acylated amino acids I exhibit the doubly hydrogen-bonded motif **4** despite the constraints imposed by **4** on molecular conformation and packing.

It is noteworthy that in crystal structures containing the chain-like molecules $HO_2C-X-CONH_2$ ($X = CH_2CH_2$, $CH{=}CH$, $CH{=}CHCH{=}CH$)[10] and in binary complexes between (primary and secondary) amides and carboxylic acids,[11] there is a far stronger tendency for the O(amide) to be doubly hydrogen-bonded and for the O(carboxyl) to be singly hydrogen-bonded than the reverse.

(b) Motif **7** is more stable than **8** which is in keeping with the fact that the singly hydrogen-bonded motif **1** [i.e., O—H···O(amide) and N—H···O(carboxyl)] is the most prevalent and that the singly hydrogen-bonded **2** [i.e., O—H···O(carboxyl) and N—H···O(amide)] occurs in only two of the observed crystal structures.

(c) The hydrogen-bonding energies of **9** and **10** (Table I) demonstrate why the hypothetical **5**, in which the carboxyl oxygen atom participates in two hydrogen bonds, does not occur.

(d) The average energies of the individual hydrogen-bond contributions (i.e., $\bar{e}_1$, $\bar{e}_2$, $\bar{e}_3$, $\bar{e}_4$ in Table I) reflect the observed preference for an O—H···O(amide) bond rather than the other three possibilities [i.e., OH···O(carboxyl), NH···O(amide), and NH···O(carboxyl)], in those crystal structures, represented by **3**, which contain only one active proton donor per molecule (i.e., $\bar{e}_2 < \bar{e}_4, \bar{e}_3, \bar{e}_1$). In this respect it is noteworthy that the O—H···O(amide) bond appears to be shorter, by up to 0.1 Å, than the O—H···O(carboxyl) bond. Furthermore, the O-H bond is a stronger proton donor than the N-H bond, as is evident from the O—H···O and N—H···O distances, i.e., 2.6 vs. 2.9 Å.

(e) The interaction energy between the two proton donors in the doubly hydrogen-bonded motif **6** is positive and was calculated to be about 0.4 kcal/mol; i.e., the two donor groups repel each other. Consequently, for amide or carboxylic acid molecules containing hydrogen-bonding groups of a single kind (i.e., amide or acid, but not both), the tendency should be for each acceptor oxygen atom to be singly hydrogen-bonded, which is in accord with the principle proposed by Etter.[6] On the other hand, for molecules which contain both amide and carboxyl groups, this principle is not all prevailing.

These calculations were carried out using a very simplified model which focused on the H-bonding groups in an isolated region, neglecting the residues and overall molecular packing. Nevertheless, these results are useful for the interpretation of the systematic features in a wide variety of crystal structures containing amides and carboxylic groups or a mixture thereof, as will be examined in a forthcoming paper.

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Registry No. *N*-Acetylglycine, 543-24-8; *S*-nitroso-*N*-acetyl-DL-penicillamine, 67776-06-1; *trans*-cinnamoyl-L-alanine, 84064-15-3; *N*-acetyl-L-tryptophan, 1218-34-4; *N*-acetyl-L-norvaline, 15891-50-6; hippuric acid, 495-69-2; *trans*-cinnamoyl-DL-alanine, 84064-16-4; *N*-acetyl-L-valine, 96-81-1; 2-chloro-*trans*-cinnamoyl-DL-alanine, 84041-42-9; *N*-acetyl-DL-valine, 3067-19-4; 2-chloro-*trans*-cinnamoyl-L-alanine, 84041-43-0.

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Quenching of Triplet States of Organic Compounds by Chromium(III) Tris(hexafluoroacetylacetonate) in Benzene Solution as a Result of Energy and Electron Transfer

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Contribution from the Department of Chemistry, University of Technology, Loughborough, Leicestershire, England. *Received June 2, 1982*

Abstract: Rate constants for quenching of the triplet states of 13 organic compounds by chromium(III) tris(hexafluoroacetylacetonate), $Cr(hfac)_3$, in benzene solution have been measured using the technique of laser flash photolysis. $Cr(hfac)_3$ is shown to be a very efficient triplet quencher, and even triplets with energies much lower than the lowest excited state of $Cr(hfac)_3$ give relatively high quenching constants, i.e., $\sim 6 \times 10^8$ dm^3 mol^{-1} s^{-1}. For five of the organic triplet donors a limiting quenching constant of 8.2×10^9 dm^3 mol^{-1} s^{-1} was observed. Spin–spin combinations are considered and the results interpreted in terms of quenching involving a combination of energy and electron transfer. It is proposed that quenching by electron transfer in benzene solution involves transfer to $Cr(hfac)_3$ (which is a much better electron acceptor than $Cr(acac)_3$, for which this type of quenching is negligible), followed by rapid reverse transfer ($k_{bt} > 10^8$ s^{-1}) to yield ground-state species. In the exciplex $D^+\cdots Q^-$, formed by electron transfer, $Q^- \equiv [Cr(hfac)_3]^-$ which is likely to be a high-spin Cr(II) complex, and therefore electron transfer via spin combinations which produce doublet states is likely to be prohibited energetically. The values obtained for the transmission coefficients and "intrinsic barriers" for both energy and electron transfer to $Cr(hfac)_3$ from these organic donors are similar to values reported for these parameters for analogous systems where either only energy or only electron transfer occurred. Finally it is suggested that where, as in the case of β-carotene, in this work it is not possible to measure the one-electron oxidation potential directly, the sensitivity of the rate constant dependence on $\Delta G^{\ominus}_{el}$ can be used as a method to obtain a good estimate for E_D^{ox}. Thus E^{ox} for β-carotene is estimated to be 0.35 ± 0.03 V (vs. SCE).

