Quenching of excited triplet states by Cr (III) and Co (III) B-diketonate complexes

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QUENCHING OF EXCITED TRIPLET STATES BY Cr(III) AND Co(III) β-DIKETONATE COMPLEXES

by

Stephen Lawrence Collins

A Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology November 1987

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TO
MUM & DAD
WITH
THANKS
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ABSTRACT

Bimolecular rate constants for the quenching of up to 15 excited triplet aromatic hydrocarbons by eight \( \beta \)-diketonate complexes of Cr(III) and four of Co(III) have been obtained using nanosecond laser flash photolysis.

The bimolecular rate constants have been plotted against donor energy and for those quenchers whose rate constants follow the available spectroscopic energy levels in the quencher, electronic energy transfer is established to be the mechanism of quenching. As the electrochemical reduction potential of the quencher is reduced by the introduction of trifluoromethyl groups into the \( \beta \)-diketonate complexes, an increase in quenching efficiency is observed which may be explained by modifying the mechanism of quenching to include electron transfer. Theoretical models have been developed in order to predict quenching constants for the different mechanistic pathways.

For the quenching of excited triplet states by \( \gamma \)-substituted chromium (III) complexes, rate constants greater than those predicted by the Debye Equation, once spin statistics have been introduced, were obtained. Diffusion theories were examined and a Spernol-Wirtz type treatment was employed, since this takes into account microfiction between solute and solvent molecules of differing molecular radii. Using this diffusion theory allowed all of the results presented to be interpreted within the framework of the theoretical models.

The effect of geometrical isomerism on the quenching efficiency of a chromium(III) complex was investigated and it was found that the \( \text{cis} \)-isomers is a more efficient electronic energy transfer quencher than the \( \text{trans} \) form, especially when energy is being accepted by the quartet state.

The general nature of the approach developed in the thesis was examined by measuring the quenching rate constants for four Co(III) \( \beta \)-diketonate complexes.
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CHAPTER I

INTRODUCTION AND THEORY

1.1 Introduction

Since the discovery of flash photolysis by Norrish and Porter (1) in 1949, the study of excited state species has received much attention. The advent of lasers and improvements in chemical instrumentation over the past three decades leaves the experimentalist in the position whereby all events down to those occurring in the picosecond time scale may now be studied.

One field of research that has been treated with particular interest is that of the quenching of electronically excited states in solution. Quenching of singlet and triplet states in solution by organic compounds has been studied in detail and the mechanism and efficiency of quenching determined. Quenching by inorganic transition metal complexes has been found to be dependent on the nature of the metal, its charge and the structure of ligands attached to the central metal atom. The aim of the work presented in this thesis is to extend the study of the quenching of electronically excited triplet states by inorganic S-diketonate complexes in order to determine the mechanism of quenching and its efficiency.

Before discussing the various mechanisms by which excited states may be quenched, it is of fundamental interest to consider the events which take place following the absorption of light. It is not however the intention of the author to provide a quantum mechanical description of these events since this may be obtained in great detail from many standard texts. (2 - 5).
1.2 State Diagram

In order to aid the discussion of the various photophysical processes which follow the absorption of radiation, Figure 1.1 presents a state diagram for a diamagnetic molecule similar to that first proposed by Jablonski. The left hand side of the diagram represents the singlet manifold of states (spins paired, \( S=0 \) and state multiplicity is given by \( m=2S+1 \), therefore \( m=1 \)), whilst the right hand side gives the triplet manifold (spins unpaired, \( S=1, m=3 \)).

As can be seen from the diagram, absorption of radiation by a molecule in its ground state, \( S_0 \), leads to population of vibrational levels in the \( S_1, S_2, \ldots, S_n \) states (\( S_2 \) state in this case). In solution rapid vibrational relaxation occurring with a rate constant in the region of \( 10^{11}-10^{13} \text{s}^{-1} \), results in the population of the lowest vibrational level of electronically excited state \( (S_2) \), which may then undergo internal conversion yielding an isoenergetic vibronic (vibrationally and electronically excited) level in the \( S_1 \) state. Again rapid vibrational relaxation will give the lowest vibrational level of \( S_1 \) which may be deactivated by four mechanisms:

1. **Fluorescence**; a radiative transition yielding the ground state, \( S_0 \).

2. **Internal conversion**; a non-radiative transition yielding a vibrational isoenergetic level of the \( S_0 \) ground state.

3. **Intersystem crossing**; a non-radiative transition to an isoenergetic vibronic level in the triplet manifold.
Fig 1-1 State Diagram

ISC - Intersystem Crossing
IC - Internal Conversion
vr Vibrational Relaxation
4. Photochemical processes; yielding products of different chemical constitution to the ground state.

Once a molecule has attained its lowest vibrational level of the $T_1$ state, deactivation may occur via three mechanisms:

1. Phosphorescence; a radiative process yield the $S_0$ ground state.

2. Intersystem crossing; a non-radiative pathway to an isoenergetic vibrational level of the $S_0$ state.

3. Photochemical processes; yielding products.

Therefore it is possible to group the various mechanisms of deactivation under two broad headings, (1) Radiative Transitions; and, (2) Non-Radiative Transitions.

1.2.1 Radiative Transitions

1.2.1.1 Fluorescence

Fluorescence is a spin-allowed process which occurs between states of the same multiplicity and proceeds with a rate constant of $10^6-10^9\text{s}^{-1}$. For most polyatomic organic molecules fluorescence occurs from the lowest vibrational level of the $S_1$ state, $S_1 \rightarrow S_0$ (Fig. 1.1), however, $S_2 \rightarrow S_0$ fluorescence has been observed in azulene (6) and related compounds (7,8). Fluorescent $^4T_{2g} \rightarrow ^4A_{2g}$ transitions have also been observed in some Cr(III) coordination complexes (9,10).
1.2.1.2 Phosphorescence

This process, with the exception of biacetyl (11) is rarely observed in fluid solution being more commonly associated with highly viscous solutions or solids at low temperatures. In organic molecules, the spin forbidden transition is represented by $T_1 \rightarrow S_0$ and occurs with an extremely long lifetime, $10^{-3}$-10 sec., compared with fluorescence. Phosphorescence is also observed from $^2E_{{g}} \rightarrow ^4A_{{2g}}$ transition in Cr(III) coordination complexes.

1.2.2 Non-Radiative Transitions

1.2.2.1 Internal Conversion

Internal conversion (IC) is a radiationless transition that occurs between states of like multiplicity and is depicted in Figure 1.1 as a wavy arrow, i.e. $S_2 \sim S_1$. IC occurs from the zero vibrational level of an electronically excited state to an isoenergetic vibronic level of a different excited state. IC of higher excited states is a highly efficient process with an associated rate constant of $\sim 10^{12}$ s$^{-1}$. The lowest triplet state $T_1$, is normally derived from higher triplet levels by internal conversion, i.e. $T_2 \rightarrow T_1$.

1.2.2.2 Intersystem Crossing

Intersystem crossing (ISC) is defined as a radiationless transition occurring between electronic states of different multiplicity. Singlet-triplet ISC usually occurs from the zero point vibrational level of $S_1$, to an isoenergetic level of $T_1$ or to some higher excited triplet level ($T_2$ or $T_q$), and proceeds at a rate similar to that of fluorescence.
(i.e. $10^6$-$10^9$ s$^{-1}$). This process is responsible for the population of the triplet manifold and occurs as a result of spin-orbit coupling (12).

The reverse process of triplet-singlet intersystem crossing has also been observed in molecules where the $T_1-S_1$ energy gap is small, allowing thermal activation of $T_1$ to occur during its lifetime, to a vibrational level isoenergetic with $S_1$. Thus $T_1\rightarrow S_1$ intersystem occurs leading to E-type delayed fluorescence. ISC will, however normally occur to an isoenergetic vibrational level of $S_0$, which will then lose its energy by vibrational relaxation.

1.3 Quenching of Electronically Excited States

Quenching of an electronically excited state in fluid solution may be defined as any intermolecular process which decreases the lifetime of an excited state. The mechanisms by which this may occur may be either chemical or physical in nature and are presented diagramatically below:

[Diagram of quenching mechanisms]

- **Photophysical Quenching**: Self-quenching
- **Chemical Quenching**: Impurity quenching
- **Heavy atom quenching**: Paramagnetic
- **Electron transfer**: Electron transfer
- **Electronic energy transfer**: Coulombic exchange

### Quenching Mechanisms

- **Self-quenching**: Processes (1.3.2)
- **Impurity quenching**: Processes (1.3.3)
- **Paramagnetic quenching**: Processes (1.3.4)
- **Electron transfer**: Processes (1.3.5)
- **Coulombic energy transfer**: Processes (1.3.6.1)
- **Exchange energy transfer**: Processes (1.3.6.2)
1.3.1 Photochemical Quenching

Photochemical reactions leading to the formation of a product are
one class of process whereby the lifetime of the excited state is reduced.

\[ M^* + Q \rightarrow \text{Products} \]  

The term 'product' refers to any species which is chemically different
to the reactants, but in the case of photochemical reactions in comparison
with ground state reactions, the 'products' may be short lived and decay,
to give the starting species:

i.e.

\[ M^* + Q \rightarrow \text{Products} \rightarrow M + Q \]  

By using this type of definition, electron transfer reactions
(sec. 1.3.5) could be classed as a photochemical reaction.

Bowen and Rohatgi (13) have studied the effect of irradiation on the
behaviour of anthracene (A) in carbon tetrachloride. They found that in
the absence of oxygen the initial step:

\[ ^1A^* + \text{CCl}_4 \rightarrow {\cdot \text{ACl}} + {\cdot \text{CCl}_3} \]  

produces radicals, which is followed by the dimerization of \( {\cdot \text{ACl}} \). Deriva-
tives of anthracene were also found to follow a similar reaction scheme.

Photochemical reactions involving inorganic complexes can be placed
under three broad headings, substitution, rearrangements and redox
reactions. A survey of this field of inorganic photochemistry has been
presented by Waltz and Sutherland (14).
1.3.2 Concentration Quenching

The fluorescence lifetime of many aromatic hydrocarbons in solution have been found to decrease with increasing solute concentration. Pyrene, which is a typical and well studied example, exhibits violet fluorescence at low concentrations \((2 \times 10^{-6} \text{M})\) but at higher concentrations \((>1 \times 10^{-4} \text{M})\) a structureless blue emission band appears, whose intensity increases with concentration. Förster and Kasper (15) showed that this was due to the formation of an excited dimer (excimer) from the combination of an excited singlet molecule and a molecule in its ground state.

\[
1_{\text{M}}^* + 1_{\text{M}} \rightarrow 1_{(\text{MM})}^* \rightarrow \text{M} + \text{M} + \text{hv}_{\text{D}}
\]

where \(\nu_{\text{M}}\) and \(\nu_{\text{D}}\) are monomer and dimer fluorescence wavenumbers respectively and \(\nu_{\text{M}} > \nu_{\text{D}}\).

Figure 1.2 depicts the formation of the excimer and shows that its structureless fluorescence is due to emission to a non-quantized ground state. In contrast with other branches of chemistry, excimers are only stable in the excited state.

Takemura et al (16) have studied triplet excimers

\[
3_{\text{M}}^* + 1_{\text{M}} \rightarrow 3_{(\text{MM})}^*
\]

of naphthalene and 1-chloronaphthalene, observing a broad structureless emission to the red of the monomer phosphorescence.

1.3.3 Heavy Atom Quenching

Triplet-singlet transitions are spin-forbidden and that they occur at all is due to spin-orbit coupling which has the effect of
Fig 1-2

Schematic Energy Surfaces showing

Excimer Formation and Emission
increasing the mixing between the singlet and triplet wavefunctions giving rise to enhanced intersystem crossing. The magnitude of this mixing increases with atomic number (Z). McClure (17) was the first worker to study this phenomena (the internal heavy atom effect) by introducing halogen atoms into a naphthalene ring. Ermolaev and Svitashev (18) furthered this study and their results are presented in Table 1.1. From this table it can be seen that for the sequence fluoro-, chloro-, bromo-, iodo-, the quantum yield of fluorescence decreases as the phosphorescence yield increases, whilst the lifetime of the phosphorescent state also decreases.

Spin-orbit coupling may also be increased without modifying the structure of the aromatic molecule if a solvent containing a heavy atom is used. This external heavy atom effect was first studied by Kasha (19) using ethyl iodide as a solvent, and proposed that intersystem crossing proceeded via an encounter complex, viz

\[
^1D^* + Q_{HA} \rightarrow ^1(DQ)_{HA} \xrightarrow{ISC} ^3(DQ)_{HA} \rightarrow ^3D^* + Q_{HA}
\]

1.6

since these encounter complexes could not be observed, the overall effect appears to be:

\[
^1D^* + Q_{HA} \rightarrow ^3D^* + Q_{HA}
\]

1.7

McGlynn et al (20) measured the quantum yields of fluorescence and phosphorescence, and the lifetime of the phosphorescent state of naphthalene in the presence and absence of heavy atom containing solvents. They showed (Table 1.2) that their results were analogous to those obtained for internal heavy atom quenching; the increase in \( \Phi_P \)
TABLE 1.1
Internal Heavy Atom Effect in Naphthalene Derivatives

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$\phi_{FM}$</th>
<th>$\phi_{PT}$</th>
<th>$\tau$(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>0.55</td>
<td>0.051</td>
<td>2.3</td>
</tr>
<tr>
<td>1-Fluoronaphthalene</td>
<td>0.84</td>
<td>0.056</td>
<td>1.5</td>
</tr>
<tr>
<td>1-Chloronaphthalene</td>
<td>0.058</td>
<td>0.30</td>
<td>0.29</td>
</tr>
<tr>
<td>1-Bromonaphthalene</td>
<td>0.0016</td>
<td>0.27</td>
<td>0.02</td>
</tr>
<tr>
<td>1-Iodonaphthalene</td>
<td>&lt;0.0005</td>
<td>0.38</td>
<td>0.002</td>
</tr>
</tbody>
</table>

TABLE 1.2
External Heavy Atom Effect in Naphthalene

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>$\phi_{FM}$</th>
<th>$\phi_{PT}$</th>
<th>$\tau$(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol/Methanol</td>
<td>0.55</td>
<td>0.055</td>
<td>2.5</td>
</tr>
<tr>
<td>EM + Propylchloride</td>
<td>0.44</td>
<td>0.080</td>
<td>2.27</td>
</tr>
<tr>
<td>EM + Propylbromide</td>
<td>0.13</td>
<td>0.24</td>
<td>1.73</td>
</tr>
<tr>
<td>EM + Propyliodide</td>
<td>0.026</td>
<td>0.35</td>
<td>1.33</td>
</tr>
</tbody>
</table>
being explained by equation 1.7, whilst the decrease in phosphorescence lifetime being a result of enhancing the $T \rightarrow S$ transition

$$^{3}D^* + Q_{HA} \longrightarrow ^{1}D + Q_{HA}$$  \hspace{1cm} (1.8)

Medinger and Wilkinson (21) studied the mechanism of fluorescence quenching of anthracene and three of its derivatives by bromobenzene. They not only found that the fluorescence intensity was decreased but also observed an increase in triplet state absorption upon flash excitation of their samples, thus giving further confirmation of the mechanism proposed by Kasha. Xenon was also shown to be an efficient external heavy atom quencher by Wilkinson et al. (22) when they measured fluorescence quenching of aromatic hydrocarbons in ethanol; xenon having the ideal properties of being chemically inert, transparent and readily soluble in organic solvents.

1.3.4 Paramagnetic Quenching

Quenching of excited states by paramagnetic species occurs by a process known as catalyzed intersystem crossing. Oxygen has been found to quench singlet states in this manner, viz

$$^{1}D^* + {^{3}}O_2 \longrightarrow ^{3}D^* + ^{3}O_2$$  \hspace{1cm} (1.9)

$^{1}D \rightarrow ^{3}D$ transitions are normally spin-forbidden, but the occurrence of an encounter complex between molecular oxygen and the excited state leads to transition becoming allowed in accordance with Wigner's Spin Rule (23)

$$^{1}D^* + {^{3}}O_2 \longrightarrow ^{3}(D\cdots O_2)^* \longrightarrow ^{3}D^* + ^{3}O_2$$  \hspace{1cm} (1.10)

encounter complex
Wigner's spin rule states that for a collisional process, spin angular momentum must be conserved. Therefore, if $S_A$ and $S_B$ are the spin quantum numbers of the reacting species, then the interactive complex must have one of the following spin quantum numbers:

$$S_A + S_B, (S_A + S_B - 1), (S_A + S_B - 2), \ldots, |S_A - S_B|$$  \hspace{1cm} (1.11)

Similarly, if $S_C$ and $S_D$ are the spin quantum numbers of the products, then it follows that one of the resultant spin quantum numbers of the series

$$S_C + S_D, (S_C + S_D - 1), (S_C + S_D - 2), \ldots, |S_C - S_D|$$  \hspace{1cm} (1.12)

must be in common with one from the series 1.11.

For the case in question we have:

$$1^* + 3^0_2 \rightarrow 3^* + 3^0_2$$  \hspace{1cm} (1.13)

where the spin quantum numbers are:

$$S_i \begin{array}{cccc} 0 & 1 & 1 & 1 \end{array}$$  \hspace{1cm} (1.14)

and the total spin of the reactant/product components are:

$$S_T \begin{array}{c} 1 \\ 2,1,0 \end{array}$$  \hspace{1cm} (1.15)

Therefore the unity component (triplet state) is common, and intersystem crossing will proceed via this.

In the case of an excited triplet state, the process may be represented by:

$$3^+_D + 3^0_Q \rightarrow (D \ldots Q)^* \rightarrow 1^* + 3^0_Q$$  \hspace{1cm} (1.16)
where \( m \) is the multiplicity of the encounter complex. Performing similar calculations to those above, the total angular momentum for the reactants gives quintet, triplet and singlet states \( (S_T = 2, 1, 0) \) whilst the products only yield a triplet \( (S_T = 1) \). Therefore the encounter complex exists as a triplet state \( (m = 3) \).

As previously discussed, paramagnetic quenching requires that an encounter complex of common multiplicity be formed. It has been shown in the cases cited that other non-common multiplicities are produced by vector addition and Porter and Wright (24) were the first to discuss these in terms of a spin-statistical factor, \( s \). The spin-statistical factor may be considered as a measure of the probability of the reactants colliding with the correct orientation of spin angular momentum and in terms of \( S_T \), defined as:

\[
s = \frac{(2S_T + 1)}{\Sigma(2S_T + 1)} \quad \text{reactive} \tag{1.17}
\]

The 'reactive' term corresponds to the common spin component, whilst the summation deals with all possible components of the reactants. Therefore, scheme 1.16 would have a spin statistical factor of:

\[
s = \frac{3}{5 + 3 + 1} = \frac{1}{3} \tag{1.18}
\]

and only one third of all collisions would lead to a complex of correct multiplicity whilst scheme 1.9 would have \( s = 1 \). Thus for a collisional process the maximum rate may be defined as:

\[
k_q = sk_d \tag{1.19}
\]
where \( k_d \) is the rate constant for diffusion.

Although paramagnetic quenching has been proposed for the quenching of triplet states by molecular oxygen:

\[
\begin{align*}
3D^* + 3O_2 & \longrightarrow 1D + 3O_2 \\
3D^* + 3O_2 & \longrightarrow 1D + 1O_2^* 
\end{align*}
\]

energy transfer to give excited singlet oxygen has been found to be more efficient.

Catalysed intersystem crossing was also proposed by Porter and Wright (25) to be the mechanism of deactivation of triplet excited states in the presence of paramagnetic transition metal complexes. Similarly, for many of these cases, electronic energy transfer has been shown to be more efficient.

1.3.5 Electron Transfer Quenching

As a result of electronic excitation a molecule can be expected to be both a better oxidant and reductant than the parent ground state molecule. This is due to a reduction in ionization potential (by \( E_T \) or \( E_S \)) as well as an increase in electron affinity. Therefore photoelectroc reactions of the type:

\[
D^* + Q \longrightarrow D^{\circ} + Q^{\circ}
\]

are more likely to occur.

Barltrop and Owers (26) showed that electron transfer was the primary process taking place when naphthalene is irradiated in the presence of ethylamine with acetonitrile as the solvent. As discussed
in the previous section concerning paramagnetic quenching, an encounter complex through which enhanced intersystem crossing took place was proposed. Rehm and Weller (27) measured the rate of quenching of many aromatic compounds by amines and were able to explain their results in terms of electron transfer via an encounter complex:

\begin{equation}
1^*_{M} + Q \rightarrow \text{encounter complex} \rightarrow (M \cdot Q)^* \rightarrow 2^\pm_{M} + 2^\pm_{Q} \downarrow \text{Products}
\end{equation}

The steady state kinetics and the various terms used to describe the electron transfer process will be presented in Section 1.4.3 when a classical treatment of both electron and energy transfer is developed. However, it can be seen from Fig. 1.3 that Rehm and Weller found a relationship between $k_q$, the quenching constant and $\Delta G_{el}$, the free energy change for electron transfer.

Quenching of excited transition metal complexes by amines has been shown by Balzani et al. (28) to proceed via electron transfer. Ohno and Lichtin have reported that methylene blue is quenched by complexes of cobalt (II) (29) and Fe(II) (30), proceeding via an electron transfer mechanism. Wilkinson and Tsiamis (31) have measured the quenching constants of 13 excited triplet state aromatic molecules using chromium (III) tris (1,1,1,5,5,5-hexafluoropentan-2,4-dionate) as a quencher and have interpreted their results in terms of both electron transfer quenching and electronic energy transfer.
Variation of $k_\text{q}$ with free energy for electron transfer

Ref (27)
1.3.6 Energy Transfer

There are two main processes by which electronic energy may be transferred from an excited state donor to a ground state acceptor, i.e. for:

\[ \text{D}^* + \text{A} \rightarrow \text{D} + \text{A}^* \]  \hspace{1cm} 1.24

Firstly, the electronically excited donor may emit a photon which is re-absorbed by the acceptor:

\[ \text{D}^* \rightarrow \text{D} + h\nu \]  \hspace{1cm} 1.25
\[ h\nu + \text{A} \rightarrow \text{A}^* \]  \hspace{1cm} 1.26

The efficiency of this process is governed primarily by the extent of overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor; the other factors being the concentration of the acceptor, the distance over which energy transfer takes place as well as the quantum efficiency of donor emission (32).

The second class of energy transfer is a non-radiative one which requires an exchange interaction between D and A. This interaction results in a perturbation \( \hat{H}' \) being added to the Hamiltonian of the system, leading to a finite probability of energy transfer (scheme 1.24) taking place. From time dependent perturbation theory the interaction given by:

\[ U = \langle \psi_{MQ}^* \mid \hat{H}' \mid \psi_{M^*Q} \rangle \]  \hspace{1cm} 1.27

where the final and initial states are represented by \( \psi_{MQ}^* \) and \( \psi_{M^*Q} \) respectively.
1.3.6.1 Coulombic Energy Transfer

Coulombic energy transfer, or long range energy transfer as it is sometimes known, proceeds via the coupling of the transition moment of the donor with that of the acceptor, resulting in the simultaneous deactivation of the donor and excitation of the acceptor. Since no actual physical contact is required, energy transfer may take place over distances considerably greater than the molecular radii. The 'interaction' may be dipole-dipole, dipole-quadrupole, quadrupole-quadrupole etc. in nature, with the former predominating in most cases. The process was considered theoretical by Förster (33) who obtained the following expression for the rate of energy transfer for a dipole-dipole mechanism:

$$
\kappa_{DA} = \frac{9000 \langle \ln 10 \rangle \kappa^2 \phi_D^2}{128 \pi^5 n^4 N_D R^6} \int_0^\infty f_D(\nu) \varepsilon_A(\nu) \frac{d\nu}{\nu^4}
$$

where $\phi_D$ is the fluorescence quantum yield of the donor, $\tau_D$ is the lifetime of the donor in the absence of quencher, $n$ is refractive index of the solvent and $R$ is the distance between the donor and acceptor. $f_D(\nu)$ is the emission spectrum of the donor (in wavenumbers) normalized to unity and $\varepsilon_A$ is the decadic molar extinction coefficient of the acceptor at the wavenumber $\nu$. The other fundamental constants taking on their normal values. The orientation factor, $\kappa$, is defined by:

$$
\kappa = \cos \theta_{DA} - 3 \cos \phi_D \cos \phi_A
$$

where $\theta_{DA}$ is the angle between the transition moment vectors of the donor and acceptor, and $\phi_D$ and $\phi_A$ are the angles between the vectors and the direction of energy transfer for species D and A respectively.
For a random distribution of vectors $x^2 = 2/3$. Equation 1.28 may also be expressed as:

$$k_{DA} = \frac{1}{\tau_D} \left( \frac{R_0}{R} \right)^n$$

the $n$ referring to whether the process is dipole-dipole ($n=6$), dipole-quadrupole ($n=8$) etc.

The distance at which deactivation of $D^*$ and energy transfer to $A$ becomes equally probable, is known as the critical transfer distance, $R_0$. Förster obtained the expression:

$$R_0^6 = \frac{9000 (1n10) k^2 \phi_A}{128 \pi^5 n^4 N} \int_0^{\infty} f_D(\tilde{\nu}) \phi_A(\tilde{\nu}) d\tilde{\nu}$$

from equation 1.28, given that $k_{DA} = \frac{1}{\tau_D}$.

By the introduction of reasonable values into equation 1.31, $R_0$'s in the region $40-100\AA$ are predicted, and $k_{DA}$'s from equation 1.28 are found to be greater than those predicted by diffusion theory (see Sec. 1.5). The theoretical predictions have been substantiated by the experimental evidence of Ware (34), who studied energy transfer between organic molecules in benzene and found $R_0$'s in good agreement with those obtained theoretically. Bowen et al (35, 36) have also studied the rate of energy transfer between 1-chloroanthracene and perylene in a variety of solvents and found $k_{DA}$'s to be excess of the diffusion controlled rate and $R_0$'s to be $\approx 40\AA$.

Coulombic energy transfer is subjected to rigorous spin selection rules which state that there should be no change in spin of either species.
Therefore processes such as:

\[ \Pi_D^* + \Pi_A \rightarrow \Pi_D + \Pi_A^* \]  
\[ \Pi_D^* + \Pi_A^* \rightarrow \Pi_D + \Pi_A^{**} \]  

are allowed, but

\[ \Pi_D^* + \Pi_A \rightarrow \Pi_D + \Pi_A^{**} \]  

is forbidden. However, Bennett et al (37) have observed triplet-singlet transfer in rigid media, since although \( \Pi_D^* \rightarrow \Pi_D \) is spin-forbidden and reduces the value of \( k_{DA} \) it also increases the lifetime of \( \Pi_D^* \) allowing energy transfer to compete with the deactivation of \( \Pi_D^* \).

1.3.6.2 Exchange Energy Transfer

Exchange, or collisional energy transfer as its name implies requires the molecules to be in physical contact, allowing the electron clouds to overlap and the electron exchange process to take place. Since physical contact is required, the maximum rate at which exchange energy transfer may take place is governed by the rate of diffusion of \( \Pi_A^* \) and \( \Pi_A \), in contrast to coulombic energy transfer.

Dexter (38) treated this problem theoretically and found the rate of electron-exchange may be expressed in the form:

\[ k_{EE} = \left( \frac{2\pi}{h} \right)^2 \exp \left[ -\frac{2R}{L} \right] \int_0^\infty F_D (\tilde{\nu}) E_A (\tilde{\nu}) d\tilde{\nu} \]  

where \( F_D (\tilde{\nu}) \) and \( E_A (\tilde{\nu}) \) are the donor emission and acceptor absorption spectra normalized to unity. L is the effective Bohr radius, R the
distance of closest approach and $z^2$ is a parameter which cannot be
directly related to optical parameters. Although both electron-exchange
and coulombic energy transfer require spectral overlap, the former is
independent of the optical transition moments.

From equation's 1.35 exponential dependence ($e^{-R}$) on $R$, it may
be concluded that exchange energy transfer is a short range mechanism in
comparison with coulombic energy transfer which exhibits a $1/R^6$ dependence.

Early calculations by Dexter (38) subjected this mechanism to
stringent spin-selection rules which were shown by Razi-Naqvi and Steel (39)
to be too rigorous when the correct exchange model was used. They
found that this process is governed by Wigner's spin rule (see Sec 1.3.4),
making the previous forbidden process:

$$^3D^* + A \longrightarrow ^1D + ^3A^*$$  \hspace{1cm} (1.36)

allowed.

1.4 A Classical Treatment of Vertical and "Non-vertical" Energy
Transfer Processes

Exchange energy transfer, as discussed in Section 1.3.6.2, requires
spatial overlap between the orbitals of the donor and acceptor, and
thus the process is governed by the rate at which these species may
diffuse together (Section 1.5). Sandros (40) obtained the following
expression:

$$k_q = \frac{k_d}{1 + \exp \left[ - \left( E(D^*, D) - E(A^*, A) \right) \right] / RT}$$  \hspace{1cm} (1.37)
for the quenching of biacetyl by a number organic acceptors. The diffusion rate constant is represented by $k_d$ and $E(D^*D)$ and $E(A^*A)$ are the energies of the donor and acceptor excited states respectively. For endoergic energy transfer (ie $E(D^*D) < E (A^*A)$) Sandros saw that the deficiency in donor energy could be made up by vibrational excitation. Systems that follow Sandros's equation are said to behave classically. (In order to take into account the spin statistics of the process, the right-hand side of equation 1.37 should contain a factor, $s$ - see Section 1.3.4). However a number of systems (41-43) exhibit higher rate constants for endoergic energy transfer than predicted from equation 1.37, by introduction of available spectroscopic data, and are thus termed to behave 'non-classically'. The common factor associated with all 'non-classical' systems is that either the donor and/or the acceptor have distorted excited states.

Hammond et al (44,45), studied the rate of energy transfer to cis-stilbene and described their results in terms of 'non-vertical excitation' and 'phantom triplet' states. Conceptually, non-vertical excitation was simultaneously followed by a change in geometry of the acceptor to give a non-spectroscopic distorted state - a phantom state. The use of these rather misleading concepts has been replaced by general treatment proposed by Balzani et al (46) and developed by Wilkinson and Tsiamis (47-49,31). This treatment which accounts for vertical and non-vertical transitions as well as lower than diffusion limited rate constants will be presented.

1.4.1 Energy Transfer Quenching

For exchange energy transfer, the following kinetic scheme may be considered to be prevalent:
\[ 3^3D^* + m_A \xrightarrow{ske_d} n(D^*\ldots A) \xrightarrow{en} n(D\ldots A^*) \xrightarrow{d} D + n_A^* \]\n
\[ 1.38 \]

\( 3^3D^* \) represents an organic donor in a triplet excited state, whilst \( m \) is the multiplicity of the ground state acceptor and \( n_A^* \) is the electronically excited acceptor. The terms \( k_d \) and \( k_d' \) are the rate constants for the formation and dissociation of the encounter complexes, which are considered to be equal for both reactants and products since only physical encounters are taking place. The various methods of calculating diffusion coefficients and hence diffusion rate constants are discussed in Section 1.5. The rate of dissociation, \( k_d' \), is given by the Eigen equation (50).

\[ k_d' = \frac{3k_d}{4\pi r^3 N} \]

\[ 1.39 \]

where \( r \) is the radii of the diffusing species. The forward and reverse energy transfer rate constants are represented by \( k_{en} \) and \( k_{en} \) respectively and the values associated with these will be discussed later. A spin statistical factor \( s \), has been introduced (47) which takes into account of the probability of the reactants colliding with the correct orientation of spin angular momentum vectors (see Section 1.3.4) Assuming that \( \frac{1}{\tau_A} >> k_d[D] \), then application of the steady-state approximation to the encounter complexes gives:

\[ d \left[ n(D^*\ldots A) \right] \frac{dt}{dt} = sk_d [D] [A] + k_{en} [n(D\ldots A^*)] - k_d [n(D^*\ldots A)] - k_{en} [n(D^*\ldots A)] = 0 \]

\[ 1.40 \]

\[ d \left[ n(D\ldots A^*) \right] \frac{dt}{dt} = k_{en} [n(D^*\ldots A)] - k_{en} [n(D\ldots A^*)] - k_d [n(D\ldots A^*)] = 0 \]

\[ 1.41 \]
From experimental work (see Chapter 2), a plot of the pseudo first order rate constant \( k'_1 \) vs \( [Q] \), the concentration of the quencher (acceptor, A) gives \( k_q \). Therefore, \( k'_1 \) is given by

\[
k'_1 = k_q [A] + \frac{1}{r_0}
\]

The pseudo first order rate constant is calculated from a plot of \( \ln A \) vs \( t \) i.e.:

\[
k'_1 = -\frac{\text{d} [\ln A]}{\text{d} t}
\]

From the Beer-Lambert law we have:

\[
A = e \cdot c \cdot l
\]

where the concentration \( c \) is equivalent to \( [D] \). Substitution of equation 1.44 into equation 1.43 gives:

\[
-\frac{\text{d} [\ln A]}{\text{d} t} = \frac{\text{d} [\ln c \cdot [D]]}{\text{d} t}
\]

and

\[
k'_1 = -\frac{\text{d} [\ln [D]]}{\text{d} t}
\]

since \( e \) and \( l \) are not functions of time. Substitution of equation 1.46 into equation 1.42 gives:

\[
-\frac{\text{d} [\ln [D]]}{\text{d} t} = k_q [A]
\]
Application of the steady-state approximation to the decay of $[D]$ in equation 1.38 gives:

$$-\frac{d[D]}{dt} = sk_d [D] [A] - k_d [^{n}(D^{*}...A)]$$  \hspace{1cm} (1.48)

and therefore equation 1.48 may be divided through by $[D]$ and combined with equation 1.47 to give:

$$-\frac{d \ln [D]}{dt} = -\frac{d[D]}{[D]dt} = sk_d [A] - k_d \frac{[^{n}(D^{*}...A)]}{[D]} = k_q [A]$$  \hspace{1cm} (1.49)

Rearrangement of equation 1.40 and substitution into equation 1.41 followed by mathematical manipulation yields:

$$\frac{[^{n}(D ...A)]}{[D]} = \frac{sk_d [A] (k_{-en} + k_{-d})}{(k_{-d} k_{-en} + k_{-d} k_{+en} k_{-d})}$$ \hspace{1cm} (1.50)

Therefore, substituting equation 1.50 into equation 1.49 gives:

$$k_q [A] = sk_d [A] - \frac{sk_d k_{-d} [A] (k_{-en} + k_{-d})}{(k_{-d} k_{-en} + k_{-d}^2 + k_{+en} k_{-d})}$$ \hspace{1cm} (1.51)

which, on rearrangement, can be shown to give a value for the quenching rate constant as being:

$$k_q = \frac{sk_d}{1 + \frac{k_{-d}}{k_{en}} + \frac{k_{-en}}{k_{en}}}$$ \hspace{1cm} (1.52)
From absolute rate theory (51) the energy transfer steps may be expressed as:

\[ k_{en} = k^0 \frac{-\Delta G^\ddagger}{RT} \]  

\[ \frac{k_{-en}}{k_{en}} = e^{\frac{\Delta G}{RT}} \]  

where \( k^0 \) is the pre-expotential factor, \( \Delta G^\ddagger \) and \( \Delta G \) are the free energy of activation and the standard free energy change for the forward energy transfer step. Substitution of equations 1.54 and 1.55 into 1.52 gives:

\[ k_q = \frac{sk_d}{1 + e^{\frac{\Delta G}{RT}} \frac{k_{-d} e^{\frac{\Delta G^\ddagger}{RT}}}{k_{en}}} \]  

The pre-expotential factor may be defined as:

\[ k_{en}^0 = \kappa \frac{kT}{h} \]  

where \( \kappa \) is the transmission coefficient and the constants take on their normal meaning. The transmission coefficient, \( \kappa \), is the probability of the system, that has reached the transition state, will continue to the final state. It is a product of both nuclear and electronic factors;
the nuclear factor accounting for the probability of nuclear tunneling which results in reactants going to products without passing through the transition state (52). The electronic factor relates to the interaction energy, $H_{if}$, (Fig. 1.4) between the initial and final states. If the electronic factor and hence the transmission coefficient are small, then the system is said to behave in a "non-adiabatic" manner. Crossing between the two curves is subject to spin-selection rules and is also governed by the amount of overlap between the initial and final states. The transmission coefficient has been treated theoretically by Zener (53) and has been discussed in detail by Glasstone et al (51) and by Reynolds and Lumay (54).

The standard free energy term, $\Delta G$, for the overall energy transfer step is:

$$D^* + A \rightarrow D + A^*$$

(1.58)

is given by:

$$\Delta G = \Delta G_t - W_r + W_p$$

(1.59)

where $W_r$ and $W_p$ are the work terms which represent the energy required to bring the reactants and products together from an infinite distance apart to their separation distance in the encounter complex. Since we are considering a process which only involves physical encounters the work terms are negligible.

From thermodynamics the standard free energy change is given by:

$$\Delta G = \Delta H - T\Delta S$$

(1.60)
Fig 1.4

Potential Energy Surfaces for Self-Exchange Energy Transfer
which for the system under study equates to:

\[-\Delta G(D, D) + \Delta G(A, A) = -\Delta H(D, D) + T\Delta S(D, D) + \Delta H(A, A) - T\Delta S(A, A)\]  \[1.61\]

If the vibrational partition functions of the ground and excited states are similar, then the enthalpy difference between the two states at room temperature is equal to the zero-zero spectroscopic energy ($E_{oo}$). Differences in entropy between the ground and excited state may occur in three ways. Firstly, excitation may lead to a change in dipole moment which would in turn effect the degree of solvation. However, in non-polar solvents (such as benzene) this is negligible and therefore neglected. Secondly, changes in internal degrees of freedom have been shown by Orlandi and Marconi (55) to only contribute a very small energy change even for large changes in vibrational frequency. The third difference is due to changes in orbital and spin degeneracy which have been calculated and found to be small. Thus $\Delta S = 0$ and the free energy change is given by:

$$
\Delta G = -hNC (\tilde{\nu}_{oo}(D) - \tilde{\nu}_{oo}(A))
$$  \[1.62\]

where $\tilde{\nu}_{oo}(D)$ and $\tilde{\nu}_{oo}(A)$ are the wavenumbers of the zero-zero electronic transitions in the donor and acceptor, respectively.

The free energy of activation has been related to the free energy change for the process by three relationships. These were proposed by Marcus (56) equation 1.63, Rehm and Weller (57) equation 1.64 and by Agmon and Levine (58) equation 1.65.

$$
\Delta G^\neq = \Delta G^\neq(0) \left(1 + \frac{\Delta G}{4\Delta G^\neq(0)}\right)^2
$$  \[1.63\]
\[ \Delta G^\ddagger = \frac{\Delta G}{2} + \left[ \left( \frac{\Delta G}{2} \right)^2 + \left( \Delta G^\ddagger(0) \right)^2 \right]^{1/2} \]

\[ \Delta G^\ddagger = \Delta G + \frac{\Delta G^\ddagger(0)}{\ln 2} \ln \left[ 1 + \exp \left( \frac{-\Delta G \ln 2}{\Delta G^\ddagger(0)} \right) \right] \]

The \( \Delta G^\ddagger(0) \) term is known as the reorganisational intrinsic barrier (which is equivalent to the free energy of activation when \( \Delta G = 0 \)) and will be discussed in due course.

Figure 1.5 gives a graphical representation of the above \( \Delta G^\ddagger \) relationships. The Marcus Theory predicts a large value of \( \Delta G^\ddagger \) when energy transfer become highly exoergonic (the Marcus inverted region \( \Delta G < -4\Delta G^\ddagger(0) \)), however, little experimental evidence for this phenomena has yet been produced. The treatment of Rehm and Weller was developed in order to explain their results (27), for the fluorescence quenching of aromatic hydrocarbons by electron donors (see Sec. 1.3.5) and their relationship has been shown to be in qualitative agreement with many systems studied (59, 60). Agmon and Levine have treated the problem theoretically and as can be seen from Fig. 1.5 their resulting function is nearly identical to that obtained by Rehm and Weller. Both functions possessing the following properties.

1. For an isoergonic reaction, the activation energy is equal to the intrinsic barrier \( \Delta G^\ddagger(0) \).

2. \( \Delta G^\ddagger \) tends asymptotically toward \( \Delta G \) for highly endoergonic reactions.

3. \( \Delta G^\ddagger \) tends asymptotically towards zero for highly exoergonic reactions.
FIG 1.5 FREE-ENERGY RELATIONSHIPS

\[ \Delta G^+(O) = 10 \text{ KJ/MOLE} \]

- MARCUS
- REHM & WELLER
- AGMON & LEVINE

\[ \Delta G^\pm \text{ KJ/MOLE} \]

\[ \Delta G \text{ KJ/MOLE} \]
The different theories and their application to experimental systems have been discussed in great detail by Balzani et al (46,61), who concluded that owing to the more general character of Agmon and Levine relationship, this should be preferred. Therefore substitution of equation 1.65 into equation 1.56 gives:

\[
\begin{align*}
\frac{sk_d}{kq} &= \frac{\Delta G}{1 + \exp\left(\frac{\Delta G}{RT}\right)} + \frac{k_d^o}{k_{en}^o} \\
&= \frac{\Delta G + \Delta G^*(0)}{1 + \exp\left(-\frac{\Delta G \ln2}{RT}\right)} + \frac{\ln\left[1 + \exp\left(\frac{-\Delta G \ln2}{RT}\right)\right]{\Delta G^*(0)}}{1 + \exp\left(\frac{-\Delta G \ln2}{RT}\right)}
\end{align*}
\]

The reorganisational intrinsic barrier, \(\Delta G^*(0)\), which is introduced by the Agmon Levine expression, for reaction 1.58, is given by:

\[
\Delta G^*_{DA}(0) = \frac{1}{2} (\Delta G_{DA}^*(0) + \Delta G_A^*(0))
\]

where \(\Delta G_{DA}^*(0)\) and \(\Delta G_A^*(0)\) are the intrinsic barriers for the donor and acceptor. The meaning of \(\Delta G^*(0)\) may be best illustrated by considering the 'self-exchange' energy transfer reaction, ie:

\[
A^* + A \longrightarrow A + A^*
\]

which is depicted schematically in Fig. 1.6 for ease, both the ground and excited state are represented by the same harmonic function having a minima at different nuclear coordinates. Energy transfer between \(A^*\) and \(A\) cannot take place because of Frank-Condon restrictions, since the energy available for the excited state (BC in Fig. 1.6) is less than that needed for ground state excitation (ie: DE), the difference being equal to the spectroscopic Stokes shift. As discussed by Sandros (40),
Fig 1.6
Schematic diagram of the relationship between spectroscopic Stokes shift and intrinsic barrier to self exchange energy transfer
the energy deficiency may be made up by either vibrational excitation of 
A* and/or A. The most convenient path is generated when both A* and A 
are in vibrational excited levels corresponding to the intersection 
between A* and A* in Fig. 1.6. Therefore the intrinsic barrier for each 
molecule is defined by $E_a$, and the intrinsic barrier for the 
'self-exchange' reaction, equation 1.68 is given by:

$$\Delta G_A^+(0) = 2(E_a + C^*)$$  \hspace{1cm} 1.69

where $C^*$ is the difference in partition function existing between the 
reactants and the transition state. If the donor-acceptor interaction is 
small then the difference in partition function between the reactants and 
transition state will also be small and therefore neglected. The 
reorganisational energy is affected by changes in 'inner-' and 'outer-' 
sphere reorganisational energies such that:

$$\Delta G^+(0) = \Delta G^+_i(0) + \Delta G^+_o(0)$$  \hspace{1cm} 1.70

where the subscripts $i$ and $o$ denote inner-sphere and outer-sphere 
contributions respectively. The inner-sphere energy relates to changes 
in nuclear coordinates whilst the outer-sphere energy equates to changes 
in the arrangement of the solvent around the molecule. In the case of 
electronic energy transfer, the reactants do not change in electronic 
charge, only small changes in dipole moment, and therefore contributions 
from $\Delta G^+_o(0)$ are negligible.

Since all the terms in equation 1.66 have now been defined, it is 
constructive to examine the properties of the equation. If for a 
particular scheme, the pre-exponential factor, $k_{en}$ is large and $\Delta G^+$ is 
small or zero, this situation arising for energy transfer to a slightly -
or non-distorted excited state, then the third term in the denominator may be neglected. Since the free energy change is given by equation 1.62 for the situation described equation 1.66 reduces to the Sandros equation (equation 1.37). If however, the opposite occurs, $\Delta G^*(0) > 0$ and $k_{en}^0$ is small then the overall energy transfer equation accounts for "non-vertical" transition behaviour i.e. transfer to distorted excited states.

In order to examine the effect of excited state distortion, a family of donors with variable excited state energy but whose excited state geometry does not vary, may transfer energy to an acceptor which has a distorted excited (or. vice-versa). Therefore, $k_d$, $k_{-d}$, $k_{en}$ and $\Delta G^*(0)$ in equation 1.66, are constant and $\Delta G$ is given by equation 1.62 Fig. 1.7 illustrates how the shape of the theoretical energy transfer curve changes with the intrinsic reorganisational barrier. Three major points of interest may be concluded from Fig. 1.7:

1. When $\bar{v}_{oo}(D) >> \bar{v}_{oo}(A)$, a plateau region is reached with
   
   $k_q = sk_d$, if $k_{en}^0 >> k_{-d}$. The point at which $k_q = sk_d$ is determined by the intrinsic reorganisational barrier.

2. When $\bar{v}_{oo}(D) < \bar{v}_{oo}(A)$, log $k_q$ can be seen to rise with an initial slope equal to $1/(2.3RT)$.

3. For the region in between, the shape of the curve is determined by $\Delta G^*(0)$, the larger the value of $\Delta G^*(0)$, the broader the curve.

N.B. A listing of the computer programs used in this thesis are given in Appendix I.
FIG 1.7 LOG(KQ) VS DONOR ENERGY

-EFFECT OF THE INTRINSIC REORGANIZATIONAL BARRIER

- $D_1=250 \text{ CM}^{-1}$ : $A_1=12000 \text{ CM}^{-1}$ : $D_1=4.00E10 \text{ S}^{-1}$
- $D_1=500 \text{ CM}^{-1}$ : $A_1=12000 \text{ CM}^{-1}$ : $D_1=4.00E10 \text{ S}^{-1}$
- $D_1=750 \text{ CM}^{-1}$ : $A_1=12000 \text{ CM}^{-1}$ : $D_1=4.00E10 \text{ S}^{-1}$
1.4.2 Energy Transfer to More than one Acceptor State
- An Introduction

In the previous section (1.4.1), a classical treatment of energy transfer to one acceptor state has been developed and the parameters that determine the efficiency of transfer discussed. However, as in the case of transition metal complexes, more than one excited state, to which energy may be transferred is available and this type of system will now be discussed. The form of the quenching expression (equation 1.38) will be altered in order to discuss a more general process i.e.

\[ 3_D^* + M_A \xrightarrow{k_1} n(D^*\cdot A) \xrightarrow{k_2} n(D^\cdot A^*) \xrightarrow{k_3} l_D + n_A^* \]  

the quenching constant being given by

\[ k_q = \frac{k_1 k_2 k_3}{(k_2^* + k_3^*)} \]

\[ \frac{k_1^* + k_2 k_3^*}{(k_2^* + k_3^*)} \]

1.4.2.1 Energy Transfer to two States of Equal Multiplicity

This process may be represented by

\[ 3_D^* + M_A \xrightarrow{k_1} n(D^*\cdot A) \]

\[ \xrightarrow{k_2} \]

\[ \xrightarrow{k_2} n(D^\cdot A^*) \xrightarrow{k_3} l_D + n_A^* \]
By application of the steady state treatment and mathematical manipulation, the quenching rate constant for scheme 1.73 is given by:

\[
k_q = \frac{\frac{k_1k_2k_3}{k_2 + k_3}}{\frac{1}{k_2 + k_3}} + \frac{\frac{k_1k_2k_3'}{k_2 + k_3'}}{\frac{1}{k_2 + k_3'}}
\]

It is interesting to note that if energy transfer to either \(A_2\) or \(A_1\) occurs with a very low or zero probability (due to \(v_{oo}(A) \gg v_{oo}(D)\)), then equation 1.24 reduces to equation 1.72 and the system acts as if only one acceptor level is present. If two accepting states lie within \(\pm 1000\text{cm}^{-1}\) of each other, and energy transfer occurs to both states, the shape of the curve depicted in Fig. 1.8 shows very little difference from the one state situation, and thus again equation 1.74 may be simplified to 1.72.

1.4.2.2 Energy Transfer to Three States of Equal Multiplicity

If the acceptor has three excited states of equal multiplicity, then the kinetic scheme may be represented diagramatically as:

\[
\begin{align*}
\text{D} + \text{A} & \xrightarrow{k_1} \text{n(D··A)} \\
\text{n(D··A)} & \xrightarrow{k_2} \text{n(D··A)} \\
\text{n(D··A)} & \xrightarrow{k_3} \text{D} + \text{n}_A
\end{align*}
\]
FIG 1.8 LOG(KQ) VS DONOR ENERGY

-EFFECT OF TWO STATES OF EQUAL MULTIPLICITY

A1=12000 CM-1 : D1=250 CM-1 : D1=4.00E10 S-1
A2=13000 CM-1 : D2=250 CM-1 : D2=2.00E10 S-1
From the steady state treatment, it can be shown that

\[ k_q \text{ is given by:} \]

\[
k_q = \frac{k_1 k_2 k_3}{(k_{-2} + k_3)} + \frac{k_1 k_2 k_3'}{(k_{-2} + k_3')} + \frac{k_1 k_2 k_3''}{(k_{-2} + k_3'')} \]

Figure 1.9 depicts the difference in shape of the theoretical curves for energy transfer to three rather than one acceptor state. It is of interest to discuss the meaning of the terms present in equation 1.76.

1. \( k_1 k_2 k_3 \) - this is the product of the forward rate constants for

\[ D^* + A \longrightarrow D + A^* \]

by each of the possible routes.

2. \( (k_{-2} + k_3) \) - takes into account the possible routes of decay of the second encounter complex in equation 1.75, and equivalent to the inverse of the complexes lifetime (\( \frac{1}{\tau} \)).

3. \( k_2 k_3 \) - is the product of the forward rate constants for the decay of the donor excited encounter complex ie

\[ (D^* \cdot A) \longrightarrow D + A^* \].