Introduction

In fluid solution transition metal complexes often quench electronically excited states with high efficiency, and the two most prevalent quenching mechanisms have been shown to involve electron[1,2] and energy transfer.[3] Variations in ligand structure as well as in the electronic configuration of the central metal atoms affect the quenching efficiencies by both these mechanisms. Many studies have been carried out to establish the parameters deter-

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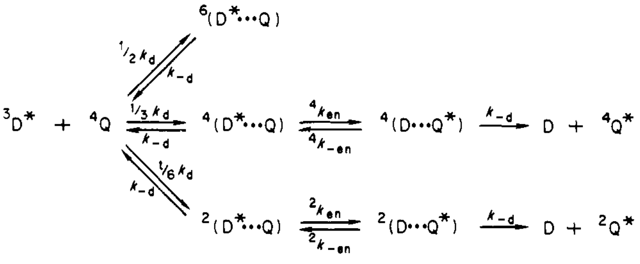
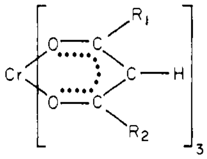
Scheme I



mining the quenching efficiency usually using systems chosen so that only one of these mechanisms operates, but not many systematic studies have been carried out which feature competition between these mechanisms. However, Caldwell et al.[4] have established that variations in the rate constants of triplet-state quenching of a series of substituted phenanthrenes by *trans-β*-methylstyrene and *trans*-anethole are best explained as a sum of energy- and charge-transfer quenching. Likewise, Ohno and Lichtin[5] demonstrated that reversible electron transfer is not the only significant mechanism of quenching of triplet methylene blue by four cobalt complexes. In this paper we present evidence that quenching of triplet states of organic compounds by chromium(III) tris(hexafluoroacetylacetonate), Cr(hfac)$_3$, involves both energy and electron-transfer processes. For convenience, chromium(III) *β*-diketonates with the general formula



are abbreviated to Cr(acac)$_3$ when $R_1 = R_2 = CH_3$, to Cr(hfac)$_3$ when $R_1 = R_2 = CF_3$, to Cr(dpm)$_3$ when $R_1 = R_2 = {}^t$Bu, and to Cr(bzac)$_3$ when $R_1 = CH_3$ and $R_2 = C_6H_5$.

Energy transfer from a triplet donor to the quartet ground state of a chromium(III) complex can be represented as shown in Scheme I,[6] where $^3D^*$ represents the electronically excited triplet donor and $^4Q^*$ the electronically excited quartet state of the quencher, etc. According to Scheme I the overall quenching constant k_q will be given by

$$k_q^{en} = {}^4k_q^{en} + {}^2k_q^{en} \quad (1)$$

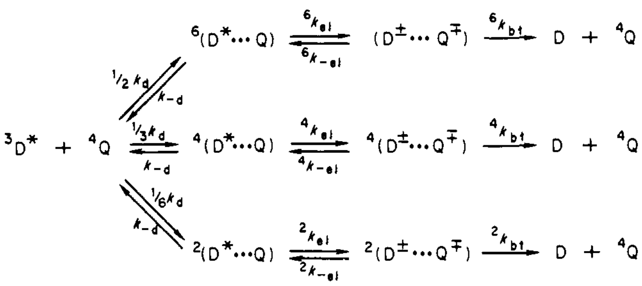
where ${}^4k_q^{en}$ and ${}^2k_q^{en}$ represent rate constants for quenching by energy transfer which proceeds via excited quartet and excited doublet states of the chromium complex. Applying the steady-state approximation to Scheme I gives

$${}^mk_q^{en} = \frac{s_m k_d}{\left[1 + \dfrac{(k_{-d} + {}^mk_{-en})}{{}^mk_{en}}\right]} \quad (2)$$

where m is the spin multiplicity of the encounter complex through which quenching proceeds, and the spin statistical factor[7] s_m equals one-sixth and one-third for the production of doublet and quartet encounter complexes, respectively.

We have recently reported[6] quenching of several triplet states of organic molecules of varying energy by Cr(acac)$_3$, Cr(bzac)$_3$, and Cr(dpm)$_3$ and established that the results can be interpreted in terms of Scheme I. Thus all three complexes show no quenching of triplet donors with energy considerably less than that of their lowest excited state (^2E_g) and "plateau values" for quenching rate constants independent of triplet energy when exothermic energy transfer is possible to produce the doublet but not the quartet state of the quencher. In the case of Cr(acac)$_3$ and Cr(bzac)$_3$ these "plateau values" are close to $k_d/6$, where k_d is the diffusion-controlled rate constant, demonstrating the importance of spin statistical factors for energy-transfer quenching. For higher energy triplet donors the quenching rate constants rise with increasing triplet energy for all three quenchers and in the case of Cr(bzac)$_3$ reach the diffusion and spin statistical factor limit of $k_d/2$ (i.e., $\sum s_m = {}^1/_2 = {}^1/_3 + {}^1/_6$). For comparison purposes the results for a typical energy-transfer quencher Cr(acac)$_3$ are shown later in Figure 3 along with the results for Cr(hfac)$_3$.

Scheme II



Electronic excitation decreases the ionization potential and increases the electron affinity of a molecule, and, as a consequence, quenching by intermolecular electron transfer often occurs as a highly efficient quenching mechanism for quenching by coordination complexes as well as by other molecules.[8-11] In nonpolar solvents separate ions are unlikely to be produced, and charge-transfer quenching is then usually represented as

$$D^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (D^*\cdots Q) \underset{k_{-el}}{\overset{k_{el}}{\rightleftharpoons}} (D^{\pm}\cdots Q^{\mp}) \xrightarrow{k_{bt}} D + Q \quad (3)$$

For charge-transfer interaction quenching of triplet states by paramagnetic species, spin statistical factors may need to be considered (cf. ref 12–14). Thus charge-transfer quenching in nonpolar solvents for a chromium(III) complex may be represented as shown in Scheme II. Note that in the scheme decay of the sextet and doublet charge-transfer exciplexes, i.e., ${}^{2\text{ and }6}(D^{\pm}\cdots Q^{\mp})$, back to ground-state species involves spin-forbidden processes. However, several studies[15-18] have demonstrated that such formally spin-forbidden intersystem crossings do often occur with relatively high rate constants (e.g., 10^9–10^{12} s^{-1}). Return to the ground state may be via the ${}^4(D^{\pm}\cdots Q^{\mp})$ exciplex which is degenerate with doublet and/or quartet "charge-transfer" exciplexes. According to this scheme

$$k_q^{el} = {}^6k_q^{el} + {}^4k_q^{el} + {}^2k_q^{el} \quad (4)$$

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and

$$^{m}k_{\mathrm{q}}^{\mathrm{el}} = \frac{s_m k_{\mathrm{d}}}{\left[1 + \frac{k_{-\mathrm{d}}}{^{m}k_{\mathrm{el}}}\left(1 + \frac{^{m}k_{-\mathrm{el}}}{^{m}k_{\mathrm{bt}}}\right)\right]} \tag{5}$$

where once more $s_m = {}^1/_6$, ${}^1/_3$, and ${}^1/_2$ when the spin multiplicity $m = 2$, 4, and 6, respectively.

Energy and electron transfer from electronically excited states can be treated classically using the same formulation as detailed recently by Balzani et al.,[19] as outlined briefly below. Thus for energy-transfer quenching

$$\ln\,(k_{\mathrm{en}}/k_{-\mathrm{en}}) = -\Delta G^{\ominus}{}_{\mathrm{en}}/RT \tag{6}$$

where $\Delta G^{\ominus}{}_{\mathrm{en}}$, the standard free-energy change for the energy-transfer process, can be obtained from the zero–zero transition wavenumbers of the energy donor and acceptor $\tilde{\nu}_{00}(^3\mathrm{D}^*)$ and $\tilde{\nu}_{00}(\mathrm{Q}^*)$, respectively, i.e., usually it is assumed that

$$\Delta G^{\ominus}{}_{\mathrm{en}} = -hNc[\tilde{\nu}_{00}(^3\mathrm{D}^*) - \tilde{\nu}_{00}(\mathrm{Q}^*)] \tag{7}$$

and

$$k_{\mathrm{en}} = \frac{\kappa kT}{h}\exp(-\Delta G^{\ominus\ddagger}{}_{\mathrm{en}}/RT) \tag{8}$$

where $\Delta G^{\ominus\ddagger}{}_{\mathrm{en}}$ represents the free energy of activation for the energy-transfer process and κ is the transmission coefficient (cf. ref 19).

In the case of charge-transfer quenching the analogous equation is

$$\ln\,(k_{\mathrm{el}}/k_{-\mathrm{el}}) = -\Delta G^{\ominus}{}_{\mathrm{el}}/RT \tag{9}$$

and the free-energy change for electron transfer to form the exciplex ($\mathrm{D}^+\cdots\mathrm{Q}^-$) is given by[9,20]

$$\Delta G^{\ominus}{}_{\mathrm{el}} = F(E_{\mathrm{D}}{}^{\mathrm{ox}} - E_{\mathrm{Q}}{}^{\mathrm{red}}) - E_{\mathrm{T}} + \Delta\omega \tag{10}$$

and that to form the exciplex ($\mathrm{D}^-\cdots\mathrm{Q}^+$) by

$$\Delta G^{\ominus}{}_{\mathrm{el}} = F(E_{\mathrm{Q}}{}^{\mathrm{ox}} - E_{\mathrm{D}}{}^{\mathrm{red}}) - E_{\mathrm{T}} + \Delta\omega' \tag{11}$$

$E_{\mathrm{D}}{}^{\mathrm{ox}}$ and $E_{\mathrm{Q}}{}^{\mathrm{ox}}$ are the oxidation potentials and $E_{\mathrm{D}}{}^{\mathrm{red}}$ and $E_{\mathrm{Q}}{}^{\mathrm{red}}$ are the reduction potentials of the triplet donor (of energy E_{T}) and of the quencher, respectively, and F is Faraday's constant. Similarly,

$$k_{\mathrm{el}} = \frac{\kappa kT}{h}\exp(-\Delta G^{\ominus\ddagger}{}_{\mathrm{el}}/RT) \tag{12}$$

where k_{el} is the rate constant for electron transfer at the encounter distance (cf. eq 8). The constants $\Delta\omega$ and $\Delta\omega'$ in eq 10 and 11 depend on the coulombic interaction energy and changes in solvation free energies of separate ions and the exciplex. Knibbe, Rehm, and Weller[10] have shown that the energy of 60 exciplexes they have studied in hexane are given by $E_{\mathrm{D}}{}^{\mathrm{ox}} - E_{\mathrm{A}}{}^{\mathrm{red}} + \Delta\omega$ with $\Delta\omega = (0.15 \pm 0.10\ \mathrm{eV})$. In agreement with this low value for $\Delta\omega$ we have shown[15] that $\Delta\omega$ values are typically (0.1 ± 0.1) eV for charge transfer from organic triplet states to amines, ketones, or quinones in benzene solution (see also ref 20). Obviously the direction of electron transfer depends on whether $E_{\mathrm{D}}{}^{\mathrm{ox}} - E_{\mathrm{Q}}{}^{\mathrm{red}}$ is greater or less than $E_{\mathrm{Q}}{}^{\mathrm{ox}} - E_{\mathrm{D}}{}^{\mathrm{red}}$. We shall assume for the present that any charge-transfer quenching by Cr(hfac)₃ will involve electron transfer to Cr(hfac)₃. Supporting evidence for this view is presented in the Discussion section. Thus for charge-transfer quenching by Cr(hfac)₃ we need to consider the electron-transfer process shown below, with electron configurations as given.

$$\begin{array}{ccccc} \mathrm{n\ or\ }\pi,\ \pi^*;\ \mathrm{d}^3 & & \mathrm{n\ or\ }\pi;\ \mathrm{d}^4 & & \mathrm{n}^2\mathrm{\ or\ }\pi^2;\mathrm{d}^3 \\ (\mathrm{D}^*\cdots\mathrm{Q}) & \rightleftarrows & (\mathrm{D}^+\cdots\mathrm{Q}^-) & \rightarrow & \mathrm{D} + \mathrm{Q} \end{array}$$

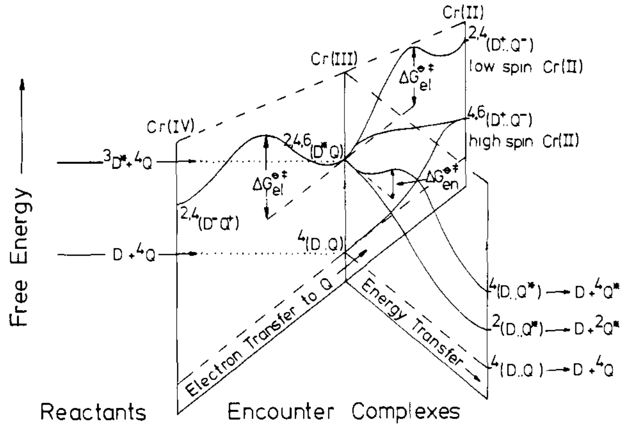

Figure 1. Schematic diagram showing various reaction pathways for energy and electron transfer from a triplet donor $^3\mathrm{D}^*$ to a quencher Q with fourfold spin multiplicity.