As with equation 1.74, if one or more energy transfer steps are neglected then equation 1.76, either reduces to equation 1.74 (one step removed) or equation 1.72 (two steps removed). Since
FIG 1.9 LOG(KQ) VS DONOR ENERGY

-EFFECT OF THREE STATES OF EQUAL MULTIPLICITY

A1=12000 CM⁻¹ ; D1=250 CM⁻¹ ; 01=4.00E10 S⁻¹
A1=12000 CM⁻¹ ; D1=250 CM⁻¹ ; 01=1.333E10 S⁻¹
A2=12500 CM⁻¹ ; D2=250 CM⁻¹ ; 02=1.333E10 S⁻¹
A3=13000 CM⁻¹ ; D3=250 CM⁻¹ ; 03=1.333E10 S⁻¹
the successive additions of one energy transfer step results only in the addition of one more expression to the overall quenching rate constant, and is not mathematically connected to the other steps, for energy transfer to n-excited states of equal multiplicity, the quenching constant is given by:

\[
k_q = \frac{k_1k_2k_3}{k_{-2} + k_3} + \frac{k_1'k_2'k_3'}{k_{-2}' + k_3'} + \cdots + \frac{k_1k_2(n-1)'k_3(n-1)'}{k_{-2} + k_3}
\]

1.4.2.3 Energy Transfer to two Coupled States of Equal Multiplicity

Scheme 1.73 as presented in Sec.1.4.2.1 may be adapted to allow for non-radiative transitions to occur between the collision complexes prior to their dissociation to yield products. This situation is represented by:

\[
D^* + M_A \xrightarrow{sk_1} n(D^* \cdot A) \xrightarrow{k_2} n(D^* \cdot A^*_2) \xrightarrow{k_3} D + n_A^*
\]

where \(k_N\) and \(k_{-N}\) are the rate constants for non-radiative energy transfer. Application of the steady state treatment to the encounter complexes yields a value of \(k_q\) as given by equation 1.79.
where $\tau = (k_3 + k_{-2} + k_{-N})^{-1}$ and $\tau' = (k_3' + k_{-2}' + k_{N})^{-1}$
This equation is in the correct form in as much as if, \( k_N \) and \( k_{-N} \) are small or zero, then it reduces to equation 1.74. If \( \nu_{oo}(A_2) >> \nu_{oo}(D) \), then the \( k' \) terms tend to zero and as expected, the overall expression may be shown to reduce to equation 1.73.

Sample calculations indicate that if non-radiative transitions are included, that the value of the plateau remains unchanged and the rising portion of the curve where \( \nu_{oo}(D) < \nu_{oo}(A) \) is only slightly altered.

1.4.2.4 Energy Transfer to Three Coupled States of Equal Multiplicity

As was the case with two excited states which were coupled by non-radiative transitions, it is also possible to envisage the case whereby three states are coupled. This possibility may be represented by:

Unfortunately, it is not possible to solve this kinetic scheme by the addition of a simple expression as was the case for energy transfer to uncoupled excited states. The reason for this is due
\[ k_q = \frac{sk_1 A}{k_1 + A} \]

where

\[ A = \left[ \frac{\frac{k_2 k_3 k_N^P_1 + k_3 k_N^T_3 + k_3^N k_N^{k_3^N}}{k_3 + k_2} + \frac{k_2 k_3^N k_3^P_3 + k_3 k_M^{T_1} + k_M k_N k_3}{k_3 + k_2}}{1.81} \right] \]

and

\[ T_1 = (k_3 + k_2 + k_N), \quad T_2 = (k_3^N + k_3 + k_N + k_M), \quad T_3 = (k_3^N + k_2 + k_M) \]

\[ P_1 = T_3 T_2 - k_M^{T_M - M} \]

\[ P_3 = T_2 T_1 - k_N^{T_N - N} \]
to the fact that $A_2$ is non-radiatively coupled to $A_3$ and $A_1$, whilst
$A_1$ and $A_3$ are only coupled to $A_2$. The non-symmetrical nature of
the scheme necessitates the use of the steady-state treatment on
the four encounter complexes giving rise to expression 1.81.

This rather complex expression is reducable:

1. If $k_M', k_N', k_N$ and $k_{-N} = 0$, then equation 1.43 becomes
equal to 1.76.

2. If $\tilde{v}_{oo}(A_3) \gg \tilde{v}_{oo}(D)$ and condition (1) also applies, then
1.81 equals 1.74.

3. If $\tilde{v}_{oo}(A_3) = \tilde{v}_{oo}(A_2) \gg \tilde{v}_{oo}(D)$ then only one excited
state is able to accept energy and equation 1.81 reduces
to the simple expression, equation 1.72.

Once again, sample calculations show that the plateau quenching
constant value is not altered and only slight differences in the
rising curve are predicted. Energy transfer to $n$-coupled excited
states is theoretically possible, however, due to the complex form
of the equation it is difficult to predict its actual form. Suffice
to say, it will contain two distinctly different expressions; one
of which will relate to a state which is only directly non-radiatively
coupled to one other state, the other being directly non-radiatively
coupled to two other states.
1.4.2.5 Energy Transfer to two States of Different Multiplicity

Energy transfer of this type has been shown by Wilkinson et al (47,48) to be operative when excited organic triplet states are quenched by transition metal co-ordination complexes (see Sec. 1.6 for greater detail). The mechanism may be represented by:

\[
\begin{align*}
4(D^* \cdot \cdot A) & \xrightleftharpoons[4k_{en}]{k_d} 4(D \cdot \cdot A^*) \xrightarrow[k_d]{4k_{en}} 4D + 4A^* \\
3D^* + 4A & \xrightarrow[k_d]{sk_d} 2(D^* \cdot \cdot A) \xrightarrow[2k_{en}]{k_d} 2(D \cdot \cdot A^*) \xrightarrow[k_d]{2k_{en}} 2D + 2A^*
\end{align*}
\]

where the superscripts 4 and 2 refer to quartet and doublet states respectively, (this situation refers to energy transfer to a chromium(III) complex). The spin statistical factor, \( s \) for transfer to a quartet state is equal to \( \frac{1}{3} \), whilst that for transfer to a doublet state equals \( \frac{1}{6} \). Since the acceptor excited states are not interacting, then scheme 1.82 may be considered as two separate one energy level transfer steps (see Sec. 1.4.1) with rate constants being given by:

\[
2k_d = \frac{k_d}{6} \left[ 1 + \frac{1}{2k_{en}} \right]^{-1}
\]

\[
1.83
\]
and
$$4_k_q = \frac{k_d}{3} \left[ 1 + \frac{1}{4 k_{en}} \frac{1}{(4 k_{en} + k_d)} \right]^{-1}$$

The overall rate constant being the sum of the individual rates of transfer to the doublet and quartet states:

$$k_q = 2 k_q + 4 k_q$$

If energy transfer to the doublet and quartet states proceeds with unit efficiency, then the maximum observable quenching constant would be expected to be $k_d / 2$ (i.e., $1/6 + 1/3 = 1/2$). Fig. 1.10 represents energy transfer to the $^2E_g$ and $^4T_{2g}$ states of a Cr(III) complex.

1.4.3 Electron Transfer Quenching

As discussed in Section 1.3.5, redox reactions are more likely to occur in the excited state rather than the ground state. Rehm and Weller (27) studied the fluorescence quenching of aromatic molecules by electron donors in acetonitrile and were able to interpret their results kinetically as occurring through encounter complexes. Balzani et al (46) have developed a classical approach to this problem which will now be discussed.

The situation of electron transfer parallels that already presented for energy transfer, and the kinetic scheme may be written as:

$$3_d^* + A \xrightarrow{k_d} (D^* \cdots A) \xrightarrow{k_{el}} (D^* \cdots A^+) \xrightarrow{k_{bt}} D + A$$

$$k_d \quad k_{el} \quad k_{bt}$$
for non-polar solvents, which would not be expected to give rise to separate ionic species. The rate constants for the forward and reverse electron transfer steps are represented by $k_{el}$ and $k_{-el}$ respectively, whilst the rate of decay of the encounter complex to give products is $k_{bt}$. As for energy transfer, the steady-state approximation may be applied to the encounter complexes yielding:

$$
m_{k_{el}} = \frac{s_m k_d}{1 + k_d} \left[ \frac{1 + \frac{m_{k_{-el}}}{k_{bt}}}{m_{k_{el}}} \right]
$$

where $m$ is the multiplicity of the state through which electron transfer proceeds and $s_m$ is the spin statistical factor associated with that state. Once again the electron transfer steps may be written in terms of the absolute rate theory,

$$
k_{el} = k_{el}^0 e^{-\Delta G^+/RT}
$$

$$
k_{-el} = \frac{e^{\Delta G/RT}}{k_{el}}
$$

where $k_{el}^0$ is the preexponential factor for electron transfer given by $k_{el}^{KT/h}$, $k_{el}$ being the transmission coefficient, $\Delta G^+$ and $\Delta G$ representing the standard free energy of activation and standard free energy change for the forward transfer step.

The standard free energy change is related to the overall process $D^* + A \rightarrow D^+ + A^-$, and is given by (28),

$$\Delta G_{el} = F(E_{D_{ox}}^{red} - E_{Q_{red}}) - E_T + \Delta \omega
$$
FIG 1.10  DOUBLET AND QUARTET CONTRIBUTIONS TO THE OVERALL QUENCHING EXPRESSION

OVERALL QUENCHING EXPRESSION
(OFFSET BY 0.2 FOR CLARITY)

DOUBLET
A1=12000 CM-1 ; D1=250 CM-1
D1=5.00E9 S-1 ; S=1/6

QUARTET
A2=15500 CM-1 ; D2=2000 CM-1
D2=5.00E9 S-1 ; S=1/3

ENERGY (1000 CM-1)
where $E_{\text{D}}^{\text{ox}}$ and $E_{\text{Q}}^{\text{red}}$ are the oxidation and reduction potentials of the donor and quencher respectively, $F$ is Faraday's constant and $E_T$ refers to the triplet energy of the donor. The $\Delta w$ term relates to the energy required to form the encounter complex together with any changes in solvation which may accompany its formation. Knibbe et al (62) and Wilkinson and co-workers (63,64) have found the value of $\Delta w$ to be small, typically $(0.1 \pm 0.1)$ eV for the systems studied.

The various expressions derived for calculating $\Delta G^\ddagger$, the standard free energy of activation, have been discussed in Sec. 1.4.1, where it was concluded that the expression of Agmon and Levine (58) gives the best fit to experimental data present in the literature. The meaning of the intrinsic reorganizational barrier, $\Delta G^\ddagger(0)$ was also discussed in Sec. 1.4.1, and for electron transfer it relates to the process:

$$D + A \rightarrow D^+ + A^-$$  \hspace{1cm} (1.91)

and takes on the value of the sum of the intrinsic barriers for the "self-exchange" electron transfer reactions, hence:

$$\Delta G^\ddagger_{DA}(0) = \frac{1}{2} (\Delta G^\ddagger_A(0) + \Delta G^\ddagger_D(0))$$  \hspace{1cm} (1.92)

$\Delta G^\ddagger(0)$, receives contributions from both "inner-sphere" and "outer-sphere" reorganizational energies. The $\Delta G^\ddagger_0(0)$ term takes into account changes in solvent orientation which are always important for electron-transfer reactions since there is a change in the charge of the reactants. The value of $\Delta G^\ddagger_1$, the "inner-sphere" reorganisational energy may be negligible if the electron is being transferred to a delocalised orbital but alternatively it may be
greater than $\Delta G^\ddagger_0$ if antibonding orbitals are involved. Balzani et al (28) have found $\Delta G^\ddagger(0)$ values of $\sim 3 - 5$ kcal/mol ($0.12 - 0.18$ ev) for transition metal bipyridyl complexes, whilst Wilkinson and Tsiamis (31) have used a $\Delta G^\ddagger(0)$ value of $0.16$ ev to describe the quenching of organic triplet states by Cr(hfac)$_3$ in benzene.

Wilkinson and Tsiamis (31) have discussed electron transfer to chromium(III) complexes which in terms of spin-statistical factors may be represented by:

\[
\begin{align*}
\frac{1}{2} k_d & \quad \leftarrow \quad 3(D^* + 4_A) \quad \rightarrow \quad \frac{1}{3} k_d \quad \leftarrow \quad \frac{1}{6} k_d \quad \rightarrow \quad k_d \\
6_k & \quad \rightarrow \quad 6(D^\ddagger + 4_A) \quad \rightarrow \quad 6_k \\
4_k & \quad \rightarrow \quad 4(D^\ddagger + 4_A) \quad \rightarrow \quad 4_k \\
2_k & \quad \rightarrow \quad 2(D^\ddagger + 4_A) \quad \rightarrow \quad 2_k
\end{align*}
\]

The overall quenching constant $k_q$, being given by the sum of the individual pathways

\[
k_q = 6_k + 4_k + 2_k
\]

A number of studies (65,66) have indicated the occurrence of rapid intersystem crossing between degenerate charge-transfer geminate radical pairs which is likely to be fast compared with the lifetime of such species.
As discussed in the previous two sections, electronically excited states are efficiently quenched by energy and by electron transfer. Most studies have been designed to determine the factors that influence the efficiency of each mechanism separately, but recently several studies have been explained in terms of competitive energy and electron transfer. Caldwell et al. (67) have explained their results in these terms when they studied the rate of quenching of a series of substituted triplet phenanthrenes by trans-β-methylstylene and trans-anethole. Ohno and Lichtin have concluded that for the quenching of triplet methylene blue by Cobalt(II) complexes (29) and Iron(II) complexes (30), that reversible electron transfer is not the only mechanism in operation. Wilkinson and Tsiamis have shown that the quenching of triplet states of organic compounds by Cr(hfac)$_3$ (31), and by Fe(hfac)$_3$ and Fe(tfac)$_3$ (49) are a result of energy and electron transfer. For Cr(hfac)$_3$ they were able to interpret these in terms of the kinetic scheme presented below:

\[
\begin{align*}
6k_e \rightarrow & 6(D^+ \cdot A^-) \\
6k_b & \rightarrow D + 4A
\end{align*}
\]

\[
\begin{align*}
4k_e \rightarrow & 4(D^+ \cdot A^-) \\
4k_b & \rightarrow D + 4A
\end{align*}
\]

\[
\begin{align*}
2k_e \rightarrow & 2(D^+ \cdot A^-) \\
2k_b & \rightarrow D + 2A^*
\end{align*}
\]
with the overall quenching constant being equal to the sum of the individual constants ie:

$$k_q = k_{q1} + k_{q2} + k_{q3}$$  \[1.96\]

The rate constants for the single transfer steps, $k_{q1}$ and $k_{q2}$ are given by equation 1.87 and 1.38 respectively, whilst quenching proceeding via the quartet exciplex is solved by application of the steady state approximation and equals:

$$k_q = \frac{1/k_d}{1 + \frac{k_{en}}{k_d} + \frac{k_{el}k_{bt}}{k_d(k_{en} + k_d)}}$$  \[1.97\]

By trial and error substitution of the appropriate terms into the above equations, Wilkinson and Tsiamis were able to fit rate constants in good agreement with those found experimentally.
1.5 Diffusion Control of Reactions

For a collisional process, the maximum rate at which it may take place is governed by the diffusion properties of the species concerned. Smoluchowski (68) developed a theory of diffusion-controlled reactions, based on classical laws of diffusion, for the rate of coagulation of colloidal particles. He obtained the time-dependent rate of diffusion as being:

\[
k(t) = 4\pi N r_{DA} D_{DA} \left( 1 + \frac{r_{DA}}{(\pi D_{DA} t)^{\frac{1}{2}}} \right)
\]

where \( r_{DA} \) and \( D_{DA} \) represent the sum of the radii \( (r_{DA} = r_D + r_A) \) and the diffusion coefficients \( (D_{DA} = D_D + D_A) \) of species \( D \) and \( A \) respectively.

Smoluchowski's equation was applied to the fluorescence quenching of dye solutions by Sveshnikoff (69), who reasoned that if a fraction \( P \) of the total number of collisions are effective in quenching, then the right hand side of equation 1.98 should contain the factor \( P \) giving:

\[
k(t) = 4\pi N r_{DA} D_{DA} P \left( 1 + \frac{r_{DA}}{(\pi D_{DA} t)^{\frac{1}{2}}} \right)
\]

The time-dependent expression in brackets above is important for short lived species and corresponds to initial transient quenching caused by the nearest neighbor being a quenching molecule. Sveshnikoff (69) obtained a complex expression to describe
this transient diffusion effect, but Umberger and LaMer (70) showed that if quenching is less than 50% then equation 1.99 may be replaced by:

\[ k = 4\pi N A D_{DA} \left[ 1 + \frac{r_{DA}}{D_{DA} \tau_{o}} \right] \]  

where \( \tau_{D} \) is the lifetime of the donor, thus giving a more useful expression for the photochemist. Equation 1.100 has been further modified by Yguerabide, Dillon and Burton (71) who suggested that the transient term should be modified to give \( (2D_{DA} \tau_{o}^{1/4}) \).

In the case of triplet excited states, long lived (>10^-7 s) species are being dealt with and hence the transient term becomes negligible. Setting \( P = 1 \), equation 1.100 reduces to:

\[ k = 4\pi N r_{DA} D_{DA} \] (P = 1)  

Thus, in order to obtain values for the two variables in equation 1.101, \( D_{DA} \) and \( r_{DA} \) it is necessary to either obtain measurements of them or be able to calculate them with some degree of certainty.

Due to the lack of experimental diffusion coefficients in the literature, it has been necessary to calculate values for \( D_{D} \) and \( D_{A} \) hence \( D_{DA} \) by application of the Stokes - Einstein relationship, whose derivation will now be discussed.

Sutherland (72) and Einstein (73) treated diffusion as being the balance between a driving force and a resistance to flow
which results in a constant average diffusion velocity. They showed independently that the diffusion coefficient, $D$, of a binary system may be represented by:

$$D = \frac{kT}{\xi}$$  \hspace{1cm} (1.102)

where $k$ is the Boltzmann constant, $T$ is absolute temperature and $\xi$ is the viscous resistance per molecule. From classical hydrodynamics, Stokes (74) was able to show that the force acting on a spherical particle of radius $r$ moving in a continuous medium of viscosity $\eta$ is given by:

$$\xi = 6\pi\eta r \left( \frac{1 + 2\eta/\beta r}{1 + 3\eta/\beta r} \right)$$  \hspace{1cm} (1.103)

$\beta$ being the coefficient of sliding friction between the diffusing particle and its surrounding. Application of boundary conditions gives:

$$\beta = 0 \hspace{0.5cm} \xi = 4\pi\eta r$$  \hspace{1cm} (1.104)

$$\beta = \infty \hspace{0.5cm} \xi = 6\pi\eta r$$  \hspace{1cm} (1.105)

When the binary system consists of a large solute molecule moving in a solvent of smaller molecules then Sutherland (72) saw the movement proceeding with 'minimum slip' and equation 1.105 being applicable. Substitution of equation 1.105 into 1.102 yields:

$$D = D_{SE} = \frac{kT}{6\pi\eta r} \hspace{0.5cm} (\beta = \infty)$$  \hspace{1cm} (1.106)
which is known as the Stokes-Einstein equation. When the reverse situation arises and solute is smaller than the solvent, 'total slip' occurs, where the solute molecules move in the free spaces between the solvent molecules and thus equation 1.104 should now be used, giving:

\[ D = \frac{kT}{4\pi \eta r} \quad (\beta = 0) \]  

1.107

since \( D_{DA} = D_D + D_A \), then for species of radii \( r_D \) and \( r_A \) equation 1.106 gives:

\[ D_{DA} = \frac{kT}{6\pi \eta} \left[ \frac{1}{r_D} + \frac{1}{r_A} \right] \]  

1.108

and substitution of equation 1.108 into 1.101 yields:

\[ k_{\text{diff}} = \frac{8RT}{3\eta} 2^{1/4} \left[ 2 + \frac{r_D}{r_A} + \frac{r_A}{r_D} \right] \]  

1.109

which reduces to:

\[ k_{\text{diff}} = \frac{8RT}{3\eta} \]  

1.110

when \( r_D = r_A = r \). Similarly equation 1.107 gives:

\[ k_{\text{diff}} = \frac{8RT}{2\eta} \]  

1.111

Equations 1.110 and 1.111 are commonly known as the Debye and the modified Debye equations, respectively.
The two unknowns in the Stokes-Einstein equation (1.106) are the viscosity of the solvent, which may be found in standard texts (75) and the radius of the solute. Gorrell and Dubois (76) have advocated the use of LeBas volume increments (77) in order to calculate molar volumes, of organic hydrocarbons quenched by Biacetyl, and thus radii. Schuh and Fischer (79) have also employed the method of LeBas to calculate diffusion coefficients of t-Butyl radicals in a number of solvents. Edward (79) has reviewed the methods of calculating molar volumes and found that the method of LeBas gives radii in reasonable agreement with those calculated from van der Waals volumes. However, Ihnat and Goring (80) have questioned the use of van der Waals volumes and concluded that molar volumes give a better measure of the radius of the diffusing entity.

Therefore molecular radii may be calculated from LeBas volumes. A number of volume relationships have been proposed but are all described by the general formulae:

\[ r = \left( \frac{3VX}{4\pi N} \right)^{1/3} \]

where \( X \) represents the space filling factor. Gorrell and Dubois (76) have advocated the use of \( X = 0.53 \) for an orderly packed cubic array. Schuh and Fischer (78) assume close packed spheres, \( X = 0.74 \), whilst Spernol and Wirtz (84) have used both \( X = 0.74 \) and \( X = 1.0 \).

The Debye and the modified Debye equations have found widespread use in calculating the maximum rate of energy transfer. Birks et al (81) found that the rate of excimer formation of pyrene was in good agreement with that predicted by equation 1.110 whilst
Dubois and Wilkinson (82) showed that the rate of energy transfer between benzene and biacetyl in n-hexane was predicted by equation 1.111.

Balzani et al (46) and Wilkinson et al (47,48) have advocated the use of equation 1.110 in order to predict the rate of diffusion of organic and coordination compounds in benzene. They have used spin statistical factors (see Sec. 1.3.4) and transmission coefficients (see Sec.1.4.1) which analogous to the $P$ factor used in equation 1.101 in order to explain their experimental quenching rate constants. Alwatter et al (83) discuss a number of systems which have been shown to obey either equation 1.110 or 1.111.

There are also a number of cases which are not adequately described by either the Debye or the modified Debye equations; or by their corresponding Stoke-Einstein relationships. Gorrell and Dubois (76) measured the diffusion coefficients of a number of organic molecules in n-hexadecane and found that neither equations 1.106 or 1.107 were applicable. This was hardly surprising since the Debye equations are based on spherical molecules and n-hexadecane is anything but spherical. They were, however, able to interpret their results by introducing a microfriction factor, $f_t$ into the denominator of equation 1.107 (equation 1.107 being used in preference of 1.106 since $r_{solvent} > r_{solute}$).

The microfriction of translation was first advocated by Spernol and Wirtz (84) and Gierer and Wirtz (85) in order to fit Stokes-Einstein diffusion coefficients to those obtained experimentally. This theoretically takes into account the migration of the solute molecule into holes of the solvent (51), which is assumed to take
place to a limited extent, and also considers the finite thickness of the solvent layers which flow round a moving solute molecule.

Spernol and Wirtz based their measurements of $f_t$ on equation 1.106 giving:

$$D = \frac{kT}{6\pi\eta r f_t}$$  \hspace{1cm} 1.113

and found that for the 137 binary systems studied (in 25 different solvents) the best fit was described by:

$$f_t = 0.16 + 0.4 \frac{r}{r_L}$$  \hspace{1cm} 1.114

where $r$ and $r_L$ are the radii of the solute and solvent respectively.

Gierer and Wirtz treated the problem theoretically and obtained the expression:

$$f_t = \left[ \frac{1.5r_L}{r} + \frac{1}{(1 + \frac{r_L}{r})} \right]^{-1}$$  \hspace{1cm} 1.115

which simplifies to:

$$f_t = 0.19 + 0.31 \frac{r}{r_L}$$  \hspace{1cm} 1.116

when $r = r_L$; this being in reasonable agreement with the empirical value of $f_t$ (equation 1.114)) previously obtained. Thus $f_t$'s may be
calculated from equation 1.114, \( D \)'s from equation 1.113 and \( k_{\text{diff}} \) from equation 1.101.

The treatment of Spernol and Wirtz has been applied to the results of many workers. Alwatter et al (83) have tabulated measured diffusion coefficients of a number of molecules in cyclohexane and have shown that the ratio \( \frac{D}{D_{SE}} \) (i.e. \( \frac{1}{f} \)) is in good agreement with that calculated from equation 1.114. Costa et al (86) have also successfully used \( f \)'s to correct calculated diffusion coefficient to those found experimentally for benzyl-1-pyrenoate in paraffin/heptane mixtures. Saltiel et al (87) studied the rate of triplet energy transfer from indeno (2,1-a) indene to azulene in a number solvents. By employing microfriction factors to correct diffusion coefficients in non-hydroxylic solvents, they were able to show that energy transfer was fully diffusion controlled. Schuh and Fischer (78) have reviewed a number of methods of calculating diffusion coefficients and concluded that in low viscosity, non-associating solvents, the correction of the Stokes-Einstein relationship by that of Spernol and Wirtz seems to work best for t-Butyl radicals.
1.6 Quenching of Electronically Excited Triplet States by Transition Metal Complexes

1.6.1 Introduction

The quenching of triplet state organic molecules by transition metal ions in fluid solution was first investigated by Porter and Wright (24), and Linschitz and Sarkanen (88) using flash photolysis. They found that paramagnetic ions quenched triplet naphthalene with bimolecular rate constants in the range $10^{-10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ whilst diamagnetic ions such as Zn$^{2+}$ proved to be inefficient quenchers. From these results, catalysed intersystem crossing was proposed to be the quenching mechanism in operation, but no correlation was found to exist between the quenching constant of the ion and its magnetic moment (e.g. Mn$^{2+}$ with a magnetic moment of 5.92BM is an inefficient quencher).

Banfield and Husain (89) studied the quenching of triplet state acridine by transition metal ions and found that quenching was only efficient when the electronic energy level of the acceptor was below that of the donor. These results therefore imply that energy transfer is an important quenching mechanism. Numerous other studies have been carried out in this field and they have been reviewed by several authors (90-93).

1.6.2 Direct Evidence for Electronic Energy Transfer

Electronic energy transfer from an excited donor molecule to a ground state acceptor molecule may be represented by:

$$D^* + A \rightarrow D + A^*$$ 1.117
and therefore the most direct way of inferring energy transfer is to monitor the sensitized emission, or transient absorption of the acceptor. Unfortunately most electronically excited states of transition metal complexes have very short lifetimes (94), thus making observations rather difficult. However, there are a limited number of chromium(III) complexes (95) and Ruthenium(II) complexes (96) which exhibit sensitized emission at room temperature, thus providing direct evidence of electronic energy transfer.

Binet et al (97) were the first workers to report the sensitized luminescence of transition metal complexes when they studied the quenching of triplet benzil at -113°C by \([\text{Cr(NCS)}_6]\)^3-, \([\text{Cr(CN)}_6]\)^3-, [Cr(acac)] and [Cr(en)]^3+; the benzil phosphorescence being replaced by emission from the \(2E_g\) state of the Cr(III) complexes. On freezing the solutions the donor phosphorescence was almost restored at the expense of the metal complex emission, indicating a collisional mechanism. Ohno and Kato (98) reported similar results when they studied the quenching of triplet benzil and erythrosine by similar Cr(III) complexes at -72°C.

Adamson et al (99) found that the quenching of biacetyl phosphorescence by the complex, \(\text{Cr(NH}_3)_5\text{(NCS)}^2+\), lead to the latters aquation, which they proposed to occur via energy transfer to the \(4T_{2g}\) state. Balzani et al (100) also studied biacetyl, which was found to sensitize \([\text{Cr(en)}_3]^3+\). Farmilo and Wilkinson (101) have also reported that \([\text{Cr(en)}_3]^3+\) may be sensitized by energy transfer from triplet acridine in DMSO at room temperature. The phenomenon of sensitized emission has been used by Bolletta et al (102) to investigate the intersystem crossing efficiencies of \([\text{Cr(en)}_3]^3+\), \([\text{Cr(bipy)}_3]^3+\) and \([\text{Cr(CN)}_6]^3-\) in \(\text{H}_2\text{O}\) and for DMSO at room
temperature. Gandolfi et al. (103) have shown that the phosphorescence emission of \( ^{2}E_g \) Cr(bipy)\(_3\)\(^{3+} \) is quenched by a series of Cobalt(III) complex ions in 0.1M \( H_2SO_4 \) aqueous solution and their results have been interpreted in terms of electronic energy transfer.

However, for the majority of systems studied, no emission is detected and therefore electronic energy transfer must be an inferred mechanism. One of the most convenient ways of studying this is to measure the bimolecular quenching constants for a single acceptor quenching a homogeneous family of donors (or vice versa) and correlating the results with the available electronic energy levels in the acceptor.

1.6.3 Correlation of Rate Constants with Electronic Energy Levels in the Quencher

As indicated in the introduction to this thesis, the quenching efficiency of transition metal complexes will be expected to depend upon the nature of the metal ion, the type and structure of the ligands and the nature of the solvent. As previously discussed in this chapter (Sec. 1.6.1), the results of Linschitz and Sarkanen (88) and Banfield and Hussain (89) demonstrate that for efficient energy transfer to take place, the quencher must possess acceptor states whose energy are below that of the excited triplet state donors.

The first work carried out to demonstrate that a correlation exists between the rate of energy transfer and the triplet energy of donors was by Adamczyk and Wilkinson (104) when they studied the quenching of several triplet states by a series of diamagnetic Ni(II) Schiff-base complexes and their free ligands. They plotted the
bimolecular rate constant \( k_q \) versus \( E_T \) (the energy of the triplet donor) and were able to distinguish between energy transfer to localized ligand states and to the ligand field states. The free ligands efficiently quenched high energy triplet donors since the free ligands possess at triplet state at \( \approx 20,000 \text{cm}^{-1} \), but the Ni(II) complexes of these ligands were found to quench methylene blue at \( 12,000 \text{cm}^{-1} \) by energy transfer to ligand field states. A drop off in quenching efficiency below methylene blue was not observed since this was outside the range of triplet energies employed by those workers (the complexes are known to have ligand field states at \( \approx 8,500 \text{cm}^{-1} \) (105,107)).

Allsopp and Wilkinson (108) studied the quenching efficiency of Palladium(II) Schiff-base complexes and found, as they had expected, that the quenching constant dropped off rapidly below the lowest excited state of the complex at \( \approx 11,500 \text{cm}^{-1} \). The quenching constants for similar complexes of Ni(II), Pd(II) and Pt(II) have been obtained by Marshall and Wilkinson (109,110).

Since quenching constants fall rapidly for endoergonic energy transfer, this phenomenon may be employed to calculate the energy of otherwise unobservable spectroscopic states. Fry et al (111) found that anthracene \( (E_T = 14,700 \text{cm}^{-1}) \) is quenched by Ferrocene at a near diffusion controlled rate of \( 4.4 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1} \). Herkstroeter (112) and Farmilo and Wilkinson (113) extended their studies to include low energy donors which they found to be inefficiently quenched. Due to rapid fall in rate constant below anthracene, it was proposed that the lowest triplet state of ferrocene is situated at \( \approx 14,000 \text{cm}^{-1} \) which is in agreement with theoretical calculations (114,115).
One particular series of transition metal complexes that have received a great deal of attention are acetylacetonates (or \(\beta\)-diketonates). Due to their ease of synthesis, wide range of available derivatives and spectroscopically well characterized nature they have provided the experimentalist with much research material. Wilkinson and Farmilo (116) studied the quenching of numerous organic triplet states by \(\text{Al(acac)}_3\), \(\text{Ru(acac)}_3\), \(\text{Fe(acac)}_3\) and \(\text{Fe(dpm)}_3\), (acac- and dpm being the abbreviations for acetylacetonate and dipivaloylmethane, respectively), in benzene, and a \(k_q\) vs \(E_T\) plot of their results is given in Fig. 1.11. These results illustrate some important features exhibited by transition metal complexes. Firstly, in the case of \(\text{Al(acac)}_3\), where the lowest acceptor state is the \(3(\pi, \pi^*)\) state of the ligand, energy transfer would not be expected to occur to low energy triplet donors and was not observed, thus illustrating the importance of the lowest excited state. Secondly, from the \(k_q\) vs \(E_T\) plot of \(\text{Fe(acac)}_3\) and \(\text{Fe(dpm)}_3\) it can be seen that there are two regions which the quenching efficiency of the complex rises rapidly. Therefore energy transfer is occurring to two different states of different multiplicity; the rise at \(\approx 10,000\,\text{cm}^{-1}\) being associated with the \(4T_{1g}\) and \(4T_{2g}\) states at \(9,790\,\text{cm}^{-1}\) and \(13,330\,\text{cm}^{-1}\) respectively, whilst the rise at \(\approx 16,000\,\text{cm}^{-1}\) is thought to be due to energy transfer to the sextet charge transfer state \((6\text{CT})\) whose maxima is observed at \(23,000\,\text{cm}^{-1}\), with a \(v_{0.05}\) value of \(18,100\,\text{cm}^{-1}\). Both quenchers exhibit these features, however, energy transfer to \(\text{Fe(dpm)}_3\) is less efficient than that to \(\text{Fe(acac)}_3\). Since orbital overlap between the donor and acceptor is required for efficient energy transfer the tertiary butyl groups of the \(\text{Cr(dpm)}_3\) complex may be seen to provide steric hinderance.

The final important conclusion of these results concerns the quenching efficiency of \(\text{Ru(acac)}_3\). \(\text{Ru(acac)}_3\) which is a second
FIG 1.11 LOG(KQ) VS DONOR ENERGY FOR AL(ACAC)_3, RU(ACAC)_3, FE(ACAC)_3 & FE(DPM)_3

ENERGY (1000 CM⁻¹)

LOG(KQ)

AL(ACAC)_3

RU(ACAC)_3

FE(ACAC)_3

FE(DPM)_3

4^T_{1g}

4^T_{2g}

CT(Ru)

CT(Fe)

3_(π,π*)
row transition metal complex has a larger $10D_{q}$ value (ligand field splitting parameter) than Fe(acac)$_3$ and therefore its lowest excited state will consequently be at higher energy. The lowest state being a doublet charge transfer ($^{2}$CT) lying at $19,800\text{cm}^{-1}$ with at $\nu_{0.05}$ (5% of maximum band intensity to the red) of $=17,000\text{cm}^{-1}$ which correlates well with the observed reduction of quenching constant occurring in the region of 16-17,000cm$^{-1}$.

Marshall (117) extended the study of the quenching efficiencies of first row transition metal acetylacetonates by studying Cr(acac)$_3$, Co(acac)$_3$, V(acac)$_3$ and Mn(acac)$_3$. He found that the later three complexes exhibited the same unique feature, that quenching efficiency reached a minima for those donors whose triplet energies lie between the available spectroscopic states of the quencher.

Wilkinson and Chapple (118) have studied the quenching of triplet donors by Cr(acac)$_3$ and Cr(hfac)$_3$ in 95% ethanol. They found that for Cr(acac)$_3$, quenching occurs via a diffusion controlled mechanism, once again illustrating the importance of spin statistical factors. Cr(hfac)$_3$ quenched the triplet donors at a less efficient rate and these results were explained in terms of a reduction in number of C-H vibrations, as compared with Cr(acac)$_3$, which reduced the rate of energy transfer between the encounter complexes $^n(D^\pi\cdot\cdotA) \rightarrow ^n(D\cdot\cdotA^\pi)$.

1.6.4 Application of a Classical Treatment of Energy Transfer

As outlined in Sec. 1.4.1., Balzani et al (46) have developed a classical treatment of vertical and "non-vertical" energy transfer
processes, the application of which will be discussed in terms of the growing wealth of experimental data.

Herkstroeter and Hammond (119) have studied the quenching of aromatic triplets by cis- and trans-stilbene and their results are presented in Fig. 1.12. From the plot of \( k_q \) vs \( E_T \) it may be observed that a larger non-linear range of the plot is covered by the cis-isomer than for the trans-isomer, thus confirming the fact that the isomers have been considered as examples of "non-vertical" and "vertical" acceptors, respectively. Balzani et al (46) have fitted the best theoretical line through these experimental points (solid line in Fig. 1.12) using equations 1.66 and 1.62, and \( k^0_{en} = 1 \times 10^{10} \text{s}^{-1} \), \( \Delta G^+(0) = 1,000 \text{cm}^{-1} \) and \( E^{oo}(*A,A) = 16,900 \text{cm}^{-1} \) for the cis-isomers, and \( k^0_{en} = 1 \times 10^{10} \text{s}^{-1} \), \( \Delta G^+(0) = 500 \text{cm}^{-1} \) and \( E^{oo}(*A,A) = 17,000 \text{cm}^{-1} \) for the trans-isomer.

Balzani et al (120) have extended the studies of Waseestain and Hammond (121) and Wilkinson and Farmilo (101) into the energy transfer efficiencies of Cr(III) complexes to quench naphthalene and acridine (in ethanol/water mixtures), respectively, by studying anthracene, the results of these studies being presented in Table 1.3. From equations 1.56 and 1.65, the preexponential factors, \( k^0_{en} \) (which are equal to \( k_{en} \times kT/h \), where \( kT/h \) is the universal frequency of the transition state theory and \( k_{en} \) is the transmission coefficient, that may be thought of as the product of nuclear and electronic factors (see Sec. 1.41)), are also listed in Table 1.3. Balzani et al have argued that for energy transfer to the non-distorted \( 2E_g \), \( \Delta G^+(0) \) is practically zero and \( k_q \) is governed by \( k^0_{en} \) values, which are a function of the electronic interaction energy between the initial and
FIG 1.12 LOG(KQ) VS DONOR ENERGY FOR CIS- AND TRANS-STILBENE
### TABLE 1.3 Electronic Energy Transfer Quenching of Aromatic Triplets by Cr(III) Complexes (ref 120)

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>$E(2E_g)_{cm}^{-1}$</th>
<th>$\beta$</th>
<th>$k_q$ dm$^3$mol$^{-1}$s$^{-1}$</th>
<th>$k_q^0$ s$^{-1}$</th>
<th>$k_{en}^o$ s$^{-1}$</th>
<th>$k_{en}$ dm$^3$mol$^{-1}$s$^{-1}$</th>
<th>$k_{en}^o$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Cr(NH$_3$)$_6$$^{3+}$</td>
<td>15120</td>
<td>0.784</td>
<td>-</td>
<td>-</td>
<td>8.0 x 10$^6$</td>
<td>9.4 x 10$^6$</td>
<td>-</td>
</tr>
<tr>
<td>(2) Cr(en)$_3$$^{3+}$</td>
<td>14975</td>
<td>0.777</td>
<td>6.2 x 10$^7$</td>
<td>7.5 x 10$^7$</td>
<td>1.0 x 10$^7$</td>
<td>1.2 x 10$^7$</td>
<td>1.1 x 10$^7$</td>
</tr>
<tr>
<td>(3) Cr(NH$_3$)$_5$Br$^{2+}$</td>
<td>14840</td>
<td>0.770</td>
<td>-</td>
<td>-</td>
<td>7.0 x 10$^7$</td>
<td>8.5 x 10$^7$</td>
<td>-</td>
</tr>
<tr>
<td>(4) Cr(NH$_3$)$_5$Cl$^{2+}$</td>
<td>14740</td>
<td>0.765</td>
<td>2.0 x 10$^8$</td>
<td>2.6 x 10$^9$</td>
<td>4.6 x 10$^7$</td>
<td>5.5 x 10$^7$</td>
<td>3.0 x 10$^7$</td>
</tr>
<tr>
<td>(5) C-Cr(en)$_3$Cl$_2$$^{3-}$</td>
<td>14420</td>
<td>0.748</td>
<td>2.0 x 10$^8$</td>
<td>2.6 x 10$^8$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(6) Cr(ox)$_3$$^{3-}$</td>
<td>14392</td>
<td>0.747</td>
<td>-</td>
<td>-</td>
<td>6.7 x 10$^7$</td>
<td>8.1 x 10$^7$</td>
<td>-</td>
</tr>
<tr>
<td>(7) Cr(urea)$_6$$^{3+}$</td>
<td>14240</td>
<td>0.739</td>
<td>5.6 x 10$^8$</td>
<td>8.7 x 10$^8$</td>
<td>-</td>
<td>-</td>
<td>3.4 x 10$^7$</td>
</tr>
<tr>
<td>(8) Cr(NH$_3$)$_2$(NCS)$_4$$^{3-}$</td>
<td>13330</td>
<td>0.691</td>
<td>1.3 x 10$^9$</td>
<td>1.3 x 10$^9$</td>
<td>1.2 x 10$^7$</td>
<td>3.0 x 10$^9$</td>
<td>5.6 x 10$^8$</td>
</tr>
<tr>
<td>(9) Cr(NCS)$_6$$^{3-}$</td>
<td>12850</td>
<td>0.667</td>
<td>-</td>
<td>-</td>
<td>1.6 x 10$^9$</td>
<td>6.2 x 10$^9$</td>
<td>-</td>
</tr>
<tr>
<td>(10) Cr(acac)$_3$</td>
<td>12840</td>
<td>0.666</td>
<td>-</td>
<td>-</td>
<td>1.3 x 10$^8$</td>
<td>1.5 x 10$^9$</td>
<td>1.3 x 10$^9$</td>
</tr>
<tr>
<td>(11) Cr(CN)$_6$$^{3-}$</td>
<td>12380</td>
<td>0.642</td>
<td>1.7 x 10$^8$</td>
<td>1.7 x 10$^8$</td>
<td>2.0 x 10$^9$</td>
<td>2.6 x 10$^8$</td>
<td>5.9 x 10$^7$</td>
</tr>
</tbody>
</table>
final states of the donor and acceptor orbitals. This argument has been further strengthened by the correlation, these workers found to exist between $k_{en}^o$ and nephelauxetic ratio $\beta_{55}$, which is a measure of the electronic delocalization (122) within the complex and will determine the amount of orbital overlap between the donor and acceptor.

Maestri and Sandrini (123) have measured the variations in the rate constants for the energy transfer quenching of ($^3$CT) in Ru(phen)$_2$(CN)$_2$ by a family of Cr(en)$_2$XY$^+$ complexes and these are given in Table 1.4. For exoergonic energy transfer to the $^2E_g$ state of the Cr(III) complexes, quenching constants lower than those predicted by Sandros's equation were obtained. Low $k_q$ values may be attributed to the free energy of activation ($\Delta G^+ = \Delta H^+$, since $\Delta S^+$ is assumed to be zero) and to the preexponential factor, $k_{en}^o$. If one assumes that $\Delta G^+$ is responsible, then $\Delta H^+$ values of 3,000 - 4,000 cm$^{-1}$ ($\Delta G^+ = \Delta H^+$) are required to explain the results rather than the experimentally observed activation enthalpies of 80 - 790 cm$^{-1}$ (see Table 1.4); these values being consistent with the fact that the excited state is not distorted. Therefore these results may be explained, like those of Balzani et al (120), in terms of the preexponential factor caused by a poor electronic interaction between the donor and acceptor. Once again a reasonable correlation between the $k_{en}^o$ and $\beta_{55}$ was found to exist.

Gandolfi et al (103) have studied the quenching of the phosphorescence emission of ($^2E_g$) Cr(bpy)$_3^{3+}$ by a series of sixteen Co(III) complexes, including geometric isomers. They have shown that the intrininc barrier, $\Delta G^+(0)$, to energy transfer is fairly high
TABLE 1.4

Electronic Energy Transfer Quenching of $^{3}$CTRU(phen)$_{2}$(CN)$_{2}$ by Cr(en)$_{2}$XY$^+$ Complexes (ref 103)

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>$E_{g}^{2}$/cm$^{-1}$</th>
<th>$\beta$</th>
<th>$\Delta G$/cm$^{-1}$</th>
<th>$k_{q}$/dm$^{-3}$/mol$^{-1}$s$^{-1}$</th>
<th>$k_{en}^{o}$/s$^{-1}$</th>
<th>$\Delta H^+$/cm$^{-1}$</th>
<th>$\Delta G^{o+}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) t-Cr(en)$<em>{2}$(NCS)$</em>{2}^+$</td>
<td>13,720</td>
<td>0.712</td>
<td>3520</td>
<td>$5.30 \times 10^8$</td>
<td>$7.30 \times 10^8$</td>
<td>790</td>
<td>3920</td>
</tr>
<tr>
<td>(2) t-Cr(en)$_{2}$NCSCI$^+$</td>
<td>14,020</td>
<td>0.727</td>
<td>3220</td>
<td>$4.15 \times 10^8$</td>
<td>$5.48 \times 10^8$</td>
<td>-</td>
<td>3680</td>
</tr>
<tr>
<td>(3) t-Cr(en)$<em>{2}$Cl$</em>{2}^+$</td>
<td>14,160</td>
<td>0.734</td>
<td>3080</td>
<td>$3.56 \times 10^8$</td>
<td>$4.64 \times 10^8$</td>
<td>640</td>
<td>3560</td>
</tr>
<tr>
<td>(4) t-Cr(en)$_{2}$ONOCl$^+$</td>
<td>14,430</td>
<td>0.748</td>
<td>2810</td>
<td>$1.92 \times 10^8$</td>
<td>$2.39 \times 10^8$</td>
<td>-</td>
<td>3400</td>
</tr>
<tr>
<td>(5) t-Cr(en)$<em>{2}$F$</em>{2}^+$</td>
<td>15,180</td>
<td>0.790</td>
<td>2060</td>
<td>$0.30 \times 10^8$</td>
<td>$0.36 \times 10^8$</td>
<td>80</td>
<td>3040</td>
</tr>
</tbody>
</table>
(950 – 2,290 cm$^{-1}$) due to the strong distortion of the Co(III)
acceptor states but this effect, is cancelled out by the large
exoergonic nature of the transition, leaving $k_{en}$ determining the
rate of quenching. It is of interest to note that these workers
found that the cis-isomers are better quenchers than the trans-isomers
which is in agreement with the earlier data of Bolletta et al (124).

Wilkinson and Tsiamis (47,48) have developed the theory of
Balzani et al (46) to deal with energy transfer to more than one
acceptor state (a review of these mechanistic pathways and their
associated kinetic expressions are given in Sec. 1.4). In their
first paper, Wilkinson and Tsiamis (47) measured the rate constants
for the quenching of thirteen triplet state donors by Cr(acac)$_3$ and
Cr(bzac)$_3$ (acac and bzac being the abbreviations for the ligands
pentan-2,4-dione and 1-phenylbutan-2,4-dione, respectively) in
benzene at room temperature using laser flash photolysis. Their
results are given in Table 1.5 and presented graphically in Fig. 1.13.
From the experimental evidence, electronic energy transfer to the
doublet ($^2E_g$, $^2T_{1g}$) and quartet ($^4T_{2g}$) states of the chromium
complexes was proposed, and once spin-statistical factors had been
introduced, almost diffusion-controlled quenching was observed in
the case of Cr(bzac)$_3$. The solid line in Fig. 1.13 represents the
best computer fit to the experimental data using equations 1.83,
1.84 and 1.66 (and expression 1.85), and Table 1.6 gives the values
of the parameters used. As expected the free energy of activation
required to produce the undistorted doublet states $^2D_{g}^*(0)$ is small
compared with that required to produce the distorted quartet state
($250 \text{ cm}^{-1} \text{ vs } 2,000 \text{ cm}^{-1}$). The increase in the preexponential factor
of the quartet state relative to that of the doublet is probably
TABLE 1.5
Rate Constants for the Quenching of Triplet Donors by Cr(III) β-diketonate Complexes

<table>
<thead>
<tr>
<th>DONOR</th>
<th>$E_T$</th>
<th>$\nu_{oo}$/1,000cm$^{-1}$</th>
<th>$k_q/10^9$ Cr(acac)$_3$</th>
<th>$k_q/10^9$ Cr(bzac)$_3$</th>
<th>$k_q/10^8$ Cr(dpm)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>2.43</td>
<td>3.10 ± 0.20</td>
<td>4.95 ± 0.20</td>
<td>8.9 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Triphenylene</td>
<td>23.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.2 ± 0.5</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>2.50 ± 0.15</td>
<td>4.56 ± 0.20</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>21.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.2 ± 0.4</td>
</tr>
<tr>
<td>2-Acetonapthione</td>
<td>20.6</td>
<td>1.80 ± 0.13</td>
<td>3.36 ± 0.14</td>
<td>3.8 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Chrysene</td>
<td>20.0</td>
<td>1.54 ± 0.09</td>
<td>2.65 ± 0.11</td>
<td>3.8 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>1.64 ± 0.10</td>
<td>2.30 ± 0.07</td>
<td>0.9 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>1,2,3,4 - DBA</td>
<td>17.8</td>
<td>1.22 ± 0.12</td>
<td>1.32 ± 0.07</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>1.34 ± 0.11</td>
<td>1.80 ± 0.11</td>
<td>0.80 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>1.28 ± 0.13</td>
<td>1.57 ± 0.09</td>
<td>0.75 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>1.25 ± 0.04</td>
<td>1.48 ± 0.05</td>
<td>0.75 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>Perylene</td>
<td>12.4</td>
<td>0.047 ± 0.01</td>
<td>0.23 ± 0.01</td>
<td>&lt;0.05</td>
<td></td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>&lt;0.002</td>
<td>-</td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>β-carotene</td>
<td>6.3</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.01</td>
<td></td>
</tr>
</tbody>
</table>

DBA - Abbreviation for Dibenzanthracene
FIG 1.13 LOG(KQ) VS DONOR ENERGY FOR CR(ACAC)₃, CR(BZAC)₃ & CR(DPM)₃

LOG(KQ)

CR(BZAC)₃

CR(ACAC)₃

CR(DPM)₃

ENERGY (1000 CM⁻¹)
### TABLE 1.6

Spectroscopic and Intrinsic Parameters for the Theoretical Fit of the Experimental Results (47,48)

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Cr(acac)$_3$</th>
<th>Cr(bzac)$_3$</th>
<th>Cr(dpm)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PARAMETER</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2E_g</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table><p>ightarrow ^4A_{2g}$, $\tilde{\nu}$/cm$^{-1}$ | 12,950       | 12,580       | 12,960       |
| $^4T_{2g}ightarrow ^4A_{2g}$, $\tilde{\nu}$/cm$^{-1}$ | 16,230       | 16,000       | 16,500       |
| $^2T_{2g}ightarrow ^4A_{2g}$, $\nu_{oo}$/cm$^{-1}$ | 19,200       | 18,116       | 19,180       |
| $k_d/10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 1.0          | 1.0          | 1.0          |
| $k_{-d}/10^{10}$ s$^{-1}$ | 1.2          | 1.2          | 1.2          |
| ($^2E_g$), $\Delta G^+(0)/$cm$^{-1}$ | 250 ± 150    | 250 ± 150    | 250 ± 150    |
| ($^4T_{2g}$), $\Delta G^+(0)/$cm$^{-1}$ | 2,000        | 2,000        | 2,000        |
| ($^2T_{2g}$), $\Delta G^+(0)/$cm$^{-1}$ | -            | -            | 250 ± 150    |
| ($^2E_g$ $^2T_{1g}$) | $3.85 \times 10^{10}$ | $1.46 \times 10^{11}$ | $6.10 \times 10^{8}$ |
| ($^4T_{2g}$), $k_{en}$, s$^{-1}$ | $4.45 \times 10^{10}$ | $3.00 \times 10^{11}$ | $6.10 \times 10^{9}$ |
| ($^2E_g$ $^2T_{1g}$) | $6.3 \times 10^{-3}$ | $2.4 \times 10^{-2}$ | $1 \times 10^{-4}$ |
| ($^4T_{2g}$), $k_{en}$ | $7.3 \times 10^{-3}$ | $4.9 \times 10^{-2}$ | $1.0 \times 10^{-3}$ |
| ($^2T_{2g}$), $k_{en}$ | - | - | $6.4 \times 10^{-4}$ |</p>
caused by the expansion of the metal orbitals in the quartet state. The differences in $k_{en}^0$ between Cr(acac)$_3$ and Cr(bzac)$_3$ may be attributed to the increased delocalization effect of the phenyl groups as opposed to that of the methyl groups.

Wilkinson and Tsiamis (48) have also measured the quenching efficiency of Cr(dpm)$_3$ (dpm = 2,2,6,6 - tetramethylheptan - 3,5 - dione) in benzene (Table 1.5 and Fig. 1.13), and have attributed the reduction in quenching efficiency with respect to Cr(acac)$_3$ to be due to the steric effect of the tert-buty1 groups (c.f. the results of Wilkinson and Farmilo (116) for Fe(acac)$_3$/Fe(dpm)$_3$) and subsequent reduction of the preexponential factor. Energy transfer to the $^{2}E_g$ state proceeds at a non-diffusion controlled rate ($sk_d = 1.66 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$: $k_q$ Acridine = $7.5 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$) and the sudden rise in quenching efficiency at $= 20,000$ cm$^{-1}$ is attributed to energy transfer to the previously unobserved $^2T_{2g}$ state of Cr(dpm)$_3$. The solid line in Fig. 1.13 is the theoretical fit to the experimental data, where the quenching rate constant is given by:

$$k_q = \Sigma^2 k_q + 4k_q$$

and $\Sigma^2 k_q$ is obtained from expression 1.74 and $^4 k_q$ from 1.72, employing spin-statistical factors of $^1/6$ and $^1/3$, respectively.

The quenching of triplet states of organic compound by chromium(III) tris (1,1,5,5,5 - hexafluoropentan - 2,4-dionate), Cr(hfac)$_3$, in benzene solution has been studied by Wilkinson and Tsiamis (31). They found that donors with energies less than the lowest excited state of Cr(hfac)$_3$ were quenched with a reasonably high rate constant $= 6 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$ and for five donors a
quenching constant of $8.2 \times 10^9 \, \text{dm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ was obtained. They were able to interpret these results in terms of electronic energy and electron transfer using the mechanistic pathway presented in Sec. 1.4.4. Table 1.7 gives a comparison of the calculated rate constants for the quenching by $\text{Cr(hfac)}_3$ with those obtained experimentally.

The use of the classical approach to energy transfer, electron transfer and competitive energy and electron transfer has recently been reviewed by Balzani and Scandola (125), Kavarnos and Turro (126) and Wilkinson (127).
### TABLE 1.7
Comparison of Calculated and Experimental Rate Constants for Quenching by Cr(hfac)$_3$ in Benzene Solution

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$\Delta G_{el}^a$</th>
<th>$k_q$ Range</th>
<th>$k_q' 10^9$ Calcd,$^b$ $dm^3\text{ mol}^{-1}\text{s}^{-1}$</th>
<th>Calcd$^c$</th>
<th>Exptl $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>-0.18</td>
<td>3.7 - 5.5</td>
<td>4.3</td>
<td>4.52 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Triphenylene</td>
<td>-0.94</td>
<td>8.5 - 8.6</td>
<td>8.6</td>
<td>8.2 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-0.70</td>
<td>8.0 - 8.4</td>
<td>8.3</td>
<td>8.2 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>-0.46</td>
<td>4.8 - 8.2$^d$</td>
<td>7.3</td>
<td>5.0 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Chrysene</td>
<td>-0.73</td>
<td>8.1 - 8.4</td>
<td>8.3</td>
<td>8.2 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Coronene</td>
<td>-0.77</td>
<td>8.2 - 8.5</td>
<td>8.3</td>
<td>8.2 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>-0.52</td>
<td>6.8</td>
<td>8.6</td>
<td>8.2 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Acridine</td>
<td>+0.02</td>
<td>1.2 - 1.6</td>
<td>1.3</td>
<td>1.20 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>-0.33</td>
<td>3.8 - 6.9</td>
<td>5.7</td>
<td>4.50 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Perylene</td>
<td>-0.29</td>
<td>2.1</td>
<td>5.5</td>
<td>3.95 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Tetracene</td>
<td>-0.11</td>
<td>0.13 - 2.1</td>
<td>0.70</td>
<td>0.67 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Pentacene</td>
<td>-0.05</td>
<td>0.04 - 1.2</td>
<td>0.30</td>
<td>0.60 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>$\beta$-carotene</td>
<td>+0.01</td>
<td>0.01 - 0.6</td>
<td>0.10</td>
<td>0.57 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Calculated using $E_{Q}^{red} = -0.40$ ev

$^b$Range assuming uncertainty of ± 0.1 ev in $\Delta G_{el}^e$

$^c$Rate constant calculated using the $\Delta G_{el}^e$ value in column 2

$^d$Assuming uncertainty of ± 0.2 ev in $\Delta G_{el}^e$.  

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CHAPTER I

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CHAPTER II

EXPERIMENTAL

2.1 Introduction

The study of fast reactions presents the experimentalist with two major difficulties. Firstly, it is necessary to initiate a reaction in a shorter time than the duration of that reaction and secondly, in order to obtain kinetic information one parameter of the system must be followed after initiation.

Many methods have been developed for the study of chemical reactions, the two commonest probably being rapid heating and mixing. Both of these methods are limited if the rate of reaction to be studied is greater than the rates of thermal conduction and diffusion respectively, since these processes would therefore become the rate determining step. Electrical discharge, temperature jump methods have resulted in initiation taking place in the microsecond time scale but for faster reactions the temperature gradient between the walls and the centre of the vessel will become important. However, the most powerful and versatile method of initiation has been found to be that of absorption of radiation.

In 1949, Norrish and Porter (1) developed the technique known as flash photolysis for which they jointly shared the Nobel Prize for Chemistry in 1967. The technique was originally designed for the study of free radicals but was soon to be used for the study of excited triplet states and subsequently singlet states.
The excited states were produced by means of a short duration, high intensity flash lamp (photoflash) and the transient produced was subsequently monitored with a lower intensity lamp (spectroflash) or even a continuous lamp.

Two experimental arrangements are possible:

1. Flash spectroscopy - where measurements are made in the frequency domain with a fixed delay between the two flash lamps yielding a spectrum.

2. Kinetic spectrophotometry - measurements made in the time domain using a fixed analysing frequency to give kinetic information, the latter being developed by Davidson et al (2) in 1951.

There are two major restrictions with this conventional apparatus. Firstly, only transients with lifetimes greater than a few microseconds could be analysed due to the duration of the flash lamps. Secondly, due to the low power output of the lamps only a low concentration of excited state, typically $10^{-6}$ M, could be generated, thus limiting the system to the detection of only strongly absorbing species.

2.2 Development of Laser Flash Photolysis

In 1960 Maiman (3) observed that optical pumping of a ruby rod using a high intensity flash lamp resulted in stimulated emission in the form of a train of sharp pulses at 694.3nm. Two years later McClung and Hellworth (4) showed that it was possible to produce a single giant
pulse (<40ns) by using a kerr cell as a Q switch. A similar giant pulse was produced by Kaflas et al (5) when they used a solution of kryptocyanine in methanol.

The ruby laser wavelength of 694.3nm is of limited use to the photochemist since few organic molecules can be excited in this region. The production of the second harmonic of the ruby laser emission at 347.1nm was first observed by Franken et al (6) when the primary beam was passed through an orientated quartz crystal. The same phenomena with increased efficiency was later observed by Maker et al (7) using a potassium dihydrogen phosphate (KDP) crystal.

Thus, over a period of a couple of years a short duration light source (of total duration < 60ns) had become available whose energy was suitable for the study of excited state organic molecules.

By 1968, Porter and Topp (8) had incorporated a laser into a photolysis system thus making the direct measurement of many triplet states and some singlet states possible. The advantages of laser flash photolysis are given below.

1. The higher power output from the laser allows weakly absorbing species to be studied.

2. The well collimated nature of the laser beam allows the power to be used efficiently thus making it unnecessary to focus the beam even after it has passed through the frequency doubling crystal.
3. The monochromatic nature of the beam allows the specific excitation of a particular molecule in a mixture. This third 'advantage' has also proved to be a disadvantage in the cases where molecules such as naphthalenes do not absorb at the laser wavelength. Therefore, it has been necessary to employ sensitization techniques.

The time resolution has been further increased to the picosecond region (9) by the uses of mode locked lasers (10), thus allowing such processes as intersystem crossing, internal conversion and vibrational relaxation to be studied. An excellent review of the development of flash photolysis from the millisecond to the pico- and sub-picosecond time scale is given by Porter and West (11).

2.3 The Nano-second Laser Photolysis Apparatus

The system used throughout this work was designed by Adams (12) and has remained unchanged except for the recording system. The system has been described in great detail by a number of workers (13-15) and therefore only an outline will be given here.

It is possible to monitor absorbance changes in two ways, either colinearily to, or at right angles to, the incident beam. The method employed in this work is the right angled arrangement as shown schematically in Figure 2.1. A full description of the colinear system was given by Adams (12).

Since it is desirable to perform experiments at a constant temperature, a thermostated box was constructed which housed the laser
Fig 2.1 Schematic Diagram of the Laser System
head, frequency doubling crystal and the sample cell. This allowed experiments to be performed at 20±1°C and also obviated the problem of readjustment of the frequency doubling crystal whose output is highly temperature sensitive.

2.3.1 The Laser Head

The ruby laser was supplied by Laser Associates (Model 211A) and consists of a 16mm diameter ruby rod cut at 60° to the crystal axis from a single crystal giving a horizontal plane polarized output. Optical pumping is achieved by the use of a high intensity xenon flash tube (E.G. and G type FX-47) which is powered by a capacitor bank whose maximum potential is 2.5kV. The system was normally run at 2.1 - 2.2kV in order to prolong the lifetime of the flash tube. The ruby rod and the flash lamp are placed at the focal axes of the reflective elipically cross-sectioned cavity.

The ruby rod and flash tube are both encased in silica tubes, through which distilled and deionised water passes in order to prevent overheating and subsequent loss of laser action. The circulating water is in turn cooled by an external cooling system which maintains the water temperature at ~15°C.

The reflection from the front end of the rod and the front window which are parallel, is of the order of 6½% whilst the rear window is misaligned by approximately 3° stopping it from acting as a mirror. The laser cavity is completed by the totally internally reflecting, TIR, prism at the rear and the Q switch which is positioned between the prism and the rear window (see Figure 2.1).
2.3.2 The Q Switch

The phenomena of Q switching occurs when the quality factor, Q, of the laser cavity is rapidly restored after it has been spoilt (either by misalignment or by having a Q switch in the cavity), resulting in the formation of a single giant pulse. Q switching may be achieved mechanically with rotating mirrors, electro-optically with a pockel cell or as in this case by using a passive Q switch consisting of a cell containing a solution of an absorbing dye, which is placed between the end of the ruby rod and the TIR prism.

The dye absorbs the laser radiation and therefore increased optical pumping is required to overcome this lost radiation. When a population inversion is achieved, the laser begins to emit weakly but it is sufficient to bleach the dye (saturate the $S_0 \rightarrow S_1$ transition of the dye and the excited state does not absorb 694nm radiation), resulting in the restoration of the Q factor to the cavity, giving rise to a giant pulse. (Half height width ~20ns) of total energy ~2J.

The dye used was a weak (~$1.5 \times 10^{-6}$ mol dm$^{-3}$) solution of vanadyl phthalocyanine in nitrobenzene ($\varepsilon_{690}=2 \times 10^5$ mol$^{-1}$ dm$^{-3}$ cm$^{-1}$) which gave an absorbance of ~0.6 at the laser wavelength. This was found to be the optimum absorbance since lower absorbances gave rise to multiple lasing whilst anything higher completely inhibited lasing.

2.2.3 Second Harmonic Generation

The generation of the second harmonic of ruby radiation was first observed by Franken et al (6) when they passed the fundamental laser
beam through a birefringent crystal. The crystal was orientated in such a manner that the velocity of the fundamental beam is matched to that of the second harmonic in order to avoid destructive interference.

The second harmonic generator (SHG) used in this work consisted of an Ammonium Dihydrogen Phosphate (ADP) crystal supplied by Electro Optic Developments Ltd. which was placed on an adjustable mount from Laser Associates Ltd. The movement of the crystal in the horizontal and vertical planes was affected by the use of two micrometer screws.

The output from the ADP crystal is highly temperature dependent due to refractive index changes and adjustments of the vertical micrometer are required in order to obtain a constant level of output. The level of output as well as its alignment with respect to the position of the fibre optics in the cell holder was checked using a piece of photochromic film (a spiropyran in PMA) which underwent a colour change on the absorption of radiation. In practice, crystal alignment was only checked at the start of each experiment since the laser system was housed in a temperature controlled box.

The passage of the fundamental laser beam through the ADP crystal results in approximately 5% of the second harmonic (347.1nm) being generated, and it is therefore necessary to filter out the red light (694nm) in order to prevent thermal shock to the sample cell. This is achieved by using a copper sulphate solution which has 80% transmittance for the second harmonic but less than 2% transmittance for the red light. If any light passes through the photolysis cell, the 347nm component is removed by a biphenylene filter whilst the red light is absorbed by a second copper sulphate filter.
2.3.4 The Monitoring System

The transient species produced during photolysis were monitored by the change in absorbance as a function of time. The monitoring light which is derived from the laser cavity, is passed along a fibre optic to the photolysis cell holder where it enters perpendicularly to the incoming laser beam. The fibre optic is placed at the front of the photolysis cell in order to transverse the maximum concentration of transient species. If the fibre optic were to be positioned further back from the front of the cell, smaller transients (due to the Beer-Lambert Law) would be observed and the increased signal to noise ratio would be evident when kinetic analysis was performed.

The monitoring light which is not absorbed by the transient species is collected by a second fibre optic and transmitted to a high intensity Bausch and Lomb UV/visible monochromator. The monochromator grating covers the range 350-700nm and has adjustable slits (0-6mm). In order to obtain the highest transmission efficiency it is necessary to have the image of the entrance slit fill that of the exit slit. This is achieved by having an entrance to exit ratio of 1.78:1.

The light from the monochromator is passed to a RCA 931A photomultiplier which is powered by a Fluke (Model 412B) power supply, operating in the region 380-450v. The current generated by the photomultiplier is fed across a load resistor and the resulting voltage is passed via a high impedance Tektronix P6045 probe to the recording system.

In order to synchronise the time base of the recording device with that of the laser pulse, a fibre optic is placed at an angle to the first
copper sulphate filter (see Figure 2.1). The light from the fibre optic is passed to a photodiode whose voltage output triggers the time base of the recording system.

2.3.5 The Recording System

The signal outputted from the Tektronix P6045 probe is fed into the Datalab DL922 transient recorder. The inputted waveform is digitised by sampling the signal amplitude at regular time intervals using an 8-bit Analogue to Digital converter. Thus the signal is stored with an accuracy of 1 part in 256 \(2^8\). The DL922 is equipped with a number of time bases ranging from 0.1 ms per sweep, the shortest, to 4 sec the longest. Since short lived species are being investigated, the smallest time base was chosen which corresponds to \(\frac{1}{2048 \times 0.1 \text{ms}}\approx 48.8\,\text{ns per point.}\) The DL922 is normally used in the pre-trigger mode with single shot but other operational modes are described in the handbook (16).

The signal stored in the transient recorder is fed via an interface cable to a Datalab DL4000B unit which consists of a DL417 function module, a DL403B display module, a DL400 store module and a DL409 transient recorder interface, as well as several other modules (17).

A visual display of the digitised trace can be seen on a Hewlett Packard hp1340A oscilloscope. A hard copy of the trace may be obtained using a facit tape punch.

The features of the DL403 display controller include an automatic scaling facility, an output facility to a X-Y recorder, independent Y-shift for four channels and the ability to display both inputted and
stored signals. The DL417 module which controls the oscilloscope display has a cursor control which includes a scanning facility for movement within a particular channel and an index button for movement between channels. This module also contains expansion and intensify features as well as being able to execute the program stored in the DL400 memory using user definables (for greater details see Ref.18).

The DL4000B unit is connected via a RS232 interface to a visual display unit with a keyboard, which allows the DL400 (1K memory) store to be programmed. A hard copy of the VDU display may be obtained by using Commodore Tractor Printer 4022P.

Using this system it is now possible to transfer a signal from the transient recorder to the DL4000B unit, display it on an oscilloscope screen, subject it to arithmetic analysis and print out information about it in a matter of minutes, with the possibility of re-analysis if required.

2.4 Experimental Procedures

The experimental work carried out in this thesis is concerned with the measurement of pseudo first order decay constants and thus calculation of bimolecular quenching constants, for various donor/acceptor pairs in benzene as presented in Chapter 4. Quenching may be defined as any process that reduces the lifetime of the excited state and since molecular oxygen is an efficient quencher (see 1.3.4) it is necessary to exclude it from solution.
2.4.1 Degassing Technique

The method of degassing employed throughout this work was one of nitrogen flushing. This is achieved by using a benzene saturated stream of oxygen free nitrogen (saturated to avoid evaporation and hence a concentration effect) passed into the photolysis cell via a hypodermic needle, the cell being sealed with a suba seal. A second shorter needle was inserted into the cell in order to remove the expelled gases. Farmilo (13) showed that degassing for a period of 5 minutes reduced the residual oxygen content to <0.2% of its original value (1.45 x 10^{-3} mol dm^{-3}) by studying the effect of fluorescene lifetime. The first order rate constant associated with the residual oxygen was shown to be of the order of 10^4 s^{-1}, which is small compared with the quenching decay constants obtained. Since no actual nitrogen flow rate has been given, the experiments carried out by Farmilo using pyrene have been repeated in order to determine a nitrogen flashing time for this system.

A stock solution of pyrene of concentration 2.5 x 10^{-5} mol dm^{-3} was chosen in order to reduce the possibility of excimer formation which would lead to a reduction in fluorescence intensity. The fluorescence spectrum of pyrene was recorded on a Perkin-Elmer MPF-44B spectrofluorimeter using an exciting wavelength of 347nm (laser wavelength), giving a fluorescence maxima at 394nm (cf. Farmilo -396nm). Into the photolysis cell exactly 2ml of solution was placed and subjected to various degassing times.

<table>
<thead>
<tr>
<th>Degassing Time/Min.</th>
<th>Lifetime/ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>294±5</td>
</tr>
<tr>
<td>3</td>
<td>295±5</td>
</tr>
<tr>
<td>5</td>
<td>298±6</td>
</tr>
</tbody>
</table>
Absorption spectra were recorded on a Pye-Unicam SP8-250 double monochromator spectrophotometer before and after nitrogen flushing in order to ensure that there were no significant changes in concentration. As can be seen from the above results, maximum fluorescence lifetime is realised in 5-6 minutes, therefore, the oxygen level is sufficiently low after 5 minutes in order to allow quenching studies to be performed.

2.4.2 Experimental Technique

Stock solutions of the triplet donors were made using Fisons spectrograde benzene, from which aliquots were taken and diluted in volumetric flasks. In order to obtain sufficiently large transients it was found that the aliquots should be diluted in such a manner that they gave an absorbance in the range 0.8 - 1.2 at the laser wavelength in a 1cm path length cell. For some donors, namely pentacene, tetracene and β-carotene, it was found to be practically undesirable to work in this concentration range. Pentacene has a low solubility in benzene whilst both tetracene and β-carotene absorb strongly at their triplet monitoring wavelengths. Pentacene and tetracene also present another problem in that they are both easily photo-oxidised. It was therefore necessary to dissolve them in light protected volumetric flasks, containing deoxygenated benzene under an atmosphere of nitrogen.

Since perylene has a low triplet quantum yield as well as a low extinction coefficient at 347nm it was necessary to employ sensitization techniques using benzophenone. Naphthalene also has a low ground state absorbance at the laser excitation wavelength and again benzophenone was

<table>
<thead>
<tr>
<th>Degassing Time/Min.</th>
<th>Lifetime/ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>298±6</td>
</tr>
<tr>
<td>8</td>
<td>292±5</td>
</tr>
<tr>
<td>10</td>
<td>291±5</td>
</tr>
</tbody>
</table>
employed as a sensitizer. In order to observe triplet \( \beta \)-carotene it was necessary to sensitize with anthracene. This also allowed the concentration of \( \beta \)-carotene to be reduced which has a favourable effect since it exhibits a high ground state absorbance at the triplet monitoring wavelength which could lead to non-ideal behaviour.

Triplet-Triplet absorptions were monitored at, or close to, values given in the literature (19) and Table 2.1 lists triplet energy, monitoring wavelength and approximate concentration of the donors used.

Stock solutions of quenchers were made up in the same manner as that for the donors and solutions used for quenching studies consisted of a constant concentration of donor and a variable concentration of quencher.

The donors and especially the quenchers were found to be stable in benzene solution. Most donors did not exhibit any spectroscopic changes after 24 hours whilst the quenchers were found to be stable even after several weeks. However, quenching studies were always completed within 4 hours of the stock solutions being made.

In order to investigate the possibility of ground state interactions taking place between the donors and the acceptor, absorption spectra of the separate solutions as well as the mixture were recorded. Figure 2.2 illustrates a typical example of the additivity found between the donor and acceptor, in this case acridine and chromium (III) tris (3-Ethylpentan-2,4-dionate), Cr (3-Etacac), whilst Table 2.2 gives a listing of the absorption values obtained together with their associated error.
TABLE 2.1

Triplet Energy, T-T Monitoring Wavelength and Approximate Concentration of Various Donors

<table>
<thead>
<tr>
<th>DONOR</th>
<th>$E_T/1000 \text{ cm}^{-1}$</th>
<th>$\lambda_{TT}/\text{nm}$</th>
<th>$(D)/\text{mmol dm}^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>535</td>
<td>10.0</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>480</td>
<td>4.0</td>
</tr>
<tr>
<td>Naphthalene$^a$</td>
<td>21.3</td>
<td>415</td>
<td>5.0</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>425</td>
<td>1.0</td>
</tr>
<tr>
<td>Chrysene</td>
<td>20.0</td>
<td>560</td>
<td>5.0</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>485</td>
<td>0.06</td>
</tr>
<tr>
<td>1,2,5,6 - DBA $^*$</td>
<td>18.3</td>
<td>500</td>
<td>0.12</td>
</tr>
<tr>
<td>1,2,3,4 - DBA $^*$</td>
<td>17.8</td>
<td>455</td>
<td>0.30</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>415</td>
<td>0.50</td>
</tr>
<tr>
<td>1,2 - Benzantracene</td>
<td>16.5</td>
<td>490</td>
<td>0.30</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>440</td>
<td>0.15</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>425</td>
<td>0.30</td>
</tr>
<tr>
<td>1,5 - Dichloroanthracene</td>
<td>14.5</td>
<td>455</td>
<td>0.30</td>
</tr>
<tr>
<td>9,10 - Dibromoanthracene</td>
<td>14.1</td>
<td>425</td>
<td>0.30</td>
</tr>
<tr>
<td>Perylene$^a$</td>
<td>12.6</td>
<td>488</td>
<td>0.20</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>460</td>
<td>0.05</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>498</td>
<td>0.01</td>
</tr>
<tr>
<td>$\beta$-Carotene $^b$</td>
<td>6.3</td>
<td>520</td>
<td>0.30</td>
</tr>
</tbody>
</table>

$^a$ Sensitized with benzophenone

$^b$ Sensitized with anthracene

$^*$ DBA - Abbreviation for Dibenzanthracene
Fig 2.2

Absorption Spectra of Acridine, Cr(3-Etacac)₃

and Acridine / Cr(3-Etacac)₃
Table 2.2

Absorbance Values for Acridine, \( \text{Cr}(3\text{-Etacac})_3 \)
and Acridine / \( \text{Cr}(3\text{-Etacac})_3 \)

<table>
<thead>
<tr>
<th>Wavelength /nm</th>
<th>Acridine (a)</th>
<th>( \text{Cr}(3\text{-Etacac})_3 ) (b)</th>
<th>(a+b)</th>
<th>Acridine / ( \text{Cr}(3\text{-Etacac})_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>0.508</td>
<td>0.852</td>
<td>1.360</td>
<td>1.349</td>
</tr>
<tr>
<td>330</td>
<td>0.802</td>
<td>0.853</td>
<td>1.655</td>
<td>1.646</td>
</tr>
<tr>
<td>340</td>
<td>1.361</td>
<td>1.052</td>
<td>2.411</td>
<td>2.397</td>
</tr>
<tr>
<td>350</td>
<td>1.241</td>
<td>1.254</td>
<td>2.495</td>
<td>2.488</td>
</tr>
<tr>
<td>360</td>
<td>1.581</td>
<td>1.262</td>
<td>2.843</td>
<td>2.829</td>
</tr>
<tr>
<td>370</td>
<td>0.614</td>
<td>0.573</td>
<td>1.187</td>
<td>1.178</td>
</tr>
<tr>
<td>380</td>
<td>0.580</td>
<td>0.119</td>
<td>0.699</td>
<td>0.699</td>
</tr>
<tr>
<td>390</td>
<td>0.049</td>
<td>0.062</td>
<td>0.111</td>
<td>0.110</td>
</tr>
<tr>
<td>400</td>
<td>0.004</td>
<td>0.054</td>
<td>0.058</td>
<td>0.057</td>
</tr>
</tbody>
</table>
The possibility of ground state interactions taking place as a result of irradiation by the laser was also investigated by subjecting the quenching solutions to 20 laser pulses. No significant changes were observed and during actual quenching experiments the solutions were only subjected to 4 irradiations.

When the possibility of ground state interactions had been investigated it was necessary to look at the possibility of interactions occurring in the excited state. In this case an excited state absorption spectrum was obtained, firstly for the donor and secondly for the donor-quencher pair, by monitoring the triplet decay at a predetermined time after the laser flash varying the analysing wavelength. Figure 2.3 gives an excited state absorption spectra for anthracene and anthracene/Cr(3-Etacac)\(_3\). If the system is acting ideally (i.e. no interactions are occurring), then it would be expected that the ratio of absorbances donor: donor/acceptor to be constant over the region analysed. In the example cited, this was found to be so, and Table 2.3 lists the values obtained.

Therefore, before quenching constants were calculated with any degree of certainty it is important that the afore-mentioned spectroscopic checks were conducted to ensure that ideal quenching systems were being studied.

2.4.3 The Acceptors

The acceptors, or quenchers, used throughout this work were pseudo octahedral \(\delta\)-diketonate complexes of cobalt (III) and chromium (III) which may be represented by the general formulae given in Table 2.4. If we consider the case where \(M\) is equivalent to chromium (III) and \(R_1 = R_2 = R_3 = CH_3\), then IUPAC nomenclature would result in the complex
Fig 2·3

Triplet–Triplet Absorption Spectra of

Anthracene and Anthracene Cr(3-Etacac)₃
Table 2.3

T-T Absorbances for Anthracene and Anthracene / Cr(3-Etacac)$_3$

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Anthracene</th>
<th>Anthracene / Cr(3-Etacac)$_3$</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>0.75</td>
<td>0.64</td>
<td>1.17</td>
</tr>
<tr>
<td>425</td>
<td>0.91</td>
<td>0.77</td>
<td>1.18</td>
</tr>
<tr>
<td>430</td>
<td>0.89</td>
<td>0.74</td>
<td>1.20</td>
</tr>
<tr>
<td>435</td>
<td>0.58</td>
<td>0.50</td>
<td>1.16</td>
</tr>
<tr>
<td>440</td>
<td>0.34</td>
<td>0.28</td>
<td>1.21</td>
</tr>
<tr>
<td>445</td>
<td>0.23</td>
<td>0.19</td>
<td>1.21</td>
</tr>
<tr>
<td>450</td>
<td>0.135</td>
<td>0.12</td>
<td>1.21</td>
</tr>
<tr>
<td>455</td>
<td>0.115</td>
<td>0.09</td>
<td>1.27</td>
</tr>
<tr>
<td>460</td>
<td>0.080</td>
<td>0.06</td>
<td>1.33</td>
</tr>
<tr>
<td>465</td>
<td>0.080</td>
<td>0.06</td>
<td>1.33</td>
</tr>
<tr>
<td>470</td>
<td>0.095</td>
<td>0.075</td>
<td>1.26</td>
</tr>
<tr>
<td>475</td>
<td>0.095</td>
<td>0.075</td>
<td>1.26</td>
</tr>
<tr>
<td>480</td>
<td>0.090</td>
<td>0.070</td>
<td>1.28</td>
</tr>
</tbody>
</table>
being named chromium (III) tris (3-methylpentan-2,4-dionate). The other ligands together with the abbreviated names for the resulting complexes are also given in Table 2.4.

2.4.3.1 Preparation

The complexes used in this thesis were prepared by standard methods as indicated by the references given in Table 2.5. In all cases reagents of the highest quality were employed in order to eliminate unwanted by-products. Many of the ligands are commercially available except for formyl ketones. These diketones were synthesised by performing a claisen condensation (20), between methyl formate and the appropriate ketone in the presence of sodium hydride yielding the sodium salt of the diketone; the free ligand being liberated in the presence of the particular transition metal ion. Great care in the choice of solvent had to be exercised when dealing with ligands containing trifluoromethyl groups e.g. hexafluoropentan-2,4-dione, since hydrolytic solvents resulted in the formation of a hydrated ligand which was unreactive towards complexation. Solvents which were found to be useful include carbon tetrachloride and 2,2-dimethylpentane.

Once the crude complex was obtained the first stage of purification was the same in all cases. The complex was dissolved in a minimum volume of benzene and passed through a chromatographic column packed with activated alumina (+100g), using benzene as the eluting solvent. This had the desired effect of removing unreacted inorganic and organic fractions as well as possible by-products. Purification of individual complexes varied from recrystallisation in mixed solvent systems to vacuum sublimate (detailed information may be found in the references cited in Table 2.5).
<table>
<thead>
<tr>
<th>METAL</th>
<th>R$_1$</th>
<th>R$_2$</th>
<th>R$_3$</th>
<th>LIGAND NAME</th>
<th>COMPLEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(III)</td>
<td>CH$_3$</td>
<td>H</td>
<td>CH$_3$</td>
<td>Pentan-2,4-dione</td>
<td>Co(acac)$_3$</td>
</tr>
<tr>
<td>Co(III)</td>
<td>CH$_3$</td>
<td>H</td>
<td>CF$_3$</td>
<td>1,1,1-Trifluoropentan-2,4-dione</td>
<td>Co(tfac)$_3$</td>
</tr>
<tr>
<td>Co(III)</td>
<td>CH$_3$</td>
<td>H</td>
<td>Ø</td>
<td>1-Phenylbutan-1,3-dione</td>
<td>Co(bzac)$_3$</td>
</tr>
<tr>
<td>Co(III)</td>
<td>CF$_3$</td>
<td>H</td>
<td>CF$_3$</td>
<td>1,1,1,5,5,5-Hexafluoropentan-2,4-dione</td>
<td>Co(hfac)$_3$</td>
</tr>
<tr>
<td>Co(III)</td>
<td>H</td>
<td>H</td>
<td>Ø</td>
<td>1-Phenylpropan-1,3-dione</td>
<td>Co( PDO)$_3$</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>3-Methylpentan-2,4-dione</td>
<td>Cr(3-Me acac)$_3$</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>CH$_3$</td>
<td>C$_2$H$_5$</td>
<td>CH$_3$</td>
<td>3-Ethylpentan-2,4-dione</td>
<td>Cr(3-Et acac)$_3$</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>CH$_3$</td>
<td>C$_3$H$_7$</td>
<td>CH$_3$</td>
<td>3-Propylpentan-2,4-dione</td>
<td>Cr(3-Pr acac)$_3$</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>CH$_3$</td>
<td>H</td>
<td>CF$_3$</td>
<td>1,1,1-Trifluoropentan-2,4-dione</td>
<td>Cr(tfac)$_3$</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>tBu</td>
<td>H</td>
<td>H</td>
<td>4,4-Dimethylpentan-1,3-dione</td>
<td>Cr(tBuPDO)$_3$</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>CF$_3$</td>
<td>H</td>
<td>Ø</td>
<td>4,4,4-Trifluoro-1-phenylbutan-1,3-dione</td>
<td>Cr(tfbzac)$_3$</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>Propan-1,3-dione</td>
<td>Cr(PDO)$_3$</td>
</tr>
</tbody>
</table>
TABLE 2.5
PHYSICAL DATA OF THE ACCEPTORS

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>m.pt, °C</th>
<th>C ANALYSIS, %</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LIT</td>
<td>FOUND\textsuperscript{a}</td>
<td>CALCD</td>
</tr>
<tr>
<td>Co(acac)\textsubscript{3}</td>
<td>220\textsuperscript{1}</td>
<td>219</td>
<td>-</td>
</tr>
<tr>
<td>Co(tfac)\textsubscript{3}</td>
<td>129(cis)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>158(trans)</td>
<td>156</td>
<td>-</td>
</tr>
<tr>
<td>Co(bzac)\textsubscript{3}</td>
<td>158(cis)</td>
<td>157</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>200\textsuperscript{1}(trans)</td>
<td>199</td>
<td>-</td>
</tr>
<tr>
<td>Co(hfac)\textsubscript{3}</td>
<td>94</td>
<td>94</td>
<td>-</td>
</tr>
<tr>
<td>Co(dpm)\textsubscript{3}</td>
<td>245</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co(\textsuperscript{4}PIDO)\textsubscript{3}</td>
<td>- (cis)</td>
<td>128</td>
<td>64.81</td>
</tr>
<tr>
<td></td>
<td>- (trans)</td>
<td>154</td>
<td>-</td>
</tr>
<tr>
<td>Cr(3-Me acac)\textsubscript{3}</td>
<td>283</td>
<td>283</td>
<td>55.24</td>
</tr>
<tr>
<td>Cr(3-Etacac)\textsubscript{3}</td>
<td>153</td>
<td>152</td>
<td>58.19</td>
</tr>
<tr>
<td>Cr(3-Pracac)\textsubscript{3}</td>
<td>-</td>
<td>118</td>
<td>60.62</td>
</tr>
<tr>
<td>Cr(tfac)\textsubscript{3}</td>
<td>113(cis)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>155(trans)</td>
<td>152</td>
<td>-</td>
</tr>
<tr>
<td>Cr(\textsuperscript{5}BuPDO)\textsubscript{3}</td>
<td>116(cis)</td>
<td>116</td>
<td>58.19</td>
</tr>
<tr>
<td></td>
<td>135(trans)</td>
<td>134</td>
<td>58.19</td>
</tr>
<tr>
<td>Cr(tfbzac)\textsubscript{3}</td>
<td>150</td>
<td>149</td>
<td>51.66</td>
</tr>
<tr>
<td>Cr(PDO)\textsubscript{3}</td>
<td>182</td>
<td>181</td>
<td>40.75</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Melting points measured on a kopfler heating mantle

\textsuperscript{b}Nottingham University microanalysis service

\textsuperscript{1}Decomposition on melting

\textsuperscript{2}Adapted by using CCl\textsubscript{4} instead of ethanol
Attempts were made to prepare mixed ligand complexes of the type \( \text{Cr(hfac)}_n\text{(acac)}_{3-n} \), where \( n = 1 \) or \( 2 \), using the method of Palmer et al (33). Four bands were detected on a TLC plate indicating the presence of the parent complexes plus the mixed ligand components, however, the yield of such components was too low to allow quenching experiments to be performed. A similar preparation using dpm instead of hfac also results in a disappointing low yield.

2.4.3.2 Separation of Isomers

The coordination of three unsymmetrical bidentate ligands to a trivalent metal ion offers the possibility of two geometrical isomers being formed. The two forms, facial (fac or cis) and meridional (mer or trans) are depicted in Figure 2.4. Cis and trans isomers were only separated in cases where a mixture of isomers did not form crystals.

The cis and trans isomers of \( \text{Co(tfac)}_3 \) were separated in accordance with the methods of Fay and Piper (22), first by utilising the solubility differences between the isomers in benzene-hexane and then by column chromatography. The complexes of formyl ketones, e.g. \( \text{Cr(tBuPDO)}_3 \) showed a marked ease of separation. The complex was dissolved in a minimum of benzene, poured onto an activated acid washed alumina column packed with benzene and eluted with a mixture of benzene-ethyl acetate (10:1). The trans isomer was eluted first in accord with the expected dipole moment whilst the more polar cis isomer was removed with acetone. The isomers were identified by the following means.

1. The relative order of elution from a chromatographic column (the trans isomer has a smaller dipole moment and is therefore eluted first).
2. Comparison with published melting point data (the trans isomer has a higher melting point).

3. Comparison with published UV/vis absorption spectra (there is little difference in band position or extinction coefficient for d-d transitions but for charge transfer transitions the trans isomer exhibits slightly higher extinction coefficients)
   e.g. cis- Co(tfac)₃  λ max = 235 nm ε = 35,000
   trans- Co(tfac)₃  λ max = 236 nm ε = 36,000

4. For diamagnetic complexes such as those containing Co(III) as the central ion, it is possible to determine the conformation of the isomer by NMR spectroscopy. As can be seen in Figure 2.4 the cis isomer has all three methyl groups, three CH protons and three trifluoromethyl groups equivalent by a threefold rotation axis but the trans isomer has no symmetry and, therefore, the three methyl groups, CH protons and CF₃ groups are non equivalent. Thus the ¹H nmr spectrum of cis Co(tfac)₃ shows two single resonance lines whilst that of the trans compound gives rise to two triplet resonances. (Figure 2.4)

In the case of paramagnetic Cr(III) complexes NMR studies do not yield such fruitful results.

2.4.3.3 Purity of Acceptors

Throughout the course of preparative work the emphasis was always placed on achieving maximum purity rather than a maximum yield of a
cis- and trans-Isomers of Co(tfac)$_3$ with their associated $^1$H nmr Spectra

Fig 2.4
particular complex. The need for high level of purity is paramount since impurities could either aid and abet or decrease the quenching efficiency of a complex; in both cases giving rise to erroneous quenching constants.

The method of purification varied from complex to complex (see 2.4.3.1) but needless to say, sublimation and recrystallisation techniques were repeated several times. However, no increase in purity was achieved by recrystallising a previously sublimed complex.

The purity of the complexes were checked in the following ways. Firstly by comparison with published melting point data and the ability to obtain a sharp melting point. Secondly by comparison with published UV/vis data including extinction coefficients and finally by carbon and hydrogen (C and H) microanalysis. The results obtained from melting points and C/H microanalysis, together with the literature values are presented in Table 2.5. The results of the UV/vis absorption spectra are discussed in chapter III.

2.4.4 The Donors

As with the acceptors, donors of the highest possible purity were used throughout this work in order to eliminate the possibility of impurity quenching. The donors were purchased from many leading chemical companies (see Table 2.6) and many were of sufficient high purity (e.g. 'Gold Label', 'Scintillation grade') that further purification was not necessary. Phenanthrene was an exception since it decomposes slowly at room temperature to give primarily anthracene which could be detected by its strong absorptions in the 320 - 380 nm region. The anthracene was removed by treating the phenanthrene with
<table>
<thead>
<tr>
<th>DONOR</th>
<th>SOURCE/PURITY</th>
<th>PURIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Acetonaphthone</td>
<td>Kodak Limited</td>
<td>Recrystallised thrice from ethanol</td>
</tr>
<tr>
<td>Acridine</td>
<td>B.D.H. Limited Laboratory Reagent</td>
<td>Recrystallised twice from ethanol/water</td>
</tr>
<tr>
<td>Anthracene</td>
<td>B.D.H. Limited Scintillation grade</td>
<td>None</td>
</tr>
<tr>
<td>1,2-Benzanthracene</td>
<td>Aldrich 99+% pure</td>
<td>None</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>B.D.H. Limited Laboratory Reagent</td>
<td>Recrystallised thrice from ethanol</td>
</tr>
<tr>
<td>8-Carotene</td>
<td>Aldrich</td>
<td>None</td>
</tr>
<tr>
<td>Chrysene</td>
<td>Koch-Light Limited Zone-refined</td>
<td>None</td>
</tr>
<tr>
<td>Coronene</td>
<td>Koch-Light Limited Puriss</td>
<td>None</td>
</tr>
<tr>
<td>1,2,3,4-Dibenzanthracene</td>
<td>Aldrich 97% pure</td>
<td>None</td>
</tr>
<tr>
<td>1,2,5,6-Dibenzanthracene</td>
<td>Aldrich 97% pure</td>
<td>None</td>
</tr>
<tr>
<td>9,10-Dibromoanthracene</td>
<td>Aldrich 97% pure</td>
<td>Recrystallised twice from ethanol/water</td>
</tr>
<tr>
<td>1,5-Dichloroanthracene</td>
<td>Eastman Kodak Limited Laboratory Reagent</td>
<td>Recrystallised twice from ethanol/water</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Merck Chemical Co. Scintillation Grade</td>
<td>None</td>
</tr>
</tbody>
</table>

continued...
### TABLE 2.6 (continued)

Source, purity and purification of donors

<table>
<thead>
<tr>
<th>DONOR</th>
<th>SOURCE/PURITY</th>
<th>PURIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentacene</td>
<td>Aldrich</td>
<td>None</td>
</tr>
<tr>
<td>Perylene</td>
<td>Koch-Light Limited Puriss</td>
<td>None</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>Eastman - Kodak Fluorescence grade</td>
<td>Refluxed with maleic anhydride. Recrystallized twice from ethanol.</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Aldrich Chemical Co. 99+% pure</td>
<td>None</td>
</tr>
<tr>
<td>Tetracene</td>
<td>Aldrich</td>
<td>None</td>
</tr>
</tbody>
</table>

**Solvent**

| BENZENE   | Fisons Limited 'Spectrograde' | None |

*Appendix II gives the Registry Numbers for both Donors and Acceptors used in this Thesis.*
maleic anhydride, filtering and recrystallising the phenanthrene twice from ethanol in accordance with the method of Kooyman and Farenhorst (30).

The purity of the donors were checked each time they were used for quenching studies by comparing their absorption spectra with published data (31). Fluorescence spectra were also run in ethanol as a further check.

2.5 Kinetic Analysis of Triplet Decay Traces

The rate of decay of a triplet state species, T, may be expressed is the general form:

\[ \frac{-d[T]}{dt} = k_1[T] + k_2[T]^2 + k_g[T][S] + k_{O_2}[T][O_2] + \sum_i k_{q_i}[T][Q_i] \ldots (2.1) \]

where \( k_1 \), \( k_2 \), \( k_g \), \( k_{O_2} \) and \( k_{q_i} \) are the rate constants for 1st order decay, 2nd order decay, ground state quenching, oxygen quenching and quenching by species \( Q_i \) respectively.

Under experimental conditions, the photolysis solutions were deoxygenated and therefore the expression involving the oxygen quenching constant, \( k_{O_2}[T][O_2] \), may be ignored. Since ground state quenching is very small, that term may also be dropped, leaving us with

\[ \frac{-d[T]}{dt} = k_1[T] + k_2[T]^2 + \sum_i k_{q_i}[T][Q_i] \ldots (2.2) \]
This equation may be further simplified since the concentration of the quencher will be in large excess of any impurity quenching that might take place. (N.B. any impurities which are present in the solvent will be constant throughout a set of experiments).

Thus

\[-\frac{dT}{dt} = k_1[T] + k_2[T]^2 + k_q[T][Q] \quad \ldots \quad (2.3)\]

may now be used as the general expression. In the absence of quencher, the rate of decay of a particular triplet will depend on the relative magnitudes of the first and second order rate constants. Decay of triplet 2-Acetonaphthone proceeds by a purely 2nd order mechanism whilst pentacene and \( \beta \)-carotene exhibit 1st order kinetics. But for most donors, mixed first and second order decay kinetics are obeyed.

In the presence of quencher, a pseudo first order rate constant, \( k'_1 \) will be used giving

\[-\frac{dT}{dt} = k'_1[T] \quad \ldots \quad (2.4)\]

where \( k'_1 = k_1 + k_q[Q] \)

Integrating equation 2.4 with respect to time gives

\[\ln[T] = k'_1 t + \text{constant} \quad \ldots \quad (2.5)\]

Observations of the decaying triplet state are made spectroscopically and, therefore, the concentration of that species at any time will be related to its absorbance via the Beer-Lambert Law.

\[A = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon \cdot L \cdot [T] \quad \ldots \quad (2.6)\]
where $A$ is the absorbance, $\varepsilon$ is the decadic molar extinction coefficient at the same wavelength and $L$ is the path length.

Substituting the value to $[T]$ into equation 2.5 gives

$$\ln A = k'_1 t + \text{constant} \quad \ldots (2.7)$$

Therefore, both plots of $\ln[T]$ and $\ln A$ vs $t$ will be linear and yield the pseudo first order rate constant. Since absorbance is related to intensity via equation 2.6, it is possible to express equation 2.7 in the form of

$$\ln (\log_{10} \frac{I_0}{I}) = k'_1 t + \text{constant} \quad \ldots (2.8)$$

where $I_0$ is the total light intensity and $I$ is the transmitted light intensity at any given time. (Figure 2.5).

A plot of $k'_1$, the pseudo first order decay constant, vs $[Q]$ will be linear giving the bimolecular quenching constant $k_q$ for a particular donor/acceptor pair.

In order to analyse the decay traces, a program was developed for the Datalab DL 400 memory store based on equation 2.8. A listing of the program is given on page 129. Since the microprocessor allows immediate analysis of the transient decays, the program was developed with a number of points in mind.

1. It must be able to store a number of decay traces - a maximum of three.

2. It is designed to correct for variations in the analysis light intensity by scaling transient traces with respect to the baseline ($I=100$) trace. (See Figure 2.5)
Fig 2.5

Schematic Diagram of the Oscilloscope Output

Indicating (a) Baseline, (b) Transient

and (c) Scatter Traces
01 "SEQ(7)"
02 "SEQ(8)"
03 "SEQ(9)"
04 "SEQ(10)"
05 "SEQ(11, 12, 13, 14, 15)"
06 "SEQ(16, 17, 18, 19, 20, 21)"
07 [A2=NC CC=NC YC=Y1 CC=1 CA=110]
08 [A2=NC-1 CC=A2 YC=Y1 CC=1]
09 [A3=NC-2 CC=A3 YC=Y1 CC=1]
10 [A4=NC-3 CC=A4 YC=Y1 CC=1]
11 [A9=CC CC=CC-2 EB(10,80) ION LSQA(Y1) AO=ZC CC=A1 LSQA(YC) B0=ZC CC=CC-2]
12 [CC=A9 LSQA(YC) B8=ZC D0=A0-B8 NC=A1 CC=A1 C0=B8-B0 YC=YC+CO IOF]
13 [IOF PNT("BLANK T="",B0,"" SCATTER =",A0)]
14 [PNT("SAMPLE T="",B8,"" 100% T="",D0,"" CHANNEL ",A9)]
15 [Y2=Y1-YC YC=YC-CC A9 Y3=Y1-1YC YC=LN(LOG(Y2/Y3)) CA=120]
16 [A9=CC ION B5=LA-FA+1 IOF D9=FA ROT(YC,FA) EB(1,B5) ION LSQA(YC)]
17 [D9=ZF B1=D3*2.048*(10**7) YZ=YC-DS*X-ZC STDV(YZ) D3=ZF YZ=X3]
18 [SUMSQ(Y3) D1=ZF SUM(Y3) D2=ZF C1=D1-(D2**2/B5) C2=D3/SQR(C1)]
19 [C3=C2**2.048*(10**7) NC=A1 D6=LA-D9+1 CC=A9 IOF ROT(YC,D6)]
20 [PNT("GRADIENT =",B1) PNT("STD DEV =",C3) PNT("X POINTS =",B5)]
21 [PNT(D1,D2,D3,C1,C2,"CHANNEL",A9) NC=A1 CA=110]
3. The transient trace is also corrected for any scatter.

The execution of the program may be most clearly explained if we deal with each line at a time.

Firstly, it is necessary to split the four channels which are already present in the microprocessor into a larger number. This is because we require to analyse three transient decay traces and for this we also need a baseline trace (analysing light alone) and a scatter trace (obtained by blanking off the analysing light), plus some computation space. Thus, it was decided to divide the 4096 points which constitute full scale x-coordinate range into eight channels, each consisting of 512 points (corresponding to : 512 x 48.8 ns = 25 μs). This is done by typing in NC = 8.

The Datalab DL 417 unit is equipped with 16 user definables (U.D's) which are initiated by using the frontpanel buttons (for a more indepth discussion see the DL 417 handbook ref.18). The buttons allow the first sixteen lines of the program to be executed (run), thus avoiding the use of the v.d.u. to type in the instructions. As it can be seen from the program listing, the first six lines consist of SEQ (sequence) expressions which also simplifies the running of the program by grouping lines which should be executed in sequence together.

Once the number of channels has been defined, the next stage of operation is to store a baseline trace. This is achieved by blocking off the laser beam from the photolysis cell by using a piece of card. The P.M.T. power supply is set in the region of 380 - 450V and the
The capacitor power bank is charged up to 2.1 - 2.2 kv, held at charge for 5 seconds and then discharged. The baseline signal is processed as previously described (section 2.3.4) and displayed on the Hewlett-Packard hp 1340A oscilloscope. The oscilloscope screen has a y-coordinate range of +127 to -128, and in order to achieve the best signal to noise ratio, it is necessary to use the full range of the screen. This was achieved by first setting the trigger offset on the transient recorder to zero and manually triggering the time base. In order to obtain a line of zero values on the oscilloscope screen, adjustments were made using the offset of the F.E.T. probe. The upper and lower limits of full scale y-deflection were set by adjusting the transient recorder trigger offset until the indicator light flashed on and off. For experimental work, the trigger offset was set to the upper limit value of +127 (a clockwise position from the zero mark). If the baseline overloads (i.e. some or all of the displayed points have a value of -128) or is displayed too far up the screen (e.g. -60), then it is necessary to adjust the slits on the monochromator. For the overload situation, too much light is passing through the monochromator and thus the slits must be closed down whilst the other situation requires them to be opened slightly (adjusting the PMT voltage will have a similar affect). It should be remembered that a front to rear slit ratio of 1.78 : 1 is required for maximum sensitivity.

Once a reasonable trace level (i.e. -110 or less) had been achieved, the first three traces obtained were cleared from the oscilloscope screen, by pressing the ENABLE - CLEAR buttons on the DL 403 unit and then the system was rearmed. The reason for doing this is to make sure that the flash tube is conditioned (i.e. up to working temperature) thus aiding reproducibility. When quenching experiments are being
carried out, it is necessary to keep the time between flashes as well as the time that the flash tube is under charge constant, thus each flash is made under 'identical' conditions.