D^+ represents the doublet radical cation of the organic molecule and $\mathrm{Q}^- \equiv [\mathrm{Cr^{II}(hfac)_3}]^-$ which might be a high- or low-spin Cr(II) complex. Most Cr(II) complexes are high spin, but high-field ligands such as CN^- form low-spin complexes.[21] If Q^- is a high-spin complex of Cr(II), the spin multiplicity of Q^- will be 5, and vector addition of the spins on D^+ (a doublet) and Q^- yield only $^6(\mathrm{D}^+\cdots\mathrm{Q}^-)$ and $^4(\mathrm{D}^+\cdots\mathrm{Q}^-)$ as spin-allowed combinations.[7] On the other hand, if Q^- is a low-spin d^4 complex, the spin multiplicity of Q^- will be 3 and only $^4(\mathrm{D}^+\cdots\mathrm{Q}^-)$ and $^2(\mathrm{D}^+\cdots\mathrm{Q}^-)$ exciplexes arise from spin-allowed vector addition. If there is a large energy difference between high- and low-spin configurations, then the quenching pathways involving either the doublet or sextet exciplexes will be energetically excluded in Scheme II, in much the same way as quenching by the sextet pathway in Scheme I for energy transfer was excluded since no low-lying sextet excited states of chromium(III) complexes exist.

It is worth noting that if quenching involved electron transfer *to* the organic molecule, the resulting radical anion D^- would be "low spin", i.e., the ground-state thermodynamic species as produced, for example, in electrochemical reduction of D. Thus for quenching involving electron transfer to the organic species, i.e., by the process

$$\begin{array}{ccccc} \mathrm{n\ or\ }\pi,\ \pi^*;\ \mathrm{d}^3 & & \mathrm{n}^2\mathrm{\ or\ }\pi^2,\ \pi^*;\ \mathrm{d}^2 & & \mathrm{n}^2\mathrm{\ or\ }\pi^2;\ \mathrm{d}^3 \\ (\mathrm{D}^*\cdots\mathrm{Q}) & \rightleftarrows & (\mathrm{D}^-\cdots\mathrm{Q}^+) & \rightarrow & \mathrm{D} + \mathrm{Q} \end{array}$$

pathways involving $^6(\mathrm{D}^-\cdots\mathrm{Q}^+)$ would not be energetically feasible. The various possibilities are shown schematically in Figure 1.

Our recent work[6] on energy transfer to Cr(acac)₃, Cr(bzac)₃, and Cr(dpm)₃ shows that in the absence of favorable charge-transfer interactions intersystem crossing between the virtually degenerate encounter complexes does not occur; i.e., processes

$$^6(\mathrm{D}^*\cdots\mathrm{Q}) \rightleftarrows {}^4(\mathrm{D}^*\cdots\mathrm{Q}) \rightleftarrows {}^2(\mathrm{D}^*\cdots\mathrm{Q})$$

are not rapid. However, several studies[15-18] indicate the occurrence of rapid intersystem crossing between degenerate charge-transfer geminate radical pairs; i.e., processes

$$^6(\mathrm{D}^\pm\cdots\mathrm{Q}^\mp) \rightleftarrows {}^4(\mathrm{D}^\pm\cdots\mathrm{Q}^\mp) \rightleftarrows {}^2(\mathrm{D}^\pm\cdots\mathrm{Q}^\mp)$$

are likely to be fast compared with the lifetime of such species provided they are virtually degenerate. In such cases exclusion of quenching via nondegenerate exciplexes leads to expected spin statistical factors of ${}^5/_6 = ({}^1/_2 + {}^1/_3)$ for quenching which involves production of only high-spin Cr(II) complexes, ${}^1/_2 = ({}^1/_3 + {}^1/_6)$ when only low spin Cr(II) complexes are involved and ${}^1/_2 = ({}^1/_3 + {}^1/_6)$ for the production of exciplexes containing Cr(IV) complexes. However, it should be borne in mind that a small admixture of charge-transfer character in the encounter complexes of the type $\mathrm{D}^*\cdots\mathrm{Q}$ could result in rapid intersystem crossing before

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[19] V. Balzani, F. Bolletta, and F. Scandola, *J. Am. Chem. Soc.*, **102**, 2152 (1980).

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Table I. Donor Concentrations and Analyzing Wavelength for Laser Flash Photolysis Experiments

compound	λ_{TT}, nm	[D], mmol dm^{-3}
xanthone	610	0.2
benzophenone	535	10.0
triphenylene[a]	415	6.1
naphthalene[b]	414	5.0
2-acetonaphthone	425	1.0
chrysene	570	2.0
coronene	465	0.08
pyrene	416	0.5
acridine	438	0.15
anthracene	425	0.3
perylene[b]	488	0.8
2,3-benzanthracene[b]	459	0.1
pentacene	498	0.01
β-carotene[c]	520	0.3

[a] Sensitized with xanthone. [b] Sensitized with benzophenone. [c] Sensitized with anthracene.

energy differences which pertain further along the reaction coordinate are established (cf. Figure 1) in which case the spin selection rules will be relaxed.