When the baseline trace is displayed on the oscilloscope screen, UD1 is pressed, and this corresponds to SEQ 7. Line 7 of the program is used to transfer the data from the first half of the memory (channels 1 - 4) to channel NC. Since NC=8, the first quarter of the data will now appear in channel 8. Before another trace can be stored into the microprocessor it is necessary to clear the trace in the first half of the memory without removing that stored in channel 8. This was achieved by moving the group lever to 1,2 and the select Y lever to 1. By pressing ENABLE-CLEAR now, only the data in the first half of the memory is removed.

The next stage of the experimental procedure is to obtain a transient decay trace. For this, the blanking material is removed from the front of the photolysis cell so that the laser beam may excite the organic donor. The capacitor bank was charged up as before and discharged after 5 seconds and the resulting transient decay trace was displayed on the oscilloscope. The button associated with UD2 was initiated and thus line 8 of the program was executed. This resulted in the displayed trace being transferred to channel 7 (this corresponds to NC-1) and the cursor being placed at current address (CA) 110 in channel 1 (the cursor was moved to CA 0 by pressing the scan left button). The same clearing and rearming procedure was repeated. Since a total of three decay traces were analysed, the previous operation was performed twice more. In these cases UD3 and UD4 were operated, thus transferring the traces into channel 6 (NC-2) and channel 5 (NC-3).
Thus we have one baseline and three transient decay traces stored in the microprocessor and only a scatter trace is required in order to perform the kinetic analysis. This was obtained by blanking out the monitoring light from the fibre optic, thus only allowing light from the laser to enter the cell. This trace is stored in the first half of the memory and is not transferred in the same manner as were the previous traces.

Pressing UD5, initiates lines 11 to 15 in the program. Starting with line 11, the first expression gives A9 the value of the channel where the cursor is present (i.e. A9 = 5 for channel 5). The CC = CC-2 term is a safety one which avoids the scatter data in channel 1 being lost if the cursor is inadvertently not moved (if CC = 1 then CC-2 is negative and the program stops. EB(10, 80) is the way of writing Enter Band of interest; the data in the region of 10 to 80 which is stored in channel 1. ION, initiates that region of interest and the least squares program which is stored in the R.O.M. is executed (LSQA (Y1)) and the value obtained is stored in the floating memory under AO. The cursor is then transferred to channel 8 which contains the baseline data and the least squares routine is carried out over the same region as before and its value is placed in another floating memory store, BO. The least squares analysis was carried out once more on the data in CC = A9, channel 5, displaying its value in B8. Therefore, we now have values for the three different traces in the region 10 to 80.

The expression DO = AO-B8 subtracts the least squares value of the transient from that of the scatter giving I_0 (see Figure 2.5). In order to allow for flash lamp jitter, a scaling expression CO = B8-BO is introduced which scales the value of the pretrigger region of the transient to that of the baseline via YC = YC + CO.
The intensification is then removed by the command IOF, and a series of parameters are printed out. In order to correct for scatter, the transient trace is subtracted from that of the scatter and displayed in channel 2 \((Y_2 = Y_1 - Y_C)\). The trace is then rescaled for the difference in level between the transient and the baseline.

The transient decay trace is then replaced by one representing \(\ln(\log_{10} \frac{I_0}{I})\) which is written as \(CC = \ln(\log(Y_2/Y_3))\) and the cursor address is set at 120. Thus, by pressing UD5, the original data has been transformed to a form which will easily lead to an evaluation of \(k_1'\), the pseudo first order rate constant.

Now that we have a \(\log_e \log_{10}\) plot of the transient decay data, it is necessary to decide what region should be analysed to give \(k_1'\). Two distinctly difference cases occur. Firstly, if a high concentration of quencher is used, Figure 2.6, then the analysis should be performed over the region AB. Going past point B would result in the analysis being made on highly scattered points. Secondly, the use of a low quencher concentration, Figure 2.7, results in the decay trace at short time being slightly curved due to the \(k_2[T]^2\) term in equation 2.3, and thus analysis must be made at longer times in order to avoid this second order region, and data would thus be used in the region CD.

For the high quencher concentration the region of interest would be typed in as EB(A,B), where A and B refer to a particular channel number, and then UD6 would be initiated. The same procedure would be employed for the low quencher concentration except the region C-D would be entered.
FIG 2.6 LOG. LN(A) VS CHANNEL NUMBER
FIG 2.7 LOG. LN(A) VS CHANNEL NUMBER

LOG. LN(A)

-7 -6 -5 -4 -3 -2 -1 0 1

CHANNEL NUMBER

0 50 100 150 200 250 300 350 400 450 500 550
Line 16 of the program includes the ION statement which intensifies the region of interest (i.e. A-B in the first case). The number of channels over which the intensification takes place is calculated by the expression \( B5 = LA - FA + 1 \) where LA and FA refer to the last and first addresses respectively. The intensification is then removed and the first address is stored in the floating memory D9. The transient decay trace under investigation is then rotated about its first address, ROT(YC, FA), in order to bring the data to the front of the microprocessor memory. This is carried out in order to avoid the microprocessor having to deal with extremely large numbers, when it is possible to use smaller ones and reduce operational time. The enter band region is now defined as EB(1, B5), where B5 is the number of channels over which the original expansion was to take place. This region is then intensified, the least squares program executed on it, and the value obtained displayed in D8. Since the value stored in D8 has been calculated in terms of channels, in order to have a meaningful value it is necessary to introduce a value for the time base. There are 2048 points for half memory and a time base for full scale deflection of 0.1 ms is set. Thus, the gradient B1 equals 
\[ D8 \times 2.048 \times (10^{7}) \text{s}^{-1}. \]

In order to have some idea of the error associated with the pseudo first order rate constant the next two lines of the program were designed to calculate the standard deviation of the points using a straight line constructed from the value of the intercept (ZC) and the gradient (ZF = D8). By calculating the sum of the squares of \( x \) and the sum of \( x \), it was possible to calculate the standard deviation via the expression \( C3 = C2 \times 2.048 \times (10^{7}) \). Once this had been completed the trace was rotated back to its original position,
ROT(YC, D6) where D6 is given by $D6 = LA - D9 + 1 \ (D9 = FA)$. The value of the gradient together with its associated standard deviation and the number of points over which both were calculated are printed out.

Thus we have a program which can yield kinetic information about a transient decay trace and allow re-examination of such transients.

The program developed for the microcomputer was checked against that in the mainframe computer and the results obtained were identical. The value of the quenching constant, $k_q$, was obtained by subjecting the values of $k_1'$, the pseudo first order rate constants, and $[Q]$ to a standard least squares program available on the University computer and also stored on disc for use with a Commodore PET microcomputer.
CHAPTER II
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CHAPTER III

SPECTROSCOPIC AND POLAROGRAPHIC PROPERTIES OF THE ACCEPTORS

3.1 Introduction

In order to aid the discussion of experimental results (Chapter V), the spectroscopic and polarographic properties of the acceptors, pertinent to such discussions will now be presented.

Over the past two decades there has been considerable interest in the spectroscopy and lately in the polarography of transition metal \( \beta \)-diketonate complexes. This interest has been largely due to the fact that many \( \beta \)-diketonates are readily synthesized thus allowing the effect of electron withdrawing and donating groups to be evaluated.

3.2 Spectroscopy of the \( \beta \)-diketonate complexes

Before discussing the nature and position of the excited states of specific Cr(III) and Co(III) \( \beta \)-diketonate complexes a more general description of the possible spectroscopic transitions will be given.

For all the complexes studied in this thesis, the central metal atom, whether it be Cr(III) or Co(III) is surrounded by six oxygen atoms at the apices of an octahedron and thus the spectra may be treated in terms of \( O_{h} \) microsymmetry. The types of transition taking place within these complexes may be divided broadly into three categories:

\[ d \rightarrow d \] or ligand field transitions.
These transitions occur between the orbitals of the central metal ion and are governed by the number of d electrons present on that ion, its local symmetry and the field strength of the associated ligands. The position and nature of the transitions are determined by ligand field theory (see Orgel (1), Jorgensen (2) and Ballhausen (3)) and are normally given their group theoretical symmetry labels (see Section 3.2.1.).

Internal Ligand Transitions.

As the name implies these transitions are mainly associated with the localized π-orbitals of the ligand. The position of the π→π* transition in acetylacetonate is little altered by complexation (4).

Charge-Transfer Transitions.

These transitions may be of two types, either metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge-transfer transitions. Due to their intermediate nature, these transitions are located between the π→π* transitions of the ligands and the d→d transitions of the central metal ion, in the β-diketonate complexes studied in this thesis (5).

3.2.1 Electronically excited states of Cr(III) complexes

Chromium (III) has a d^3 configuration and the energy levels that arise for such an ion in an octahedral field are depicted in Fig. 3.1. The absorption spectra of chromium (III) β-diketonate complexes have been studied in great detail (5-10) and Table 3.1. presents the spectral data of the complexes in chloroform, since this allowed internal ligand transitions to be measured. (Some complexes not used in this study have
A Tanabe–Sugano Diagram for the $d^3$ Configuration
### Table 3.1: Transition Energies (1000 cm\(^{-1}\)) and Nephelauxetic Parameters (cm\(^{-1}\)) for Cr(III) Complexes

| COMPOUND       | \(4^2_A_{2g}\) | \(4^2_A_{2g}\) | \(4^2_A_{2g}\) | \(\delta_4(e)\) | \(\delta_4(e)\) | \(\pi_3(a)\) | \(\pi_3(e)\) | \(\pi_3(e)\) | \(\pi_4(a)\) | \(\pi_4(a)\) | \(\pi_4(a)\) | \(\pi_4(a)\) | \(\beta_{35}\) | \(\beta_{55}\) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Cr(acac)_3     | 12.95          | 17.86          | 23.26          | 29.76          | 33.56          | 36.76          | 39.22          | 505            | 0.55           | 0.678          | 0.74           |                |                |                |
| Cr(3-Meacac)_3 | 12.39          | 17.60          | 24.40          | -              | 28.30          | 35.10          | 36.82          | -              | 647            | 0.70           |                |                |                |                |
| Cr(3-Etacac)_3 | 12.47          | 17.45          | 24.10          | -              | 28.70          | 35.20          | 37.60          | -              | 652            | 0.71           |                |                |                |                |
| Cr(3-Pracac)_3 | 12.44          | 17.50          | 24.30          | -              | 28.20          | 34.70          | 36.60          | -              | 650            | 0.71           |                |                |                |                |
| Cr(tfac)_3     | 12.20          | 17.64          | 22.55          | 25.38          | 28.99          | 32.26          | 35.34          | 37.74          | 453            | 0.49           | 635            | 0.69           |                |                |
| Cr(tfbzac)_3   | 12.28          | 17.54          | 21.42          | -              | 27.75          | -              | 32.26          | 36.36          | 348            | 0.38           | 671            | 0.73           |                |                |
| Cr(bzac)_3     | 12.58          | 17.76          | 21.74          | -              | 27.93          | 32.79          | 33.90          | 38.61          | 358            | 0.39           | 630            | 0.68           |                |                |
| e-Cr\(^{t}\)BuPDO)_3 | 12.69          | 17.86          | 23.59          | 25.77          | 29.24          | 32.47          | 35.59          | 38.31          | 541            | 0.59           | 663            | 0.72           |                |                |
| t-Cr\(^{t}\)BuPDO)_3 | 12.69          | 17.86          | 23.59          | 25.77          | 29.24          | 32.47          | 35.59          | 38.31          | 541            | 0.59           | 663            | 0.72           |                |                |
| Cr(dpm)_3      | 12.96          | 17.70          | 23.26          | 25.71          | 29.41          | 33.06          | 35.56          | 39.33          | 523            | 0.57           | 679            | 0.74           |                |                |
| Cr(dbm)_3      | 12.13          | 17.48          | 20.83          | 21.98          | 25.91          | 32.47          | 33.77          | 35.01          | 297            | 0.32           | 632            | 0.69           |                |                |
| Cr(BDO)_3      | 12.69          | 17.86          | 23.42          | 25.97          | 29.15          | 29.67          | 32.89          | 36.10          | 522            | 0.57           | 663            | 0.72           |                |                |
| Cr(hfac)_3     | 12.56          | 17.45          | 21.68          | 24.69          | 27.78          | 28.27          | 32.89          | 34.33          | 38.36          | 383            | 0.42           | 630            | 0.68           |                |
been included to aid later discussions). Spectra were recorded in various solvents including benzene, dichloromethane, chloroform and ethanol, and within experimental error there was found to be no solvent dependence. The absorption spectra of Cr(acac)$_3$ in chloroform is presented in Fig. 3.2.

The high spin nature of the complexes, $t^3_{2g} e^0_g$, gives rise to the $4A_{2g}$ ground state. From Fig. 3.1 it can be seen that three doublet states $^2E_g$, $^2T_{1g}$ and $^2T_{2g}$ lie above the ground state and although they all have the same electronic configuration as the ground state, $t^3_{2g}$, they differ in multiplicity due to an inversion of electron spin. The $^2T_{1g} \rightarrow 4A_{2g}$ transition is not observed in the absorption spectra since it lies beneath the more intense $^4T_{2g} \rightarrow 4A_{2g}$ transition. However, it is possible to calculate the position of this transition from standard equations (11) which include configurational interactions. The results and the equations used to calculate them are given in Table 3.2. From these calculations it can be seen that the $^2T_{1g}$ state is situated some $\approx 590-670$ cm$^{-1}$ above that of the $^2E_g$ state.

Promotion of an electron from the non-bonding $t_{2g}$ set of orbitals to the anti-bonding $e_g$ orbitals gives rise to the lowest quartet state $^4T_{2g}$ ($t^2_{2g} e^{-1}_g$). The consequence of this excitation is that the metal-ligand bond will be weakened and thus the $^4T_{2g}$ state will exhibit a distorted geometry with respect to the ground and lowest doublet state, Fig. 3.3. The transition presented under the heading $^4T_{2g} \rightarrow 4A_{2g}$ in Table 3.1 does not represent the zero-zero band for that transition. Fleischauer et al. (12) have calculated $^4T_{2g}(0,0)$ values for a number of Cr(III) complexes by measuring the point to
FIG 3.2  ABSORPTION SPECTRA OF CR(ACAC)3 IN CHLOROFORM
### TABLE 3.2
Quartet - Doublet transition Energies (cm\(^{-1}\))
for Cr(III) \(\delta\)-diketonate complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>(v_{\text{Eg} \rightarrow \text{A}_{2g}})</th>
<th>(v_{\text{T}<em>{1g} \rightarrow \text{E}</em>{g}})</th>
<th>(v_{\text{T}<em>{1g} \rightarrow \text{A}</em>{2g}})</th>
<th>(v_{\text{T}<em>{2g} \rightarrow \text{A}</em>{2g}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cr(acac)}_3)</td>
<td>12950</td>
<td>670</td>
<td>13620</td>
<td>19200</td>
</tr>
<tr>
<td>(\text{Cr(3-Meacac)}_3)</td>
<td>12390</td>
<td>618</td>
<td>13008</td>
<td>18460</td>
</tr>
<tr>
<td>(\text{Cr(3-Etacac)}_3)</td>
<td>12470</td>
<td>635</td>
<td>13105</td>
<td>18520</td>
</tr>
<tr>
<td>(\text{Cr(3-Pracac)}_3)</td>
<td>12440</td>
<td>627</td>
<td>13067</td>
<td>18500</td>
</tr>
<tr>
<td>(\text{Cr(tfac)}_3)</td>
<td>12200</td>
<td>594</td>
<td>12794</td>
<td>18200</td>
</tr>
<tr>
<td>(\text{Cr(bztfac)}_3)</td>
<td>12800</td>
<td>667</td>
<td>13467</td>
<td>18970</td>
</tr>
<tr>
<td>(\text{C-Cr(\text{tBuPDO})}_3)</td>
<td>12690</td>
<td>640</td>
<td>13330</td>
<td>18870</td>
</tr>
<tr>
<td>(\text{t-Cr(\text{tBuPDO})}_3)</td>
<td>12690</td>
<td>640</td>
<td>13330</td>
<td>18870</td>
</tr>
<tr>
<td>(\text{Cr(bzac)}_3)</td>
<td>12580</td>
<td>581</td>
<td>13146</td>
<td>18116</td>
</tr>
<tr>
<td>(\text{Cr(dpm)}_3)</td>
<td>12960</td>
<td>677</td>
<td>13637</td>
<td>19180</td>
</tr>
<tr>
<td>(\text{Cr(dbm)}_3)</td>
<td>12130</td>
<td>594</td>
<td>12724</td>
<td>18098</td>
</tr>
<tr>
<td>(\text{Cr(BD0)}_3)</td>
<td>12690</td>
<td>640</td>
<td>13330</td>
<td>18873</td>
</tr>
</tbody>
</table>

\[ E(\text{Eg} \rightarrow \text{A}_{2g}) = 9B_{55} + 3C - \frac{50B_{55}^2}{10Dq} \]

\[ E(\text{T}_{1g} \rightarrow \text{A}_{2g}) = 9B_{55} + 3C - \frac{24B_{55}^2}{10Dq} \]

\[ E(\text{T}_{1g} \rightarrow \text{E}_{g}) = \frac{26B_{55}^2}{10Dq} \]

\[ E(\text{T}_{2g} \rightarrow \text{A}_{2g}) = 15B_{55} + 5C - \frac{176B_{55}^2}{10Dq} \]

Assuming \( C = 4B \)
Figure 3.3 Potential Energy Curves For An Octahedral Cr(III) Complex
the red of the maxima, at which the absorbance of the $^4T_{2g}$ band reaches 5\% of its maximum value, $(\bar{v}_{0.05})$ and substituting $\bar{v}_{0.05}$ (in $kk$) into the expression:

$$^4T_{2g} (0,0) = 1.11\bar{v}_{0.05} - 0.88 \quad \ldots \quad 3.1$$

which was derived from the results of fluorescent chromium complexes. The results of the above calculations performed on the absorption spectra of the complexes used in this thesis are given in Table 3.3. In their work, Fleischauer et al. (12) calculated $^4T_{2g}(0,0)$ for Cr(acac)$_3$ to lie at 16,230 cm$^{-1}$ as opposed to 15,614 cm$^{-1}$ calculated in this work. The discrepancy is explained by the fact that they have based their calculations of $\bar{v}_{0.05}$ as $\bar{v}_{^4T_{2g}} (\text{max})$ being equal to 18,150 cm$^{-1}$ whereas this work and that of Fatta and Lindvelt (6) measure the quartet maxima to occur at 17,860 cm$^{-1}$.

In Table 3.1 the nephelauxetic parameters $B_{35}$ and $B_{55}$ are given together with $\beta_{35}$ and $\beta_{55}$, which are the ratios of $B_{\text{complex}}/B_0$, where $B_0 = 920$ cm$^{-1}$, the value for the free ion. The $B_{35}$ values were calculated from the spectroscopic data presented in Table 3.1 using the equation:

$$E(^4T_{1g} - ^4A_{2g}) = 7.5 B_{35} + 15Dq - \frac{1}{2} (225B_{35}^2 + 100(Dq)^2 - 180DqB_{35})^{\frac{1}{2}} \quad \ldots \quad 3.2$$

where $10Dq$ is equal to the energy of the first spin allowed transition, $^4T_{2g} - ^4A_{2g}$. Using the energy of the spin forbidden transition $^2E_g - ^4A_{2g}$, the value of $B_{55}$ may be calculated using:

$$E(^2E_g - ^4A_{2g}) = 9B_{55} + 3C - \frac{50B_{55}^2}{10Dq} \quad \ldots \quad 3.3$$

assuming that $C = 4B$. 

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$^{4}\text{T}<em>{2g}$$\rightarrow$$^{4}\text{A}</em>{2g}$ $\nu$ max</th>
<th>$\nu_{0.05}$</th>
<th>$^{4}\text{T}<em>{2g}$$\rightarrow$$^{4}\text{A}</em>{2g}$ $\nu_{oo}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(acac)$_3$</td>
<td>17860</td>
<td>14859</td>
<td>15614</td>
</tr>
<tr>
<td>Cr(3-meacac)$_3$</td>
<td>17600</td>
<td>14663</td>
<td>15390</td>
</tr>
<tr>
<td>Cr(3-Etacac)$_3$</td>
<td>17400</td>
<td>14599</td>
<td>15315</td>
</tr>
<tr>
<td>Cr(3-Pracac)$_3$</td>
<td>17500</td>
<td>14535</td>
<td>15260</td>
</tr>
<tr>
<td>Cr(tfac)$_3$</td>
<td>17640</td>
<td>14793</td>
<td>15540</td>
</tr>
<tr>
<td>Cr(tfbzac)$_3$</td>
<td>17540</td>
<td>14620</td>
<td>15350</td>
</tr>
<tr>
<td>c-Cr(5Bu-PDO)$_3$</td>
<td>17860.</td>
<td>14838</td>
<td>15590</td>
</tr>
<tr>
<td>t-Cr(5Bu-PDO)$_3$</td>
<td>17860.</td>
<td>14838</td>
<td>15590</td>
</tr>
</tbody>
</table>
Fatta and Lintvedt (6) have discussed the meaning of the nephelauxetic parameters in detail concluding that $\beta_{35}$ values are determined by the magnitude of the repulsions within the $\pi$- and $\sigma$-bonding subsets and the ability to expand the d-orbitals follows the sequence $\text{C}_6\text{H}_5:\text{CF}_3:\text{H}:\text{CH}_3:\text{t-C}_4\text{H}_9$. Values of $\beta_{35}$ less than unity are interpreted as indicating $\pi$-type interactions between the ligand and the metal.

3.22 Electronically Excited States of Co(III) Complexes

Cobalt(III) has a d$^6$ electronic configuration and in an octahedral field, low-spin ($t_{2g}^6e_g^0$) complexes result, giving rise to a $^1A_{1g}$ ground state. The spectroscopic situation is analogous to that for an organic molecule, namely a succession of singlet and triplet states. The lowest single excited state, $t_{2g}^5e_g^1$ (anti-parallel spin), is the result of an electron being promoted to an antibonding orbital giving rise to a weakened metal-ligand bond and a distorted excited state. Triplet states arise when a spin flip occurs, giving weak $^3T_{1g} + ^1A_{1g}$ and $^3T_{2g} + ^1A_{1g}$ transitions. Fig.3.4 predicts the existence of a spin quintet state, $^5T_{2g}$, lying at approximately $>5000 \text{ cm}^{-1}$. The actual position of this state is not important, however, since triplet $\rightarrow$ quintet energy transfer is spin forbidden.

Table 3.4 gives the energies of the spectroscopic states for the cobalt 8-diketonate complexes studied in this Thesis (13-15). As was observed in the case of the Cr(III) complexes, only small shifts in band position occur as a result of changes in the R-groups attached to the basic ligand skeleton. The absorption spectra of Co(acac)$_3$ in chloroform is presented in Fig.3.5.
A Tanabe–Sugano Diagram for the d^6 Configuration
TABLE 3.4

Transition Energies (1000 cm$^{-1}$) for Co(III) Complexes

<table>
<thead>
<tr>
<th>Transition</th>
<th>Co(acac)$_3$</th>
<th>Co(bzac)$_3$</th>
<th>Co(4PDO)$_3$</th>
<th>Co(tfac)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3T_{1g} \rightarrow ^1A_{1g}$</td>
<td>9.09</td>
<td>9.01</td>
<td>9.04</td>
<td>9.0 - 10.0</td>
</tr>
<tr>
<td>$^3T_{2g} \rightarrow ^1A_{1g}$</td>
<td>12.50</td>
<td>12.40</td>
<td>12.60</td>
<td>12.0 - 13.0</td>
</tr>
<tr>
<td>$^1T_{1g} \rightarrow ^1A_{1g}$</td>
<td>16.86</td>
<td>-</td>
<td>16.80</td>
<td>16.60</td>
</tr>
<tr>
<td>$^1T_{2g} \rightarrow ^1A_{1g}$</td>
<td>25.00</td>
<td>24.60</td>
<td>-</td>
<td>25.00</td>
</tr>
<tr>
<td>CT $\rightarrow ^1A_{1g}$</td>
<td>30.90</td>
<td>-</td>
<td>27.00</td>
<td>30.40</td>
</tr>
</tbody>
</table>
FIG 3.5  ABSORPTION SPECTRA OF CO(ACAC)3 IN CHLOROFORM

WAVELENGTH / NM

LOG (E)
3.3 Polarography of Transition Metal β-diketonate Complexes

The polarographic reduction potentials of a number of transition metal β-diketonate complexes have been measured in order to determine the effect of substituents. The central metal ions studied include Cr(III) (16,17), Co(III) (18,19), Fe(III) (19,20), Ru(III) (21,17), Os(III) (21), Mn(III) (22) and Cu(II) (18). All the above metal complexes exhibit the same property; the attachment of electron releasing groups (ie - tBu) causes the reduction potential to shift to more negative values in contrast with -CF3 groups which are electron withdrawing and shift the reduction to more positive values, resulting in an ease of reduction as compared with the 1,3-propandione complex as a reference. The absolute values of the reduction potentials being dependent on the nature of the central ion. Changes of 1-2V have been observed as a result of introduced substituents.

The following discussions will be in general limited to the Cr(III) and Co(III) β-diketonate complexes, which have been employed in quenching studies.

3.3.1 Polarographic Study of Cr(III) β-diketonate Complexes

The reduction potentials of a series of 20 chromium (III) tris (β-diketonate) complexes were studied by Handy and Lintvedt (16) in
Dimethyl sulfoxide (DMSO) and 85% dioxane - 15% water employing the technique of cyclic voltammetry. The $E_1'$s for 11 of those complexes in DMSO and 4 complexes in 85% dioxane - 15% water are presented in Table 3.5.

In DMSO, multiple waves similar to those presented in Fig. 3.6 for Cr(dbm)$_3$ ($R_1 = R_3 = \Phi$, $R_2 = H$) were obtained. The first wave which is the only one that will be discussed, has been assigned to the reduction process:

$$\text{Cr(\beta-diketonato)$_3$} + e^- \rightarrow \text{Cr(\beta-diketonato)$_3^-$} \quad \cdots 3.4$$

since plots of $E_{\text{dme}}$ vs $\log i/(i_{d^-}i)$ for this wave have slopes close to the theoretical value of 59.15mv for a reversible one electron reduction (Cr(acac)$_3$ 58mV, Cr(bzac)$_3$ 60mV, Cr(dpm)$_3$ 58mV).

In the other solvent system, Handy and Lintvedt found that only one wave was observed and that it was more irreversible than for the DMSO system. Due to the high water content of the solvent (15%), the workers suggested that the reduced complex underwent chemical decomposition. However, in the cases where the complexes were studied in both solvents, $E_1'$s were obtained in reasonable agreement ($\pm 10\%$ values in 85% dioxane - 15% water being usually more negative). It was found necessary to study the complexes substituted in the 2-position in 55% dioxane for reasons of solubility.
TABLE 3.5
Electrochemical reduction potential for Cr(III) and Co(III) β-diketonate complexes

<table>
<thead>
<tr>
<th>NO.</th>
<th>LIGAND</th>
<th>Cr(III)</th>
<th>Co(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E'_1/\text{V}$ vs SCE-DMSO</td>
<td>$E'_1/\text{V}$ vs SCE - MeCN</td>
</tr>
<tr>
<td>1</td>
<td>H</td>
<td>-1.32</td>
<td>-0.30 (calc) $^a$</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$</td>
<td>-1.58</td>
<td>-0.28</td>
</tr>
<tr>
<td>3</td>
<td>CH$_3$</td>
<td>-1.64</td>
<td>-0.19</td>
</tr>
<tr>
<td>4</td>
<td>CH$_3$</td>
<td>-1.73</td>
<td>-0.34</td>
</tr>
<tr>
<td>5</td>
<td>CH$_3$</td>
<td>-1.85 (calc) $^a$</td>
<td>-0.38</td>
</tr>
<tr>
<td>6</td>
<td>CF$_3$</td>
<td>-1.04</td>
<td>+0.05</td>
</tr>
<tr>
<td>7</td>
<td>CF$_3$</td>
<td>-1.50</td>
<td>-0.21</td>
</tr>
<tr>
<td>8</td>
<td>CF$_3$</td>
<td>-0.40</td>
<td>+0.50</td>
</tr>
<tr>
<td>9</td>
<td>CF$_3$</td>
<td>-1.10</td>
<td>+0.05 (calc) $^a$</td>
</tr>
<tr>
<td>10</td>
<td>CF$_3$</td>
<td>-0.79</td>
<td>+0.25</td>
</tr>
<tr>
<td>11</td>
<td>CF$_3$</td>
<td>-1.24</td>
<td>-0.13</td>
</tr>
<tr>
<td>12</td>
<td>CF$_3$</td>
<td>-1.67 (calc) $^a$</td>
<td>-0.27</td>
</tr>
<tr>
<td>13</td>
<td>CF$_3$</td>
<td>-1.96 (calc) $^a$</td>
<td>-0.40 (calc) $^a$</td>
</tr>
<tr>
<td>14</td>
<td>CF$_3$</td>
<td>-1.75 $^b$</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>CH$_3$</td>
<td>-1.78 $^b$</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>CH$_3$</td>
<td>-1.84 $^b$</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ see text

$^b$ 85% dioxane - 15% water
Fig 3.6 Cyclic voltammetric current vs potential for Cr(dbm)$_3$ in DMSO

Fig 3.7 $E_{1/2}$ (V) vs sum of Hammett sigma constants
The addition of an electron to the Cr(III) complexes (process 3.4) results in the formation of a high-spin chromium (II) complex with the preferred $t_{2g}^3 e_g^1$ configuration ($\beta$-diketonates being weak field ligands).

In order to assess the additivity effect of the substituents on the value of $E_1$, a scale similar to the Hammett $\sigma_p$ functions (24) was constructed using Cr(propan-1,3-dione)$_3$ as a reference. Handy and Lintvedt found that the experimentally derived group electronic effects showed a better correlation with Hammett $\sigma_p$ values rather than $\sigma_m$. Fig. 3.7 represents a plot of $E_1$ vs the sum of the Hammett constants. In Table 3.5, three complexes appear with calculated $E_1$ values, the reason being that complexes 6 and 13 are experimentally difficult to synthesize and compound 14, Cr(dpm)$_3$ has a low solubility. The reduction potentials of these complexes were calculated using the formulae:

$$E_1 = E_1^{\text{Cr(PDO)$_3$}} + \Delta/R_1 + \Delta/R_3 \quad \cdots \quad 3.5$$

where $\Delta/R_1$ and $\Delta/R_3$ are the group electronic effects for the substituents at positions 1 and 3 respectively.

From Fig. 3.8 it can be seen that the 1,3-substituents are ortho and para to the oxygen atoms and since values similar to $\sigma_p$'s are used the major electronic effect is therefore experienced by the oxygen atoms rather than by the metal. Patterson and Holm (21) interpreted their results for Ru(III) $\beta$-diketonate complexes in terms of Hammett $\sigma_m$ constants, however as discussed by Handy and Lintvedt (16), a better correlation would have been obtained using Hammett $\sigma_p$ values.
Since the spectral properties of chromium(III) β-diketonate complexes have been extensively studied (5-15), and previously discussed, a correlation between the ligand field parameters (10Dq, B_{35}, B_{55}) and E_{1} has been sought. By comparing the 10Dq values given in Table 3.1 (10Dq being equal to the energy of the $^{4}T_{2g} \rightarrow ^{4}A_{2g}$ transition), with the E_{1} values of Table 3.5 no simple relationship appears to exist. Thus the large variations in E_{1} values occur with an invariant 10Dq since the energy of the d-orbitals (t_{2g} and e_{g}) are determined by a spherically symmetric term, V_{s}, and an octahedrally symmetric term, V_{o}, (25). Handy and Lintvedt (16) and more recently Lintvedt and Fenton (17) have argued that the changes in E_{1} must be related directly to the V_{s} term since V_{o} (10Dq) shows little or no substituent dependence. Since V_{s} is a repulsive term, substituents that are electron-releasing would be expected to have higher energy antibonding "d" orbitals than a complex containing electron-withdrawing groups. (E_{1} Cr(dpm)_{3} = -1.96V \ E_{1} Cr(hfac)_{3} = -0.40 V). This argument being in agreement with the linear relationship found with Hammett $\sigma_{p}$ constants.

**Fig 3·8**

Electronic effect of 1,3-Substituents
3.3.2. Polarographic study of Co(III) β-diketonate complexes

The reduction potentials of 11 cobalt (III) tris (β-diketonate) complexes have been measured by Tsiamis et al. (18) whilst Endo et al. (19) have also obtained values for 4 of these complexes. The work of Tsiamis et al. is of more use in the following discussions since their results cover a larger range of complexes and the conditions under which the results were obtained are more compatible with the results of Handy and Lintvedt (16) for Cr(III) complexes which were discussed in the previous section. Table 3.5 lists the $E_1'$s for the 11 complexes in Acetonitrile studied by Tsiamis et al. using DC polarography.

These workers found that the cobalt (III) complexes exhibited a greater degree of solvent dependence than for the chromium (III) analogues and acetonitrile was the only solvent they employed that gave well defined polarographic waves for all of the complexes. The slope of the first wave was found to be equal to the theoretical value for a reversible one electron transfer, (59mV) thus allowing the step to be assigned to:

$$\text{Co(β-diketonato)}_3^+ + e^- \rightarrow \text{Co(β-diketonato)}_3^- \quad \ldots \quad 3.6$$

unlike the Cr(III) situation where three one-step electron transfer were observed, Fig. 3.6, the second wave in the Co(III) system has been designated to represent a two electron transfer step:

$$\text{Co(β-diketonato)}_3^- + 2e^- \rightarrow \text{Co(β-diketonato)}^{3-} \quad \ldots \quad 3.7$$

A similar relationship, using Hammett $\sigma_p$ functions as proposed by Handy and Lintvedt (16) for chromium (III) complexes, has been
obtained, with the $E_1$ value being related to $c_p$ by:

$$E_1 = -0.16 + 0.61 \Sigma_p \cdots 3.8$$

thus again indicating that the effect of substituents is to perturb the electron density of the oxygen atoms.

The reduction of the low spin $d^6$ cobalt (III) complexes (i.e. process 3.6) results in the addition of an electron to the $e_g$ set of antibonding orbitals. Therefore, the $t_2^6e_1^1$ configuration represents an excited state (octahedral Co(II) complexes have a $t_2^5e_2^2$ configuration) which is likely to have different bond lengths and angles as compared with the ground state.

3.4 Polarographic Properties of the donors

In order to discuss the results presented in this thesis in terms of the mechanistic pathways outlined in Chapter I (Sec. 1.4.4), a knowledge of the redox potentials of the donor molecules is required. The reduction (26-28) and oxidation (29-30) potentials of aromatic hydrocarbons have been studied in great detail by many workers and Table 3.6 lists the values for the donors used in the quenching studies. For some of the donors, notably compounds containing heteroatoms (benzophenone and 2-Acetonaphthone) oxidation potentials in acetonitrile relative to the standard calomel electrode (SCE) were not available and it was therefore necessary to estimate them in some way. Several groups of workers (30-32) have found a correlation between the ionization potential of the molecule and its polarographic oxidation potential. The results of Pysh and Yang (30) appear to be most
TABLE 3.6

Triplet Energies ($E_T$), Ionization Potentials (IP), Reduction Potentials ($E_{\text{red}}$) and oxidation potentials ($E^{\text{ox}}$) for the donors used Experimentally.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$E_T$/ev$^1$</th>
<th>IP/ev$^2$</th>
<th>$E_{\text{red}}$/V$^3$</th>
<th>$E^{\text{ox}}$/V$^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>3.01</td>
<td>9.45</td>
<td>1.55</td>
<td>2.46$^5$</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>2.68</td>
<td>7.86</td>
<td>2.44</td>
<td>1.50</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2.64</td>
<td>8.12</td>
<td>2.58</td>
<td>1.54</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>2.55</td>
<td>8.31</td>
<td>1.72</td>
<td>1.69$^5$</td>
</tr>
<tr>
<td>Chrysene</td>
<td>2.48</td>
<td>7.75</td>
<td>2.30</td>
<td>1.35</td>
</tr>
<tr>
<td>Coronene</td>
<td>2.40</td>
<td>7.60</td>
<td>2.04</td>
<td>1.23</td>
</tr>
<tr>
<td>1,2,5,6-DBA$^*$</td>
<td>2.27</td>
<td>7.38</td>
<td>2.04</td>
<td>1.19</td>
</tr>
<tr>
<td>1,2,3,4-DBA$^*$</td>
<td>2.21</td>
<td>7.39</td>
<td>2.04</td>
<td>1.25</td>
</tr>
<tr>
<td>Pyrene</td>
<td>2.08</td>
<td>7.55</td>
<td>2.10</td>
<td>1.16</td>
</tr>
<tr>
<td>Acridine</td>
<td>1.96</td>
<td>7.78</td>
<td>1.81</td>
<td>1.58</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.82</td>
<td>7.23</td>
<td>1.96</td>
<td>1.09</td>
</tr>
<tr>
<td>Perylene</td>
<td>1.54</td>
<td>7.15</td>
<td>1.65</td>
<td>0.85</td>
</tr>
<tr>
<td>Tetracene</td>
<td>1.28</td>
<td>6.88</td>
<td>1.55</td>
<td>0.77</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0.99</td>
<td>6.61</td>
<td>1.36</td>
<td>0.54$^5$</td>
</tr>
<tr>
<td>β-carotene</td>
<td>0.78</td>
<td>6.40</td>
<td>1.68</td>
<td>0.39$^5$</td>
</tr>
</tbody>
</table>

$^1$from ref 33

$^2$from ref's 34,35

$^3$vs SCE in Acetonitrile or dimethylformamide ref's 26-28

$^4$vs SCE in Acetonitrile 29,30

$^5$calculated from equation 3-9

* Abbreviation for Dibenzanthracene
relevant since they measured $E_D^{\text{ox}}$ for nine of the ten aromatic hydrocarbons used in this study. The relationship they found to exist is:

$$IP = (1.473 \pm 0.027) E_D^{\text{ox}} + (5.821 \pm 0.009) \cdots 3.9$$

thus allowing estimates for $E_D^{\text{ox}}$ to be calculated (Table 3.6).
CHAPTER III
REFERENCES

1. L. Orgel, "An introduction to Transition Metal Chemistry", (Methuen) 1960


CHAPTER IV

RESULTS

4.1 Introduction

The results presented in this chapter were obtained in accordance with the experimental procedure outlined in chapter II. The experiments were designed to investigate the mechanism and efficiency by which excited triplet states of aromatic compounds are quenched by a series of transition metal 8-diketonate complexes. The aim of this work being to see how subtle changes in the molecular structure of the ligands in the complexes dictate the mechanistic pathway by which that molecule may quench. As discussed in Chapter I (section 1.6), previous studies have found that certain 8-diketonate complexes quench by energy transfer (1) and by energy transfer/electron transfer (2). It is also the intention of this work to fit theoretical models, based on different mechanistic pathways, to the experimental data obtained.

The results may be categorised under two major headings:

1. An investigation into the quenching ability of Chromium (III) 8-diketonate complexes.

2. An investigation into the quenching ability of Cobalt (III) 8-diketonate complexes.

Bimolecular quenching constants \( (k_q)'s \) were calculated by plotting the pseudo first order rate constant \( (k'_1) \) against \([Q]\), the concentration of the quencher and subjecting the data to linear least squares
regression analysis; the programme of which was present in the Commodore CBM 3032 microcomputer. For most donors between 3 - 5 different quencher concentrations, excluding zero were employed, thus allowing a ten fold change in \( k_1 \) to be followed. For each concentration, six decay traces were analysed. Quenching constants are quoted to ± one standard deviation which were usually better than ± 10%. For some of the low energy triplet donors notably tetracene and pentacene, the quencher concentration range was limited by the absorption of the quencher at the laser wavelength, and therefore correspondingly more decay traces were analysed.

The purity of the donors and acceptors were checked as described in chapter II, and ground state as well as excited state absorption spectra were obtained in order to investigate the possibility of donor/acceptor interactions. Some sample spectra are presented in chapter II, section 2.4.3 and the spectroscopic data pertinent to the acceptors is given in chapter III, (section 3.2).

4.2 Quenching by Chromium (III) β-diketonate complexes

Under the general heading of quenching of excited triplet states by Chromium (III) β-diketonate complexes, the investigations were designed to look at three particular aspects:

1. How the quenching efficiency of the complex is affected by the substitution of successively larger aliphatic groups (differing by one \(-\mathrm{CH}_2^-\) unit) in the \( \gamma \)-position, as compared with the case where the \( \gamma \)-substituent is hydrogen.
2. To observe how the mechanism of quenching is affected by
the reduction potential of the quencher (see chapter III,
section 3.3) which may be altered by the introduction of
trifluoromethyl groups.

3. To investigate the possible effect of geometrical isomerism
on the quenching ability of Cr(tBu-PDO)$_3$.

4.2.1 Quenching by γ-substituted chromium (III) β-diketone complexes

The complexes studied under this heading were chromium (III)
tris (3-methylpentan-2,4-dionate), Cr(3-Meacac)$_3$, chromium (III)
tris (3-Ethylpentan-2,4-dionate), Cr(3-Etacac)$_3$ and chromium (III)
tris (3-n-Propylpentan-2,4-dionate), Cr(3-Pracac)$_3$. The results on
the aforementioned complexes are presented in Tables 4.1, 4.2 and 4.4,
respectively. In each table, the donor and its associated triplet
energy are listed together with the range and number of quencher
concentrations used, the final column being the bimolecular quenching
constant. In order to obtain some feel for the values of psuedo
first order quenching constants associated with the quencher concentrations
employed, Table 4.3 lists the values of [Q] and $k_1'$ for the pyrene-
Cr(3-Etacac)$_3$ system. Figures 4.1, 4.2 and 4.3 present graphically
a number of stern-volmer plots for quenching by Cr(3-Meacac)$_3$,
Cr(3-Etacac)$_3$ and Cr(3-Pracac)$_3$ respectively.

A limited number of quenching constants for chromium (III) tris
(pentan-2,4-dionate) have been remeasured and compared with a more
extensive list of quenching constants obtained by Wilkinson and Tsiamis (1).
These are listed in Table 4.5.
TABLE 4.1

Quenching by Cr(3-Meacac)₃
in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_\text{T}/$ 1000 cm⁻¹</th>
<th>No. of Conc.'s</th>
<th>Range [Q]/ m mol</th>
<th>$kq/10^9$ 3⁻¹ 1⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>3</td>
<td>0.15-0.25</td>
<td>4.78±0.32</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>5</td>
<td>0.08-0.25</td>
<td>4.33±0.13</td>
</tr>
<tr>
<td>Naphthalene a</td>
<td>21.3</td>
<td>4</td>
<td>0.08-0.30</td>
<td>3.74±0.20</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.11-0.33</td>
<td>2.77±0.14</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>4</td>
<td>0.06-0.11</td>
<td>2.42±0.07</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.04-0.14</td>
<td>2.40±0.12</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>4</td>
<td>0.17-0.42</td>
<td>2.10±0.06</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>4</td>
<td>0.11-0.44</td>
<td>2.15±0.09</td>
</tr>
<tr>
<td>Perylene a</td>
<td>12.6</td>
<td>3</td>
<td>0.02-0.04</td>
<td>0.61±0.06</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>1</td>
<td>0.25</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.25</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>â- Carotene b</td>
<td>6.3</td>
<td>1</td>
<td>0.25</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

1 Excluding zero

a Sensitized with benzophenone

b Sensitized with Anthracene
(a) Acetonaphthone
$Q = 1.082 \times 10^{-4} \text{ mol dm}^{-3}$

(b) Anthracene
$Q = 1.087 \times 10^{-4} \text{ mol dm}^{-3}$

(c) Pyrene
$Q = 3.546 \times 10^{-5} \text{ mol dm}^{-3}$

Fig 4.1 Quenching of various donors by Cr(3-Meacac)$_3$
TABLE 4.2

Quenching by Cr(3-Etacac)$_3$

in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_T/\text{cm}^{-1}$</th>
<th>No. of Conc.'s</th>
<th>Range $[\text{Q}]/\text{m mol}$</th>
<th>$k_q/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>3</td>
<td>0.08-0.24</td>
<td>4.05±0.16</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>5</td>
<td>0.09-0.35</td>
<td>3.88±0.13</td>
</tr>
<tr>
<td>Naphthalene $^a$</td>
<td>21.3</td>
<td>4</td>
<td>0.10-0.30</td>
<td>3.54±0.16</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.12-0.37</td>
<td>2.35±0.05</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>4</td>
<td>0.06-0.12</td>
<td>2.00±0.05</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>5</td>
<td>0.04-0.20</td>
<td>1.77±0.08</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>4</td>
<td>0.15-0.37</td>
<td>1.72±0.08</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>4</td>
<td>0.09-0.38</td>
<td>1.79±0.06</td>
</tr>
<tr>
<td>Perylene $^a$</td>
<td>12.6</td>
<td>4</td>
<td>0.09-0.37</td>
<td>0.58±0.03</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>1</td>
<td>0.22</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.22</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>$\beta$-Carotene $^b$</td>
<td>6.3</td>
<td>1</td>
<td>0.22</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

1 Excluding zero
$a$ Sensitized with benzophenone
$b$ Sensitized with Anthracene
(a) Acetonaphthone; \( Q = 1.232 \times 10^{-4} \text{ mol dm}^{-3} \)
(b) Pyrene; \( Q = 3.912 \times 10^{-5} \text{ mol dm}^{-3} \)
(c) Perylene; \( Q = 9.154 \times 10^{-5} \text{ mol dm}^{-3} \)

**Fig 4.2** Quenching of various donors by \( \text{Cr(3-Etacac)}_3 \)
### TABLE 4.3

**Psuedo First Order Rate constants and Quencher Concentrations for the Pyrene - Cr(3-Etacac)$_3$ System**

<table>
<thead>
<tr>
<th>[Q]/dm$^3$mol$^{-1}$</th>
<th>$-k'_1$/s$^{-1}$</th>
<th>[Q]/dm$^3$mol$^{-1}$</th>
<th>$-k'_1$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.01 x 10$^4$</td>
<td>7.824 x 10$^{-5}$</td>
<td>1.91 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.94 x 10$^4$</td>
<td>&quot;</td>
<td>1.88 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>5.03 x 10$^4$</td>
<td>&quot;</td>
<td>2.01 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>5.00 x 10$^4$</td>
<td>&quot;</td>
<td>1.86 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.97 x 10$^4$</td>
<td>&quot;</td>
<td>1.82 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>5.04 x 10$^4$</td>
<td>&quot;</td>
<td>1.87 x 10$^5$</td>
</tr>
<tr>
<td>11.736 x 10$^{-5}$</td>
<td>2.63 x 10$^5$</td>
<td>19.560 x 10$^{-5}$</td>
<td>4.02 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.69 x 10$^5$</td>
<td>&quot;</td>
<td>4.06 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.61 x 10$^5$</td>
<td>&quot;</td>
<td>3.98 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.51 x 10$^5$</td>
<td>&quot;</td>
<td>4.01 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.61 x 10$^5$</td>
<td>&quot;</td>
<td>4.01 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.53 x 10$^5$</td>
<td>&quot;</td>
<td>4.05 x 10$^5$</td>
</tr>
<tr>
<td>15.648 x 10$^{-5}$</td>
<td>3.08 x 10$^5$</td>
<td>3.912 x 10$^{-5}$</td>
<td>1.28 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>3.18 x 10$^5$</td>
<td>&quot;</td>
<td>1.28 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>3.21 x 10$^5$</td>
<td>&quot;</td>
<td>1.10 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>3.15 x 10$^5$</td>
<td>&quot;</td>
<td>1.02 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>3.36 x 10$^5$</td>
<td>&quot;</td>
<td>1.15 x 10$^5$</td>
</tr>
<tr>
<td>&quot;</td>
<td>3.13 x 10$^5$</td>
<td>&quot;</td>
<td>1.17 x 10$^5$</td>
</tr>
</tbody>
</table>

$k_q = 1.77 \pm 0.08 \times 10^9$ dm$^3$mol$^{-1}$ s$^{-1}$

intercept on y - axis = 50424

Pearson's correlation coefficient = 0.99527

sum of errors squared = 2.3940 x 10$^9$
TABLE 4.4

Quenching by Cr\((3\text{-Pracac})_3\)

in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_T$/1000 cm$^{-1}$</th>
<th>No. of Conc.'s</th>
<th>Range $[Q]$/m mol</th>
<th>$k_q$/10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>4</td>
<td>0.10-0.17</td>
<td>3.80±0.10</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>4</td>
<td>0.06-0.24</td>
<td>3.58±0.08</td>
</tr>
<tr>
<td>Naphthalene $^a$</td>
<td>21.3</td>
<td>4</td>
<td>0.11-0.26</td>
<td>3.31±0.09</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.15-0.30</td>
<td>2.28±0.06</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>4</td>
<td>0.08-0.21</td>
<td>1.86±0.07</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.08-0.21</td>
<td>1.75±0.07</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>4</td>
<td>0.17-0.44</td>
<td>1.58±0.03</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>4</td>
<td>0.15-0.39</td>
<td>1.70±0.04</td>
</tr>
<tr>
<td>Perylene $^a$</td>
<td>12.6</td>
<td>3</td>
<td>0.12-0.37</td>
<td>0.50±0.03</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>1</td>
<td>0.26</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.26</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>β-Carotene $^b$</td>
<td>6.3</td>
<td>1</td>
<td>0.26</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

$^1$ excluding zero

$^a$ sensitized with benzophenone

$^b$ sensitized with anthracene
(a) Phenanthrene: $Q = 5.896 \times 10^{-5}$ mol dm$^{-3}$

(b) Naphthalene: $Q = 5.249 \times 10^{-5}$

(c) Acridine: $Q = 8.874 \times 10^{-5}$

Fig 4.3 Quenching of various donors by Cr(3-Pr acac)$_3$
TABLE 4.5
Quenching of Cr(acac)$_3$ - Comparison with Published Results

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_T/1000\text{cm}^{-1}$</th>
<th>$k_{q/1}\times 10^9\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$</th>
<th>$k_{q/2}\times 10^9\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>1.80±0.13</td>
<td>1.85±0.10</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>1.64±0.10</td>
<td>1.66±0.10</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>1.34±0.11</td>
<td>1.27±0.09</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>1.28±0.13</td>
<td>1.24±0.07</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>1.25±0.04</td>
<td>1.29±0.05</td>
</tr>
</tbody>
</table>

1 Results of Wilkinson and Tsiamis (1)
2 Results from this work
4.2.2 Quenching by chromium (III) \(\beta\)-diketonate complexes containing trifluoromethyl groups

The two complexes studied under this heading were chromium (III) tris (1,1,1-Trifluoro pentan-2,4-dionate), \(\text{Cr}(\text{tfac})_3\), and chromium (III) tris (4,4,4 - Trifluoro - 1 - phenylbutan - 1,3-dionate), \(\text{Cr}(\text{tfbzac})_3\), whose method of synthesis and purification was reported in chapter II. As discussed in chapter III, complexes containing trifluoromethyl groups have larger (less negative) reduction potentials than the corresponding complex which does not contain these groups. The intention of these studies being to investigate any change in quenching mechanism that may be associated with a change in the reduction potential of the acceptor.