Finally, we need to consider the kinetic factors which determine the rate constants k_{en} and k_{el}. As written, both eq 8 and 11 involve transmission coefficients κ and free energies of activation $\Delta G^{\ominus\ddagger}$. Several free-energy relationships have been and still are being used to relate $\Delta G^{\ominus\ddagger}{}_{el}$ to $\Delta G^{\ominus}{}_{el}$, the free-energy change for the electron-transfer process. These include those associated with the names of Polyani,[22] Marcus,[23] Rehm and Weller,[24] and Agmon and Levine.[25] All of these have been applied with various degrees of success and support by different groups. The failure of the Marcus relationship which, contrary to many experimental findings, predicts an increase in $\Delta G^{\ominus\ddagger}$ when $\Delta G^{\ominus} \ll 0$ in the so-called "Marcus-inverted region" has been much discussed (see ref 26 and references therein). Among the relationships which do not suffer from this disadvantage and predict $\Delta G^{\ominus\ddagger} \rightarrow 0$ as $\Delta G^{\ominus} \rightarrow -\infty$ is that of Agmon and Levine,[25] viz.

$$\Delta G^{\ominus\ddagger} = \Delta G^{\ominus} + \frac{\Delta G^{\ominus\ddagger}(0)}{\ln 2} \ln\left[1 + \exp\left(-\frac{\Delta G^{\ominus}\ln 2}{\Delta G^{\ominus\ddagger}(0)}\right)\right] \quad (13)$$

Balzani et al.[19] have pointed to the advantages of this relationship and applied it to both electron- and energy-transfer quenching. This is the approach which we have chosen to adopt in our discussions of the quenching results we have obtained using Cr(hfac)$_3$ in our attempts to increase understanding of excited-state quenching by coordination complexes.

Experimental Section

Materials. Chromium(III) tris(1,1,1,5,5,5-hexafluoro-2,4-pentanodionate), Cr(hfac)$_3$, was prepared by the method suggested by Charles.[27] Unreacted reagents and byproducts were removed by column chromatography on activated alumina with benzene as eluent. Further purification was achieved by repeated sublimation under vacuum and recrystallization from benzene–pentane.

The sources of the donors and the purification methods used have been described elsewhere[6] except for triphenylene (Aldrich) which was zone-refined. β-Carotene was obtained from BDH and was stored under nitrogen in the dark at 0 °C. The purity of the donors was checked by careful examination of their respective fluorescence and excitation spectra from ethanol solutions. All quenching experiments were carried out using Fisons spectrograde benzene as solvent.

Instruments. The excitation source was a frequency-doubled ruby laser, Q-switched to produce a pulse of ~25 mJ at 347 nm, with a fwhm of ~20 ns. The triplet–triplet absorption changes were followed photoelectrically. The analyzing wavelengths for triplet–triplet absorption of the various donors together with the actual concentrations of solutions used are given in Table I. The transient signal monitoring arrangement has already been described, and further details of the laser system can be found in ref 28. The data-processing system has also been described elsewhere.[6]

Absorption spectra in the range 190–900 nm were recorded on a Pye-Unicam SP8-250 double monochromator spectrophotometer. Fluorescence spectra were measured on a Perkin-Elmer MPF-44B recording spectrofluorimeter.

Technique. The general procedure for conducting quenching experiments was to prepare benzene stock solutions of the various donors. Aliquots were then taken and diluted in graduated flasks so that the absorbance with a 10-mm path length of donor solution at 347 nm in the photolysis sample was in the range 0.9 to 1.2. In a number of cases this was either not desirable nor attainable. For instance, triphenylene has low ground-state absorption at 347 nm, the excitation wavelength, so that relatively large amounts would be required to obtain solutions with the preferred absorbance. However, an exceptionally high concentration of donor as well as a significant amount of quencher might lead to nonideal behavior. Therefore, lower concentrations were employed and use was made of xanthone as a sensitizer in the case of most quenching experiments involving triplet triphenylene.

Sensitization techniques were also employed in several other cases, i.e., β-carotene, 2,3-benzanthracene, and perylene. Perylene has a low extinction coefficient at the laser excitation wavelength and, in addition, a low triplet quantum yield in benzene. As a result, direct detection of triplet perylene is difficult. It was therefore necessary to use a sensitizer, and in this case benzophenone was chosen as sensitizer. Benzophenone was also used to sensitize triplet 2,3-benzanthracene. This procedure, although not essential in the case of 2,3-benzanthracene, was found useful for two reasons. Firstly, comparison could be made between quenching results from direct excitation and from sensitization experiments, and as in the case of triphenylene the results were found to be equal. Secondly, the ground-state molecule absorbs at the triplet decay monitoring wavelength and the extinction coefficient is comparable to that at 347 nm, so that low concentrations are preferable. β-Carotene also exhibits strong ground-state absorption at the triplet monitoring wavelength. Again its concentration had to be lowered. Sensitization was inevitable, in this case with anthracene, as β-carotene gives no transient upon direct laser photolysis.

Low absorbance solutions (~0.4) were also employed in the case of pentacene as this compound has very low solubility in benzene. Sensitization was found unnecessary as the triplet quantum yield and lifetime were sufficient to ensure accurate enough measurements. This compound, as well as 2,3-benzanthracene, is easily photooxidized so precautions were taken in making up solutions. They were therefore dissolved in deoxygenated benzene in light-protected flasks under nitrogen. Oxygen was also excluded from all samples during photoexcitation. Flushing with nitrogen gas saturated with benzene vapor was shown to be an efficient means of reducing the amounts of dissolved oxygen sufficiently to give results identical with those obtained using as an alternative the usual repetitive freeze–pump–thaw method with a vacuum system.

Results

The absorption spectra of mixtures of each donor and Cr(hfac)$_3$ were equal to that expected by adding the spectra of separate solutions of each donor to that of Cr(hfac)$_3$ alone. Thus there was no evidence for the formation of any ground-state complexes between the donors and Cr(hfac)$_3$. Thus the addition of $\sim 10^{-2}$ mol dm^{-3} of most of the donors to 10^{-3} mol dm^{-3} of Cr(hfac)$_3$ showed no detectable change in the absorption spectra from which one can estimate that the association constants for ground-state complexes of Cr(hfac)$_3$ with the donors are $K_{as} \leq 5$ mol^{-1} dm^3. However, pentacene is so insoluble in benzene that in this case one could only say that $K_{as} \leq 5 \times 10^3$ mol^{-1} dm^3. The absorption spectra were also shown to undergo no significant changes when subjected to 20 laser pulses. During actual experiments each solution was exposed to the laser beam for no more than four exposures.