Bimolecular quenching constants for \(\text{Cr}(\text{tfac})_3\) and \(\text{Cr}(\text{tfbzac})_3\) are presented in Tables 4.6 and 4.7 respectively. Figures 4.4 and 4.5 present some of the results graphically.

4.2.3 Quenching by Geometrical isomers of \(\text{Cr}(\text{tBuPD0})_3\)

Chromium (III) tris (4,4-dimethylpentan -1,3-dionate), \(\text{Cr}(\text{tBuPD0})_3\), was synthesised in accordance with the procedure outlined in chapter II. The geometrical isomers of this formyl \(\beta\)-diketonate were separated by column chromatography on activated alumina, using ethyl acetate/benzene (1:10) to elute the less polar \(\text{trans}\)-isomer and acetone to remove the \(\text{cis}\)-isomer from the column.

The bimolecular quenching constants for the \(\text{cis}\)- and \(\text{trans}\)-isomers of \(\text{Cr}(\text{tBuPD0})_3\) are presented in Tables 4.8 and 4.9 respectively. Figures 4.6 and 4.7 represent some of the data graphically. Both quenchers were found to undergo some ground state interaction with anthracene, as illustrated in Figure 4.8 by the hypsochromatic shift in
### TABLE 4.6

Quenching by Cr(tfac)$_3$

in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_T$ 1000 cm$^{-1}$</th>
<th>No. of Conc.'s</th>
<th>Range [Q]/m·mol$^{-1}$</th>
<th>$k_q/10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>3</td>
<td>0.16-0.32</td>
<td>4.13±0.29</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>3</td>
<td>0.10-0.30</td>
<td>3.86±0.30</td>
</tr>
<tr>
<td>Naphthalene $^a$</td>
<td>21.3</td>
<td>3</td>
<td>0.10-0.40</td>
<td>4.12±0.22</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.11-0.32</td>
<td>1.99±0.16</td>
</tr>
<tr>
<td>Chrysene</td>
<td>20.0</td>
<td>3</td>
<td>0.17-0.34</td>
<td>1.90±0.11</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>4</td>
<td>0.02-0.11</td>
<td>1.75±0.09</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.03-0.15</td>
<td>1.77±0.12</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>4</td>
<td>0.12-0.48</td>
<td>1.12±0.03</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>4</td>
<td>0.18-0.46</td>
<td>1.43±0.08</td>
</tr>
<tr>
<td>Perylene $^a$</td>
<td>12.6</td>
<td>3</td>
<td>0.24-0.48</td>
<td>0.33±0.02</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>1</td>
<td>0.31</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.31</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

---

1 excluding zero

$a$ sensitized with benzophenone
Quenching of various donors by Cr(tfac)$_3$

(a) Phenanthrene; $Q = 1.086 \times 10^{-4}$ mol dm$^{-3}$
(b) Acetonaphthone; $Q = 1.066 \times 10^{-4}$ 
(c) Coronene; $Q = 2.848 \times 10^{-5}$
### TABLE 4.7

Quenching by Cr(tfbzac)$_3$ in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$\varepsilon_T$ / 1000 cm$^{-1}$</th>
<th>No. of Conc.'s</th>
<th>$[^{[Q]}]/$ mmol</th>
<th>$[^{k_q}/10^9$ dm$^3$ mol$^{-1}$s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>3</td>
<td>0.08-0.14</td>
<td>6.29±0.31</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>4</td>
<td>0.07-0.17</td>
<td>6.19±0.21</td>
</tr>
<tr>
<td>Naphthalene a</td>
<td>21.3</td>
<td>4</td>
<td>0.03-0.12</td>
<td>6.10±0.23</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.04-0.18</td>
<td>3.75±0.13</td>
</tr>
<tr>
<td>Chrysene</td>
<td>20.0</td>
<td>4</td>
<td>0.04-0.11</td>
<td>5.85±0.20</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>4</td>
<td>0.03-0.08</td>
<td>4.00±0.13</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.03-0.08</td>
<td>4.20±0.15</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>3</td>
<td>0.04-0.12</td>
<td>1.18±0.08</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>4</td>
<td>0.11-0.28</td>
<td>1.99±0.04</td>
</tr>
<tr>
<td>Perylene a</td>
<td>12.6</td>
<td>3</td>
<td>0.02-0.09</td>
<td>0.88±0.14</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>1</td>
<td>0.15</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.15</td>
<td>&lt;0.002</td>
</tr>
</tbody>
</table>

$[^{1}]$ excluding zero

$[^{a}]$ sensitized with benzophenone
(a) Chrysene; \( Q = 3.785 \times 10^{-5} \text{ mol dm}^{-3} \)
(b) Benzophenone; \( Q = 2.647 \times 10^{-5} \)
(c) Pyrene; \( Q = 1.620 \times 10^{-5} \)

Fig 4.5 Quenching of various donors by \( \text{Cr(tfbzac)}_3 \)
TABLE 4.8

Quenching by cis-Cr(tBuPD0)$_3$

in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_T$ / 1000cm$^{-1}$</th>
<th>No. of Conc.'s</th>
<th>Range $[Q]$ / mmol</th>
<th>$k_q$ / $10^9$ 3 mol$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>4</td>
<td>0.06-0.19</td>
<td>5.33±0.38</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>4</td>
<td>0.08-0.21</td>
<td>4.71±0.22</td>
</tr>
<tr>
<td>Naphthalene a</td>
<td>21.3</td>
<td>4</td>
<td>0.10-0.33</td>
<td>3.70±0.13</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.16-0.33</td>
<td>2.10±0.07</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>4</td>
<td>0.10-0.21</td>
<td>1.83±0.06</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.10-0.21</td>
<td>1.47±0.05</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>4</td>
<td>0.14-0.35</td>
<td>1.32±0.04</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>-</td>
<td>-</td>
<td>REACTS</td>
</tr>
<tr>
<td>Perylene a</td>
<td>12.6</td>
<td>3</td>
<td>0.09-0.21</td>
<td>0.21±0.02</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>1</td>
<td>0.27</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.27</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

1 excluding zero

a sensitized by benzophenone
(a) Phenanthrene; \( Q = 4.226 \times 10^{-5} \ \text{mol dm}^{-3} \)
(b) Naphthalene; \( Q = 3.765 \times 10^{-5} \ \text{mol dm}^{-3} \)
(c) Acridine; \( Q = 7.105 \times 10^{-5} \ \text{mol dm}^{-3} \)

Fig 4.6 Quenching of various donors by cis-Cr(tBu-PDO)₃
### TABLE 4.9

Quenching by $\text{trans-Cr(tBuPDO)}_3$ in benzene solution at $20^\circ\text{C}$

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E^*_T/1000\text{cm}^{-1}$</th>
<th>No. of Conc.'s</th>
<th>Range $[Q]/\text{mmol}$</th>
<th>$k_q/10\text{ dm mol}^{-1}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>4</td>
<td>0.08-0.20</td>
<td>$4.14\pm0.40$</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>4</td>
<td>0.15-0.25</td>
<td>$2.83\pm0.19$</td>
</tr>
<tr>
<td>Naphthalene $^a$</td>
<td>21.3</td>
<td>4</td>
<td>0.10-0.33</td>
<td>$3.16\pm0.12$</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.16-0.34</td>
<td>$1.92\pm0.11$</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>4</td>
<td>0.10-0.21</td>
<td>$1.47\pm0.05$</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.10-0.21</td>
<td>$1.26\pm0.03$</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>4</td>
<td>0.15-0.37</td>
<td>$1.26\pm0.05$</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>-</td>
<td>-</td>
<td>REACTS</td>
</tr>
<tr>
<td>Perylene $^a$</td>
<td>12.6</td>
<td>3</td>
<td>0.11-0.22</td>
<td>$0.19\pm0.02$</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>1</td>
<td>0.28</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.28</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

1 excluding zero  

$a$ sensitized by benzophenone
Fig 4.7 Quenching of various donors by trans-Cr(tBu-PDO)$_3$
Fig 4.8  Ground State Interaction between Anthracene and Cr(tBu-PDO)$_3$. 

3·0
2·0
1·0
0·0
320
360
400
420
Wavelength / nm
Abs
Anthracene, Cr(tBu-PDO)$_3$
356 nm
Anthracene
Cr(tBu-PDO)$_3$
band position at 356 nm of 2 nm. None of the other donors studied with these quenchers exhibited any observable absorption changes.

4.2.4 Quenching by Cr(PDO)$_3$

Chromium(III) tris(propan-1,3-dionate), Cr(PDO)$_3$ is the parent complex of the acetylacetonate series where $R_1 = R_2 = R_3 = H$. Before quenching studies were attempted, ground state spectroscopic checks in the 450 - 320 nm region revealed a lack of additivity between donor and acceptor solutions, indicating a ground state interaction. Similar studies in the excited state also exhibited differences and therefore quenching experiments using Cr(PDO)$_3$ were abandoned.

4.3 Quenching by Cobalt (III) B-diketonate complexes

The quenching studies conducted using the Cobalt (III) complexes were designed to investigate three particular aspects of their quenching ability.

1. To further the study of Marshall (3), who investigated the quenching efficiency of Co(acac)$_3$ in benzene solution.

2. To investigate how the quenching efficiency of the complexes is affected by the introduction of phenyl groups into the ligand and to compare these results with those obtained using Co(acac)$_3$.

3. To investigate the influence substituted trifluoromethyl groups have on the quenching mechanism and efficiency.
4.3.1 Quenching by Co(acac)$_3$

Cobalt (III) tris (pentan-2,4-dionate), Co(acac)$_3$ was purchased from Aldrich Chemical Company and purified by recrystallisation. Earlier studies by Marshall (3) had indicated the presence of a dip in the quenching curve ($k_q$ vs $E_T$) centred at approximately 20,000 cm$^{-1}$. In this study an attempt was made to define this dip with more precision and to confirm some of the previous results.

Bimolecular quenching constants are given in Table 4.10 and Figure 4.9 presents some of the quenching plots graphically. The quenching of two halo-substituted anthracenes, namely 9,10-dibromoanthracene and 1,5-dichloroanthracene, was attempted and in both cases good first order plots were obtained. However, changes in ground state absorption spectra were observed in the 450 - 320 nm region when the donor and acceptor were mixed, thus indicating a ground state interaction. Therefore, these results have been eliminated from Table 4.10.

4.3.2 Quenching by Cobalt(III) S-diketonate complexes containing Phenyl groups

Two complexes were studied under this heading. Cobalt (III) tris (1-phenylbutan-1,3-dionate), Co(bzac)$_3$ and Cobalt (III) tris (1-phenylpropan-1,3-dionate), Co($\beta$-PDO)$_3$ were synthesised and purified using the methods given in the reference of Table 2.5. In both cases it was necessary to separate their geometrical isomers since the mixtures provided difficult to purify and the trans-isomer was used in the quenching experiments.

The bimolecular quenching constants for Co(bzac)$_3$ and Co($\beta$-PDO)$_3$ are given in Table 4.11 and 4.12 respectively. Figures 4.10 and 4.11 present some of the data graphically.
TABLE 4.10

Quenching by Co(acac)$_3$

in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_T$ / 1000 cm$^{-1}$</th>
<th>Conc.'s</th>
<th>Range [Q]/ mmol</th>
<th>$k_q$ / 10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>3</td>
<td>0.27–0.76</td>
<td>2.7±0.2 $^c$</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>3</td>
<td>0.09–0.25</td>
<td>2.6±0.2 $^c$</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>5</td>
<td>0.43–0.99</td>
<td>0.46±0.02</td>
</tr>
<tr>
<td>Chrysene</td>
<td>20.0</td>
<td>4</td>
<td>0.16–0.64</td>
<td>0.46±0.03</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>4</td>
<td>0.10–0.40</td>
<td>0.36±0.02</td>
</tr>
<tr>
<td>1,2,5,6 – DBA *</td>
<td>18.3</td>
<td>4</td>
<td>0.20–0.80</td>
<td>0.60±0.03</td>
</tr>
<tr>
<td>1,2,3,4 – DBA *</td>
<td>17.8</td>
<td>4</td>
<td>0.20–0.80</td>
<td>0.71±0.02</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.08–0.34</td>
<td>0.50±0.04</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>5</td>
<td>0.26–0.78</td>
<td>0.58±0.04</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>5</td>
<td>0.15–0.75</td>
<td>0.73±0.07</td>
</tr>
<tr>
<td>Perylene $^a$</td>
<td>12.6</td>
<td>3</td>
<td>0.32–0.52</td>
<td>0.74±0.02 $^c$</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>2</td>
<td>0.25–0.49</td>
<td>0.66±0.03 $^c$</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.63</td>
<td>0.16±0.07 $^c$</td>
</tr>
<tr>
<td>β-Carotene $^b$</td>
<td>6.3</td>
<td>2</td>
<td>0.44–0.85</td>
<td>&lt;0.03 $^c$</td>
</tr>
</tbody>
</table>

1 excluding zero

$a$ sensitized by benzophenone

$b$ sensitized by anthracene

$c$ results of Marshall

* DBA - abbreviation for Dibenzanthracene
Fig 4.9 Quenching of various donors by Co(acac)$_3$
TABLE 4.11

Quenching by trans-Co(bzac)$_3$ in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_T/1000\text{cm}^{-1}$</th>
<th>No. of Conc.'s</th>
<th>Range $[Q]/\text{mmol}$</th>
<th>$k_q/10^9\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>3</td>
<td>0.06-0.17</td>
<td>5.12±0.25</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>4</td>
<td>0.04-0.17</td>
<td>5.34±0.20</td>
</tr>
<tr>
<td>Naphthalene $^a$</td>
<td>21.3</td>
<td>4</td>
<td>0.04-0.17</td>
<td>4.64±0.15</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.12-0.31</td>
<td>2.15±0.08</td>
</tr>
<tr>
<td>Chrysene</td>
<td>20.0</td>
<td>4</td>
<td>0.05-0.20</td>
<td>4.15±0.20</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>3</td>
<td>0.13-0.20</td>
<td>1.85±0.09</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.10-0.27</td>
<td>1.30±0.05</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>4</td>
<td>0.20-0.34</td>
<td>1.21±0.04</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>4</td>
<td>0.17-0.35</td>
<td>1.35±0.05</td>
</tr>
<tr>
<td>Perylene $^a$</td>
<td>12.6</td>
<td>4</td>
<td>0.05-0.21</td>
<td>1.32±0.06</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>1</td>
<td>0.29</td>
<td>0.78±0.03</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.28</td>
<td>0.23±0.02</td>
</tr>
</tbody>
</table>

$^a$ excluding zero

$^a$ sensitized by benzophenone
(a) Phenanthrene ; \( Q = 4.417 \times 10^{-5} \text{ mol dm}^{-3} \)

(b) Acetonaphthone ; \( Q = 6.246 \)

(c) Pyrene ; \( Q = 5.420 \)

Fig 4.10 Quenching of various donors by trans-Co(bzac)$_3$
### TABLE 4.12

Quenching by trans-Co(Ø-PDO)$_3$

in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_T$/1000cm$^{-1}$</th>
<th>No. of Conc.'s</th>
<th>Range $[Q]/$mmol</th>
<th>$k_q$/$10^3$ dm$^3$ mol$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>3</td>
<td>0.06-0.18</td>
<td>6.36±0.29</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>4</td>
<td>0.05-0.20</td>
<td>6.73±0.32</td>
</tr>
<tr>
<td>Naphthalene $^a$</td>
<td>21.3</td>
<td>4</td>
<td>0.04-0.11</td>
<td>7.23±0.25</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.07-0.27</td>
<td>3.34±0.09</td>
</tr>
<tr>
<td>Chrysene</td>
<td>20.0</td>
<td>4</td>
<td>0.06-0.25</td>
<td>4.85±0.19</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>4</td>
<td>0.05-0.13</td>
<td>2.93±0.09</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.05-0.13</td>
<td>2.21±0.06</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>4</td>
<td>0.12-0.32</td>
<td>1.85±0.05</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>5</td>
<td>0.12-0.38</td>
<td>2.30±0.06</td>
</tr>
<tr>
<td>Perylene $^a$</td>
<td>12.6</td>
<td>3</td>
<td>0.18-0.28</td>
<td>2.28±0.16</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>3</td>
<td>0.12-0.26</td>
<td>1.12±0.06</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>1</td>
<td>0.26</td>
<td>0.37±0.03</td>
</tr>
</tbody>
</table>

$^1$ excluding zero

$^a$ sensitized by benzophenone
(a) Chrysene; \( Q = 6.131 \times 10^{-5} \) mol dm\(^{-3}\)
(b) Naphthalene; \( Q = 2.346 \)
(c) Pyrene; \( Q = 2.658 \)

Fig 4.11 Quenching of various donors by \( \text{trans-} \text{Co(\(\phi\)-PDO)}_3 \)
4.3.3 Quenching by Cobalt (III) β-diketonate complexes containing trifluoromethyl groups

Cobalt (III) tris (1,1,1-trifluoropentan-2,4-dionate), Co(tfac)$_3$ and Cobalt (III) tris (1,1,1,5,5,5-hexafluoropentan-2,4-dionate), Co(hfac)$_3$ were synthesised in accordance with the methods given in chapter II (Table 2.5). In the case of Co(tfac)$_3$, geometrical isomers are possible, and the trans-isomer was separated and used for quenching experiments.

The results for the quenching of excited triplet states by trans-Co(tfac)$_3$ are presented in Table 4.13 together with the associated donor energy and the concentration range employed. Some $-k_1'$ vs $[Q]$ plots are given in Figure 4.12. Quenching experiments were attempted using Co(hfac)$_3$ with anthracene and pyrene as donors. The complications of these systems is described below.

Figure 4.13 gives a plot of the Y-coordinate of the oscilloscope versus its time base, in terms of channel numbers (1 channel number being equivalent to 48.8 ns), for the experimental triplet decay curves of anthracene in the presence and absence of Co(hfac)$_3$. For the freshly prepared solutions containing Co(hfac)$_3$, the shape of the decay curve in the channel number region 200 - 400 indicates the presence of a long-lived transient not normally associated with previous quenching studies. A Triplet - Triplet absorption spectra taken 50 channel numbers after the flash, Figure 4.14 being obtained for anthracene and anthracene/Co(hfac)$_3$ indicating the presence of an excited state interaction.

Ground state absorption spectra were also obtained. Co(hfac)$_3$ dissolved in benzene showed no change in absorption or band shifts in
TABLE 4.13
Quenching by trans-Co(tfac)$_3$

in benzene solution at 20°C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_T^{1}$</th>
<th>No. of 1 Conc.'s</th>
<th>Range $[Q]$/$\text{mmol}$</th>
<th>$k_q^{1}$/$10^9 \text{dm mol}^{-1} \text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>4</td>
<td>0.05–0.20</td>
<td>4.73±0.32</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>21.6</td>
<td>4</td>
<td>0.04–0.20</td>
<td>4.86±0.40</td>
</tr>
<tr>
<td>Naphthalene *</td>
<td>21.3</td>
<td>4</td>
<td>0.17–0.20</td>
<td>5.06±0.12</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4</td>
<td>0.22–0.55</td>
<td>1.19±0.06</td>
</tr>
<tr>
<td>Chrysene</td>
<td>20.0</td>
<td>4</td>
<td>0.13–0.47</td>
<td>4.10±0.27</td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>5</td>
<td>0.03–0.08</td>
<td>3.89±0.12</td>
</tr>
<tr>
<td>1,2,5,6-DBA *</td>
<td>18.3</td>
<td>4</td>
<td>0.05–0.19</td>
<td>3.37±0.17</td>
</tr>
<tr>
<td>1,2,3,4-DBA *</td>
<td>17.8</td>
<td>4</td>
<td>0.10–0.30</td>
<td>2.16±0.13</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>4</td>
<td>0.03–0.11</td>
<td>3.01±0.07</td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>5</td>
<td>0.26–0.66</td>
<td>0.51±0.05</td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>4</td>
<td>0.22–0.69</td>
<td>1.05±0.06</td>
</tr>
<tr>
<td>Perylene *</td>
<td>12.6</td>
<td>4</td>
<td>0.10–0.42</td>
<td>1.03±0.07</td>
</tr>
<tr>
<td>Tetracene</td>
<td>10.3</td>
<td>5</td>
<td>0.08–0.30</td>
<td>0.58±0.05</td>
</tr>
<tr>
<td>Pentacene</td>
<td>8.0</td>
<td>3</td>
<td>0.07–0.36</td>
<td>0.17±0.02</td>
</tr>
</tbody>
</table>

1 excluding zero
* DBA – abbreviation for dibenzanthracene
a sensitized by benzophenone
(a) Anthracene; \( Q = 1.147 \times 10^{-4} \) mol dm\(^{-3} \)

(b) Pyrene; \( Q = 2.639 \times 10^{-5} \) mol dm\(^{-3} \)

(c) Coronene; \( Q = 1.594 \times 10^{-5} \) mol dm\(^{-3} \)

Fig 4.12  Quenching of various donors by trans-Co(tfac)\(_3\)
FIG 4.13 TRIPLET DECAY TRACES

CHANNEL NUMBER

CO-ORD

Y

0

50

100

150

0 100 200 300 400 500 600 700 800 900 1000

CHANNEL NUMBER
Fig 4.14 Triplet - Triplet Absorption Spectra of Anthracene and Anthracene/Co(hfac)$_3$

(a) Anthracene $2.443 \times 10^{-4}$ mol dm$^{-3}$

(b) Anthracene $2.443 \times 10^{-4}$

Co(hfac)$_3$ $9.896 \times 10^{-5}$
the 450-750 nm region over a 24 hour period; Anthracene does not absorb in this region. The same spectral region was monitored for a mixture of anthracene and Co(hfac)$_3$ and on dissolution of the anthracene a reduction in absorption of the d-d band of Co(hfac)$_3$ was noted. Spectra were rerun at hourly intervals and Figure 4.15 illustrates the reduction in absorption which was found to approach zero after 3 hours. An insoluble crystalline residue was observed at the base of the spectroscopic cell after this period. Similar results were obtained for the pyrene/Co(hfac)$_3$ system.
FIG 4.15  ABSORPTION SPECTRA OF ANTHRACENE / ANTHRACENE - CO(HFAC)3

- CO(HFAC)3  TIME=00 MINS
- CO(HFAC)3 + ANTHRACENE  TIME=30 MINS
- CO(HFAC)3 + ANTHRACENE  TIME=60 MINS
- CO(HFAC)3 + ANTHRACENE  TIME=90 MINS

ABSORPTION vs. WAVELENGTH (NM)
CHAPTER IV

REFERENCES


5.0 Introduction

In this Chapter, the results presented in Chapter IV will be discussed in terms of the classical treatment of electronic energy transfer and electron transfer which was developed in Chapter I. The results have been divided into two main parts. The first dealing with the quenching of electronically excited triplet donors by Cr(III) \( \beta \)-diketonate complexes, and the second part of the discussion is concerned with the quenching of triplet donors by Co(III) \( \beta \)-diketonate complexes. At the end of each part, a brief summary will be given, and any general trends discussed. This Chapter will close with a section concerned with the overall conclusions pertaining to the research presented in this thesis.

Before discussing the results, a brief resume of the classical treatment of electronic energy transfer (see Chapter 1.4 for greater detail) will be given. Special reference being made to the factors which determine the profile of a \( k_q \) vs. \( E_T \) plot.

5.1 Classical Treatment of Electronic Energy Transfer: A Review

Electronic energy transfer from a triplet donor to a quencher with one accepting state may be represented by the scheme:

\[
\begin{align*}
3D^* + nA & \xrightarrow{sk_d} n(D^*\cdot\cdot\cdot A) \xrightarrow{k_{en}} n(D\cdot\cdot\cdot A^*) \xrightarrow{k_d} 1_D + nA^* \\
& \xrightarrow{k_{d-}} \frac{1}{\tau_A} \\
& \xrightarrow{k_{-d}} \xrightarrow{k_{-en}}
\end{align*}
\] 5.1
Assuming $\frac{1}{\tau^o_{A^*}} \gg k_d [B]$ , then application of steady state
treatment to the encounter complexes gives the value for the bimolecular
quenching constant, $k_q$, as:

$$
\frac{sk_d}{1 + k_d} \left( \frac{1 + k_{-en}}{k_{en}} \right)
$$

or alternatively as:

$$
\frac{sk_d}{1 + \left( \frac{1}{k_{en}} \right) \left( \frac{k_{en}}{k_{-en} + k_d} \right)}
$$

From absolute rate theory (1), the rate constants for the energy
transfer steps, $k_{en}$ and $k_{-en}$, may be expressed as:

$$
k_{en} = k^o_{en} e^{-\Delta G^*/RT}
$$

$$
\frac{k_{-en}}{k_{en}} = e^{\Delta G/RT}
$$

where $\Delta G^*$ and $\Delta G$ are the free energy of activation and the standard
free energy change for the forward energy transfer process respectively.

$k^o_{en}$ is the pre-exponential factor which is given by:

$$
k^o_{en} = \frac{k_{en} kT}{h}
$$
where \( \frac{kT}{h} \) is the universal frequency and \( \kappa \) is the transmission coefficient, which is a measure of the probability of the system which has reached the transition state will continue to the final state.

The standard free energy change, \( \Delta G \), for the energy transfer step

\[
\text{D}^* + \text{A} \rightarrow \text{D} + \text{A}^*
\]

is given by:

\[
\Delta G = \Delta G_t - W_r + W_p
\]

and the work terms \( (W_r \text{ and } W_p) \) are assumed to be zero since only physical encounters of uncharged species are being considered. Therefore, \( \Delta G \) may be calculated from thermodynamics:

\[
\Delta G = \Delta H - T \Delta S
\]

which, for the system under discussion is given by:

\[
-\Delta G(D^*,D) + \Delta G(A^*,A) = -\Delta H(D^*,D) + T \Delta S(D^*,D) + \Delta H(A^*,A) - T \Delta S(A^*,A)
\]

Entropy differences between the ground and excited states have been shown by Balzani et al (2) to be zero and therefore, the enthalpy difference between these states at room temperature is equal to the zero-zero spectroscopic energy \( (E_{oo}) \). Thus, \( \Delta G \) is given by:

\[
\Delta G = -hNc \left[ \bar{\nu}_{oo}(D^*) - \bar{\nu}_{oo}(A^*) \right]
\]
where $\tilde{\nu}_{00} (D^*)$ and $\tilde{\nu}_{00} (A^*)$ refer to the wavenumbers of zero-zero transitions of the donor and acceptor, respectively.

As discussed in detail in Chapter I (Sec. 1.4.1), there are a number of equations for calculating $\Delta G^+$, the free energy of activation, however, the expression derived by Agmon and Levine (3) is preferred:

$$
\Delta G^+ = \Delta G + \frac{\Delta G^+ (0)}{\ln 2} \ln \left[ 1 + \exp \left( \frac{-\Delta G \ln 2}{\Delta G^+ (0)} \right) \right]
$$

This expression introduces another variable into the system, namely $\Delta G^+ (0)$ which is known as the intrinsic reorganisational barrier. For a reaction of the type considered here, i.e. scheme 5.7, the overall value of $\Delta G^+ (0)$ is given by:

$$
\Delta G^+_{DA} (0) = \frac{1}{2} \left( \Delta G^+_{D} (0) + \Delta G^+_{A} (0) \right)
$$

Therefore, substitution of equations 5.4, 5.5, 5.11, 5.12 and 5.13 into either equation 5.2 or 5.3 allows $k_q$ (experimental) to be fitted by varying $k_{en}^o$ (and therefore $\kappa_{en}$).

As discussed in Chapter I (Sec. 1.6.4), energy transfer to transition metal complexes involves energy being accepted by at least two acceptor states (to be discussed later), in the case of chromium complexes, one doublet state ($^2E_g$, $^2T_{1g}$) and one quartet state $^4T_{2g}$. Theoretical calculations (Chapter III, Table 3.2) show that the $^2T_{1g}$ state of the Cr(III) $\beta$-diketonate complexes studied in this thesis lie between 580-680 cm$^{-1}$ above that of the $^2E_g$ state. In Chapter I (Sec. 1.4.2), $k_q$ vs $E_T$ calculations carried out on energy transfer to two acceptor states lying up to...
1000 cm\(^{-1}\) apart showed (Fig. 1.8) that the curve for two acceptor states exhibited only a slight broadening over that for one acceptor state. On the basis of these calculations and since the differences between the energy transfer profiles are within experimental error of the quenching constants obtained, the pair of doublet states (\(^2E_g\) and \(^2T_{1g}\)) will be treated as a degenerate pair.

Therefore, energy transfer to these acceptors may be described by:

\[
\begin{align*}
3_{D^*} + 4_A & \rightarrow \frac{1}{6} k_d \\
& \rightarrow \frac{1}{3} k_d \rightarrow 4_{D^*} \rightarrow 4_{D^*} \rightarrow 1_D + 4_{A^*} \\
& \rightarrow 2_{D^*} \rightarrow 2_{D^*} \rightarrow 1_D + 2_{A^*} \\
& \rightarrow k_{-d} \\
& \rightarrow k_{-d} \\
& \rightarrow k_{-en} \\
& \rightarrow k_{-en} \\
\end{align*}
\]

and the bimolecular quenching constant is given by:

\[
k_q = 4k_q + 2k_q
\]

where,

\[
m_{k_q} = \frac{s_m k_d}{1 + \frac{1}{\frac{s_m k_{en}}{(k_{-en} + k_{-d})}}}
\]

\[
5.16
\]
m being the multiplicity of the state under discussion.

Wilkinson and Tsiamis (4) measured the bimolecular rate constants for thirteen triplet states of organic donors quenched by Chromium(III) tris(2,2,6,6-tetramethylheptan-3,5-dionate), \( \text{Cr(dpm)}_3 \). In order to explain the sudden rise in quenching efficiency observed at \( \lambda = 20,000 \text{ cm}^{-1} \), energy transfer to produce the higher non-distorted \( ^2\text{T}_{2g} \) state of \( \text{Cr(dpm)}_3 \) was postulated. The mechanistic pathway for energy transfer to \( \text{Cr(dpm)}_3 \) being given by:

\[
\begin{align*}
\text{3}D^* + \text{4}A^* & \quad \begin{array}{c}
\text{1/6 } k_d \\
\text{2}D^* \cdots \text{A}\text{)} \end{array} \\
\text{2}D^* \cdots \text{A}\text{)} & \quad \begin{array}{c}
\text{2}k_\text{en} \\
\text{2}D^* \cdots \text{A}\text{)} \end{array} \\
\text{2}D^* \cdots \text{A}\text{)} & \quad \begin{array}{c}
\text{1/3 } k_d \\
\text{4}k_\text{en} \\
\text{4}D^* \cdots \text{A}\text{)} \\
\text{1}D + \text{4}A^* \\
\text{1}D + \text{2}A^*_2 \\
\text{1}D + \text{2}A^*_1 \\
\end{array}
\end{align*}
\]

and \( k_q \) is given by:

\[
k_q = \Sigma 2k_\text{en} + 4k_q
\]

where \( 4k_q \) is given by expression 5.3 and \( \Sigma 2k_q \) may be represented by:

\[
\Sigma 2k_q = \frac{1/6 k_d}{1 + \left( \frac{2k_\text{en}}{(2k_\text{en} + k_d)} + \frac{2k'_\text{en}}{(2k'_\text{en} + k_d)} \right)}
\]
In a previous study, Wilkinson and Tsiamis (5) had advocated the use of the kinetic expression 5.14 to describe the quenching of organic triplet donors by Cr(acac)$_3$ and Cr(bzac)$_3$. Since the quenching constants for these complexes were close to diffusion control once spin-statistics were included, these workers concluded that it would be difficult to experimentally detect energy transfer to the higher doublet state and therefore this energy transfer step was not included.

Since a number of mechanistic pathways have been developed to describe energy transfer, it is of interest to examine how, and to what degree the various parameters affect the predicted value of $k_q$.

1. The rate of constant for diffusion $k_d$ determines the maximum rate at which the donor and acceptor may diffuse together and therefore if all other factors are constant, it also determines $k_q$.

2. The position and nature (multiplicity) of the acceptor's excited state energy levels determines the manner in which $k_q$ may increase and the maximum value of $k_q$

$$k_q^{(\text{max})} = s \ k_d$$  \hspace{1cm} (5.20)

associated with the particular state.

3. The intrinsic reorganisational barrier, $\Delta G^\ddagger(0)$ dictates the manner in which the quenching efficiency rises for a given excited state of the acceptor.
4. If all of the above factors are held constant, then the quenching efficiency of a system is determined by the pre-exponential factor, $k_0$ or the transmission coefficient, $k_{en}$ ($k_{en} = k_{en}^0 kT/h$).

Each of the above-mentioned parameters will be discussed in turn, values assigned where appropriate and for experimental and theoretical "values" an indication of their variability assessed.

5.1.1 Evaluation of the Diffusion Control Rate Constant

Triplet anthracene ($E_T = 14,700$ cm$^{-1}$) has been shown by Wilkinson and Tsiamis (6) to typify a plateau quenching constant for energy transfer to the doublet state ($^2E_g$, $^2T_{1g}$) in Cr(acac)$_3$ and Cr(bzac)$_3$. For these two complexes they have shown that energy transfer is essentially diffusion controlled ($k_q = 1.25 \pm 0.04 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ for anthracene/Cr(acac)$_3$ and $1.48 \pm 0.05 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ for anthracene/Cr(bzac)$_3$), when the appropriate spin statistical factor is introduced and $k_d$ is taken to be $1 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$, as predicted by the Debye equation ($k_d = \frac{8RT}{3n}$), i.e. $sk_d = 1.66 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. Examination of the results presented in Chapter IV show that for the quenching of anthracene by the $\gamma$-substituted $\delta$-diketonate complexes of Chromium(III), i.e. Cr(3-Meacac)$_3$, Cr(3-Etacac)$_3$ and Cr(3-Pracac)$_3$, rate constants in the region $2.15 - 1.70 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ have been obtained. Substitution of these experimental $k_q$ values into equation 5.20 yield $k_d$'s in the region $1.29 - 1.04 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$, assuming a fully diffusion controlled mechanism. These predicted $k_d$ values are higher than those calculated from the Debye equation which leaves us with three possibilities:

i. Another quenching mechanism is becoming operable.

ii. The diffusion controlled rate constant as defined by the Debye equation is an underestimate of the real value of $k_d$. 
iii. That spin selection rules are being contravened in some manner.

Dealing with the first point, Wilkinson and Tsiamis have found in subsequent papers (6,7) that energy transfer and electron transfer may compete as the mechanism of quenching at the same time. In the case of Cr(hfac)\textsubscript{3} with a reduction potential of -0.40V vs S.C.E. (see Table 3.5) electron transfer was found to efficiently compete with energy transfer, with a \( \Delta G \) for electron transfer of -0.46 eV for anthracene, whilst Cr(acac)\textsubscript{3} and Cr(bzac)\textsubscript{3} (reduction potentials of -1.73V and -1.50V; vs SCE; \( \Delta G_{el} \) of +0.87 eV and 0.64 eV respectively) quench by electronic energy transfer only. Since the three \( \gamma \)-substituted complexes, Cr(3-Meacac)\textsubscript{3}, Cr(3-Etacac)\textsubscript{3} and Cr(3-Pracac)\textsubscript{3} have reduction potentials of -1.75V, -1.78V and -1.79V vs S.C.E. respectively, electron transfer may be discounted as a possible competing mechanism and it is unlikely that any other quenching mechanism will operate with such a high efficiency.

Moving on to the second point, the various methods of calculating diffusion coefficients and hence \( k_d \) have been discussed in Chapter I (Sec. 1.5). It was found that for the many systems which were not adequately described by the Debye equation, that the treatment of Spernol and Wirtz (8) was able to give satisfactory agreement with experimental results for low viscosity, non-associating solvents. The Spernol and Wirtz treatment makes use of a microfriction factor, \( f_c \), to correct the Debye equation for the movement of the solute molecule into holes in the solvent and also considers the finite thickness of the solvent layers which flow round a moving solute molecule. The diffusion coefficient may be calculated from:

\[
D = \frac{kT}{6\pi\eta f_c} \]

5.21
and the microfriction factor is given by:

$$ f_t = 0.16 + 0.4 \frac{r}{r_L} $$  \hspace{1cm} (5.22) 

where \( r \) and \( r_L \) are the radii of the solute and solvent respectively.

The empirical value of \( f_t \) was obtained by analysis of measurements made on 137 different binary systems in 25 different solvents (9). Since benzene was used as a solvent throughout the work contained in this thesis, the 51 systems that employed benzene as presented by Spernol and Wirtz were reanalysed giving a new working expression for the microfriction factor of:

$$ f_t = -0.04 + 0.53 \frac{r}{r_L} $$  \hspace{1cm} (5.23) 

In order to calculate diffusion coefficients, equation 5.21, molecular radii must be determined, and the use of Le Bas molar volume increments (9) have been advocated by many workers (see Sec. 1.5 for more detail). These increments are listed in Appendix IIIa, but in the case of determining the volume of the acceptors, values for Chromium(III) and Cobalt(III) were not available. However, any increase in molar volume that may occur on the addition of the central atoms increment would be offset by the fact that three, six-atom ring systems are formed, which according to Le Bas necessitates a reduction in volume. Since no estimated molar volume was used for the central atom, these reductions were not made. The Le Bas volumes of the acceptors and donors are given in Appendices IIIb and IIIc respectively.

The three methods of calculating radii from Le Bas volumes were also discussed in Chapter I and may all be described by the equation:
\[ r = \left( \frac{3Vx}{4\pi N} \right)^{\frac{1}{3}} \]  

where \( x \) is the space filling factor. Since the treatment of Spernol and Wirtz is being used to calculate diffusion coefficients, it is necessary therefore to employ the same relationship for calculating \( r \), i.e. \( x = 0.74 \) for close packed spheres. The radii of the acceptors and donors are presented in Appendices IIIb and IIIC respectively. From the radii, diffusion coefficients may be calculated via equation 5.21 utilising the microfriction factor, \( f \), (equation 5.23) and the diffusion rate constant can be calculated from:

\[ k_d = 4\pi N r_{DA} D_{DA} \]  

where \( r_{DA} = r_D + r_A \) and \( D_{DA} = D_D + D_A \). Table 5.1 lists the calculated values of \( D_D \), \( D_A \) and \( D_{DA} \) as well as the associated \( r_{DA} \) and \( k_d \), for a number of organic donor molecules with \( \text{Cr(acac)}_3 \) as the constant acceptor. Table 5.2 illustrates the variation of \( k_d \) with different acceptors (not all of which were studied in this thesis) using a constant donor, anthracene.

Excluding the value of naphthalene in Table 5.1 and that of \( \text{Cr(PDO)}_3 \) in Table 5.2, which give \( k_d \)'s higher than average due to their low radii and subsequently high diffusion coefficients, the values of \( k_d \) calculated are 1.39 ± 0.07 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) from Table 5.1 and 1.43 ± 0.04 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) from Table 5.2 giving a working average of 1.41 ± 0.07 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}. An average value for \( k_d \) rather than \( k_d \)'s for a particular donor/acceptor pair will be advocated, since the range associated with the diffusion rate constant is \( \sigma \pm 5\% \) which is of the same order as that found for the experimental error of the quenching constants. Therefore,
TABLE 5.1

Variation in Diffusion Constant for Organic Donor Molecules with Cr(acac)$_3$ as a Constant Acceptor in Benzene at 20°C

<table>
<thead>
<tr>
<th>DONOR$^1$</th>
<th>ACCEPTOR$^2$</th>
<th>$D_D/10^{-6}$ cm$^2$s$^{-1}$</th>
<th>$D_A/10^{-6}$ cm$^2$s$^{-1}$</th>
<th>$D_{DA}/10^{-6}$ cm$^2$s$^{-1}$</th>
<th>$r_{DA}/\text{Å}$</th>
<th>$k_d/10^{10}$ dm$^3$ mol$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>Cr(acac)$_3$</td>
<td>16.40</td>
<td>8.99</td>
<td>25.39</td>
<td>8.21</td>
<td>1.58</td>
</tr>
<tr>
<td>Anthracene</td>
<td>&quot;</td>
<td>13.47</td>
<td>&quot;</td>
<td>22.46</td>
<td>8.56</td>
<td>1.46</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>&quot;</td>
<td>13.47</td>
<td>&quot;</td>
<td>22.46</td>
<td>8.56</td>
<td>1.46</td>
</tr>
<tr>
<td>Pyrene</td>
<td>&quot;</td>
<td>12.72</td>
<td>&quot;</td>
<td>21.71</td>
<td>8.67</td>
<td>1.42</td>
</tr>
<tr>
<td>Tetracene</td>
<td>&quot;</td>
<td>11.37</td>
<td>&quot;</td>
<td>20.36</td>
<td>8.89</td>
<td>1.37</td>
</tr>
<tr>
<td>Chrysene</td>
<td>&quot;</td>
<td>11.37</td>
<td>&quot;</td>
<td>20.36</td>
<td>8.89</td>
<td>1.37</td>
</tr>
<tr>
<td>1,2-benzanthracene</td>
<td>&quot;</td>
<td>11.37</td>
<td>&quot;</td>
<td>20.36</td>
<td>8.89</td>
<td>1.37</td>
</tr>
<tr>
<td>Perylene</td>
<td>&quot;</td>
<td>10.95</td>
<td>&quot;</td>
<td>19.94</td>
<td>8.97</td>
<td>1.35</td>
</tr>
<tr>
<td>Pentacene</td>
<td>&quot;</td>
<td>10.00</td>
<td>&quot;</td>
<td>18.99</td>
<td>9.16</td>
<td>1.32</td>
</tr>
<tr>
<td>1,2,3,4 - DBA$^*$</td>
<td>&quot;</td>
<td>10.00</td>
<td>&quot;</td>
<td>18.99</td>
<td>9.16</td>
<td>1.32</td>
</tr>
<tr>
<td>1,2,5,6 - DBA$^*$</td>
<td>&quot;</td>
<td>10.00</td>
<td>&quot;</td>
<td>18.99</td>
<td>9.16</td>
<td>1.32</td>
</tr>
<tr>
<td>Coronene</td>
<td>&quot;</td>
<td>10.19</td>
<td>&quot;</td>
<td>18.18</td>
<td>9.12</td>
<td>1.32</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>&quot;</td>
<td>12.99</td>
<td>&quot;</td>
<td>21.98</td>
<td>8.63</td>
<td>1.44</td>
</tr>
<tr>
<td>Acridine</td>
<td>&quot;</td>
<td>13.61</td>
<td>&quot;</td>
<td>22.60</td>
<td>8.54</td>
<td>1.46</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>&quot;</td>
<td>13.61</td>
<td>&quot;</td>
<td>22.60</td>
<td>8.54</td>
<td>1.46</td>
</tr>
</tbody>
</table>

* Abbreviation for Dibenzanthracene

1 Donor radii - from appendix III

2 Acceptor radius - 4.70 Å

Excluding naphthalene (see text) $\bar{k_d} = 1.39 \pm 0.07 \times 10^{10}$ dm$^3$ mol$^{-1}$s$^{-1}$
**TABLE 5.2**

Variation in Diffusion Constant for Cr(III) \(\beta\)-diketonate Complexes with a Constant Donor Molecule Anthracene in Benzene at \(20^\circ\)C

<table>
<thead>
<tr>
<th>DONOR(^1)</th>
<th>ACCEPTOR(^2)</th>
<th>(D_D) /10(^{-6}) cm(^2)s(^{-1})</th>
<th>(D_A) /10(^{-6}) cm(^2)s(^{-1})</th>
<th>(D_{DA}) /10(^{-6}) cm(^2)s(^{-1})</th>
<th>(R_{DA}) /(\AA)</th>
<th>(k_d) /10(^{10}) dm(^3)mol(^{-1})s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>Cr(acac)(_3)</td>
<td>13.47</td>
<td>8.99</td>
<td>22.46</td>
<td>8.56</td>
<td>1.46</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(tfac)(_3)</td>
<td>&quot;</td>
<td>8.25</td>
<td>21.72</td>
<td>8.76</td>
<td>1.44</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(hfac)(_3)</td>
<td>&quot;</td>
<td>7.69</td>
<td>21.16</td>
<td>8.93</td>
<td>1.43</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(bzac)(_3)</td>
<td>&quot;</td>
<td>6.61</td>
<td>20.08</td>
<td>9.32</td>
<td>1.42</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(dbm)(_3)</td>
<td>&quot;</td>
<td>4.99</td>
<td>18.46</td>
<td>10.14</td>
<td>1.42</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(dpdm)(_3)</td>
<td>&quot;</td>
<td>5.33</td>
<td>18.80</td>
<td>9.91</td>
<td>1.41</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr((\phi)-PDO)(_3)</td>
<td>&quot;</td>
<td>6.79</td>
<td>10.26</td>
<td>9.25</td>
<td>1.42</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(BDO)(_3)</td>
<td>&quot;</td>
<td>10.34</td>
<td>23.81</td>
<td>8.25</td>
<td>1.49</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(t)BuPDO(_3)</td>
<td>&quot;</td>
<td>7.22</td>
<td>20.69</td>
<td>9.09</td>
<td>1.42</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(PDO)(_3)</td>
<td>&quot;</td>
<td>12.38</td>
<td>25.85</td>
<td>7.88</td>
<td>1.54</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(tfbzac)(_3)</td>
<td>&quot;</td>
<td>6.00</td>
<td>19.47</td>
<td>9.60</td>
<td>1.42</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(3-Meacac)(_3)</td>
<td>&quot;</td>
<td>7.98</td>
<td>21.45</td>
<td>8.84</td>
<td>1.44</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(3-Etacac)(_3)</td>
<td>&quot;</td>
<td>7.22</td>
<td>20.69</td>
<td>9.09</td>
<td>1.42</td>
</tr>
<tr>
<td>&quot;</td>
<td>Cr(3-Pracac)(_3)</td>
<td>&quot;</td>
<td>6.61</td>
<td>20.08</td>
<td>9.32</td>
<td>1.42</td>
</tr>
</tbody>
</table>

1 Donor radius = 3.86 \(\AA\)

2 Acceptor radii = from Appendix III

Acceptor abbreviations (Chapter II Table 2.4)

Excluding Cr(PDO)\(_3\) (see text) av \(k_d\) = 1.43 ± 0.04 \times 10\(^{10}\) dm\(^3\)mol\(^{-1}\)s\(^{-1}\)
any trend which may pertain to the calculated diffusion constants would
be lost in the error of the quenching constants. However, the average
will not be rigidly enforced if better theoretical fits to experimental
points are likely to be obtained using individual donor/acceptor \( k_d \)'s.
(Quenching of naphthalene might be such a case).

As mentioned previously, no values for the Le Bas volumes of the
central atoms have been found and therefore it would be of interest to
calculate the variation of \( k_d \) with acceptor volume. The pyrene/Cr(acac)\(_3\)
system was chosen as typical donor-acceptor pair and the acceptor volume
was varied from +20% to -20% of its original value. This resulted in \( k_d \)'s
taking on the values \( 1.40 \times 10^{10} \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1} \) (+20% on \( V_A \)) and \( 1.46 \times 10^{10} \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1} \) (-20% on \( V_A \)), i.e. \( \approx 3\% \) change in \( k_d \). (See Appendix IIId).
This small change in \( k_d \) is not particularly surprising since \( D_A \) is
inversely proportional to \( r_A \) (see equation 5.21) and \( k_d \) is proportional
to both \( D_{DA} \) and \( r_{DA} \) (equation 5.25). Therefore, any change in volume
(occurring through addition of the Le Bas volume of Cr(III) or Co(III)),
and hence radius, have a self-cancelling effect which in turn only
varies \( k_d \) by a small amount.

In conclusion, the use of the diffusion rate constant derived from
the SW treatment (\( k_d = 1.41 \pm 0.07 \times 10^{10} \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1} \)), allows non-
diffusion controlled energy transfer to be attributed to all the systems
studied within this thesis. Thus, the \( \gamma \)-substituted \( \beta \)-diketonate com-
plexes may be interpreted without invoking any contravention of spin
statistics.
The value of $k_d$, the rate of dissociation, is given by the Eigen equation:

$$k_d = \frac{3k_d}{4\pi N r^3}$$

A value of $8 \times 10^9$ s$^{-1}$ was obtained when the average of the donor/acceptor pair radii are substituted into equation 5.26. Since $k_d$ is inversely proportional to $r^2$, ($k_d$ is proportional to $r$), changes in donor/acceptor volume are likely to have a more pronounced effect on $k_d$ than on $k_d$ (as previously calculated).

Changes in donor/acceptor volumes and hence in $k_d$, affects the overall value of $k_q$, however the magnitude of this effect is highly dependent on the efficiency of energy transfer. Sample calculations show that for highly efficient energy transfer, $k_{en}^0 = 4 \times 10^{11}$ s$^{-1}$, variations in donor/acceptor volume of $\pm 20\%$ affect the overall rate constant by less than one percent. For less efficient energy transfer, $k_{en}^0 = 1 \times 10^{10}$, these changes in volume have a more pronounced effect on $k_q$, approximately $\pm 8\%$. These variations being of the same order as the observed experimental errors.

5.1.2 Position of the Quencher Excited State Energy Levels

The spectroscopy of the acceptors has been discussed in detail in Chapter III and the position of the excited states determined. The following discussions will give errors associated with the measurements/calculations of the band positions.
5.1.2.1 Low Lying Doublet States $^{2}_{Eg}$ and $^{2}_{T_{1g}}$

The values used for $^{2}_{Eg}$ (Table 3.1) were obtained from the work of Fatta and Lintvedt (10) and are in good agreement with the values of other workers (11,12). The $^{2}_{T_{1g}}$ state is not readily observed but it may be calculated from:

$$E^{2}_{T_{1g} \rightarrow ^{4}_{A_{2g}}} = 9B_{55} + 3C - \frac{24B_{55}^2}{10Dq}$$

assuming $C = 4B$ or the difference in energy between the two states from:

$$E^{2}_{T_{1g} \rightarrow ^{2}_{Eg}} = \frac{26B_{55}^2}{10Dq}$$

$10Dq$ being equal to the energy of the $^{4}_{T_{2g} \rightarrow ^{4}_{A_{2g}}}$ transition and $B_{55}$ is obtained from the energy of the $^{2}_{Eg} \rightarrow ^{4}_{A_{2g}}$ transition. Table 3.3 (Chapter 3) lists the calculated energy level of the $^{2}_{T_{1g}}$ state for a number of Cr(III) complexes and they all lie $580 - 680$ cm$^{-1}$ above the $^{2}_{Eg}$ state. The error associated with these theoretical calculations is probably of the order $\pm 300$ cm$^{-1}$, thus allowing the $^{2}_{T_{1g}}$ state to be up to $1000$ cm$^{-1}$ above that of the $^{2}_{Eg}$ state.

5.1.2.2 The Quartet State $^{4}_{T_{2g}}$

As discussed in Chapter III, the wavenumber value for the $^{4}_{T_{2g} \rightarrow ^{4}_{A_{2g}}}$ transition in Table 3.1 represents a band maxima, not the $\tilde{v}_{\infty}$ value, since this transition involves the promotion of an electron to the antibonding, $e_{g}$ orbitals, with subsequent geometric distortion. Fleischauer et al (13) have advocated the use of $\tilde{v}_{0.05}$ (the wavenumber that represents 5% of the maximum absorbance, to the red of that maxima)
in order to calculate $\bar{\nu}_{oo}$, by substitution of $\bar{\nu}_{0.05}$ into an equation derived from fluorescent Cr(III) complexes. In the region where the $^{4}\text{T}_{2g} \rightarrow ^{4}\text{A}_{2g}$ band reaches 5% of its maxima there is possibly overlap with the $^{2}\text{E}_{g} \rightarrow ^{4}\text{A}_{2g}$ band, thus introducing a further error into the estimation of $\bar{\nu}_{oo}$. Therefore, the values of $\bar{\nu}_{oo}$, as presented in Table 3.3 have an estimated associated error of ± 1000 cm$^{-1}$.

5.1.2.3 The High Energy Doublet State – $^{2}\text{T}_{2g}$

This transition is not observed in the absorption measurements of these complexes, but may however, be calculated from standard equations:

$$E^{^2\text{T}_{2g} \rightarrow ^4\text{A}_{2g}} = 15\beta_{55} + 5C - \frac{176\beta_{55}^2}{10Dq}$$

Assuming $C = 4B$

The values obtained from the above equation for a series of Cr(III) $\beta$-diketonates are given in Table 3.2 (Chapter III). From these theoretical calculations, the $^{2}\text{T}_{2g}$ state for Cr(dpm)$_3$ is predicted to lie at 19,180 cm$^{-1}$. Wilkinson and Tsiamis (4) measured the quenching rate constants for a series of organic donors quenched by Cr(dpm)$_3$ and were able to attribute the rapid increase in the $k_q$ vs $E_T$ plot, occurring at $\approx$20,000 cm$^{-1}$, to electronic energy transfer to the $^{2}\text{T}_{2g}$. On the basis of this experimental evidence, 800 cm$^{-1}$ will be added to the theoretical predictions when interpreting quenching data.
5.2 Reexamination of Published Data

The results of Wilkinson and Tsiamis (4,5) for the quenching of electronically excited triplet states by Cr(acac)$_3$, Cr(bzac)$_3$ and Cr(dpm)$_3$ have been reexamined in terms of the rate constants $k_d$ and $k_{d'}$ derived from the Spernol-Wirtz treatment. The parameters used by Wilkinson and Tsiamis to give the best theoretical fit to the experimental data, together with the reexamined ones are given in Table 5.3. The more general kinetic scheme 5.17, proposed by these workers (4) to explain the quenching rate constants for Cr(dpm)$_3$, has been employed for the reanalysis of the quenching data for Cr(acac)$_3$ and Cr(bzac)$_3$. Using scheme 5.17 introduces electronic energy transfer to the $^2T_{2g}$ state.

In the case of Cr(dpm)$_3$, Fig 5.5, a sudden rise in quenching at $\approx 20,000$ cm$^{-1}$ was observed, which has been attributed to energy transfer to the doublet $^2T_{2g}$ state. The best fit to the experimental data was achieved with $^2K_{en} (^2T_{2g}) = 2.8 \times 10^{-4}$ as compared to $^2K_{en} (^2E_g, ^2T_{1g}) = 4.4 \times 10^{-5}$ (i.e. a 12.7 fold increase, since the $^2E_g, ^2T_{1g}$ states are treated as a degenerate pair). On the basis of these experimental findings, Fig 5.1 gives a plot of log $k_q$ vs $E_T$ for energy transfer to two doublet states positioned at 12,500 cm$^{-1}$ and 19,500 cm$^{-1}$ (the av. $^2E_g, ^2T_{1g}$ and $^2T_{2g}$ energy levels for chromium(III) β-diketonate complexes), the transmission coefficient for the upper state being 12.7 times greater than that for the lower states. The curves in Fig 5.1 depict three different situations. Firstly, for low efficiency quenchers (blue curve), energy transfer to the high energy doublet state has a pronounced effect on the shape of the quenching curve. Secondly, as $k_q$ approaches $sk_d$ (red curve), the effect of energy transfer to the upper state becomes virtually undetectable. Finally, for the intermediate case (green curve) $^2K (^2E_g, ^2T_{1g}) = 1.3 \times 10^{-3}$ ($^2K_{en} = 8 \times 10^9$; $k_q = 1.15 \times 10^9$ dm$^3$ mol$^{-1}$
<table>
<thead>
<tr>
<th></th>
<th>Cr(acac)₃</th>
<th>Cr(bzac)₃</th>
<th>Cr(dpm)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_d/10^3$ dm⁻³ mol⁻¹ s⁻¹</td>
<td>1.41</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td>$k_\perp/10^3$ s⁻¹</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$^{2}E_g$/cm⁻¹</td>
<td>12950</td>
<td>12580</td>
<td>12980</td>
</tr>
<tr>
<td>$^{2}\Delta^{\pm}(\omega)$/cm⁻¹</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>$^{2}k_\perp(2^{E_g} - 2^{T_g})/10^3$ s⁻¹</td>
<td>0.96</td>
<td>1.55</td>
<td>0.027</td>
</tr>
<tr>
<td>$^{4}k_\perp(2^{E_g} - 1^{g})/10^3$ cm⁻¹</td>
<td>15614</td>
<td>15400</td>
<td>16500</td>
</tr>
<tr>
<td>$^{4}T_{1g}$/cm⁻¹</td>
<td>16230</td>
<td>16000</td>
<td>16500</td>
</tr>
<tr>
<td>$\Delta^{\pm}(\omega)$/cm⁻¹</td>
<td>2200</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>$^{4}k_\perp/10^3$ s⁻¹</td>
<td>1.60</td>
<td>4.00</td>
<td>0.30</td>
</tr>
<tr>
<td>$^{4}k_\perp/10^3$ cm⁻¹</td>
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<td>6.6</td>
<td>0.5</td>
</tr>
<tr>
<td>$^{2}T_{2g}$/cm⁻¹</td>
<td>20000</td>
<td>19000</td>
<td>20000</td>
</tr>
<tr>
<td>$\Delta^{\pm}(\omega)$/cm⁻¹</td>
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<td>250</td>
<td>250</td>
</tr>
<tr>
<td>$^{2}k_\perp/10^3$ s⁻¹</td>
<td>0.48</td>
<td>0.78</td>
<td>0.17</td>
</tr>
<tr>
<td>$^{2}k_\perp/10^3$ cm⁻¹</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
</tr>
<tr>
<td>$^{2}k_\perp/10^3$ cm⁻¹</td>
<td>0.79</td>
<td>1.3</td>
<td>0.28</td>
</tr>
<tr>
<td>$^{2}k_\perp/10^3$ cm⁻¹</td>
<td>-</td>
<td>-</td>
<td>1.10</td>
</tr>
</tbody>
</table>
FIG 5.1 LOG(KQ) VS DONOR ENERGY

-EFFECT OF TWO DOUBLET STATES AT 12,500 CM⁻¹ AND 19,500 CM⁻¹

D1=250 CM⁻¹ : D1=8.00E10 S⁻¹ ; D2=250 CM⁻¹ : D2=5.08E11 S⁻¹

D1=250 CM⁻¹ : D1=8.00E9 S⁻¹ ; D2=250 CM⁻¹ : D2=5.08E10 S⁻¹

D1=250 CM⁻¹ : D1=8.00E8 S⁻¹ ; D2=250 CM⁻¹ : D2=5.08E9 S⁻¹
s\(^{-1}\)), a substantial contribution from the \(^2T_{2g}\) pathway can be seen. This intermediate case is representative of many of the quenchers studied in this thesis, and the rapid increase in quenching efficiency predicted to occur at 19,500 ± 500 cm\(^{-1}\) as a result of energy transfer the \(^2T_{2g}\) state is not evident. Clearly the ratio of \(2k_{en}^{T_{2g}} : 2k_{en}^{E_{g}, T_{1g}}\) is less than 12.7 but its actual value is difficult to elucidate since its effect becomes indistinguishable from energy transfer to the \(^4T_{2g}\) state. For Iron(III) \(\beta\)-diketonates, the ratio of transmission coefficients for energy transfer to higher and lower quartet states was found to decrease with increasing quenching efficiency (7). Due to the lack of any other evidence, for quenchers with \(k_q > \frac{1}{2} k_d\) best fits were obtained by making the assumption that \(2k_{en}^{T_{2g}} = \frac{1}{2} 2k_{en}^{E_{g}, T_{1g}}\) and this situation is depicted in Fig 5.2.

Figs. 5.3, 5.4 and 5.5 give the best theoretical fits to the experimental data of Cr(acac)\(_3\), Cr(bzac)\(_3\) and Cr(dpm)\(_3\) respectively, and wherever possible the parameters used by Wilkinson and Tsiamis have been advocated, varying only the preexponential factors, \(k_{en}^0\)'s, in order to obtain the best fit. However, in the case of Cr(acac)\(_3\), these workers used a value of \(\bar{C}_{oo}^{4T_{2g}}\) obtained by Fleischauer et al (13) which as previously discussed in Chapter 3 (3.2.1) is not in agreement with this work or with that of Fatta and Lintvedt (10) and has therefore been replaced for this reinterpretation. This change in quartet energy level has necessitated the use of a slightly larger quartet intrinsic reorganizational barrier of 2,200 cm\(^{-1}\) as compared with 2,000 cm\(^{-1}\) to give the best fit.

In conclusion, the experimental results of Wilkinson and Tsiamis have been successfully reinterpreted in terms of the modified kinetic scheme 5.17 and the derived value of the diffusion rate constant \(k_d\),
FIG 5.2  LOG(KQ) VS DONOR ENERGY
-EFFECT OF TWO DOUBLET STATES AT 12,500 CM⁻¹ AND 19,500 CM⁻¹

ENERGY (1000 CM⁻¹)

LOG (KQ)

D1=250 CM⁻¹ : D1=8.00E10 S⁻¹ ; D2=250 CM⁻¹ : D2=4.00E10 S⁻¹
D1=250 CM⁻¹ : D1=8.00E9 S⁻¹ ; D2=250 CM⁻¹ : D2=4.00E9 S⁻¹
D1=250 CM⁻¹ : D1=8.00E8 S⁻¹ ; D2=250 CM⁻¹ : D2=4.00E8 S⁻¹
FIG 5.3 LOG(KQ) VS DONOR ENERGY FOR CR(ACAC)3

\[ A1 = 12950 \text{ cm}^{-1}, \quad D1 = 250 \text{ cm}^{-1}, \quad 01 = 0.96 \times 10^{10} \text{ S}^{-1} \]

\[ A2 = 15614 \text{ cm}^{-1}, \quad D2 = 2200 \text{ cm}^{-1}, \quad 02 = 1.60 \times 10^{10} \text{ S}^{-1} \]

\[ A3 = 20000 \text{ cm}^{-1}, \quad D3 = 250 \text{ cm}^{-1}, \quad 03 = 0.48 \times 10^{10} \text{ S}^{-1} \]
FIG 5.4  LOG(KQ) VS DONOR ENERGY FOR CR(BZAC)3

A1=12580 CM⁻¹,  D1=250 CM⁻¹,  D1=1.55E10 S⁻¹
A2=15400 CM⁻¹,  D2=2000 CM⁻¹,  D2=4.00E10 S⁻¹
A3=19000 CM⁻¹,  D3=250 CM⁻¹,  D3=0.76E10 S⁻¹
FIG 5.5  LOG(KQ) VS DONOR ENERGY FOR CR(DPM)3

A1=12960   CM-1   :   D1=250   CM-1   :   D1=2.70E8   S-1
A2=16500   CM-1   :   D2=2000   CM-1   :   D2=3.00E9   S-1
A3=20000   CM-1   :   D3=250   CM-1   :   D3=1.70E9   S-1
presented in this thesis. The value of $k_d$ has a pronounced effect on the preexponential factors (see Table 5.3) especially for complexes whose upper plateaus are close to the theoretical maxima of $s k_d$. Sample calculations show as we would expect, that as the theoretical maxima is approached, large variations in $k_0^{\text{en}} (\pm 20\%)$ have little effect on the best fit obtainable through the experimental points. Therefore these variations in the values assigned to those parameters must be carefully considered when comparisons are being made between the quenching efficiencies of a series of complexes.
PART A

5.3 Quenching of Electronically Excited States by γ-substituted Cr(III) β-diketonate Complexes

The bimolecular rate constants for quenching by Cr(3-Meacac)₃, Cr(3-Etacac)₃, and Cr(3-Pracac)₃ are given in Tables 4.1, 4.2 and 4.4 (Chapter IV), and are presented graphically in Figs. 5.6, 5.7 and 5.8, respectively. The results, as represented by plots of ln kᵢ vs Eᵢ, all exhibit a common feature, namely the existence of a plateau region. The plateau region which extends from 14,000 cm⁻¹ to 18,000 cm⁻¹ is attributed to electronic energy transfer to the two low lying doublet states, \(^2\)E₉ and \(^2\)T₁₂g, which are treated as a degenerate pair (see Sec. 5.1.2.3). The region after the plateau, > 18,000 cm⁻¹ rises slowly, never quite reaching a second plateau (over the range of donors studied). The rise in the rate constants observed in this region indicates that electronic energy is being transferred to one or more other states. By studying the Tables in Chapter III (3.1, 3.2 and 3.3), the states which are available for energy transfer are the quartet \(^4\)T₂g state and high energy doublet \(^2\)T₂g state. The \(\nu_\infty\) value for the \(^4\)T₂g state places it at \(= 15,500\) cm⁻¹ and since no rise in quenching efficiency is observed until \(\nu_\infty(T) > 18,000\) cm⁻¹, it may be concluded that energy is being transferred to a highly distorted state. The distortion being associated with the fact that Cr(III) in its ground state has a d-electron configuration of \(^3\)e₀ \(^2\)g and the \(^4\)T₂g is a \(^2\)e \(^1\)g state. Since energy transfer to the doublet states \(^2\)E₉, \(^2\)T₁₂g and \(^2\)T₂g involves no change of electron configuration, it proceeds with a low intrinsic barrier (12,000 cm⁻¹ - 14,000 cm⁻¹ region being an example). Energy transfer to the \(^2\)T₂g state is masked by the more efficient transfer of electronic energy to the \(^4\)T₂g state.
FIG 5.6  LOG(KQ) VS DONOR ENERGY FOR CR(3-MEACAC)3

A1 = 12390 CM⁻¹, D1 = 250 CM⁻¹, 01 = 8.55E10 S⁻¹

A2 = 15390 CM⁻¹, D2 = 2400 CM⁻¹, 02 = 5.70E10 S⁻¹

A3 = 19400 CM⁻¹, D3 = 250 CM⁻¹, 03 = 4.30E10 S⁻¹
FIG 5.7 LOG\((KQ)\) VS DONOR ENERGY FOR CR\((3\text{-ETACAC})3\)

\[
\begin{align*}
A1 &= 12470 \text{ CM}^{-1} ; D1 = 250 \text{ CM}^{-1} ; D1 = 2.60E10 \text{ S}^{-1} \\
A2 &= 15315 \text{ CM}^{-1} ; D2 = 2400 \text{ CM}^{-1} ; D2 = 4.70E10 \text{ S}^{-1} \\
A3 &= 19500 \text{ CM}^{-1} ; D3 = 250 \text{ CM}^{-1} ; D3 = 1.30E10 \text{ S}^{-1}
\end{align*}
\]
FIG 5.8  LOG(KQ) VS DONOR ENERGY FOR CR(3-PRACAC)3

A1=12440 CM-1; D1=250 CM-1;  D1=2.30E10 S-1
A2=15260 CM-1; D2=2400 CM-1;  D2=4.00E10 S-1
A3=19500 CM-1; D3=250 CM-1;  D3=1.15E10 S-1
On the basis of these and previous arguments (Sec. 1.6), an analysis of the kinetic scheme (5.17) involving energy transfer to the degenerate $^2E_g$, $^2T_{1g}$ states, the $^4T_{2g}$ state and the $^2T_{2g}$ state is now given. Table 5.4 gives the values of energy transfer parameters used to obtain the best fit to the experimental data; this being achieved by varying the pre-exponential factors, $k^0_{en}$. For energy transfer to the degenerate doublet pair, a reorganization intrinsic barrier, $\Delta G^\ddagger(0)$ of 250 cm$^{-1}$ was found to fit the results which according to equation 5.13 results in the energy for self-exchange of the organic donors being $\approx 500$ cm$^{-1}$; the contribution from the acceptor being practically zero since energy transfer is taking place to the undistorted $^2E_g$ state. Over the region where $k_q$ vs $E_q$ rises most steeply, 12000 cm$^{-1} - 14000$ cm$^{-1}$, only one donor, perylene, is available. Unfortunately, the exact position of the triplet energy of perylene is open to some discussion (14,15) and the value of 12600 cm$^{-1}$ could be subject to an error of $\pm 500$ cm$^{-1}$. However, from the results to be discussed, it seems that $^2\Delta G^\ddagger(0) = 250$ cm$^{-1}$ gives a reasonable fit.

For energy transfer to the distorted $^4T_{2g}$ state, a $^4\Delta G^\ddagger(0)$ of 2200 $\pm$ 200 cm$^{-1}$, fits all the experimental data. From equation 5.13 a self-exchange free energy of $\approx 4000$ cm$^{-1}$ is required, which corresponds to a Stokes shift of $\approx 8000$ cm$^{-1}$; making the assumption that $\Delta S$ contributions to $\Delta G^\ddagger(0)$ are negligible, equation 5.10. Although this value is higher than one might expect, it does not eliminate the $^4T_{2g}$ state from the quenching scheme. The dotted curves in Figs. 5.6, 5.7 and 5.8 represent the best fit of the experimental data and Table 5.4 also gives the values of the transmission coefficients. The $^2T_{2g}$ state is given a transmission coefficients equal to half of that found to describe the plateau region (since both the $^2E_g$ and $^2T_{1g}$ state accept energy in the plateau region), the closer the plateau is to the diffusion controlled limit the less effect
### TABLE 5.4

Energy Transfer Parameters for Cr(acac)$_3$ and $\gamma$-Alkyl Substituted Complexes

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>Cr(acac)$_3$</th>
<th>Cr(3-Meacac)$_3$</th>
<th>Cr(3-Etacac)$_3$</th>
<th>Cr(3-Pracac)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2E_g \bar{v}$/cm$^{-1}$</td>
<td>12950</td>
<td>12390</td>
<td>12470</td>
<td>12440</td>
</tr>
<tr>
<td>$2\Delta G^+(0)/$cm$^{-1}$</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>$2k_{en}(2E_g, 2T_{1g})/10^{10}$s$^{-1}$</td>
<td>0.96</td>
<td>8.55</td>
<td>2.60</td>
<td>2.30</td>
</tr>
<tr>
<td>$2k_{en}$</td>
<td>$1.57 \times 10^{-3}$</td>
<td>$1.40 \times 10^{-2}$</td>
<td>$4.26 \times 10^{-3}$</td>
<td>$3.77 \times 10^{-3}$</td>
</tr>
<tr>
<td>$4T_{2g} \bar{v}$</td>
<td>15614</td>
<td>15390</td>
<td>15315</td>
<td>15260</td>
</tr>
<tr>
<td>$4\Delta G^+(0)/$cm$^{-1}$</td>
<td>2200</td>
<td>2400</td>
<td>2400</td>
<td>2400</td>
</tr>
<tr>
<td>$4k_{en}/10^{10}$s$^{-1}$</td>
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<td>5.70</td>
<td>4.70</td>
<td>4.00</td>
</tr>
<tr>
<td>$4k_{en}$</td>
<td>$2.62 \times 10^{-3}$</td>
<td>$9.34 \times 10^{-3}$</td>
<td>$7.70 \times 10^{-3}$</td>
<td>$6.55 \times 10^{-3}$</td>
</tr>
<tr>
<td>$2T_{2g} \bar{v}$/cm$^{-1}$</td>
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<td>19400</td>
<td>19500</td>
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</tr>
<tr>
<td>$2\Delta G^+(0)/$cm$^{-1}$</td>
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<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>$2k_{en}/10^{10}$s$^{-1}$</td>
<td>0.48</td>
<td>4.30</td>
<td>1.30</td>
<td>1.15</td>
</tr>
<tr>
<td>$2k_{en}$</td>
<td>$7.86 \times 10^{-4}$</td>
<td>$7.04 \times 10^{-3}$</td>
<td>$2.13 \times 10^{-3}$</td>
<td>$1.88 \times 10^{-3}$</td>
</tr>
<tr>
<td>$k_d/10^{10}$dm$^3$mol$^{-1}$s$^{-1}$</td>
<td>1.41</td>
<td>1.41</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td>$k_d/10^9$s$^{-1}$</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
</tr>
</tbody>
</table>
this energy transfer step will have (see Sec. 5.2 and Figs. 5.1 and 5.2).

Table 5.4 also lists the parameters used to obtain the best theoretical fit in the reinterpretation of the experimental data of Wilkinson and Tsiamis (5) for the quenching of electronically excited triplet donors by Cr(acac)$_3$. The attachment of an alkyl group in the $\gamma$-position might well be expected to increase the steric blocking effect in the complex, reducing the donor overlap with the chelated metal ion and subsequently reducing its quenching constant. However, examination of the tabulated results shows that the opposite effect is observed, namely an increase in quenching efficiency. Steric enhancement could be a possible mechanism whereby the $\gamma$-alkyl substituted complexes with increased molecular radii, have a larger collisional cross-section and may be able to more easily 'trap' a donor, facilitating the energy transfer process. A more reasonable argument concerns the electron donating properties of alkyl groups. From basic organic chemistry, in a benzoid system alkyl groups have an ortho- para-directing effect (16) towards substitution; the para-directing effect dominating. If one acetylacetone ring in a Cr(III) complex is considered, together with the central metal, we have a quasi-aromatic system (9), with the metal atom being para to the $\gamma$-substituent.

The Hammett constants (17), $\sigma_p$, for Methyl, Ethyl and n-Propyl groups are $-1.170$, $-1.151$ and $-1.126$, respectively (the negative value indicating an electron donating effect: Hydrogen being zero by definition).
Therefore, electron density will be donated to the metal orbitals in the sequence Me > Et > Pr. This will have the effect of expanding the metal d-orbitals with the consequence of increasing the possible overlap between the donor and acceptor orbitals, thus aiding electronic energy transfer. Electronic energy transfer to give the $^{2}\text{E}_g$ state ($t_{2g}^{3} e_{g}^{0}$) involves the $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals which for an octahedral complex position their nodes in the spaces between the metal – oxygen bonds. The $e_g$ set of orbitals, $d_{x^2-y^2}$ and $d_{z^2}$ position their nodes along the $X-Z$ direction of the metal – oxygen bonds, these are important for energy transfer to the $^{4}\text{T}_{2g}$ state ($t_{2g}^{2} e_{g}^{1}$).

In terms of the above discussions, the question arises - How does the inductive effects of the alkyl groups relate to the calculated preexponential factors, $k_{en}^0$? Firstly, the values of $k_{en}^0$ increase in the same manner as $\sigma_p$, however $2k_{en}^0$ (Cr(Meacac)$_3$) appears to be out of step with the others since it has a much higher value. Secondly, a steric blocking effect by the alkyl groups must also be considered. Molecular models show that both ethyl and propyl groups are successful in sterically blocking some of the free space which previously existed in Cr(acac)$_3$, this mainly affects overlap with the $t_{2g}$ orbitals. Thus, the benefits gained from the electron releasing properties of ethyl and propyl groups are offset to a certain extent by steric blocking. The methyl group has a slightly higher electron releasing effect but must have a substantially lower steric blocking effect than the other two groups. Thus this electron releasing/steric blocking argument can explain the $2k_{en}^0$ values but does it also explain the calculated $4k_{en}^0$ values?

Examination of $4k_{en}^0$ for these complexes shows them to be in better agreement if we assume that differences are due purely to an
electron releasing effect. $\Delta \sigma_p \ (Et - Pr) = 0.025$ and this is associated with a $0.70 \times 10^{10} \text{s}^{-1}$ change in $4_{\text{en}}^o$. Since $\Delta \sigma_p \ (Me-Et) = 0.020$ a difference in $4_{\text{en}}^o$ of $0.56 \times 10^{10} \text{s}^{-1}$ would be predicted against the observed difference of $1.0 \times 10^{10} \text{s}^{-1}$. These differences could be explained by introducing an associated error of $\pm 20\%$ in the value of $4_{\text{en}}^o$ but it is probable that energy transfer to produce the $4_{T_{2g}}^r$ state experiences a mild steric blocking effect. Examination of a molecular model of an acetylacetonate complex shows that the $e_g$ orbitals which point along the $M-O$ bonds are less affected by the steric effect of $\gamma$-substituents, however ethyl and propyl groups will have a greater steric effect than methyl.

Examination of Table 5.4 shows that for Cr(3-Meacac)$_3$ $2_{\text{en}}^o (2_{E_g}^2 2_{T_{1g}}^s) > 4_{\text{en}}^o$. However, it must be noted that $2_{\text{en}}^o$ takes on a value associated with both the $2_{E_g}^2$ and $2_{T_{1g}}^s$ states and therefore in order to compare it with quartet state its value should be halved thus making $4_{\text{en}}^o > 2_{\text{en}}^o$. Table 5.5, lists the ratio's of $4_{\text{en}}^o : 2_{\text{en}}^o$ (for one doublet state) for Cr(acac)$_3$ and the three $\gamma$-substituted complexes. As would be expected on the basis of the previous discussion, the ratio $4_{\text{en}}^o : 2_{\text{en}}^o$ is much smaller for Cr(3-Meacac)$_3$ indicating its smaller steric blocking effect for the $t_{2g}$ orbitals as compared with the case for the ethyl-/Propyl derivatives.
TABLE 5.5

Ratio of Quartet : Doublet Preexponential Factors

<table>
<thead>
<tr>
<th></th>
<th>Cr(acac)$_3$</th>
<th>Cr(3-Meaca)$_3$</th>
<th>Cr(3-Etacac)$_3$</th>
<th>Cr(3-Pracac)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4k^o_{en}/10^{10}$ s$^{-1}$</td>
<td>1.60</td>
<td>5.70</td>
<td>4.70</td>
<td>4.00</td>
</tr>
<tr>
<td>$2k^o_{en}/10^{10}$ s$^{-1}$</td>
<td>0.48</td>
<td>4.28</td>
<td>1.30</td>
<td>1.15</td>
</tr>
<tr>
<td>$4k^o_{en} : 2k^o_{en}$</td>
<td>3.33</td>
<td>1.33</td>
<td>3.62</td>
<td>3.48</td>
</tr>
</tbody>
</table>
5.4 Quenching by Geometrical Isomers of Cr(\(^t\)Bu PDO)\(_3\)

Unsymmetrical \(\beta\)-diketones complexed with metal ions result in the possibility of geometrical isomerism. Huang and Gafney (18) have measured the bimolecular quenching rate constants for the quenching of five organic triplet donors by \(cis\)- and \(trans\)- isomers of Co(tfac)\(_3\), Co(bzac)\(_3\), Cr(tfac)\(_3\) and Cr(bzac)\(_3\). They found that for each geometrical isomer pair that the rate constants were identical within experimental error. More recently, Gandolfi et al (19) studied the quenching of the \(2E_g\) excited state of tris(2,2'-bipyridine) Chromium(III) by a series of Co(III) complexes, concluding that the \(cis\)-isomers are better quenchers than the \(trans\)- isomers. In a similar study by Sandrini et al (20), the rate constants for electron transfer quenching of Cr(bpy)\(_3\)^{3+} by \(cis\)- Co(en)\(_2\)Cl\(_2\)^{+} was found to be 18 times larger than that for the \(trans\)- isomer. This type of study was furthered, using \(cis\)- and \(trans\)- Cr(\(^t\)Bu PDO)\(_3\), together with a larger number of donors, the results from which are tabulated graphically in Figs. 5.9 and 5.10, respectively. The \(cis\)- isomer was found to be a more efficient quencher than the \(trans\)-, being in agreement with the later two workers, especially when energy is being transferred to the \(4T_{2g}\) state of Cr(\(^t\)Bu PDO)\(_3\). The parameters used to obtain the best fit to the experimental data are given in Table 5.6.

Before continuing with the discussion, it should be made clear that alternative avenues of explanation for the differences in quenching rate constants were pursued. Firstly, the possibility of spectral differences between the isomers was investigated. However, from Tables 3.1, 3.2 and 3.3 it can be seen that the position of the \(2E_g\), \(4T_{2g}\) and \(2T_{2g}\) states are identical. Secondly, ground state and excited state spectra were ran for solutions of donor and \(cis\/-\(trans\)- isomer. Ground state spectra were found to be additive and no differences in spectral characteristics were
FIG 5.9  LOG(KQ) VS DONOR ENERGY FOR CIS-CR(TBUPDD)3

A1=12690 CM\(^{-1}\) : D1=250 CM\(^{-1}\) : D1=1.15E10 S\(^{-1}\)

A2=15590 CM\(^{-1}\) : D2=2300 CM\(^{-1}\) : D2=8.30E10 S\(^{-1}\)

A3=19800 CM\(^{-1}\) : D3=250 CM\(^{-1}\) : D3=0.60E10 S\(^{-1}\)
FIG 5.10  LOG(KQ) VS DONOR ENERGY FOR TRANS-CR(TBUPDO)3

A1=12690 CM-1, D1=250 CM-1, D1=0.94E10 S-1
A2=15590 CM-1, D2=2300 CM-1, D2=5.70E10 S-1
A3=19820 CM-1, D3=250 CM-1, D3=0.47E10 S-1
TABLE 5.6

Energy Transfer Parameter for cis- and trans-
Cr(\textsuperscript{t}BuPDO\textsubscript{3}) \textsubscript{3} and Cr(BD\textsubscript{3})

<table>
<thead>
<tr>
<th>Parameters</th>
<th>cis- Cr(\textsuperscript{t}BuPDO\textsubscript{3})</th>
<th>trans- Cr(\textsuperscript{t}BuPDO\textsubscript{3})</th>
<th>Cr(BD\textsubscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2E_g/\text{cm}^{-1})</td>
<td>12690</td>
<td>12690</td>
<td>12690</td>
</tr>
<tr>
<td>(2\Delta G^\ddagger(0)/\text{cm}^{-1})</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>(2k_e/10^3 \text{s}^{-1})</td>
<td>1.15</td>
<td>0.94</td>
<td>1.55</td>
</tr>
<tr>
<td>(4\nu_{so}/\text{cm}^{-1})</td>
<td>15590</td>
<td>15590</td>
<td>15590</td>
</tr>
<tr>
<td>(4\Delta G^\ddagger(0)/\text{cm}^{-1})</td>
<td>2300</td>
<td>2300</td>
<td>2300</td>
</tr>
<tr>
<td>(4k_e/10^3 \text{s}^{-1})</td>
<td>8.30</td>
<td>5.70</td>
<td>4.30</td>
</tr>
<tr>
<td>(2T_{2g}/\text{cm}^{-1})</td>
<td>19800</td>
<td>19800</td>
<td>19800</td>
</tr>
<tr>
<td>(2\Delta G^\ddagger(0)/\text{cm}^{-1})</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>(2k_e/10^3 \text{s}^{-1})</td>
<td>0.60</td>
<td>0.47</td>
<td>0.80</td>
</tr>
<tr>
<td>(2k_e/\text{cm}^{-1})</td>
<td>9.8 \times 10^{-4}</td>
<td>7.7 \times 10^{-4}</td>
<td>1.3 \times 10^{-3}</td>
</tr>
</tbody>
</table>

* Results of Wilkinson and Tsiamis (22)
recorded after lasing 20 times. Excited state spectra similarly showed no differences and the possibility of a long-lived species may be ruled out. The third avenue pursued was the possibility of competitive electron transfer adding the overall quenching constant observed for the cis-isomer. The individual reduction potentials for cis- and trans- Cr(tBu PDO)\textsubscript{3} have not been measured but Table 3.5 lists an $E_1 \approx -1.64$ V vs. SCE for Cr(tBu PDO)\textsubscript{3}. Gamache et al (21) have measured the reduction potentials of cis- and trans- Cr(bzac)\textsubscript{3} in CH\textsubscript{2}Cl\textsubscript{2} ref. ferrocene and found them to be -2.09 V and -2.11 V respectively, indicating, not surprisingly, little dependence on isomeric structure. Both Cr(acac)\textsubscript{3} and Cr(bzac)\textsubscript{3} ($E_1 = -1.73$ V and -1.50V, respectively) have been successfully interpreted in terms of energy transfer mechanism (5.17) and since $E_1$ Cr(tBu PDO)\textsubscript{3} lies between the two, it seems reasonable to assume that electron transfer has no part to play in the quenching of cis- Cr(tBu PDO)\textsubscript{3}.

In order to aid the rationalization of the differences in quenching efficiency between the isomers, Figs. 5.11a and 5.11b illustrate their configurations in a diagramatic form. The list of numbers to the side of the diagrams represent the numbers of groups (whether tert-butyl or hydrogen) present on each face of an octahedron, and within these figures lies the reasons for the differences in observed quenching rate constants.

The low triplet energy plateau extending from $\approx 14,000 \text{cm}^{-1}$ to $18,000 \text{cm}^{-1}$ is attributed to electronic energy transfer to the degenerate doublet pair ($^2E_g$, $^2T_{1g}$). This involves the overlap with the $t_2g$ 'd-electrons' of the central metal ion, whose orbitals ($d_{xy}$, $d_{xz}$, $d_{yz}$) are pointing into the vacant spaces between the metal-oxygen bonds. Although the preexponential factor $^2k_0^e$ ($^2E_g$, $^2T_{1g}$) is only slightly
FIGURES 5.1la and 5.1lb

Cis/Trans Isomers of Cr(tBu PDO)₃

Cis-

Trans-

<table>
<thead>
<tr>
<th>t_Bu</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>-</td>
<td>3</td>
</tr>
</tbody>
</table>
larger for the cis- isomer than for the trans-, and could be easily explained in terms of experimental errors, this difference may alternatively be considered to be a result of greater steric blocking on the part of trans- isomer. Steric blocking having the effect of reducing orbital overlap between the donor and acceptor, therefore reducing $k_q$.

This steric blocking effect is more pronounced when electronic energy transfer to the $4t_{2g}$ state is considered. This state has an $d$-electron configuration $t_{2g}^2e_{g}^1$ and thus overlap with the $e_g$ orbitals is also required. The $d_{x^2-y^2}$ and $d_{z^2}$ orbitals which constitute the $e_g$ subset, have their nodes pointing in the direction of the metal-oxygen bonds. Examination of Figs.5.1a and 5.1b and molecular models, show that approach to the $e_g$ orbitals is more successfully sterically blocked in the case of the trans- isomer than it is for the cis- isomer. Simplistically, the differences may be related to the fact that the cis- isomer possesses one face of the octahedron with no tert-butyl groups (and one with three), whilst the faces of the trans- isomer representation has either one or two tert-butyl groups. Therefore, the one "good" face with no tert-butyl groups more than compensates for the "bad" face with three tert-butyl groups.

It is of interest to examine how the results for the quenching of Cr($t^\text{BuPD}O)_3$ compare with data already published. Wilkinson and Tsiamis (5) have studied the quenching of Cr(dpm)$_3$ ($R_1 = R_3 = t^\text{Bu}$) and have attributed to the low quenching rate constants to the steric blocking effect of the tert-butyl groups. Therefore, the increase in quenching constants for Cr($t^\text{BuPD}O)_3$ ($R_1 = t^\text{Bu}$, $R_3 = H$) over Cr(dpm)$_3$, can be attributed to better donor/acceptor overlap at the hydrogen atom sites in the complexes. The rate constants for quenching by Cr(acac)$_3$ have an almost identical preexponential factor for electronic energy transfer to the low lying degenerate doublet pair ($2g^2$, $2T_{1g}$); $2k^e_{en}$ for Cr(acac)$_3$ =
0.96 \times 10^{10} \text{ s}^{-1}, \quad 2k_{en}^{\circ} \text{ for cis- and trans-Cr(tBuPDO)}_3 = 1.15 \times 10^{10} \text{ s}^{-1} and 0.94 \times 10^{10} \text{ s}^{-1}, respectively. Therefore, it may be concluded that the t_{2g} orbitals of the Cr(III) ion are sterically blocked to the same degree by two methyl groups as they are for one tButyl group and one hydrogen atom. For electronic energy transfer to the ^4T_{2g} state, \( 4k_{en}^{\circ} \text{ cis/trans-Cr(tBuPDO)}_3 > 4k_{en}^{\circ} \text{ Cr(acac)}_3 \), indicating that the six methyl groups of Cr(acac)_3 are more efficient at blocking the e_g orbitals of the central ion, than Cr(tBuPDO)_3.

Table 5.6 also gives the parameters used to fit the quenching constants obtained for another formyl ketone complex, Cr(BDO)_3 \((R_1 = \text{CH}_3, R_3 = \text{H})\), these results being kindly donated for discussion by F Wilkinson and C Tsiamis (22) and are acknowledged as such. The geometrical isomers of this complex have not been separated but statistically the trans-form will dominate. Electronic energy transfer to the doublet state \( (^2E_g, ^2T_{1g}) \) of Cr(BDO)_3 proceeds with a larger preexponential factor than for either cis- and trans-Cr(tBuPDO)_3, the reverse situation occuring for energy transfer to the quartet state, \(^4T_{2g}\). In the previous section the results were explained in terms of a balance between the electron-releasing effect of the \( \gamma \)-substituents (correlated with Hammett \( \sigma_p \) values) and a steric blocking effect. The Hammett \( \sigma_p \) values for methyl and tButyl groups are -0.171 and -0.197, respectively, since \( \beta \)-diketones may be treated as quasi-aromatic systems, the position para to the \( \beta \)- (or 1) position corresponds to the oxygen atom. As discussed earlier, the e_g orbitals of the metal ion point in the direction of the M-O bonds and are therefore more likely to be effected by charge directed towards the oxygen atom than the t_{2g} orbitals which point between them.
The lower $2_{en}^{2}\kappa$ plateau constants for Cr(\textsuperscript{t}BuPDO)\textsubscript{3} may be attributed to the steric blocking effect of the \textsuperscript{t}Butyl groups, the electron releasing effect of the group having little effect on the $t_2g$ orbitals. For energy transfer to the $4_{T_{2g}}$ state ($e_g$ orbitals) the greater steric blocking effect of \textsuperscript{t}Bu groups as compared with the methyl groups is overcome by the difference in the $\sigma_p$ constants for those groups, $\Delta \sigma_p^{(\text{t}Bu-Me)} \approx 0.026$. It may therefore be concluded that electron donating groups, whether they direct their charge onto the metal or onto its nearest neighbour expand the orbitals, increasing donor/acceptor overlap and thereby $k_q$. 
5.5 Quenching by Chromium(III) Complexes Containing Trifluoromethyl Groups

The quenchers studied under this heading were Cr(tfbzac)\textsubscript{3} and Cr(tfac)\textsubscript{3} (23), whose results were tabulated in Chapter IV (4.6 and 4.7) and are presented graphically in Figs. 5.12 and 5.13, respectively. Wilkinson and Tsiamis (6) found the quenching of electronically excited donors by Cr(hfac)\textsubscript{3}(R\textsubscript{1}=R\textsubscript{3}=CF\textsubscript{3}) could be interpreted in terms of a competitive mechanism between energy and electron transfer (Scheme 1.95, Chapter 1).

The experiments presented here were designed to determine the point (value of \(E_{\text{red}}^Q\)) at which energy transfer no longer becomes the only important quenching mechanism. The reduction potentials vs. SCE (as presented in Table 3.5) for Cr(tfac)\textsubscript{3} and Cr(tfbzac)\textsubscript{3} are \(-1.04\) V and \(-0.79\) V, respectively, compared with a value of \(-0.40\) V for Cr(hfac)\textsubscript{3}.

Wilkinson and Tsiamis (6) have discussed the direction in which the electron is transferred in detail, i.e. the processes:

\[
\begin{align*}
(D^*..Q) & \longrightarrow (D^+..Q^-) & & 5.30 \\
(D^*..Q) & \longrightarrow (D^-..Q^+) & & 5.31
\end{align*}
\]

and have argued that the electron will be transferred to the quencher (process 5.30). This statement is substantiated if we examine the differences between a complex such as Cr(acac)\textsubscript{3}, which is known to quench by energy transfer only, and Cr(hfac)\textsubscript{3}. The reduction potential of Cr(hfac)\textsubscript{3} is 1.33 V larger relative to Cr(acac)\textsubscript{3} indicating that the substitution of CF\textsubscript{3} groups makes Cr(hfac)\textsubscript{3} a better electron acceptor than Cr(acac)\textsubscript{3}. Although the oxidation potentials of Cr(acac)\textsubscript{3} and Cr(hfac)\textsubscript{3} have not been reported, their gas-phase appearance potentials have (24), with values of 8.11 V and 10.13 V, respectively. Thus, electron donation
is less likely to occur from Cr(hfac)$_3$ than it is from Cr(acac)$_3$, which has been shown to quench by energy transfer only. These workers also found a better correlation between $k_q$ and $FE_\text{D}^{\text{ox}} - E_T$ than they did for $FE_\text{D}^{\text{red}} - E_T$, when they examined Cr(hfac)$_3$.

The direction of electron transfer has been defined, but the possibility of forming a high- or low-spin Cr(II) complex must also be considered. In general, Cr(II) forms high-spin complexes with low-field ligands in the spectrochemical series, however, high-spin ligands such as CN$^-$ are known to form low-spin complexes (25). If we assume that Cr(II) is high-spin ($t_{2g}^3, e_g$), then vector addition of its spin multiplicity with that of the doublet donor (D) leads to the formation of sextet $^6(D^+..Q^-)$ and a quartet $^4(D^+..Q^-)$ charge transfer complexes. The low spin complex ($t_{2g}^3, e_g$) would give rise to quartet $^4(D^+..Q^-)$ and doublet $^2(D^+..Q^-)$ species. The various pathways for the quenching of a quartet state by electron transfer may be represented by:

\[
\begin{align*}
\frac{1}{3}k_d & \quad \frac{1}{3}k_d \\
 undue & \quad undue \\
\rightarrow & \quad \rightarrow \\
6(D^+..Q^-) & \quad 4(D^+..Q^-)
\end{align*}
\]

\[
\begin{align*}
\frac{6}{k_e} & \quad \frac{4}{k_e} \\
\frac{6}{k_{bt}} & \quad \frac{4}{k_{bt}} \\
\rightarrow & \quad \rightarrow \\
D + 4Q & \quad D + 4Q
\end{align*}
\]

5.32
However, if the energy difference between the high- and low-spin configuration of Cr(II) is large, then either the doublet or the sextet state would become energetically excluded. In terms of spin statistics, electron transfer to form a high-spin Cr(II) complex would proceed with $s = \frac{5}{6} \left( \frac{1}{2} + \frac{1}{3} \right)$, whilst for the low-spin situation, $s = \frac{1}{2} \left( \frac{1}{3} + \frac{1}{6} \right)$ would be obtained.

In their study of Cr(hfac)$_3$, Wilkinson and Tsiamis found that 5 of the 13 $k_q$'s measured had a value of $8.2 \times 10^9 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$, which was close to the maximum rate for charge transfer quenching proceeding via the high-spin complex, i.e. $\frac{5}{6} k_d = 8.33 \times 10^9 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$, assuming $k_d = 1.0 \times 10^{10} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$. Quenching via the low-spin complex could only proceed with a maximum rate of $5 \times 10^9 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ and is therefore excluded. In this Thesis, a diffusion controlled rate constant of $1.41 \times 10^{10} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ is advocated, thus giving $\frac{5}{6} k_d$ a value of $1.17 \times 10^{10} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$. This difference does not, however, question the conclusion of these workers, that electron transfer proceeds via the high-spin complexes, since $\frac{1}{2} k_d$, the maximum value attainable by quenching with low-spin Cr(II), would assume a value of $7 \times 10^9 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$, which is still lower than the observed rate constants.

Since competitive energy- and electron-transfer has been shown to be quenching mechanism of these complexes, combinations of Scheme 5.17 and 5.32 (minus the doublet step) gives the kinetic pathway:
with the rate constant for Quenching being equal to:

\[ k_q = \frac{6k_{qel} + 4k_{q} + 2k_{qen}}{k_q} \]

where:

\[ 6k_{qel} = \frac{1}{1 + \frac{1}{k_d}} \]

\[ k_d \left( 6k_{bt} + k_{el} \right) \]
\[ \frac{4k_q}{1/3k_d} = \frac{1}{1 + \frac{1}{\left(k_d + \frac{4k_{en}}{2k_{en}}\right)}} \]

\[ \frac{4k_{en}}{k_d + 4k_{en}} + \frac{4k_{el} \cdot 4k_{bt}}{k_d(4k_{bt} + 4k_{el})} \]

and \( 2k_{q \, en} \) is given by expression 5.19.

Using the above kinetic pathway, together with a \( k_d \) of \( 1.41 \times 10^{10} \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\), the results of Wilkinson and Tsiamis (6) for the quenching of triplet excited states by Cr(hfac)_3 have been reanalysed. The parameters used to obtain the best fit, together with those of Wilkinson and Tsiamis, are presented in Table 5.7. As expected, one difference between the two sets of parameters lies in the transmission coefficients, which have been reduced in the reanalysed data due to the higher \( k_d \).

The other difference between the reinterpreted results of Cr(hfac)_3 and the originals lies in the introduction of the second doublet state, \( ^2T_{2g} \), at 19,000 cm\(^{-1}\). The reasons for its introduction have been discussed previously (see Section 5.2), but predictably no major effect is observed in this case since the quenching constants are approaching those for the maximum diffusion controlled rate.
TABLE 5.7

Parameters for the Reinterpretations of the Results of Wilkinson and Tsiamis for Cr(hfac)$_3$

<table>
<thead>
<tr>
<th>Parameters</th>
<th>This Work</th>
<th>Wilkinson</th>
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<tbody>
<tr>
<td>$^{2}$E$_g$ $\nu$/cm$^{-1}$</td>
<td>12560</td>
<td>12560</td>
</tr>
<tr>
<td>$^{2}$AG$^{*}$(o)/cm$^{-1}$</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>$^{2}$k$_{en}$ ($^{2}$E$<em>g$, $^{2}$T$</em>{1g}$)/10$^{10}$ s$^{-1}$</td>
<td>0.80</td>
<td>3.00</td>
</tr>
<tr>
<td>$^2$k$_{en}$</td>
<td>$1.32 \times 10^{-3}$</td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^4$T$_{2g}$ $\nu$/cm$^{-1}$</td>
<td>15900</td>
<td>15900</td>
</tr>
<tr>
<td>$^4$AG$^{*}$(o)/cm$^{-1}$</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>$^4$k$_{en}$/10$^{10}$ s$^{-1}$</td>
<td>2.0</td>
<td>6.1</td>
</tr>
<tr>
<td>$^4$k$_{en}$</td>
<td>$3.3 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^2$T$_{2g}$ $\nu$/cm$^{-1}$</td>
<td>19000</td>
<td>-*</td>
</tr>
<tr>
<td>$^2$AG$^{*}$(o)/cm$^{-1}$</td>
<td>250</td>
<td>-*</td>
</tr>
<tr>
<td>$^2$k$<em>{en}$ ($^2$T$</em>{2g}$)/10$^{10}$ s$^{-1}$</td>
<td>0.40</td>
<td>-*</td>
</tr>
<tr>
<td>$^2$k$_{en}$</td>
<td>$6.6 \times 10^{-4}$</td>
<td>-*</td>
</tr>
<tr>
<td>$E_2$/V</td>
<td>$-0.40$</td>
<td>$-0.40$</td>
</tr>
<tr>
<td>$\Delta G_{el}$(o)/cm$^{-1}$</td>
<td>1200 (0.15)</td>
<td>1300 (0.16)</td>
</tr>
<tr>
<td>$k_{el}$/10$^{10}$ s$^{-1}$</td>
<td>1.50</td>
<td>9.70</td>
</tr>
<tr>
<td>$\kappa_{el}$</td>
<td>$2.48 \times 10^{-3}$</td>
<td>$1.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>$k_{d}$/10$^{10}$ dm$^3$mol$^{-1}$s$^{-1}$</td>
<td>1.41</td>
<td>1.00</td>
</tr>
<tr>
<td>$k_{-d}$/10$^{10}$</td>
<td>0.80</td>
<td>1.20</td>
</tr>
</tbody>
</table>

* The $^2$T$_{2g}$ state was not included in the Wilkinson and Tsiamis interpretation.
5.6 Quenching by Cr(tfbzac)$_3$

From Fig. 5.12 and the tabulated results given in Table 4.7, two main features become apparent when considering the quenching efficiency of Cr(tfbzac)$_3$. Firstly, four of the high energy donors (> 20,000 cm$^{-1}$) studied have quenching constants in the region of $6.00 \pm 0.30 \times 10^9$ dm$^3$ mol$^{-1}$s$^{-1}$. Secondly, both 2-Acetonaphthone and acridine have quenching constants considerably lower than their nearest neighbours. Clearly, this behaviour is not consistent with quenching by energy transfer, which has been shown to proceed in a series smooth and well-defined steps. Since Cr(tfbzac)$_3$ has a reduction potential of $-0.79$ V vs. SCE, the experimental data will be examined in terms of competitive energy and electron transfer as represented by kinetic scheme 5.33.

The direction of electron transfer has been discussed in the introduction to this section and from Table 5.8 it can be seen that a better correlation exists between $F_E^{OX} - E_T$ and $k_q$ than for $-F_E^{red} - E_T$, further confirmation that the electron is transferred to the quencher. The values of $E_D^{OX}$ and $E_D^{red}$ are presented and discussed in Chapter 3 (Table 3.7).