Following laser excitation triplet-state decay was studied by monitoring triplet–triplet absorption at the wavelength of maximum absorption (see Table I and ref 29). First-order decay constants, k_1, were evaluated and shown to be linearly dependent

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Table II. Rate Constants in Benzene Solution at Room Temperature for Quenching by Chromium(III) Tris(hexafluoroacetylacetonate) of the Triplet States of Organic Compounds (k_q) Together with Their Triplet Energies (E_T), Ionization Potentials (IP), Reduction Potentials (E^{red}), and Oxidation Potentials (E^{ox})

compound	E_T,[a] eV	IP,[b] eV	$-E^{red}$,[c] V	E^{ox},[d] V	$-FE^{red} - E_T$, eV	$FE^{ox} - E_T$, eV	k_q, 10^9 dm^3 mol^{-1} s^{-1}
benzophenone	3.01	9.45	1.55	2.46[e]	−1.46	−0.58	4.52 ± 0.2
triphenylene	2.89	7.80	2.41	1.55	−0.48	−1.34	8.2 ± 0.4
naphthalene	2.64	8.12	2.58	1.54	−0.06	−1.10	8.2 ± 0.4
2-acetonaphthone	2.55	8.31	1.72	1.69[e]	−0.83	−0.86	5.0 ± 0.3
chrysene	2.48	7.75	2.30	1.35	−0.18	−1.13	8.2 ± 0.3
coronene	2.40	7.60	2.04	1.23	−0.36	−1.17	8.2 ± 0.4
pyrene	2.08	7.55	2.10	1.16	+0.02	−0.92	8.2 ± 0.4
acridine	1.96	7.78	1.81	1.58	−0.15	−0.38	1.20 ± 0.08
anthracene	1.82	7.23	1.96	1.09	+0.14	−0.73	4.50 ± 0.2
perylene	1.54	7.15	1.65	0.85	+0.11	−0.69	3.95 ± 0.2
2,3-benzanthracene	1.28	6.88	1.55	0.77	+0.27	−0.51	0.67 ± 0.03
pentacene	0.99	6.61	1.36	0.54[e]	+0.37	−0.45	0.60 ± 0.06
β-carotene	0.78	6.40	1.68	0.39[e]	+0.90	−0.39	0.57 ± 0.03

[a] From ref 6 and 29. [b] From ref 37, 39–41, and F. I. Vilesov, *Dokl. Akad. Nauk SSR*, 132, 632, 1332 (1960). [c] Vs. SCE, acetonitrile, or dimethylformamide as solvent from ref 20 and C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Non-Aqueous Systems", Marcel Dekker, New York, 1960; A. J. G. Barwise, A. A. Gorman, R. L. Leyland, R. G. Smith, and M. A. J. Rodgers, *J. Am. Chem. Soc.*, 100, 1814 (1978); J. Tabner and J. R. Yandle in "Reactions of Molecules at Electrodes", N. S. Hush, Ed., Wiley-Interscience, New York, 1971, p 283. [d] Vs. SCE, in acetonitrile from ref 35 and L. Marcoux and R. N. Adams, *Electroanal. Chem. Interfacial Electrochem.*, 49, 111 (1974). [e] Estimated values from IP using eq 15.

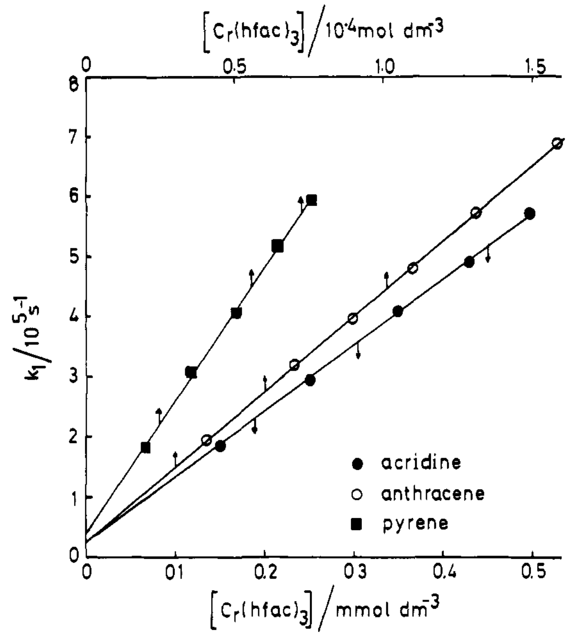

Figure 2. Dependence of the first-order decay constants k_1 of the triplet states of (●) acridine, (○) anthracene, and (■) pyrene on the concentration of the quencher Cr(hfac)$_3$ in deoxygenated benzene solution.

on the concentration of Cr(hfac)$_3$ which was varied up to 4×10^{-3} mol dm^{-3}, i.e.

$$k_1 = k_1^0 + k_q[\mathrm{Cr(hfac)_3}] \qquad (14)$$

where k_1^0 is the first-order constant for triplet-state decay in the absence of quencher and k_q is the bimolecular quenching constant.

A selection of quenching plots which demonstrate the linear dependence of k_1 on [Cr(hfac)$_3$] is shown in Figure 2. k_q values were obtained from the slopes of such plots. The quenching constants obtained are given together with standard errors in Table II.

Discussion

There has been a great deal of interest shown recently in the effect of ligands on the redox potentials of transition metal ions. Several studies have been carried out in which the metal atom is unchanged and where the ligands are systematically varied.[30–32]

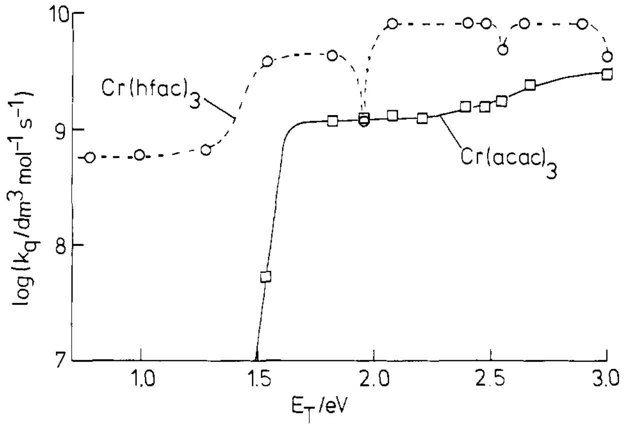

Figure 3. Dependence of the bimolecular quenching constants, k_q, on the energies E_T of the triplet state being quenched in the case of (○) Cr(hfac)$_3$ and (□) Cr(acac)$_3$.