The free energy for electron transfer may be calculated from:

$$
\Delta G_{el}^\Theta = (E_D^{OX} - E_Q^{red}) F - E_T + \Delta W
$$

5.37

In Chapter I (Section 1.4.3), the value of $\Delta W$, was found to be small, typically $\pm 0.1$ eV, and the values derived from Equation 5.37 are given in the second column of Table 5.9.
FIG 5.12 Log(KQ) vs Donor Energy for Cr(TFBZAC)3

Log(KQ)

9.5
9
8.5
8
7.5
7
6.5

10
9
8
7
6.5

ENERGY (1000 CM-1)

10
12
14
16
18
20
22
24
26

↑ Indicating Electron Transfer Contribution

A1 = 12280 CM-1 ; D1 = 250 CM-1 ; 01 = 0.85E10 S-1
A2 = 15350 CM-1 ; D2 = 2000 CM-1 ; 02 = 4.00E10 S-1
A3 = 19700 CM-1 ; D3 = 250 CM-1 ; 03 = 0.43E10 S-1
D6 = 500 CM-1 ; 06 = 0.35E10 S-1
### TABLE 5.8

Correlation between Reduction and Oxidation Potentials of the Donors and $k_q$ for Cr(tfbzac)$_3$

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_{T'}^{\text{red}}$ - $E_{T'}$ (eV)</th>
<th>$E_{T'}^{\text{ox}}$ - $E_{T'}$ (eV)</th>
<th>$10^9 k_q$ (dm$^3$mol$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>-1.46</td>
<td>-0.58</td>
<td>6.29 ± 0.31</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-0.24</td>
<td>-1.18</td>
<td>6.19 ± 0.21</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-0.06</td>
<td>-1.10</td>
<td>6.10 ± 0.23</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>-0.83</td>
<td>-0.86</td>
<td>3.75 ± 0.13</td>
</tr>
<tr>
<td>Chrysene</td>
<td>-0.18</td>
<td>-1.13</td>
<td>5.85 ± 0.20</td>
</tr>
<tr>
<td>Coronene</td>
<td>-0.36</td>
<td>-1.17</td>
<td>4.00 ± 0.13</td>
</tr>
<tr>
<td>Pyrene</td>
<td>+0.02</td>
<td>-0.92</td>
<td>4.20 ± 0.15</td>
</tr>
<tr>
<td>Acridine</td>
<td>-0.15</td>
<td>-0.38</td>
<td>1.18 ± 0.08</td>
</tr>
<tr>
<td>Anthracene</td>
<td>+0.14</td>
<td>-0.73</td>
<td>1.99 ± 0.04</td>
</tr>
<tr>
<td>Perylene</td>
<td>+0.11</td>
<td>-0.69</td>
<td>0.38 ± 0.14</td>
</tr>
<tr>
<td>Tetracene</td>
<td>+0.27</td>
<td>-0.15</td>
<td>&lt;0.002</td>
</tr>
</tbody>
</table>
TABLE 5.9

Calculated and Experimental Quenching rate constants for \( \text{Cr(tfbzac)}_3 \)

\[
\begin{array}{cccccc}
\text{Donor} & \Delta G_{el}^{\circ} & k_q & \text{Range} & \text{Calc.} & k_q & \text{Exp.} \\
\text{Benzophenone} & +0.21 & 4.81 - 4.83 & 4.81 & 4.81 & 6.29 \pm 0.31 \\
\text{Phenanthrene} & -0.39 & 6.11 - 6.32 & 6.27 & 6.27 & 6.19 \pm 0.21 \\
\text{Naphthalene} & -0.31 & 5.67 - 6.15 & 6.02 & 6.02 & 6.10 \pm 0.23 \\
\text{2-Acetonaphthone} & -0.07 & 3.30 - 5.05 & 4.08 & 4.08 & 3.75 \pm 0.13 \\
\text{Chrysene} & -0.34 & 5.06 - 5.48 & 5.37 & 5.37 & 5.85 \pm 0.20 \\
\text{Coronene} & -0.38 & 4.88 - 5.15 & 5.08 & 5.08 & 4.00 \pm 0.13 \\
\text{Pyrene} & -0.13 & 1.93 - 4.15 & 3.24 & 3.24 & 4.20 \pm 0.15 \\
\text{Acridine} & +0.41 & 1.18 - 1.18 & 1.18 & 1.18 & 1.18 \pm 0.08 \\
\text{Anthracene} & +0.06 & 1.19 - 2.02 & 1.29 & 1.29 & 1.99 \pm 0.04 \\
\text{Perylene} & +0.10 & 0.57 - 0.96 & 0.60 & 0.60 & 0.38 \pm 0.14 \\
\text{Tetracene} & +0.26 & 0 - 0.002 & \text{=} & \text{=} & <0.002 \\
\end{array}
\]

*Range of values calculated by varying \( \Delta G_{el}^{\circ} \) by \( \pm 0.1 \) eV

†Best Fit parameters from Table 510
Since spectroscopic energy levels in the series of Cr(III) β-
diketonate complexes studied are similar (see Chapter III, Table 3), the
values assigned to $^2\Delta^+(o)$ and $^4\Delta^+(o)$ for Cr(tfbzac)$_3$, were typical of
those associated with the analysis of previous quenching results, i.e.
250 cm$^{-1}$ and 2000 - 2400 cm$^{-1}$ (0.02 eV and 0.25 - 0.3 eV), respectively.
In order to obtain reasonable values for $^2k_{en}^0$ and $^4k_{en}^0$, the following
approach was adopted. From Table 5.9 acridine is found to have the
most endoergonic free energy of electron transfer, thus indicating that
quenching of this donor proceeds purely by energy transfer. Quenching
of triplet acridine by the quartet state, $^4T_{2g}$, is energetically
unfavourable, thus leaving the degenerate doublet pair ($^2E_g$, $^2T_{1g}$) as the
excepting state. Therefore, the value of $^2k_{en}^0$ was fixed using acridine
(see Table 5.10). $^2k_{en}^0$ for energy transfer to the $^2T_{2g}$ state was assigned
in the same manner as for all of the other quenchers studied, namely given
half the value of $^2k_{en}^0$ ($^2E_g$, $^2T_{1g}$). In order to make a reasonable estimate
for $^4k_{en}^0$ and $^4\Delta^+(o)$, the values assigned to Cr(bzac)$_3$, the most
structurally related complex were chosen, namely $4.0 \times 10^{10}$ s$^{-1}$ and
2000 cm$^{-1}$.

Since the analysis of experimental results is based on the kinetic
scheme 5.33, it is necessary to consider the other undefined quantities.
The free energy electron transfer, $\Delta G_{el}^+$, is the same for both quartet
and sextet exciplexes and since electron transfer to Cr(tfbzac)$_3$ does
not result in a change of spin,

$$\Delta G_{el}^+(o) = ^4\Delta G_{el}^+(o) = ^6\Delta G_{el}^+(o)$$ \hspace{1cm} 5.38

and

$$\kappa_{el} = ^4\kappa_{el} = ^6\kappa_{el}$$ \hspace{1cm} 5.39
The rate constants for exoergonic electron transfer, $k_{bt}$ and $k_{bt}'$, may be taken as being $> 10^8 \text{ s}^{-1}$, since no transient species were observed during flash photolysis studies. Sample calculations show that variation in $k_q$ of only 1% are predicted if $k_{bt}$ is given values ranging from $10^8$ to $10^{12} \text{ s}^{-1}$. Due to this lack of sensitivity, $k_{bt}$ and $k_{bt}'$ were given a rate constant of $10^{10} \text{ s}^{-1}$.

The best fit to the experimental data was achieved by making $K_{el} = 6.6 \times 10^{-4}$ and $\Delta G^\pm_{el}(o)$ and 0.06 eV, and Table 5.9 shows the excellent agreement which exists between calculated and experimental values, indicating that quenching may be explained in terms of competing energy and electron transfer. As discussed earlier, an uncertainty of $\pm 0.1$ eV exists in the value assigned to $\Delta G^\pm_{el}$ and Table 5.9 also includes the range of rate constants calculated when this uncertainty is introduced. Table 5.11 lists the calculated values of $k_{en}$, $k_q$ and $k_{el}$ using the parameters given in Table 5.10.

Two donors, benzophenone and coronene, were found to have experimental rate constants lying outside those obtained from the best fit program. In the case of benzophenone ($E_T = 24,300 \text{ cm}^{-1}$), the program predicted a lower rate constant than that experimentally observed, however energy transfer to the $^4T_{1g}$ and charge transfer states (Table 3.1) become energetically favourable and are able to explain why the calculated value is low. The standard kinetic expression 5.17 has not been modified to take into account the possibility of energy transfer to these states since there is insufficient experimental data from high energy triplet donors and all the other quenching systems so far studied are well defined by it. The predicted value for the quenching of coronene by Cr(tfbzac)$_3$ lies approximately $1.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ above that observed.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2E_g$ $\bar{\nu}/$cm$^{-1}$</td>
<td>12280</td>
</tr>
<tr>
<td>$^2\Delta G^+(o)/$cm$^{-1}$</td>
<td>250</td>
</tr>
<tr>
<td>$^2k_{en}(^2E_g, ^2T_{1g})/10^{10}$ s$^{-1}$</td>
<td>0.85</td>
</tr>
<tr>
<td>$^2\kappa_{en}$</td>
<td>$1.40 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^4T_{2g} \bar{\nu}/$cm$^{-1}$</td>
<td>15350</td>
</tr>
<tr>
<td>$^4\Delta G^+(o)/$cm$^{-1}$</td>
<td>2000</td>
</tr>
<tr>
<td>$^4k_{en}/10^{10}$ s$^{-1}$</td>
<td>4.00</td>
</tr>
<tr>
<td>$^4\kappa_{en}$</td>
<td>$6.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^2T_{2g} \bar{\nu}/$cm$^{-1}$</td>
<td>19700</td>
</tr>
<tr>
<td>$^2\Delta G^+(o)/$cm$^{-1}$</td>
<td>250</td>
</tr>
<tr>
<td>$^2k_{en}/10^{10}$ s$^{-1}$</td>
<td>0.43</td>
</tr>
<tr>
<td>$^2\kappa_{en}$</td>
<td>$7.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$E_1/V$</td>
<td>-0.79</td>
</tr>
<tr>
<td>$\Delta G^+(o)/$cm$^{-1}$</td>
<td>500</td>
</tr>
<tr>
<td>$k_{el}/10^{10}$ s$^{-1}$</td>
<td>0.35</td>
</tr>
<tr>
<td>$\kappa_{el}$</td>
<td>$6.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$k_{bt}/10^{10}$ s$^{-1}$</td>
<td>1.0</td>
</tr>
</tbody>
</table>
TABLE 5.11

Contributions to $k_q$ from Doublet, Quartet and Sextet States.

A Comparison with Experimental Data

$k_q / 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

<table>
<thead>
<tr>
<th>Donor</th>
<th>$2_k\text{ en}_q$</th>
<th>$4_k\text{ q}_q$</th>
<th>$6_k\text{ el}_q$</th>
<th>$k_q\text{ (theor)}$</th>
<th>$k_q\text{ (exp)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>1.41</td>
<td>2.92</td>
<td>-</td>
<td>4.81</td>
<td>6.29</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1.41</td>
<td>2.79</td>
<td>2.06</td>
<td>6.27</td>
<td>6.19</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.41</td>
<td>2.65</td>
<td>1.96</td>
<td>6.02</td>
<td>6.10</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>1.39</td>
<td>1.95</td>
<td>0.74</td>
<td>4.08</td>
<td>3.75</td>
</tr>
<tr>
<td>Chrysene</td>
<td>1.31</td>
<td>2.05</td>
<td>2.01</td>
<td>5.37</td>
<td>5.85</td>
</tr>
<tr>
<td>Coronene</td>
<td>1.21</td>
<td>1.82</td>
<td>2.05</td>
<td>5.08</td>
<td>4.00</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1.18</td>
<td>0.84</td>
<td>1.22</td>
<td>3.24</td>
<td>4.20</td>
</tr>
<tr>
<td>Acridine</td>
<td>1.18</td>
<td>0.003</td>
<td>-</td>
<td>1.18</td>
<td>1.18</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.18</td>
<td>0.04</td>
<td>0.07</td>
<td>1.29</td>
<td>1.99</td>
</tr>
<tr>
<td>Perylene</td>
<td>0.57</td>
<td>0.01</td>
<td>0.02</td>
<td>0.60</td>
<td>0.38</td>
</tr>
<tr>
<td>Tetracene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.002</td>
</tr>
</tbody>
</table>
experimentally. Spectroscopic investigations of the system, both in the ground state and the excited state, did not reveal any abnormal behaviour that could explain the differences in the rate constants. Coronene with a triplet energy of 19,800 cm\(^{-1}\) lies 100 cm\(^{-1}\) above the position at which energy transfer to the \(2\,T_{2g}\) state is introduced. Sample calculations show that even if the \(2\,T_{2g}\) state is introduced above the triplet energy of coronene, only a minimal reduction in predicted rate constant (\(= 1.0 \times 10^8\) dm\(^3\)mol\(^{-1}\)s\(^{-1}\)) will be realised. The most likely explanation lies with the oxidation potential of coronene (and thus \(\Delta G^0_{el}\)) being 0.2 eV too low.
5.7 Quenching by Cr(tfac)$_3$

As discussed in Sec. 5.4, Huang and Gafney (18) have measured the rate constants for quenching of five organic triplet donors by cis- and trans-
Cr(tfac)$_3$. Although the geometrical isomers were not separated in the
work presented in this Thesis, statistically the trans- isomer will
dominate. Three of the donors used by these workers are in common with
this study, namely anthracene, pyrene and phenanthrene, however in each
case their rate constants for quenching were 25%, 56% and 18% higher,
respectively; these values being well outside quoted experimental errors.
There does not appear to be any obvious explanation for these differences,
however it should be noted that the results of Huang and Gafney follow
the same trend as those presented in Table 4.6.

Kutal et al (26) have undertaken a detailed photochemical study of
trans- Cr(tfac)$_3$ in several non-aqueous solvents. Continuous photolysis
of trans- Cr(tfac)$_3$ in benzene at wavelengths $> 366$ nm was found to
result in trans- to cis- isomerisation taking place with low quantum
yields, $\phi_{\text{isom}} = 9 \times 10^{-4}$. Flash photolysis studies in alcoholic solvents
resulted in the formation of a long-lived species which in deaerated
solutions decayed with a rate constant of $\sim 1$ s$^{-1}$. These studies were,
however, not extended to benzene, but Kutal et al concluded that if the
solvent is a poor hydrogen atom donor, then no redox products are likely
to be detected. Before quenching studies were performed in this thesis,
a solution of the acceptor was subjected to lasing 20 times and without
exception no long-lived species were detected. Neither were any ground
state changes observed.

In the previous section, it was shown that the quenching of organic
triplet states by Cr(tfbzac)$_3$ could be explained in terms of competitive
energy and electron transfer. In order to determine the approximate position (value of the quenchers reduction potential) at which electron transfer becomes important, the quenching ability of Cr(tfac)$_3$, whose reduction potential is -1.04 V vs. SCE, was studied. The results are presented graphically in Fig. 5.13 and tabulated in Table 4.6.

From the profile of Fig. 5.13 it is clear that energy transfer is the predominate mechanism of quenching. However the $k_q$ value for acridine is slightly lower than neighbouring rate constants, which has been shown to be indicative of an electron transfer contribution. In Table 5.12, the free energy changes for electron transfer are listed, and by virtue of the exoergonic values displayed by phenanthrene, naphthalene, chrysene and coronene, an electron transfer contribution from these donors may be expected. In order to evaluate this contribution sample calculations were performed using the kinetic expression based on Scheme 5.33. The rate constant for quenching of triplet Acridine was used to define energy transfer to the doublet states ($^2E_g$, $^2T_{1g}$), whilst the use of intrinsic barriers and transmission coefficients based on those values obtained for Cr(hfac)$_3$ fit the experimental data within experimental errors except for naphthalene (see Table 5.12). A better fit to naphthalene may have been achieved by increasing the value of $^4\kappa_{en}$ ($^4T_{2g}$), however this does not seem justified since $^4\kappa_{en}$ for Cr(acac)$_3$ ($R_1 = R_3 = CH_3$) and Cr(hfac)$_3$ ($R_1 = R_3 = CF_3$) are $2.6 \times 10^{-3}$ and $3.3 \times 10^{-3}$ respectively. However the nature of unsymmetrically substituted Cr(tfac)$_3$ may give rise to an increase in $^4\kappa_{en}$ but until more data is available, the parameters listed in Table 5.13 will be used.

On the basis of these discussions, it may be concluded that for complexes which are structurally similar to Cr(hfac)$_3$, (i.e. contain
FIG 5.13  \( \log(KQ) \) VS DONOR ENERGY FOR CR(TFAC)_3

\[
\begin{align*}
\text{INDICATES ELECTRON TRANSFER CONTRIBUTION} \\
A1 &= 12200 \text{ CM}^{-1}, D1 = 250 \text{ CM}^{-1}, D1 = 0.85E10 \text{ S}^{-1} \\
A2 &= 15540 \text{ CM}^{-1}, D2 = 2000 \text{ CM}^{-1}, D2 = 2.00E10 \text{ S}^{-1} \\
A3 &= 19000 \text{ CM}^{-1}, D3 = 250 \text{ CM}^{-1}, D3 = 0.43E10 \text{ S}^{-1} \\
D6 &= 1200 \text{ CM}^{-1}, D6 = 1.50E10 \text{ S}^{-1}
\end{align*}
\]
TABLE 5.12

Experimental and Calculated Quenching Constants
for Cr(tfac)$_3$

<table>
<thead>
<tr>
<th>Donor</th>
<th>$\Delta G_{el}$/ev</th>
<th>Range$^{(a)}$</th>
<th>Calc $k_q/10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>Expt $k_q/10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>+0.46</td>
<td>3.72-3.74</td>
<td>3.72</td>
<td>4.13±0.29</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-0.14</td>
<td>2.68-3.76</td>
<td>3.06</td>
<td>3.86±0.30</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-0.06</td>
<td>2.42-2.97</td>
<td>2.58</td>
<td>4.12±0.22</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>+0.18</td>
<td>1.96-1.97</td>
<td>1.96</td>
<td>1.99±0.16</td>
</tr>
<tr>
<td>Chrysene</td>
<td>-0.09</td>
<td>1.82-2.66</td>
<td>2.02</td>
<td>1.90±0.11</td>
</tr>
<tr>
<td>Coronene</td>
<td>-0.13</td>
<td>1.64-2.82</td>
<td>2.04</td>
<td>1.75±0.09</td>
</tr>
<tr>
<td>Pyrene</td>
<td>+0.12</td>
<td>1.27-1.38</td>
<td>1.27</td>
<td>1.77±0.12</td>
</tr>
<tr>
<td>Acridine</td>
<td>+0.66</td>
<td>1.12-1.12</td>
<td>1.12</td>
<td>1.12±0.03</td>
</tr>
<tr>
<td>Anthracene</td>
<td>+0.31</td>
<td>1.12-1.14</td>
<td>1.12</td>
<td>1.45±0.08</td>
</tr>
<tr>
<td>Perylene</td>
<td>+0.35</td>
<td>0.62-0.62</td>
<td>0.62</td>
<td>0.33±0.02</td>
</tr>
<tr>
<td>Tetracene</td>
<td>+0.51</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
</tbody>
</table>

(a) Range of values obtained by varying $\Delta G_{el}$ by ±0.1 eV
### TABLE 5.13

Best Fit Parameters for Cr(tfac)$_3$

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2E_g$ $\nu$/cm$^{-1}$</td>
<td>12200</td>
</tr>
<tr>
<td>$2\Delta G^*(o)/$cm$^{-1}$</td>
<td>250</td>
</tr>
<tr>
<td>$2k^o_{en} (2E_g, 2T_{1g})/10^{10}$ s$^{-1}$</td>
<td>0.85</td>
</tr>
<tr>
<td>$2\kappa_{en}$</td>
<td>$1.40 \times 10^{-3}$</td>
</tr>
<tr>
<td>$4T_{2g}$ $\nu_{oo}$/cm$^{-1}$</td>
<td>15540</td>
</tr>
<tr>
<td>$4\Delta G^*(o)/$cm$^{-1}$</td>
<td>2000</td>
</tr>
<tr>
<td>$4k^o_{en}/10^{10}$ s$^{-1}$</td>
<td>2.00</td>
</tr>
<tr>
<td>$4\kappa_{en}$</td>
<td>$3.29 \times 10^{-3}$</td>
</tr>
<tr>
<td>$2T_{2g}$ $\nu$/cm$^{-1}$</td>
<td>19000</td>
</tr>
<tr>
<td>$2\Delta G^*(o)/$cm$^{-1}$</td>
<td>250</td>
</tr>
<tr>
<td>$2k^o_{en}/10^{10}$ s$^{-1}$</td>
<td>0.43</td>
</tr>
<tr>
<td>$2\kappa_{en}$</td>
<td>$7.00 \times 10^{-4}$</td>
</tr>
<tr>
<td>$k_d/10^{10}$ dm$^3$mol$^{-1}$s$^{-1}$</td>
<td>1.41</td>
</tr>
<tr>
<td>$k_{-d}/10^{10}$ s$^{-1}$</td>
<td>0.80</td>
</tr>
<tr>
<td>$k_{el}/10^{10}$ s$^{-1}$</td>
<td>1.51</td>
</tr>
<tr>
<td>$\kappa_{el}$</td>
<td>$2.48 \times 10^{-3}$</td>
</tr>
<tr>
<td>$E_1/V$ vs. SCE</td>
<td>-1.04</td>
</tr>
<tr>
<td>$\Delta G^+_e l (o)$ / cm$^{-1}$</td>
<td>1200</td>
</tr>
</tbody>
</table>
aliphatic rather than aryl substituents) quenching by competitive energy and electron transfer is still experimentally detectable at -1.04 V vs. SCE. The point at which the competitive mechanism becomes unimportant is likely to occur at approximately -1.15 V vs. SCE.

The best fit parameters used for those quenchers interpreted in terms of competitive energy and electron transfer are given in Table 5.14. It is interesting to note that for Cr(tfbzac)_3 both $\Delta G_{el}^\neq$ and $\kappa_{el}$ values are less than those of Cr(hfac)_3. Structural differences are the likely cause, with the phenyl group of Cr(tfbzac)_3 lowering the intrinsic barrier considerably compared with CH_3 and CF_3 groups. The decrease in $\kappa_{el}$ being due to the increased steric effect of the bulky phenyl group.
TABLE 5.14

Transmission coefficients and Intrinsic Barriers for
Cr(III) β-diketonate complexes quenching by
competitive Energy- and Electron- Transfer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cr(tfac)$_3$</th>
<th>Cr(tfbzac)$_3$</th>
<th>Cr(hfac)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2\kappa_{\text{en}}(^2E_g ^2T_{1g})/10^{-3}$</td>
<td>1.4</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>$^2\Delta G^\pm(o)/\text{cm}^{-1}$</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>$^4\kappa_{\text{en}}(^4T_{2g})10^{-3}$</td>
<td>3.3</td>
<td>6.5</td>
<td>3.3</td>
</tr>
<tr>
<td>$^4\Delta G^\pm(o)/\text{cm}^{-1}$</td>
<td>2000</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>$\kappa_{\text{el}}/10^{-3}$</td>
<td>2.5</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>$\Delta G_{\text{el}}^\pm(o)/\text{cm}^{-1}$</td>
<td>1200</td>
<td>500</td>
<td>1200</td>
</tr>
</tbody>
</table>
The classical treatment of energy transfer developed by the author has been employed with considerable success in the interpretation of the rate constants for quenching of triplet excited organic donors by Cr(III) β-diketonate complexes. The spectroscopic energy levels of the series are well defined, diffusion and dissociation rate constants, $k_d$ and $k_d^{-1}$ have been calculated, leaving the intrinsic reorganizational barriers, $\Delta G_{en}^\ddagger(o)$ and transmission coefficients $\kappa_{en}$ as the variables used to obtain the best fit to the experimental data.

The intrinsic reorganizational barrier governs the shape of the rising portion of a $k_q$ vs. $E_T$ plot and may be considered as due to two contributions with

$$\Delta G_{en}^\ddagger(o) = \frac{1}{2} (\Delta G_{D}^\ddagger(o) + \Delta G_{A}^\ddagger(o))$$  \hspace{1cm} \text{5.40}$$

where $\Delta G_{D}^\ddagger(o)$ and $\Delta G_{A}^\ddagger(o)$ refer to the free energies of activation for self exchange energy transfer of the donor and acceptor, respectively. The barrier receives contributions from both the "inner-sphere" reorganization energy $\Delta G_{I}^\ddagger$ (which relates to changes in bond length and configuration) and the "outer-sphere" reorganizational energy $\Delta G_{O}^\ddagger$ (relating to changes in the solvent arrangement around the molecule) with

$$\Delta G_{en}^\ddagger(o) = \Delta G_{I}^\ddagger + \Delta G_{O}^\ddagger$$  \hspace{1cm} \text{5.41}$$

In the case of energy transfer there is no change in the charge of the species and therefore contributions from the "outer-sphere" energy are likely to be negligible.
Both ground state Cr(III), $^4A_{2g}$ and the doublet excited state $^2E_g$, have a d-electron configuration of $t^3_{2g}e^0_{g}$ and are therefore likely to be of equal size which would indicate a negligible contribution to the "inner-sphere" reorganizational energy, leaving $\Delta G^\dagger_i$ for the donor as the parameter dictating the shape of the curve. For the quenching systems studied, a $\Delta G^\dagger_{en}(o)$ of $250 \text{cm}^{-1}$ was able to fit the experimental data indicating a contribution of approximately $500 \text{cm}^{-1}$ from the "self-exchange" energy transfer of the donor. However it should be noted that the only donor which covers the range $12,000$-$14,000 \text{ cm}^{-1}$ is perylene, and there has been some doubt over the exact position of the $\nu_{oo}(T)$ band (5), which suggests that $\Delta G^\dagger(\omega) = 250 \pm 150 \text{ cm}^{-1}$.

For energy transfer to the $^4T_{2g}$ state, the best fit was achieved with $\Delta G^\dagger_{en}(\omega) = 2200 \pm 200 \text{ cm}^{-1}$. This larger intrinsic reorganizational barrier is the result of the distortion caused by the promotion of an electron to the $e_g$ subset giving rise to a contribution from $\Delta G^\dagger_i$. From equation 5.40, the free energies of self-exchange to form the distorted $^4T_{2g}$ for the series of Cr(III) $\beta$-diketonate complexes are in the range of $3500$-$4300 \text{ cm}^{-1}$. When energy transfer is sufficiently exoergonic to compensate for the intrinsic barrier, then the plateau quenching rate constant is controlled by the transmission coefficient and the value of $k_d$ and $k_{-d}$. The transmission coefficients calculated to give the best fit to the experimental data are listed in Table 5.1.5. Attempts will be made to see if the values of $\kappa$ obtained for the complexes with various substituent groups could be attributed to a simple addition of substituent $\kappa$ contributions. This type of approach was adopted by Handy and Linvedt (27) for evaluating the substituent group electronic effects in Cr(III) $\beta$-diketonate complexes and comparing them with polarographic half wave potentials. In this case the group effects were measured relative to the
TABLE 5.15

Transmission coefficients and Intrinsic Barriers for

Cr(III) β-diketonate complexes quenching by Energy Transfer

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{2}\kappa_{en}/10^{-3}$</th>
<th>$^{2}\Delta G^{\mp}(o)$</th>
<th>$^{4}\kappa_{en}/10^{-3}$</th>
<th>$^{4}\Delta G^{\mp}(o)$</th>
<th>$^{2}\kappa_{en}/10^{-3}$</th>
<th>$^{2}\Delta G^{\mp}(o)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(dpm)$_3$*</td>
<td>0.04</td>
<td>250</td>
<td>0.49</td>
<td>2000</td>
<td>0.28</td>
<td>250</td>
</tr>
<tr>
<td>Cr(acac)$_3$*</td>
<td>1.60</td>
<td>250</td>
<td>2.60</td>
<td>2200</td>
<td>0.80</td>
<td>250</td>
</tr>
<tr>
<td>Cr(3-Meacac)$_3$</td>
<td>14.0</td>
<td>250</td>
<td>9.40</td>
<td>2400</td>
<td>7.00</td>
<td>250</td>
</tr>
<tr>
<td>Cr(3-Etacac)$_3$</td>
<td>4.30</td>
<td>250</td>
<td>7.70</td>
<td>2400</td>
<td>2.15</td>
<td>250</td>
</tr>
<tr>
<td>Cr(3-Pracac)$_3$</td>
<td>3.80</td>
<td>250</td>
<td>6.60</td>
<td>2400</td>
<td>1.90</td>
<td>250</td>
</tr>
<tr>
<td>Cr(bzac)$_3$*</td>
<td>2.50</td>
<td>250</td>
<td>6.60</td>
<td>2000</td>
<td>1.25</td>
<td>250</td>
</tr>
<tr>
<td>Cr(BDO)$_3$*</td>
<td>2.50</td>
<td>250</td>
<td>7.00</td>
<td>2300</td>
<td>1.25</td>
<td>250</td>
</tr>
<tr>
<td>c-Cr(5BuPDO)$_3$</td>
<td>1.90</td>
<td>250</td>
<td>14.00</td>
<td>2300</td>
<td>0.95</td>
<td>250</td>
</tr>
<tr>
<td>t-Cr(5BuPDO)$_3$</td>
<td>1.50</td>
<td>250</td>
<td>9.30</td>
<td>2300</td>
<td>0.75</td>
<td>250</td>
</tr>
</tbody>
</table>

*Results of Wilkinson and Tsiamis (4,5,22)
parent complex \( \text{Cr(PDO)}_3 (R_1 = R_2 = R_3 = H) \). Unfortunately it was not possible to obtain quenching rate constants for \( \text{Cr(PDO)}_3 \) since ground state absorption spectra revealed interactions between donors and the acceptor.

The following approach was adopted. In section 5.3, the increase in quenching rate constants associated with the introduction of aliphatic groups of increasing chain length in the \( \gamma \)- or \( R_2 \) position was explained in terms of inductive effect. The increases were correlated with Hammett \( \sigma \) constants which define the inductive effect of hydrogen to be zero. From Table 5.15, energy transfer to the \( ^2E_g, ^2T_{1g} \) states of \( \text{Cr(dpm)}_3 \) proceeds with a transmission coefficient of \( 4 \times 10^{-5} \), indicating the possibility of contributions to \( \kappa \) (complex) from both \( R_1 = R_3 = t-C_4H_9 \) and \( R_2 = H \). It follows that for this study of the group additivity of transmission coefficients, the contribution from \( R_2 = H \) has to be \( < 4 \times 10^{-5} \). Since \( ^2\kappa_{en} \) values for the other complexes studied are significantly greater, the value assigned to \( ^2\kappa (R_2 = H) \) will not have any measurable effect on calculated \( \kappa \) (complex) values and for convenience has been assigned a value of zero (see Table 5.16). In the case of energy transfer to \( ^4\tau_{2g} \), for \( R_2 = H \) the contribution to \( \kappa \) (complex) is likely to be more significant and a value of \( 0.2 \times 10^{-3} \) has been assigned (the author acknowledges the possibility of alternative approaches to this problem).

For Tris complexes, where \( R_1 = R_3 \) and \( R_2 = H \), the group effect for energy transfer to the doublet state was given a value of half that of the transmission coefficient for the complex; in the case of \( ^4\kappa_{en} \), the \( 2 \times 10^{-4} \) contribution from \( R_2 \) was taken into account. Where \( R_1 \neq R_3 \) (or when \( R_2 \neq H \) ), the contribution from the unknown group was calculated by simple subtraction using the equation
TABLE 5.16

Doublet Transmission Coefficients for Cr(III) \( \beta \)-diketonates complexes together with their proposed \( R_1 \), \( R_2 \) and \( R_3 \) contributions

<table>
<thead>
<tr>
<th>Complex</th>
<th>( 2\kappa_{en}/10^{-3} ) ( ^2E_g \rightarrow ^2T_{1g} )</th>
<th>( 2\kappa_{en}/10^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t\text{Bu} ) H ( t\text{Bu} )</td>
<td>0.04</td>
<td>( 0.02 ) 0 ( 0.02 )</td>
</tr>
<tr>
<td>CH\text{3} H CH\text{3}</td>
<td>1.6</td>
<td>( 0.8 ) 0 ( 0.8 )</td>
</tr>
<tr>
<td>CH\text{3} CH\text{3} CH\text{3}</td>
<td>14.0</td>
<td>( 0.8 ) 12.4 ( 0.8 )</td>
</tr>
<tr>
<td>CH\text{3} C\text{2H}5 CH\text{3}</td>
<td>4.3</td>
<td>( 0.8 ) 2.7 ( 0.8 )</td>
</tr>
<tr>
<td>CH\text{3} n-C\text{3H}7 CH\text{3}</td>
<td>3.8</td>
<td>( 0.8 ) 2.2 ( 0.8 )</td>
</tr>
<tr>
<td>CH\text{3} H ( \emptyset )</td>
<td>2.5</td>
<td>( 0.8 ) 0 ( 1.7 )</td>
</tr>
<tr>
<td>CH\text{3} H H</td>
<td>2.5</td>
<td>( 0.8 ) 0 ( 1.7 )</td>
</tr>
</tbody>
</table>

For \( R_2 = H \) \( 2\kappa_{en} \leq 0.04 \)
\[
\kappa \text{(complex)} = \kappa R_1 + \kappa R_2 + \kappa R_3 \quad 5.42
\]

The group effect values derived from this treatment for both \(2\kappa_{_{en}}\) and \(4\kappa_{_{en}}\) are given in Tables 5.16 and 5.17, respectively. This approach may be taken further extended to mixed ligand complexes of the form \(M(L_1)_n(L_2)_{3-n}\) by calculating the \(R\) group contribution per ligand i.e. \(R/3\) for the values listed in the aforementioned tables.

The validity of this additive treatment may be tested by comparing the predicted values with those derived from the experimental data of \(\sigma\text{is} - \text{and trans} - \text{Cr(tBu PDO)}_3 \text{(R}_1 = \text{tBu}, \text{R}_2 = \text{R}_3 = \text{H})\). For energy transfer to the \(2\text{E}_g, 2\text{T}_{1g}\) states \(2\kappa \text{(pred)} = 1.72 \times 10^{-3}\) which is in excellent agreement with the average value derived from the experimental data \(\sigma\text{is} = 1.9 \times 10^{-3}, \text{trans} = 1.5 \times 10^{-3}\) av. \(2\kappa \text{(expt)} = 1.7 \times 10^{-3}\).

For energy transfer to \(4\text{T}_{2g}\), \(4\kappa \text{(pred)} = 5.95 \times 10^{-3}\) compared with av. \(4\kappa \text{(expt)} = 11.7 \times 10^{-3}\), however it should be noted that \(4\kappa \text{ (tBu)}\) is derived from the quenching data of \(\text{Cr(dpm)}_3\) where there is a large contribution from energy transfer to the \(2\text{T}_{2g}\) state, which results in a considerable reduction in the contribution from the quartet pathway.

In Section 5.4, the difference in quenching efficiency of \(\text{Cr(tBu PDO)}_3 \text{(R}_1 = \text{tBu}, \text{R}_2 = \text{R}_3 = \text{H})\) compared with \(\text{Cr(BDO)}_3 \text{(R}_1 = \text{CH}_3, \text{R}_2 = \text{R}_3 = \text{H})\) was attributed to the larger inductive effect of \(\text{tBu}\) compared with that of \(\text{CH}_3\) \(\sigma_p \text{tBu} = -0.197, \text{CH}_3 = -0.171\), which was able to overcome steric considerations. Thus contributions from the inductive effect may need to be included into the expression for the prediction of transmission coefficients. Whether this takes the form of a summation or a product is however not clear from this single result and further experimental data is required.
TABLE 5.17

Quartet Transmission coefficients for Cr(III) \( \beta \)-diketonate complexes together with their proposed \( R_1 \), \( R_2 \), and \( R_3 \) contributions

<table>
<thead>
<tr>
<th>Complex</th>
<th>( 4^{\kappa_{en}} / 10^{-3} ) ( (4^{T_{2g}}) )</th>
<th>( 4^{\kappa_{en}} / 10^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_{Bu} )</td>
<td>0.5</td>
<td>0.15</td>
</tr>
<tr>
<td>( CH_3 )</td>
<td>2.6</td>
<td>1.2</td>
</tr>
<tr>
<td>( CH_3 )</td>
<td>9.3</td>
<td>1.2</td>
</tr>
<tr>
<td>( CH_3 )</td>
<td>7.7</td>
<td>1.2</td>
</tr>
<tr>
<td>( CH_3 )</td>
<td>6.6</td>
<td>1.2</td>
</tr>
<tr>
<td>( CH_3 )</td>
<td>6.6</td>
<td>1.2</td>
</tr>
<tr>
<td>( CH_3 )</td>
<td>7.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

*For Cr(dpm) \(_3\) a large contribution from energy transfer to the \( 2T_{2g} \) state may influence the value listed

for \( R_2 = H \) \( 4^{\kappa_{en}} = 0.02 \)
In unpublished work, Wilkinson and Tsiamis have measured rate constants for quenching of the triplet states of organic donors by Cr(dbm)$_3$ (28), where $R_1 = R_3 = \emptyset$ and $R_2 = H$. Quenching is likely to proceed by energy transfer only since Cr(dbm)$_3$ has an $E_T$ of $-1.26$ V vs. SCE, and from Section 5.7 it was concluded that electron transfer becomes improbable below $-1.15$ V vs. SCE. The predicted best fit values from this treatment are $k_{2E_g \rightarrow 2T_{1g}} = 3.4 \times 10^{-3}$ and $k_{4T_{2g} \rightarrow 2T_{2g}} = 10.6 \times 10^{-3}$ (energy transfer to $2T_{2g}$ being assigned a contribution of $1.7 \times 10^{-3}$). As previously discussed in Section 5.2, transmission coefficients are likely to be subject to variations of $\pm 20\%$ and Table 5.18 shows an excellent agreement between the predicted $+20\%$ rate constants and those obtained experimentally. The slightly low values predicted for Benzophenone, Triphenylene and Naphthalene can be accounted for if energy transfer to $4T_{1g}$ and CT states at 20,830 cm$^{-1}$ and 21,980 cm$^{-1}$, respectively is advocated.

In conclusion, the additive effect of substituent groups to the transmission coefficient has a notable success in predicting the quenching rate constants for Cr(dbm)$_3$ ($R_1 = R_3$) and slightly less success for Cr(tBu PDO)$_3$ ($R_1 \neq R_3$) where an inductive effect has been proposed. Clearly it is going to require considerably more quenching data in order to elucidate the role played by both steric and inductive factors in determining the transmission coefficients for any complex. It is therefore suggested that in further quenching experiments the Cr(III) $\beta$-diketonate complexes are divided into five distinct classes with similar substituents i.e. all aliphatic, all aromatic, all mixed aliphatic/aromatic, all aliphatic/aromatic + $R_3 = H$ and $\gamma$-substituents, varying one substituent at a time in order to assess its effect. Further, the step-wise nature of the treatment in predicting transmission coefficients may be tested by
TABLE 5.18

Experimental* and Predicted Values of Quenching rate constants for \text{Cr\(\text{dbm}\)_3}

<table>
<thead>
<tr>
<th>Donor</th>
<th>(E_T/1000)</th>
<th>Prediction</th>
<th>(k_q/10^9\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1})</th>
<th>(-20%)</th>
<th>(+20%)</th>
<th>expt/</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>24.3</td>
<td>5.67</td>
<td>5.40</td>
<td>5.87</td>
<td>7.4±0.4</td>
<td></td>
</tr>
<tr>
<td>Triphenylene</td>
<td>23.3</td>
<td>5.49</td>
<td>5.21</td>
<td>5.66</td>
<td>7.1±0.4</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>21.3</td>
<td>4.73</td>
<td>4.39</td>
<td>4.95</td>
<td>5.8±0.4</td>
<td></td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>20.6</td>
<td>4.25</td>
<td>3.91</td>
<td>4.50</td>
<td>4.7±0.3</td>
<td></td>
</tr>
<tr>
<td>Chrysene</td>
<td>20.0</td>
<td>3.75</td>
<td>3.41</td>
<td>3.99</td>
<td>4.7±0.3</td>
<td></td>
</tr>
<tr>
<td>Coronene</td>
<td>19.4</td>
<td>3.15</td>
<td>2.86</td>
<td>3.37</td>
<td>2.3±0.2</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.8</td>
<td>1.75</td>
<td>1.62</td>
<td>1.80</td>
<td>2.1±0.2</td>
<td></td>
</tr>
<tr>
<td>Acridine</td>
<td>15.8</td>
<td>1.70</td>
<td>1.58</td>
<td>1.74</td>
<td>1.6±0.1</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>14.7</td>
<td>1.69</td>
<td>1.57</td>
<td>1.73</td>
<td>1.7±0.1</td>
<td></td>
</tr>
</tbody>
</table>

* Results of Tsiamis and Wilkinson (28)

Parameters used

\[2\kappa_{en} = 3.4 \times 10^{-3}\]

\[2\Delta G^\circ(\text{o}) = 250 \text{ cm}^{-1}\]

\[4\kappa_{en} = 10.6 \times 10^{-3}\]

\[4\Delta G^\circ(\text{o}) = 2000 \text{ cm}^{-1}\]
measuring quenching constants for mixed ligand quenchers of the type Cr(dpm)_n(acac)_{3-n}, where n=1 or 2, since quenching for the respective parent complexes have been measured. Work of this nature is currently planned.

PART B

5.9 Quenching by Co(III) β-diketonate complexes

In the preceding part of this discussion chapter, it was shown that theoretical calculations based upon the kinetic schemes developed by the author are able to account for the experimental results presented. The results have been interpreted in terms of energy transfer and competitive energy- and electron- transfer, with the reduction potential of the quencher dictating the mechanism followed. Wilkinson and Tsiamis (7) and G. Michael (29) have successfully used the same approach when they studied quenching by Fe(III) β-diketonates. In order to further these studies and test the general nature of this type of approach, rate constants for quenching of triplet excited organic donors by Co(III) β-diketonates were measured.
5.10 Kinetic Scheme for quenching by Co(III) complexes

In an octahedral field Co(III) has a low spin configuration \( t^6 \), which gives rise to the singlet ground state, \( ^1A_{1g} \). Both singlet and triplet excited states are expected, however energy transfer to singlet excited states, Scheme 5.43 is forbidden by Wigner's spin rules. From the \( d^6 \) Tanabe - Sugano diagram in Chapter 3, a quintet excited state is predicted to lie at \(-7500\) cm\(^{-1}\) but again energy transfer to this state is forbidden by Wigner's spin rules.

\[
\begin{align*}
3^D* + ^1Co & \rightarrow 1^D + ^1Co^* \\
3^D* + ^1Co & \rightarrow 1^D + ^5Co^* \\
3^D* + ^1Co & \rightarrow 1^D + ^3Co^*
\end{align*}
\]

Quenching of electronically excited triplet donors by Co(III) complexes is therefore expected to proceed via Scheme 5.45, with a spin statistical factor, of unity. The energy levels of the \( 3^T_{1g} \) and \( 3^T_{2g} \) states are given in Table 3.4.

Schematically, quenching by energy transfer may be represented by

\[
\begin{align*}
3^D* + ^1Q & \overset{k\text{-en}}{\underset{k\text{-d}}{\rightleftharpoons}} 3^D + ^1Q^* \\
3^D + ^1Q & \overset{k\text{-en}}{\underset{k\text{-d}}{\rightleftharpoons}} 3^D + ^3Q^* \\
3^D* + ^3Q^* & \overset{k\text{-d}}{\rightarrow} 1^D + ^3Q^* \\
3^D + ^3Q^* & \overset{k\text{-en}}{\rightarrow} 3^D + ^3Q^*
\end{align*}
\]

Previous results and discussions have shown that quenching by electronic energy transfer is characterized by well defined steps and plateau's in a plot of \( k_q \) vs. \( E_T \). The results presented in Fig's 5.14-5.17 clearly
do not exhibit this phenomena and thus it may be concluded that another quenching mechanism must be important. In the sections dealing with the quenching by Cr(III) β-diketonates containing trifluromethyl groups (5.5-5.7), it was necessary to introduce competitive electron transfer into the kinetic scheme in order to account for the observed quenching behaviour. It was found that electron transfer was observable, even when the reduction potential of the quencher reached -1.04 V vs. SCE. The reduction potentials for the Cobalt(III) complexes studied lie in range -0.34V to +0.05 V vs. SCE and thus the free energy changes for electron transfer ΔG_{el} as given by equation 5.37 are more exoergonic for these complexes, which is further confirmation for the inclusion of an electron transfer pathway into Scheme 5.46 Ohno and Lichtin (30) concluded that reversible electron transfer is not the only significant mechanism of quenching of triplet methylene blue by four cobalt complexes. Several other studies (31-35) have come into similar conclusions.

For charge transfer quenching by Co(III) complexes Creaser et al (31) have concluded that it involves electron transfer to the Co(III) complex. Thus we have the situation

\[ \text{D}^* \cdot \text{Q} \rightarrow \text{D}^+ + \text{Q}^- \rightarrow \text{D} + \text{Q} \]  

5.47

Where D^+ represents the doublet radical cation of the organic molecule and Q^- represents the reduced Co(III) complex. Co(III) has a d^7 configuration which may be either low spin t_{2g}^6 e_g^1, (S=1) or high spin t_{2g}^5 e_g^2 (S=3/2) but most Co(II) complexes with weak field ligands are high-spin (25). Vector addition of the spin multiplicities of D^+ and high-spin Q^- yield \( ^3(D^* \cdot Q^-) \) as the spin-allowed combination. This pathway has been added to Scheme 5.46, and the experimental results presented will be analysed in terms of Scheme 5.48.
with a rate constant

\[
k_q = \frac{sk_d}{1 + \frac{1}{k_{el}k_{bt}}}
\]

\[
\frac{k_{en}}{k_{en} + k_{d}} + \frac{k_{en}}{k_{en} + k_{d}} + k_{el}k_{bt}
\]

The excited triplet states of Co(III) are expected to be distorted with respect to the ground state configuration $^1A_{1g}$ since an electron has been promoted to antibonding $e_g$ orbitals. Gandolifi et al (19) have reported a $\Delta G^+ (o)$ value of 1420 cm$^{-1}$ for the self-exchange reaction

\[
^1A_{1g} + ^3T_{1g} \rightarrow ^3T_{1g} + ^1A_{1g}
\]

since $\Delta G^+ (o)$ is likely to be negligible for energy transfer a $\Delta G_{en}^+ (o)$ value of $-1000$ cm$^{-1}$ as given by equation 5.13 ($\Delta G_{en}^+ (o)$ $= 500$ cm$^{-1}$ from the study of Cr(III) complexes) will be considered a reasonable starting point for the interpretation of the experimental results. As for Cr(III), $k_{bt}$ will be taken as $10^{10}$ s$^{-1}$.
Some quenching rate constants for Co(acac)$_3$ have been previously measured by Marshall (36) who locating a "dip" in a $k_q$ vs. $E_T$ plot with a minima at ~ 20,000 cm$^{-1}$. The study presented here has reconfirmed the existence of the dip and increased the number of donors studied over this region. The results are presented in Table 4.10 and a plot of log $k_q$ vs. $E_T$ is given in Fig. 5.14. The lowest rate constant for quenching in the dip is represented by coronene ($E_T = 19,400$ cm$^{-1}$) with $k_q = 0.36 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ compared with perylene ($E_T = 12,600$ cm$^{-1}$) $k_q = 0.74 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ which represents the highest quenching constant of the low energy donors, i.e. there is a two fold reduction in $k_q$ over a range of ~ 7,000 cm$^{-1}$. Co(acac)$_3$ has an $E_T = -0.34$ V vs. SCE, and Table 5.19 lists the free energy changes for electron transfer. For coronene and perylene $\Delta G_{el}$ equals -0.79 eV and -0.35 eV, respectively which indicates that irrespective of the magnitude of the intrinsic reorganizational barrier a larger contribution from the electron transfer pathway rate for coronene would be predicted. Experimentally $k_q$ (perylene) > $k_q$ (coronene) and clearly these results cannot be explained within the general framework of the kinetic approach previously adopted.

Quenching rate constants have been measured for three other Co(III) $\beta$-diketonate complexes. These results will now be discussed before returning to possible reasons for the difference between experimental and calculated rate constants for Co(acac)$_3$. 
FIG 5.14  LOG(KQ) VS DONOR ENERGY FOR CO(ACAC)₃
TABLE 5.19

Experimental and Calculated Quenching Rate Constants for Co(acac)₃

<table>
<thead>
<tr>
<th>DONOR</th>
<th>$\Delta G_{el}^\theta$ (eV)</th>
<th>Range* (eV)</th>
<th>Calcd. $k_q$ ($10^9$ dm³ mol⁻¹ s⁻¹)</th>
<th>Expt. $k_q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>-0.24</td>
<td>0.57</td>
<td>0.57</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-0.84</td>
<td>1.33 - 3.14</td>
<td>2.06</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>-0.52</td>
<td>0.60 - 0.86</td>
<td>0.67</td>
<td>0.46 ± 0.02</td>
</tr>
<tr>
<td>Chrysene</td>
<td>-0.79</td>
<td>1.08 - 2.58</td>
<td>1.66</td>
<td>0.46 ± 0.03</td>
</tr>
<tr>
<td>Coronene</td>
<td>-0.83</td>
<td>1.31 - 3.11</td>
<td>2.04</td>
<td>0.36 ± 0.02</td>
</tr>
<tr>
<td>1,2,5,6-DBA</td>
<td>-0.74</td>
<td>0.90 - 2.07</td>
<td>1.33</td>
<td>0.60 ± 0.03</td>
</tr>
<tr>
<td>1,2,3,4-DBA</td>
<td>-0.62</td>
<td>0.67 - 1.21</td>
<td>0.84</td>
<td>0.71 ± 0.02</td>
</tr>
<tr>
<td>Pyrene</td>
<td>-0.58</td>
<td>0.64 - 1.06</td>
<td>0.77</td>
<td>0.50 ± 0.04</td>
</tr>
<tr>
<td>Acridine</td>
<td>-0.04</td>
<td>0.57 - 0.57</td>
<td>0.57</td>
<td>0.58 ± 0.04</td>
</tr>
<tr>
<td>Anthracene</td>
<td>-0.39</td>
<td>0.57 - 0.64</td>
<td>0.59</td>
<td>0.73 ± 0.07</td>
</tr>
<tr>
<td>Perylene</td>
<td>-0.35</td>
<td>0.45 - 0.52</td>
<td>0.46</td>
<td>0.74 ± 0.02</td>
</tr>
<tr>
<td>Tetracene</td>
<td>-0.17</td>
<td>0.27 - 0.28</td>
<td>0.27</td>
<td>0.66 ± 0.03</td>
</tr>
<tr>
<td>Pentacene</td>
<td>-0.11</td>
<td>0.02</td>
<td>0.02</td>
<td>0.16 ± 0.07</td>
</tr>
</tbody>
</table>

* Range values calculated by allowing an uncertainty of ± 0.1 eV in $\Delta G_{el}^\theta$. 

-288-
5.12 Quenching by Co(III) β-diketonate complexes containing Phenyl groups.