The outcome is often surprisingly large changes in redox potentials brought about by subtle variations in the ligands. These observations indicate that by using a "family" of ligands it should be possible to change the mechanism of quenching to order. Thus the reduction potential (vs. SCE) in dimethyl sulfoxide of Cr(hfac)$_3$ is reported to be −0.40 V while that of Cr(acac)$_3$ is −1.73 V under the same conditions.[32] It follows that quenching by a charge-transfer mechanism involving electron transfer to these Cr(III) complexes should be much more likely in the case of Cr(hfac)$_3$ than for Cr(acac)$_3$. It is interesting to note that the electronic energy levelss in Cr(hfac)$_3$ are very similar to those in Cr(acac)$_3$ (see Table III). Thus very little difference is expected in the free energy of activation for quenching of any donor by the mechanism of electronic energy transfer. In Figure 3 quenching by Cr(hfac)$_3$ is compared with that of Cr(acac)$_3$ under identical conditions,[6] since Cr(acac)$_3$ has been shown to quench triplet states of organic compounds by the mechanism of electronic energy transfer as depicted in Scheme I.

Examination of Figure 3 and the data given in Table II reveals some interesting features concerning quenching by Cr(hfac)$_3$.

1. There are several triplet donors for which k_q values do not correlate well with E_T, the energy of the triplet state being quenched. In particular, acridine, benzophenone, and, to a lesser

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Table III. Spectroscopic Transitions and Nephelauxetic Parameters for $Cr(acac)_3$ and $Cr(hfac)_3$

acceptor	$^2E_g \leftarrow {}^4A_{2g}$ $\bar{\nu}$/ μm^{-1}	$^4T_{2g} \leftarrow {}^4A_{2g}$ $\bar{\nu}_{max}$/ μm^{-1}	$^4T_{2g} \leftarrow {}^4A_{2g}$ $\bar{\nu}_{oo}$/ μm^{-1}	$^4T_{1g} \leftarrow {}^4A_{2g}$ $\bar{\nu}_{max}$/ μm^{-1}	B_{55}/ cm^{-1}	D_q/ B_{55}
$Cr(acac)_3$	1.295	1.786	1.623[a]	2.326	678[b]	2.63[b]
$Cr(hfac)_3$	1.256	1.745	1.590[a]	2.168	624[b]	2.80[b]

[a] Calculated as in P. D. Fleischauer, A. W. Adamson, and G. Satori, *Proc. Inorg. Chem.*, 17, 1 (1972). [b] Calculated from standard equations: (a) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon, London, 1962; (b) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, 1962; (c) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, New York, 1968.

extent, 2-acetonaphthone are quenched relatively inefficiently (see Figure 3).

2. Quenching by $Cr(hfac)_3$ of donors with energy $E_T \ll E(^2E_g)$, i.e., when energy transfer is energetically excluded, is relatively efficient.

3. Many of the quenching constants exceed $k_d/2$, the maximum rate constant expected for exothermic energy transfer to produce both doublet and quartet excited states of the Cr(III) complex. The diffusion-controlled rate constant,[33] $k_d = 1.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, for benzene solutions at 20 °C and 5 of the 13 donors give quenching constants of 8.2×10^9 dm^3 mol^{-1} s^{-1} which is close to $^5/_6k_d$, the maximum limit for charge-transfer quenching which results in only high-spin Cr(II) exciplexes (see Introduction).

It is obvious that the quenching constants reported in Table II cannot be explained by the mechanism of energy transfer alone. When considering possible contributions to quenching from a charge-transfer mechanism, the first thing to establish is the direction of the electron transfer. This undoubtably involves $Cr(hfac)_3$ acting as the electron acceptor. The evidence for this viewpoint is as follows. Firstly, the increase in the reduction potential[32] of $Cr(hfac)_3$ of 1.3 V relative to $Cr(acac)_3$ demonstrates that as expected substitution of the CH_3 groups in the ligand by CF_3 groups makes $Cr(hfac)_3$ a much better electron acceptor than $Cr(acac)_3$. Secondly, although the oxidation potentials of $Cr(acac)_3$ and $Cr(hfac)_3$ have not been reported, gas-phase appearance potentials of 8.11 and 10.13 V have been reported[34] from mass spectrometric measurements on $Cr(acac)_3$ and $Cr(hfac)_3$, respectively, demonstrating the expected increase in ionization potential for $Cr(hfac)_3$. Thus electron donation is much less likely from $Cr(hfac)_3$ than from $Cr(acac)_3$ which, as mentioned above, gives negligible quenching by electron donation under identical conditions. Finally according to eq 10 and 11 the free energies for electron transfer for a set of triplet donors D and, therefore, from eq 13, also the free energies of activation for quenching involving electron transfer to or from a single common quencher Q will be proportional to $FE_D^{ox} - E_T$ or $-FE_D^{red} - E_T$, respectively. These values are tabulated in Table II, and it is apparent that there is a better correlation of k_q with the former than the latter.

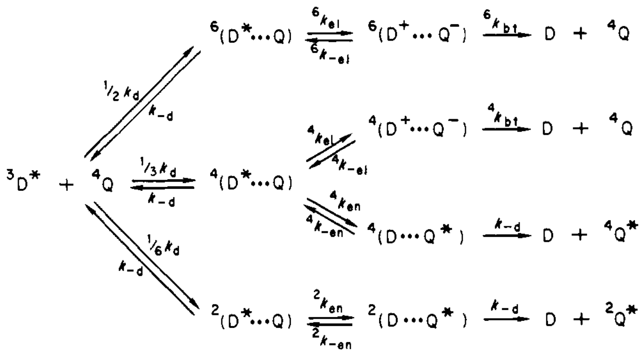
Having established that any charge-transfer quenching will involve electron transfer to $Cr(hfac)_3$, values of $\Delta G^\ominus_{el}$ can be estimated using eq 10. Where E_D^{ox} values measured in acetonitrile relative to a standard calomel electrode (SCE) were not available in the literature, estimates were calculated from measured ionization potentials. Pysh and Yang[35] who measured E_D^{ox} for eight out of the nine aromatic hydrocarbons used in this study found, as have several other groups,[36-38] a linear correlation between ionization potentials IP and E_D^{ox} values. The equation they give[35] is