The two quenchers studied under this heading were trans-Co(bzac)$_3$ ($R_1 = \emptyset, R_3 = CH_3$) and trans-Co(β-PDO)$_3$ ($R_1 = \emptyset, R_3 = H$) whose experimental quenching rate constants are given in Tables 4.11 and 4.12, respectively. Log $k_q$ vs. $E_T$ plots are represented by Figs. 5.15 and 5.16. Huang and Gafney (18) have reported quenching constants for triplet anthracene, pyrene and phenanthrene in the presence of both cis- and trans- Co(bzac)$_3$. Their values for anthracene and phenanthrene are in agreement with the results presented in this thesis, however $k_q$ for pyrene is 1.8 times higher. A similar unexplainable high value was reported for pyrene in the presence of Cr(tfac)$_3$ (see Section 5.7).

As discussed previously (Section 5.9) a significant contribution from competitive electron transfer is expected since $E'_k$'s for Co(bzac)$_3$ and Co(β-PDO)$_3$ have been reported as $-0.21$ V and $-0.19$ V vs. SCE respectively. Free energy changes for electron transfer as given by equation 5.37 are tabulated in 5.20 and 5.21.

The same approach to competitive energy- and electron- transfer as used for the Cr(III) complexes has been adopted, namely the transmission coefficients for energy transfer to the low lying triplet excited states of Co(III) being determined by the quenching constant of triplet acridine which has the most endoergic free energy of electron transfer. From Table 3.4, the Co(III) β-diketonate complexes studied have fairly invariant $^3T_{1g}$ and $^3T_{2g}$ energy levels with $\tilde{\nu}_{max}$ of 9,000 cm$^{-1}$ and 12,500 cm$^{-1}$, respectively. The position of $\tilde{\nu}_{\infty}$ will be somewhat lower, and as discussed by Gandolfi et al (19) have intrinsic reorganizational barriers approaching $\approx 1,000$ cm$^{-1}$. 
FIG 5.15 LOG(KQ) VS DONOR ENERGY FOR TRANS-CO(BZAC)3

PREDICTED ELECTRON TRANSFER CONTRIBUTION

BEST FIT PARAMETERS GIVEN IN TABLE 5.23
TABLE 5.20

Experimental and Calculated Quenching Rate Constants for trans-Co(bzac)$_3$~Ge

<table>
<thead>
<tr>
<th>DONOR</th>
<th>$\Delta G_{el}^9$ (eV)</th>
<th>Range* ($\text{cm}^{-1}$)</th>
<th>Calcd. $k_q$ ($10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)</th>
<th>Expt. $k_q$ ($10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>-0.37</td>
<td>1.22 - 1.30</td>
<td>1.24</td>
<td>5.12 ± 0.25</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-0.97</td>
<td>3.61 - 6.53</td>
<td>5.02</td>
<td>5.34 ± 0.20</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-0.89</td>
<td>2.14 - 5.37</td>
<td>3.91</td>
<td>4.64 ± 0.15</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>-0.65</td>
<td>1.42 - 2.39</td>
<td>1.75</td>
<td>2.15 ± 0.08</td>
</tr>
<tr>
<td>Chrysene</td>
<td>-0.92</td>
<td>3.04 - 5.80</td>
<td>4.31</td>
<td>4.15 ± 0.20</td>
</tr>
<tr>
<td>Coronene</td>
<td>-0.96</td>
<td>3.58 - 6.49</td>
<td>4.98</td>
<td>1.85 ± 0.09</td>
</tr>
<tr>
<td>Pyrene</td>
<td>-0.71</td>
<td>1.58 - 2.96</td>
<td>2.08</td>
<td>1.30 ± 0.05</td>
</tr>
<tr>
<td>Acridine</td>
<td>-0.17</td>
<td>1.21 - 1.22</td>
<td>1.21</td>
<td>1.21 ± 0.04</td>
</tr>
<tr>
<td>Anthracene</td>
<td>-0.52</td>
<td>1.26 - 1.62</td>
<td>1.36</td>
<td>1.35 ± 0.05</td>
</tr>
<tr>
<td>Perylene</td>
<td>-0.48</td>
<td>1.00 - 1.39</td>
<td>1.11</td>
<td>1.32 ± 0.06</td>
</tr>
<tr>
<td>Tetracene</td>
<td>-0.30</td>
<td>0.61 - 0.64</td>
<td>0.62</td>
<td>0.78 ± 0.03</td>
</tr>
<tr>
<td>Pentacene</td>
<td>-0.24</td>
<td>0.05 - 0.07</td>
<td>0.06</td>
<td>0.23 ± 0.02</td>
</tr>
</tbody>
</table>

* Range values calculated by allowing an uncertainty of ± 0.1 eV in $\Delta G_{el}^9$
FIG 5.16 LOG(KQ) VS DONOR ENERGY FOR TRANS-CO(Ø-PDO)₃

PREDICTED ELECTRON TRANSFER CONTRIBUTION

BEST FIT PARAMETERS GIVEN IN TABLE 5.23
<table>
<thead>
<tr>
<th>DONOR</th>
<th>$\Delta G^\theta_{el}$ (eV)</th>
<th>Range*</th>
<th>Calcd. $k_q$ (10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})</th>
<th>Expt. (k_q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>-0.39</td>
<td>1.89 - 2.00</td>
<td>1.92</td>
<td>6.36 ± 0.29</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-0.99</td>
<td>4.78 - 7.73</td>
<td>6.26</td>
<td>6.73 ± 0.32</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-0.91</td>
<td>3.78 - 6.61</td>
<td>5.11</td>
<td>7.23 ± 0.25</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>-0.67</td>
<td>2.16 - 3.39</td>
<td>2.59</td>
<td>3.34 ± 0.09</td>
</tr>
<tr>
<td>Chrysene</td>
<td>-0.94</td>
<td>4.13 - 7.04</td>
<td>5.53</td>
<td>4.85 ± 0.19</td>
</tr>
<tr>
<td>Coronene</td>
<td>-0.98</td>
<td>4.74 - 7.70</td>
<td>6.22</td>
<td>2.93 ± 0.09</td>
</tr>
<tr>
<td>Pyrene</td>
<td>-0.73</td>
<td>2.38 - 4.05</td>
<td>3.01</td>
<td>2.21 ± 0.06</td>
</tr>
<tr>
<td>Acridine</td>
<td>-0.19</td>
<td>1.87 - 1.89</td>
<td>1.88</td>
<td>1.85 ± 0.05</td>
</tr>
<tr>
<td>Anthracene</td>
<td>-0.54</td>
<td>1.94 - 2.42</td>
<td>2.08</td>
<td>2.30 ± 0.06</td>
</tr>
<tr>
<td>Perylene</td>
<td>-0.50</td>
<td>1.55 - 2.08</td>
<td>1.71</td>
<td>2.28 ± 0.16</td>
</tr>
<tr>
<td>Tetracene</td>
<td>-0.32</td>
<td>0.97 - 1.02</td>
<td>0.98</td>
<td>1.12 ± 0.06</td>
</tr>
<tr>
<td>Pentacene</td>
<td>-0.26</td>
<td>0.09 - 0.11</td>
<td>0.10</td>
<td>0.37 ± 0.03</td>
</tr>
</tbody>
</table>

* Range values calculated by allowing an uncertainty of ± 0.1 eV in $\Delta G^\theta_{el}$
For both states plateau quenching will be achieved before 15,800 cm\(^{-1}\) (\(E_T\) acridine), and equal \(\kappa\) values will be attributed to both states. The author acknowledges the possibility of unequal \(\kappa\) values, however the lack of quenching constants over the region 8,000-12,000 cm\(^{-1}\) does not define the use of any other values. The best fit to the experimental data was achieved by varying the values of \(\Delta G_{el}^+(o)\) and \(K_{el}\).

Tables 5.20 and 5.21 list calculated and experimental rate constants for \(\text{trans- Co(bzac)}_3\) and \(\text{trans- Co(\beta-PDO)}_3\), respectively; the best fit parameters being given in Table 5.23. For both quenchers the predicted quenching constants for benzophenone and coronene do not correlate with experimental values. In the case of benzophenone lower values were predicted, however energy transfer to charge transfer states, as advocated for some Cr(III) \(\beta\)-diktonates, become likely and may explain the low value. For coronene, higher values have been predicted which is analogous to the situation for quenching by Cr(tfbzac)\(_3\) (see Section 5.6). It was suggested that the oxidation potential of coronene might be 0.2 eV too low which would also account for these results. However, in the next section dealing with quenching by \(\text{trans- Co(tfac)}_3\) reasonable agreement between \(k_q\) (pred) and \(k_q\) (expt) for coronene will be found. It should be noted that a reduction in \(\Delta G\) of 0.2 eV for coronene/\(\text{trans- Co(tfac)}_3\) would underpredict the experiment rate constant for quenching by ~ 40%.

It should be noted that the common denominator in the three complexes whose experimental rate constants are low, is the presence of phenyl groups. It is suggested that an additional barrier to electron transfer exists between coronene, which is a bulky molecule consisting of seven fused benzene rings, and phenyl substituted complexes. Further work is clearly required to investigate this suggestion.
Overall there is reasonable agreement between predicted and experimental quenching constants for both trans-Co(bzac)$_3$ and trans-Co(0-PD0)$_3$ using the generalised kinetic approach, which was not evident for quenching by Co(acac)$_3$. It is interesting to note that for energy transfer $3\kappa_{en}^{\text{Cr}(0-PD0)} > 3\kappa_{en}^{\text{Cr}(bzac)}$ which is in agreement with the values predicted for the analogous Cr(III) complexes (see Section 5.8).

5.13 Quenching by trans-Co(tfac)$_3$

The experimental quenching constants for trans-Co(tfac)$_3$ ($R_1=CF_3$, $R_2=CH_3$) are tabulated in 4.13 and Fig.5.17 gives a plot of $\log k_q$ vs $E_T$. Once again Huang and Gafney (18) have studied the same three donors quenched by trans-Co(tfac)$_3$ and in each case their results are within quoted experimental errors of the values presented in this thesis.

The $E_f$ of Co(tfac)$_3$ has been further reduced by 0.39V with respect to Co(acac)$_3$, to $+0.05V$ vs SCE by the introduction of a trifluoromethyl group. The free energy changes for electron transfer are given in Table 5.22, together with the calculated best fit quenching constants and the best fit parameters are given in Table 5.23. The predicted quenching rate constant for benzophenone is low, however the inclusion of energy transfer to charge transfer states as previously advocated would account for this low value. Once again there is reasonable agreement between predicted and experimental quenching rate constants.
FIG 5.17  LOG(KQ) VS DONOR ENERGY FOR TRANS-CO(TFAC)3

PREDICTED ELECTRON TRANSFER CONTRIBUTION

BEST FIT PARAMETERS GIVEN IN TABLE 5.23
<table>
<thead>
<tr>
<th>DONOR</th>
<th>$\Delta G_{el}^{\theta}$ (eV)</th>
<th>Range*</th>
<th>Calcd. $k_q$ $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>Expt. $k_q$ $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>-0.63</td>
<td>0.57 - 0.88</td>
<td>0.67</td>
<td>4.73 ± 0.32</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-1.23</td>
<td>3.71 - 5.81</td>
<td>4.77</td>
<td>4.86 ± 0.40</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-1.15</td>
<td>2.92 - 5.02</td>
<td>3.95</td>
<td>5.06 ± 0.12</td>
</tr>
<tr>
<td>2-Acetonaphthone</td>
<td>-0.91</td>
<td>1.19 - 2.57</td>
<td>1.76</td>
<td>1.19 ± 0.06</td>
</tr>
<tr>
<td>Chrysene</td>
<td>-1.18</td>
<td>3.21 - 5.32</td>
<td>4.26</td>
<td>4.10 ± 0.27</td>
</tr>
<tr>
<td>Coronene</td>
<td>-1.22</td>
<td>3.68 - 5.79</td>
<td>4.74</td>
<td>3.89 ± 0.12</td>
</tr>
<tr>
<td>1,2,5,6-DBA</td>
<td>-1.13</td>
<td>2.71 - 4.79</td>
<td>3.71</td>
<td>3.37 ± 0.17</td>
</tr>
<tr>
<td>1,2,3,4-DBA</td>
<td>-1.01</td>
<td>1.71 - 3.49</td>
<td>2.51</td>
<td>2.16 ± 0.13</td>
</tr>
<tr>
<td>Pyrene</td>
<td>-0.97</td>
<td>1.50 - 3.14</td>
<td>2.21</td>
<td>3.01 ± 0.07</td>
</tr>
<tr>
<td>Acridine</td>
<td>-0.43</td>
<td>0.51 - 0.56</td>
<td>0.51</td>
<td>0.51 ± 0.05</td>
</tr>
<tr>
<td>Anthracene</td>
<td>-0.79</td>
<td>0.75 - 1.55</td>
<td>1.05</td>
<td>1.05 ± 0.06</td>
</tr>
<tr>
<td>Perylene</td>
<td>-0.74</td>
<td>0.65 - 1.49</td>
<td>0.97</td>
<td>1.03 ± 0.07</td>
</tr>
<tr>
<td>Tetracene</td>
<td>-0.56</td>
<td>0.27 - 0.45</td>
<td>0.33</td>
<td>0.58 ± 0.05</td>
</tr>
<tr>
<td>Pentacene</td>
<td>-0.50</td>
<td>0.01 - 0.11</td>
<td>0.02</td>
<td>0.17 ± 0.02</td>
</tr>
</tbody>
</table>

* Range values calculated by allowing an uncertainty of ± 0.1 eV in $\Delta G_{el}^{\theta}$
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Co(acac)$_3$</th>
<th>Co(bzac)$_3$</th>
<th>Co(φ-PDO)$_3$</th>
<th>Co(tfac)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3T_{1g}$ $\tilde{\nu}$/cm$^{-1}$</td>
<td>9000</td>
<td>9000</td>
<td>9000</td>
<td>9000</td>
</tr>
<tr>
<td>$3T_{2g}$ $\tilde{\nu}$/cm$^{-1}$</td>
<td>12500</td>
<td>12500</td>
<td>12500</td>
<td>12500</td>
</tr>
<tr>
<td>$3\Delta G^\dagger_{en}$ (o)/cm$^{-1}$</td>
<td>750</td>
<td>750</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td>$3k^o_{en}/10^8$ s$^{-1}$</td>
<td>1.70</td>
<td>3.80</td>
<td>6.20</td>
<td>1.50</td>
</tr>
<tr>
<td>$3\kappa_{en}/10^{-5}$</td>
<td>2.79</td>
<td>6.23</td>
<td>10.16</td>
<td>2.46</td>
</tr>
<tr>
<td>$E_i/\nu$ vs. SCE</td>
<td>-0.34</td>
<td>-0.21</td>
<td>-0.19</td>
<td>+0.05</td>
</tr>
<tr>
<td>$3\Delta G^\dagger_{el}$ (o)/cm$^{-1}$</td>
<td>3000</td>
<td>3000</td>
<td>3000</td>
<td>3000</td>
</tr>
<tr>
<td>$k^o_{el}/10^{10}$ s$^{-1}$</td>
<td>6.00</td>
<td>9.50</td>
<td>12.00</td>
<td>3.00</td>
</tr>
<tr>
<td>$\kappa_{el}/10^{-3}$</td>
<td>9.84</td>
<td>15.57</td>
<td>19.68</td>
<td>4.92</td>
</tr>
<tr>
<td>$k_d/10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$</td>
<td>1.41</td>
<td>1.41</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td>$k_{-d}/10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>$k_{br}/10^{10}$ s$^{-1}$</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>
To summarise:

Returning to the question of the quenching rate constants obtained for Co(acac)$_3$, it needs to be recognised that it is the only Co(III) $\beta$-diketonate quencher where the general theory does not seem to adequately explain the results. Of the four Co(III) complexes investigated Co(acac)$_3$ has the lowest reduction potential and therefore the other quenchers are likely to have larger electron transfer contributions, indicating that the energy transfer pathways do not obey the classical model. This may also be true for the other quenchers but the effect is masked by the electron transfer contributions. There does not seem to be any obvious reasons why Co(acac)$_3$ should behave in this manner however, there is a large gap of $\approx 15000 \text{cm}^{-1}$ between the $3T_2g$ state and the next state which can accept energy by a spin allowed process, which is the spin allowed charge transfer state. Maybe the plateau tips slightly for highly exoergonic energy transfer in the direction expected by Marcus. With a lack of confirmation of such an effect with any other complex it is suggested that this is a possible explanation. Note that for Cr(III) $\beta$-diketonate complexes the largest energy gap between excited states is $\approx 5000 \text{cm}^{-1}$.

Overall there has been a surprisingly good fit between the experimentally measured quenching rate constants and those calculated from models based upon classical theory. It has been assumed that the donors represent a homogeneous series which for energy transfer to a given acceptor state requires $s,k_d,k_{-d},k_{en}$ and $\Delta G^*_{en}(o)$ to be treated as constants. For competitive energy and electron-transfer the situation requires similar assumptions to be made concerning $s,k^O_{el},k_{pt}$ and $\Delta G^*_{el}(o)$. If one or more of these criteria are not fulfilled for a particular donor/acceptor pair then deviations from the model are likely to occur.
CONCLUSIONS

1. The diffusion rate constant predicted by the Debye equation 
$(1 \times 10^{-10} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ was not able to adequately describe all of the 
data presented in this thesis. For the $\gamma$-substituted complexes, energy 
transfer to the doublet states $(^2E_g, ^2T_{1g})$ proceed with rate constants 
in the range $2.15-1.70 \times 10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$, which would predict the 
diffusion rate constant to be $1.29-1.04 \times 10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ($k_q = sk_d = s^{-1/6}$), 
assuming a fully diffusion controlled mechanism. The approach of 
Spernol and Wirtz was adopted which introduces a microfriction factor, 
f_t, into the Debye equation to correct for the movement of solute mole­
cules into holes in the solvent. Using this method, $k_d$ was calculated 
to be $1.41 \times 10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ allowing all of the results presented to 
be interpreted within the framework of the classical treatment.

2. The introduction of alkyl substituents (methyl, ethyl and $n$-propyl) 
into the $\gamma$- or $R_2$ position of Cr(acac)$_3$ unexpectedly resulted in an 
increase in quenching efficiency with respect to Cr(acac)$_3$, where 
$R_2=H$. The experimental rate constants following the sequence 
$\text{CH}_3 > \text{C}_2\text{H}_5 > \text{n-C}_3\text{H}_7 > \text{H}$ and the increased efficiency has been interpreted to 
be the result of the electron donating properties (inductive effect) 
of the $\gamma$-substituents, which relates to the Hammett $\sigma_p$ constants. 
This may be considered to expand the metal orbitals, with a subsequent 
increase in overlap with the orbitals of the donor and hence $k_q$ is 
increased. As the length of the alkyl chain is increased, the en­
hancement of $k_q$ as a result of the electron donating nature of the 
substituent is reduced by an increase in steric hindrance.
3. Quenching rate constants for cis- and trans- \textit{Cr}(^t\text{BuPDO})_3 (R_1 = ^t\text{Bu}, R_3 = \text{H}) were measured in order to evaluate the effect of geometrical isomers. It was found that the cis-isomer was a more efficient quencher especially when energy was being transferred to the \textit{4}^T_{2g} state \((^2T_{2g} e_i^1)\). From molecular models, overlap with the orbitals is more sterically blocked in the case of trans-isomer than it is for the cis, resulting in lower \(k_q\) values.

Comparing the quenching rate constants of \textit{Cr}(^t\text{BuPDO})_3 with those of another formyl ketone complex, \textit{Cr}(BDO)_3 \((R_1 = \text{CH}_3 R_3 = \text{H})\) revealed some interesting differences. From a steric viewpoint \textit{Cr}(BDO)_3 would be expected to be a more efficient quencher than \textit{Cr}(^t\text{BuPDO})_3 and this was found to be the case when energy was being transferred to the doublet state \((^2E_g, ^2T_{1g})\). However for energy transfer to the \textit{4}^T_{2g} state both cis- and trans- \textit{Cr}(^t\text{BuPDO})_3 were found to be more efficient quenchers than \textit{Cr}(BDO)_3 (the isomers of which were not separated, however statistically the trans-form will dominate). As was the case for the \(\gamma\)-substituted complexes, these results may also be explained in terms of a balance between electron releasing and steric blocking effects, with Hammett \(\sigma_p^t\text{Bu} > \text{CH}_3\). Thus for \textit{Cr}(^t\text{BuPDO})_3, the larger contribution from the electron releasing nature of \(^t\text{Bu}\) more than compensates for its greater size.

4. For energy transfer quenching of \textit{Cr}(III)\(\beta\)-diketonate complexes, a simple addition of substituent \(\kappa\) contributions to give \(\kappa\) for the complex has been proposed. For \textit{Cr}(dbm)_3, where \(R_1 = R_3 = \emptyset, R_2 = \text{H}\), the \(\kappa\) values predicted on the basis of this approach were in good agreement with experimental values, once associated errors were taken into account. For \textit{Cr}(^t\text{BuPDO})_3, where \(R_1 = ^t\text{Bu}, R_2 = R_3 = \text{H}\), the value of \(4\kappa(^t\text{Bu})\) was below that found experimentally.
however $\kappa(tBu)$ was calculated from quenching data of Cr(dpm)$_3$ where energy transfer to the $^2T_{2g}$ state competes strongly with that to $^4T_{2g}$.

In the previous section, the electron-releasing nature of the $tBu$ group was advocated to explain the experimental results, and thus for complexes where $R_1R_3$, a contribution from the inductive effect may need to be included into the expression for predicting transmission coefficients.

5. Expressions have been developed to interpret quenching by energy transfer and competitive energy and electron transfer based upon classical theory. For the Cr(III)$\beta$-dikonates studied in this thesis calculation based upon these expressions have predicted rate constants in reasonable agreement with those measured experimentally. This approach has also been successfully extended to Fe(III) $\beta$-dikonate by other workers(7,29). Quenching rate constants for four Co(III)$\beta$-dikonates have been measured with three of them being adequately fitted by competitive energy and electron transfer. The fourth Co(acac)$_3$ shows deviations from the model which should be seen as a cautionary note to the universal application of this type of treatment.
CHAPTER V

REFERENCES


28. F. Wilkinson and C. Tsiamis, Private Communication


APPENDIX I
LISTINGS OF THE COMPUTER PROGRAMS
USED IN THIS THESIS
10 NN=120
20 P=.1
30 REM ONE STATE PLOT
40 DIM D(500),K0(500),X(500),Y(500)
50 OPEN 3,4,1
60 PRINT#3,"H"
70 T=10000;IN=100;A1=12000;01=250;01=4.00E10;KD=1.4E10;KS=0.8E10;S=1/6
80 FOR I=0 TO NN STEP P
90 D(I)=T+IN*I
100 G1=A1-D(I)
110 IF -G1/D1>50 GOTO 130
120 F1=G1+(G1/0.69315)*LOG(-0.69315*G1/D1))
125 GOTO 140
130 F1=G1
140 K1=01*EXP(-F1/203.6)
150 B1=01*EXP(G1-F1/203.6)
160 K0(I)=S*KD/(1+(KS/K1)*(1+B1/KS))
165 X(I)=D(I)/1000
166 Y(I)=LOG(K0(I))/2.303
167 IF Y(I)>6.5 GOTO 170
168 IF X(I)>15.99 GOTO 230
169 GOTO 500
170 NEXT I
180 PRINT#5,"PA0,0;SP0;"
230 END
500 CLOSE5
510 OPEN5,5
520 PRINT#5,"IN;SP2;LT0;VS0;"
530 PRINT#5,"IP1200,300,10000,6250;"
540 PRINT#5,"SC10,16,6.5,10;"
550 PRINT#5,"PA";X(I);Y(I);"PO"
560 PRINT X(I),Y(I),K0(I)
570 GOTO 170
READY.

where

- $A_1$ = Acceptor Energy level $E^{00}(^A_A)$
- $D_1$ = Intrinsic Reorganisation Barrier $\Delta G^\ddagger (o)$
- $O_1$ = Preexponential factor $k_{en}$
- $K_D$ = Rate constant for diffusion $k_d$
- $K_S$ = Rate constant for dissociation $k_d$
- $S$ = Spin statistical factor
- $F_1$ = Free Activation energy $\Delta G^\dagger$
- $G_1$ = Free Energy change $\Delta G$
- $K_1$ = Rate Constant for forward energy transfer $k_{en}$
- $B_1$ = Rate Constant for back energy transfer $k_{en}$
5 REM PLOTAXIS
10 OPEN 5,5
20 PRINT#5,"IN:SP1;VS5;"
30 PRINT#5,"IP1200,500,10000,6500;"
40 PRINT#5,"SC6,26,7.5,10;"
50 PRINT#5,"PU5,7.5 PD 26,7,5,26,10,6,10,6,7.5,PU"
60 PRINT#5,"SI.2,.3;TL0.2.5"
70 FOR X=6 TO 26 STEP 2
80 PRINT#5,"PA",X,".7,5;XT;"
90 IF X<10 THEN PRINT#5,"CP-1.33,-1.5;LB",X; CHR$(3)
100 IF X>9 THEN PRINT#5,"CP-1.80,-1.5;LB",X; CHR$(3)
110 NEXT X
120 PRINT#5,"PA16.0,7.5;CP-8,-3.5;LBENERGY(1000 CM-1)"CHR$(3)
130 FOR Y=7.5 TO 10.0 STEP 0.5
140 PRINT#5,"PA 6.,",Y,"YT;"
150 PRINT#5,"CP-5,-.25;LB",Y;CHR$(3)
160 NEXT Y
170 PRINT#5,"PA3.8,8.75 CP-1,-.25 LBOUND(KO)"CHR$(3)
180 PRINT#5,"PA12,10.2 CP-1,-.25 LBOUND(KO) VS DONOR ENERGY"CHR$(3)
190 PRINT#5,"PA0,0;SP0;"
200 END
READY.
10 NN=100
20 P=2
30 REM TWO STATE PLOT
40 DIM D(300), KQ(300), X(300), Y(300)
50 OPEN 3, 4, 1
60 T=9000: IN=100: R1=1200: Q1=250: Q2=2.00E10: KD=1.4E10: KS=0.8E10: S=1/
70 A2=12500: D2=250: D2=2.00E10
80 FOR I=0 TO NN STEP P
90 D(I)=T+IN*IN
100 G1=A1-D(I)
110 G2=A2-D(I)
120 IF -G1/D1>50 GOTO 150
130 F1=G1+(D1/0.69315)*LOG(1+EXP(-0.69315*G1/D1))
140 GOTO 160
150 F1=0
160 IF -G1/D1>50 GOTO 150
170 F2=G2+(D2/0.69315)*LOG(1+EXP(-0.69315*G2/D2))
180 GOTO 200
190 F2=0
200 K1=G1*EXP(-F1/203.6)
210 B1=01*EXP(-Q1-F1)/203.6
220 K2=02*EXP(-F2/203.6)
230 B2=02*EXP(-Q2-F2)/203.6
240 KQ(I)=S*KD/(1+1/(K1/B1+KS)+K2/(B2+KS))
244 X(I)=D(I)/1000
245 Y(I)=LOG(KQ(I))/2.303
246 IF Y(I)<6.5 GOTO 250
248 GOTO 500
250 NEXT I
255 PRINT#5; "PA0,0; SP0;".
260 END
500 CLOSE 5
510 OPEN 5, 5
520 PRINT#5; "IN; SP2; LT0; VS0";
530 PRINT#5; "IP1200,300,10000,6250;";
540 PRINT#5; "SC10,26,6.5,10;";
550 PRINT#5; "PA0; X(I); Y(I); "P0";
560 PRINT X(I), Y(I), KQ(I)
570 GOTO 250
READY.
10 NN=170
20 P=2
30 REMTHEESTATEPLOT
40 DIM D(300),KQ(300)
50 OPEN 3,4,1
60 T=9000:IN=100:A1=12000:D1=250:Q1=1.33E10:KD=1.4E10:KS=0.8E10:S=1/6
70 A2=12500:D2=250:Q2=1.33E10:A3=13000:D3=250:Q3=1.33E10
80 FOR I=0 TO NN STEP P
90 D(I)=T+IN*I
100 G1=A1-D(I)
110 G2=A2-D(I)
120 G3=A3-D(I)
130 IF -G1/D1>50 GOTO 150
140 FI=G1+(01/0.69315)*LOG(1+EXP(-0.69315*G1/01))
150 GOTO 160
160 IF -G2/D2>50 GOTO 190
170 F2=G2+(02/0.69315)*LOG(1+EXP(-0.69315*G2/02))
180 GOTO 192
190 F2=0
192 IF -G3/D3>50 GOTO 195
193 F3=G3+(03/0.69315)*LOG(1+EXP(-0.69315*G3/03))
194 GOTO 200
195 F3=0
200 K1=01*EXP(-F1/203.6)
210 B1=01*EXP((G1-F1)/203.6)
220 K2=02*EXP(-F2/203.6)
230 B2=02*EXP((G2-F2)/203.6)
233 K3=03*EXP(-F3/203.6)
235 B3=03*EXP((G3-F3)/203.6)
240 K0(I)=S*KD/(1+1/(K1/(B1+KS)+K2/(B2+KS)+K3/(B3+KS))
244 X(I)=D(I)/1000
245 Y(I)=LOG(K0(I))/2.303
246 IF Y(I)<6.5 GOTO 250
248 GOTO 500
250 NEXT I
255 PRINT#5,"PA0,0;SP0;"
260 END
500 CLOSE 5
510 OPEN 5,5
520 PRINT#5,"IN;SF2;LT0;VS0"
530 PRINT#5,"IF1200,300,10000,6250;"
540 PRINT#5,"SC10,26,6.5,10;"
550 PRINT#5,"PA";X(I);Y(I);"PD"
560 PRINT X(I),Y(I),KQ(I)
570 GOTO 250
READY.
10 NN=160
20 P=2
30 REMTWOSTATEDIFFMP
40 DIM D(500),LQ(500),HQ(500),KQ(500),Y(500),X(500)
50 OPEN 3,4,1
60 T=9000;IN=100;A1=12390;D1=400;G1=8.55E10;KD=1.4E10;K3=0.8E10;S1=1/t
70 A2=15390;D2=2400;G2=6.00E10;S2=1/3
80 FOR I=0 TO NN STEP P
90 D(I)=T+IN*I
100 G1=A1-D(I)
110 Q2=A2-D(I)
120 IF -G1/D1>50 GOTO 150
130 F1=G1+(01/0.69315)*LOG(1+EXP(-0.69315*G1/D1))
140 GOTO 160
150 F1=0
160 FOR I=0 TO NN STEP P
170 G2=A2-D(I)
180 IF -G2/D2>50 GOTO 190
190 F2=G2+(02/0.69315)*LOG(1+EXP(-0.69315*G2/D2))
200 GOTO 200
210 F2=0
220 K1=G1*EXP(-F1/203.6)
230 K2=G2*EXP(-F2/203.6)
240 LQ(I)=S1*KD/(1+K5/K1)*(1+B1/K5)
250 HQ(I)=S2*KD/(1+K5/K2)*(1+B2/K5)
260 KQ(I)=LQ(I)+HQ(I)
270 Y(I)=LOG(KQ(I))/2.303
280 X(I)=D(I)/1000
290 IF Y(I)<6.5 GOTO 250
300 GOTO 500
310 NEXT I
320 PRINT#5,"PRA0,0;SP0;"
330 END
340 CLOSE5
350 OPEN5,5
360 PRINT#5,"IN;SP2;LT0;VS0"
370 PRINT#5,"IP1200,300,10000,6250;"
380 PRINT#5,"SC10,25,6.5,10;"
390 IF Y(I)<6.5 GOTO 250
400 PRINT X(I),Y(I),KQ(I)
410 GOTO 250
420 READY.
10 NN=200
20 P=1.0
30 REM AGNON LEVINE
40 DIM G(300),F1(300),X(300),Y(300)
50 OPEN 3,4,1
60 T=100;IN=1;D1=10
80 FOR I=0 TO NN STEP P
90 G(I)=T+IN*I
100 G1=G(I)
130 F1(I)=G1+(D1/0.69315)*LOG(1+EXP(-0.69315*G1/D1))
244 X(I)=G(I)
245 Y(I)=F1(I)
248 GOTO 500
250 NEXT I
255 PRINT#5,"PA0,0;SP0;"
260 END
500 CLOSE 5
510 OPEN 5,5
520 PRINT#5,"IN;SP2;LT0;VS0"
530 PRINT#5,"IP1200,1000,1000,6250;"
540 PRINT#5,"SC-100,100,0,0.120;"
550 PRINT#5,"PA";X(I);Y(I);"PD"
560 PRINT X(I),Y(I),F1(I)
570 GOTO 250
READY.

10 NN=200
20 P=1.0
30 REM WEVER WELLE
40 DIM G(300),F1(300),X(300),Y(300)
50 OPEN 3,4,1
60 T=100;IN=1;D1=10
80 FOR I=0 TO NN STEP P
90 G(I)=T+IN*I
100 G1=G(I)
130 F1(I)=G1/2+(G1/2)*T2+(D1)*T2*T0.5
244 X(I)=G(I)
245 Y(I)=F1(I)
248 GOTO 500
250 NEXT I
255 PRINT#5,"PA0,0;SP0;"
260 END
500 CLOSE 5
510 OPEN 5,5
520 PRINT#5,"IN;SP2;LT0;VS0"
530 PRINT#5,"IP1200,1000,1000,6250;"
540 PRINT#5,"SC-100,100,0,0.130;"
550 PRINT#5,"PA";X(I);Y(I);"PD"
560 PRINT X(I),Y(I),F1(I)
570 GOTO 250
READY.
10 NN=200
20 P=1.0
30 REMMARCUS
40 DIM G(300),F1(300),X(300),Y(300)
50 OPEN 3,4,1
60 T=-100:IN=1:D1=10
80 FOR I=0 TO NN STEP P
90 G(I)=T+IN*I
100 G1=G(I)
110 F1(I)=D1*(1+(G1/(4*D1)))^2
244 X(I)=G(I)
245 Y(I)=F1(I)
248 GOTO 500
250 NEXT I
255 PRINT#5,"PA0,0;SP0;"
260 END
500 CLOSE 5
510 OPEN 5,5
520 PRINT#5,"IN;SP2;LT0;VS0"
530 PRINT#5,"IP1200,1000,10000,6250;"
540 PRINT#5,"SC-100,100,0,0,130;"
550 PRINT#5,"PA";X(I);Y(I);"PO"
560 PRINT X(I),Y(I),F1(I)
570 GOTO 250

READY.
10 N=160
20 P=2
30 RENTWOODHEQP4
40 DIM D(500),L0(500),H0(500),K0(500),Y(500),X(500)
50 OPEN 3,4,1
60 T=9000:IN=100:A1=12690:D1=250:G1=0.94E10:K0=1.4E10:Ks=0.3E10:S=1/3:
70 A2=15590:D2=2300:G2=5.00E10:S2=1/3:A3=13870:D3=250:G3=0.50E10
80 FOR I=0 TO N STEP P
90 D(I)=T+IN*I
100 G1=A1-D(I)
110 G2=A2-D(I)
115 G3=A3-D(I)
120 IF -G1/D1>50 GOTO 150
130 F1=G1+<D1/0.69315)*LOG(1+EXP(-0.69315*G1/01))
140 GOTO 160
150 F1=0
160 IF -G2/D2>50 GOTO 190
170 F2=G2+<D2/0.69315)*LOG(1+EXP(-0.69315*G2/02))
180 GOTO 191
190 F2=0
191 IF -G3/D3>50 GOTO 195
192 F3=G3+<D3/0.69315)*LOG(1+EXP(-0.69315*G3/03))
193 GOTO 200
194 F3=0
200 K1=01*EXP(-F1/203.6)
210 B1=01*EXP(<G1-F1)/203.6)
220 K2=02*EXP(-F2/203.6)
230 B2=02*EXP(<G2-F2)/203.6)
232 K3=03*EXP(-F3/203.6)
234 B3=03*EXP(<G3-F3)/203.6)
240 L0(I)=S1*KD/<1+1/<(K1*(B1+KS))+<K3/(B3+KS)))
241 H0(I)=S2*KD/<1+(K5/K2)*(1+B2/KS))
242 K0(I)=L0(I)+H0(I)
243 Y(I)=LOG(K0(I))/2.303
244 X(I)=DO(I)/1000
245 IF Y(I)<6.5 GOTO 250
246 GOTO 500
250 NEXT I
260 PRINT#5,"PA0,0;SP0;"
300 END
500 CLOSE5
510 OPEN5,5
520 PRINT#5,"IN;SP2;LT0;VS0"
530 PRINT#5,"IP1200,300,10000,6250;"
540 PRINT#5,"SC10,26,6.5,10;"
550 PRINT#5,"PA";X(I);Y(I);"PD"
555 PRINT X(I),Y(I),K0(I)
560 GOTO 250

READY.
1 REM CR(TFEZAC)
10 N#="TRIPHENYLENE"
15 J=0
17 GOTO30
20 OPEN3,4,1
25 PRINT#3,"COMPOUND","IP/EV";SPC(5);"RP/EV";SPC(5);"OD/EV";"ET/CM-1";"K0/10^9"
26 PRINT#3,
30 GOTO1000
60 G2=K2-TE
75 REM PRINT#3,N#;SPC(6);IP;SPC(5);RP;SPC(5);OD/8067;SPC(8);TE;SPC(8);EV
76 REM PRINT#3,
80 F2=G2+(D2/0.69315)*LOG(1+EXP(-0.69315*G2/D2))
110 K2=02*EXP(-F2/203.6)
120 B2=02*EXP((G2-F2)/203.6)
130 G3=03-TE
135 F3=G3+(D3/0.69315)*LOG(1+EXP(-0.69315*G3/D3))
140 K3=03*EXP(-F3/203.6)
145 B3=03*EXP((G3-F3)/203.6)
150 O2=KD/(1*(K2/(B2+KS))+(K3/(B3+KS)))
160 G6=06-RA-TE
165 F6=G6+(D6/0.69315)*LOG(1+EXP(-0.69315*G6/D6))
210 K6=06*EXP(-F6/203.6)
220 B6=06*EXP((G6-F6)/203.6)
250 G6=KD/(2*(1+(KS*IS+B6*KS)/(K6*IS)))
260 G4=04-TE
265 F4=G4+(D4/0.69315)*LOG(1+EXP(-0.69315*G4/D4))
310 K4=04*EXP(-F4/203.6)
320 B4=04*EXP((G4-F4)/203.6)
350 O4=KD/(3*(1+(K6*KI/(KS*(K1+B6))))+(K4/(K6+B4)))
360 K0=02+O4+O6
420 PRINTK0,EV
430 GOTO482
440 OPEN3,4
445 PRINT#3,N#
450 PRINT#3,02;04;06;K0;EV;CHR$(13)
455 PRINT#3,02;04;KI;IS;RA;TE;OD/8067;G6;D6;06;CHR$(13)
480 CLOSE3
482 J=J+1
490 ONJGOTO3000,3500,4000,5000,6000,7000,8000,9000,10000,11000,12000
495 CLOSE3
```
1001 TE=2330:02=8.0E7:0D=1.55*Z:RA=5566:D6=500:Z=8067:EV=8.2E9:IP=7.8:RP=2.5
1002 KS=1.0E10:IS=1.0E10:06=0.40E10:A3=19700:D3=250:03=2.00E10
1003 GOT060
2000 A2=12560:D2=250:02=0E01:A4=16000:D4=2000:04=4E01:KS=1.2E10:KD=1.0E10
2001 TE=20000:00=38590:RA=-3146:D6=1000:Z=8067
2002 KS=1.0E11:IS=1.0E10:06=8.0E10
2003 GOT0620
3000 N#="BENZOPHENONE":TE=24300:0D=2.43*Z:EV=6.2E9:RP=1.73:IP=1.35
3001 GOT060
3500 N#="PHENANTHRENE":TE=21600:0D=1.50*Z:EV=6.1E9:RP=2.47:IP=7.86
3501 GOT0 60
4000 N#="NAPHTHALENE":TE=21300:0D=1.54*Z:EV=6.1E9:RP=2.58:IP=8.12
4001 GOT060
5000 N#="ACETONATHONE":TE=20600:0D=1.69*Z:EV=3.75E9:RP=1.96:IP=8.31
5001 GOT060
6000 N#="CHRYSENE":TE=20000:0D=1.35*Z:EV=5.85E9:RP=2.30:IP=1.22
6001 GOT060
7000 N#="CORONENE":TE=19400:0D=1.23*Z:EV=4.0E9:RP=2.10:IP=0.93
7001 GOT060
8001 GOT060
9000 N#="ACRIDINE":TE=15800:0D=1.58*Z:EV=1.18E9:RP=1.62
9001 GOT060
10000 N#="ANTHRACENE":TE=14700:0D=1.09*Z:EV=1.99E9:RP=2.07:IP=7.23
10001 GOT060
11000 N#="PERYLENE":TE=12400:0D=0.85*Z:EV=0.38E9:IP=7.15:RP=1.73
11001 GOT060
12000 N#="TETRACENE":TE=10300:0D=0.77*Z:EV=6.7E8:IP=6.88:RP=1.64
12001 GOT060
13000 N#="PENTACENE":TE=8000:0D=0.54*Z:EV=6.0E8:RP=1.29:IP=6.61
13001 GOT060
14000 N#="CAROTENE":TE=6300:0D=0.39*Z:EV=5.7E8:RP=1.92:IP=6.40
14001 GOT060
15000 END
15001 GOT060
READY.
```
APPENDIX II

Registry Numbers of the Donors and Acceptors
<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS Number</th>
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<tbody>
<tr>
<td>2-Acetonaphthone</td>
<td>93-08-3</td>
</tr>
<tr>
<td>Acridine</td>
<td>260-94-6</td>
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<tr>
<td>Anthracene</td>
<td>120-12-7</td>
</tr>
<tr>
<td>1,2-Benzanthracene</td>
<td>56-55-3</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>119-61-9</td>
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<tr>
<td>β-Carotene</td>
<td>7235-40-7</td>
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<tr>
<td>Chrysene</td>
<td>218-01-9</td>
</tr>
<tr>
<td>Coronene</td>
<td>191-07-1</td>
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<tr>
<td>1,2,3,4-Dibenzanthracene</td>
<td>215-58-7</td>
</tr>
<tr>
<td>1,2,5,6-Dibenzanthracene</td>
<td>53-70-3</td>
</tr>
<tr>
<td>9,10-Dibromoanthracene</td>
<td>523-27-3</td>
</tr>
<tr>
<td>1,5-Dichloroanthracene</td>
<td>6406-96-8</td>
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<tr>
<td>Naphthalene</td>
<td>91-20-3</td>
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<tr>
<td>Pentacene</td>
<td>135-48-8</td>
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<tr>
<td>Perylene</td>
<td>198-55-0</td>
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<tr>
<td>Phenanthrene</td>
<td>85-01-8</td>
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<tr>
<td>Pyrene</td>
<td>129-00-0</td>
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<tr>
<td>Tetracene</td>
<td>92-24-0</td>
</tr>
<tr>
<td>Triphenylene</td>
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<td>Acceptors</td>
<td>Formula</td>
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<tr>
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<td>---------------</td>
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<tr>
<td>Cr(acac)$_3$</td>
<td>C$<em>{15}$H$</em>{21}$Cr$_6$O$_6$</td>
</tr>
<tr>
<td>Cr(bzac)$_3$</td>
<td>C$<em>{30}$H$</em>{27}$Cr$_6$O$_6$</td>
</tr>
<tr>
<td>Cr(dpm)$_3$</td>
<td>C$<em>{33}$H$</em>{27}$Cr$_6$O$_6$</td>
</tr>
<tr>
<td>Cr(3-Me acac)$_3$</td>
<td>C$<em>{18}$H$</em>{27}$Cr$_6$O$_6$</td>
</tr>
<tr>
<td>Cr(3-Et acac)$_3$</td>
<td>C$<em>{21}$H$</em>{33}$Cr$_6$O$_6$</td>
</tr>
<tr>
<td>Cr(3-Pr acac)$_3$</td>
<td>C$<em>{24}$H$</em>{39}$Cr$_6$O$_6$</td>
</tr>
<tr>
<td>Cr(tfac)$_3$</td>
<td>C$<em>{15}$H$</em>{12}$CrF$_9$O$_6$</td>
</tr>
<tr>
<td>Cr(hfac)$_3$</td>
<td>C$_{15}$H$<em>3$CrF$</em>{18}$O$_6$</td>
</tr>
<tr>
<td>Cr(t'Bu PDO)$_3$</td>
<td>C$<em>{21}$H$</em>{33}$Cr$_6$O$_6$</td>
</tr>
<tr>
<td>Cr(PDO)$_3$</td>
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</tr>
<tr>
<td>Cr(BDO)$_3$</td>
<td>C$<em>{12}$H$</em>{15}$Cr$_6$O$_6$</td>
</tr>
<tr>
<td>Cr(tfbzac)$_3$</td>
<td>C$<em>{30}$H$</em>{18}$CrF$_9$O$_6$</td>
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<table>
<thead>
<tr>
<th>Acceptors</th>
<th>Formula</th>
<th>CAS Number</th>
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</thead>
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<tr>
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<td>C$<em>{15}$H$</em>{21}$Co$_6$</td>
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<td>16827-64-8</td>
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<td>Co(bzac)$_3$</td>
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<tr>
<td>Co(hfac)$_3$</td>
<td>C$_{15}$H$<em>3$CoF$</em>{18}$O$_6$</td>
<td>16702-37-7</td>
</tr>
<tr>
<td>Co(ØPDO)$_3$</td>
<td>C$<em>{27}$H$</em>{21}$Co$_6$</td>
<td>53749-20-5</td>
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APPENDIX III
DATA FOR DIFFUSION ANALYSIS
### IIa

**Le Bas Volume Increments for Calculating Molar Volumes**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Volume Increment $cm^3/g$ mole</th>
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<tr>
<td>Carbon</td>
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<td>Hydrogen</td>
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</tr>
<tr>
<td>Oxygen</td>
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</tr>
<tr>
<td>Doubly bound</td>
<td>7.4</td>
</tr>
<tr>
<td>Methyl esters and ethers</td>
<td>9.1</td>
</tr>
<tr>
<td>Ethyl esters and ethers</td>
<td>9.9</td>
</tr>
<tr>
<td>Higher esters and ethers</td>
<td>11.0</td>
</tr>
<tr>
<td>Acids</td>
<td>12.0</td>
</tr>
<tr>
<td>Joined to S,P,N</td>
<td>8.3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
</tr>
<tr>
<td>Primary amines</td>
<td>10.5</td>
</tr>
<tr>
<td>Secondary amines</td>
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<tr>
<td>Fluorine</td>
<td>8.7</td>
</tr>
<tr>
<td>Chlorine</td>
<td>21.6</td>
</tr>
<tr>
<td>Bromine</td>
<td>27.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td>25.6</td>
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<tr>
<td>Ring</td>
<td></td>
</tr>
<tr>
<td>3-Membered</td>
<td>-6.0</td>
</tr>
<tr>
<td>4-Membered</td>
<td>-8.5</td>
</tr>
<tr>
<td>5-Membered</td>
<td>-11.5</td>
</tr>
<tr>
<td>6-Membered</td>
<td>-15.0</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-30.0</td>
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<tr>
<td>Anthracene</td>
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Le Bas Volumes and Calculated Radii of the Acceptors

<table>
<thead>
<tr>
<th>ACCEPTOR</th>
<th>MOLECULAR FORMULAE</th>
<th>LE BAS VOLUME cm$^3$/g mol</th>
<th>RADIUS r/Å</th>
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<tbody>
<tr>
<td>Cr(PDO)$_3$</td>
<td>$C_9H_9CrO_6$</td>
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<tr>
<td>Cr(BDO)$_3$</td>
<td>$C_{12}H_{15}CrO_6$</td>
<td>288.3</td>
<td>4.39</td>
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<tr>
<td>Cr(hfac)$_3$</td>
<td>$C_{15}H_3CrF_{18}O_6$</td>
<td>444.9</td>
<td>5.07</td>
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<tr>
<td>Cr(tfac)$_3$</td>
<td>$C_{15}H_{12}CrF_9O_6$</td>
<td>399.9</td>
<td>4.90</td>
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<td>Cr(acac)$_3$</td>
<td>$C_{15}H_{21}CrO_6$</td>
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<td>4.70</td>
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<td>Cr(3-Meacac)$_3$</td>
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<td>Cr(3-Etacac)$_3$</td>
<td>$C_{21}H_{33}CrO_6$</td>
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<td>5.23</td>
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<tr>
<td>Cr(3-Bu PDO)$_3$</td>
<td>$C_{21}H_{33}CrO_6$</td>
<td>488.1</td>
<td>5.23</td>
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<tr>
<td>Cr(3-Pracac)$_3$</td>
<td>$C_{24}H_{39}CrO_6$</td>
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<td>5.46</td>
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<tr>
<td>Cr(ØPDO)$_3$</td>
<td>$C_{27}H_{21}CrO_6$</td>
<td>532.5</td>
<td>5.39</td>
</tr>
<tr>
<td>Cr(bzac)$_3$</td>
<td>$C_{27}H_{27}CrO_6$</td>
<td>554.7</td>
<td>5.46</td>
</tr>
<tr>
<td>Cr(tfbzac)$_3$</td>
<td>$C_{30}H_{18}CrF_9O_6$</td>
<td>644.1</td>
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<td>Cr(dpm)$_3$</td>
<td>$C_{33}H_{37}CrO_6$</td>
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<td>Cr(dbm)$_3$</td>
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### Le Bas Volumes and Calculated Radii of the Donors

<table>
<thead>
<tr>
<th>DONOR</th>
<th>MOLECULAR FORMULAE</th>
<th>LE BAS VOLUME cm³/g mol</th>
<th>RADIUS Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>C₁₀H₈</td>
<td>147.6</td>
<td>3.51</td>
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<tr>
<td>2-Acetonaphthone</td>
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</tr>
<tr>
<td>Acridine</td>
<td>C₁₃H₉N</td>
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<tr>
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<td>3.86</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>C₁₄H₁₀</td>
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<td>3.86</td>
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<tr>
<td>Pyrene</td>
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<td>3.97</td>
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<td>4.19</td>
</tr>
<tr>
<td>Tetracene</td>
<td>C₁₈H₁₂</td>
<td>250.8</td>
<td>4.19</td>
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<tr>
<td>1,2-Benzanthracene</td>
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<td>4.19</td>
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<tr>
<td>Perylene</td>
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<td>Pentacene</td>
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<tr>
<td>1,2,3,4-Dibenzanthracene</td>
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<tr>
<td>1,2,5,6-Dibenzanthracene</td>
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<td>Coronene</td>
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<td>Benzene</td>
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## III(d)

### Variation in $k_d$ with % Change of Acceptor Volume

Volume for the Cr(acac)$_3$/Pyrene System

<table>
<thead>
<tr>
<th>$V_A$ (cm$^3$/g mol)</th>
<th>%</th>
<th>$r_A$</th>
<th>$r_D$</th>
<th>$r_{DA}$</th>
<th>$D_A$</th>
<th>$D_D$</th>
<th>$D_{DA}$</th>
<th>$k_d/10^{10}$ (dm$^3$/mol s$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>354.9</td>
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<td>8.75</td>
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<td>8.83</td>
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<td>3.97</td>
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