Table IV. Comparison of Calculated Rate Constants for Quenching by $Cr(hfac)_3$ in Benzene Solution, Using $\Delta G^\ominus_{el}$, the Standard Free Energy Change for Electron Transfer at Encounter Distances, with Experimental Values

compound	$\Delta G^\ominus_{el}$,[a] eV	k_q range calcd,[b] 10^9 dm^3 mol^{-1} s^{-1}	k_q, 10^9 dm^3 mol^{-1} s^{-1}	
			calcd[c]	exptl
benzophenone	−0.18	3.7–5.5	4.3	4.52 ± 0.2
triphenylene	−0.94	8.5–8.6	8.6	8.2 ± 0.4
naphthalene	−0.70	8.0–8.4	8.3	8.2 ± 0.4
2-acetonaphthone	−0.46	4.8–8.2[d]	7.3	5.0 ± 0.3
chrysene	−0.73	8.1–8.4	8.3	8.2 ± 0.3
coronene	−0.77	8.2–8.5	8.3	8.2 ± 0.4
pyrene	−0.52	6.8–8.0	7.6	8.2 ± 0.4
acridine	+0.02	1.2–1.6	1.3	1.20 ± 0.08
anthracene	−0.33	3.8–6.9	5.7	4.50 ± 0.2
perylene	−0.29	2.1–5.5	4.0	3.95 ± 0.2
2,3-benzanthracene	−0.11	0.13–2.1	0.70	0.67 ± 0.03
pentacene	−0.05	0.04–1.2	0.30	0.60 ± 0.06
β-carotene	+0.01	0.01–0.6	0.10	0.57 ± 0.03

[a] Calculated from eq 16 using E_D^{ox} and E_T values from Table II and $E_Q^{red} = -0.40$ eV.[32] [b] Range of values assuming an uncertainty of ±0.1 eV in $\Delta G^\ominus_{el}$. [c] Rate constant calculated using the $\Delta G^\ominus_{el}$ value given in column 2. [d] Assuming uncertainty of ±0.2 eV in $\Delta G^\ominus_{el}$.

Scheme III



$$\mathrm{IP} = (1.473 \pm 0.027)E_D^{ox} + (5.821 \pm 0.009) \qquad (15)$$

Equation 15 has been used to obtain estimates for E_D^{ox} for benzophenone, acetonaphthone, pentacene, and β-carotene from reported ionization potentials.[39-44] Unfortunately, the reduction potential of $Cr(hfac)_3$ has only been measured in dimethylsulfoxide and 85% dioxane–water mixtures, but these values show very little solvent dependence, being −0.40 and −0.39 V, respectively.[43] As mentioned earlier, $\Delta\omega$ in eq 10 is expected to be small. Thus eq 16 below is likely to give quite a good estimate for $\Delta G^\ominus_{el}$, viz.

$$\Delta G^\ominus_{el} = (E_D^{ox} - E_Q^{red})F - E_T \qquad (16)$$

Values calculated according to eq 16 are given in Table IV. They are expected to have uncertainties of around ±0.1 eV.

It is apparent from Table IV that $\Delta G^\ominus_{el}$ is definitely negative for many of the triplet aromatic hydrocarbons. However, the value of $\Delta G^\ominus_{el}$ for acridine is close to zero while for the ketones $\Delta G^\ominus_{el}$ values are less negative than for aromatic hydrocarbons with similar triplet energies. Since there is very little change in the energy levels of Cr(III) complexes and therefore in ligand field

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strength when the CH$_3$ groups in the acetylacetonate ligand is replaced by CF$_3$ (cf. Table III and ref 44), it is likely that Cr(II) complexes of the β-diketonates will be high-spin Cr(II) complexes.[21] Scheme III shows a mechanism for combined quenching via energy transfer and charge transfer via only high-spin exciplexes of $[\mathrm{Cr^{II}(hfac)_3}]^- \equiv \mathrm{Q}^-$. Using Scheme III it follows that

$$k_q = {}^6k_q^{el} + {}^4k_q + {}^2k_q^{en} \tag{17}$$

where ${}^2k_q^{en}$ and ${}^6k_q^{el}$ are given by eq 2 and 5, respectively, i.e., the same values as those based on Schemes I and II, respectively. Applying the steady-state approximation to the quartet spin combinations in Scheme III gives eq 18. Quenching by either

$${}^4k_q = \frac{s_m k_d}{\left[1 + \dfrac{1}{\dfrac{{}^4k_{en}}{(k_{-d} + {}^4k_{-en})} + \dfrac{{}^4k_{el}{}^4k_{bt}}{k_{-d}({}^4k_{bt} + {}^4k_{-el})}}\right]} \tag{18}$$

energy transfer[6,19] or electron transfer[9-11,20] for a homogeneous series of donors to a single acceptor often results in a correlation between $\Delta G^{\ominus}_{en}$ or $\Delta G^{\ominus}_{el}$, respectively, and ln k_q. In order to see how closely Scheme III fits these experimental observations, we have assumed the donors can be treated as a homogeneous series; i.e., $\Delta G^{\ominus\ddagger}(0)$ and κ values for substitution into eq 8, 12, and 13 may be considered constant (cf. ref 26). This assumption has already been shown to be a good one in the case of energy transfer to Cr(acac)$_3$, Cr(bzac)$_3$, and Cr(dpm)$_3$ from the triplet states of these same donors.[6]

In view of the similarities in the energy levels of Cr(III)-substituted β-diketonates,[44] we have used the same values for ${}^2\Delta G^{\ominus\ddagger}(0)$ and ${}^4\Delta G^{\ominus\ddagger}(0)$ as found recently by us[6] to fit quenching by energy transfer, which were 0.03 and 0.25 eV, respectively. Following Balzani et al.[19] we have taken $k_d = 1.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1} and $k_{-d} = 1.2 \times 10^{10}$ s^{-1}. Values for ${}^2\kappa_{en}$ and ${}^4\kappa_{en}$ were chosen as follows. Quenching by electron transfer and by energy transfer via the quartet excited state of Cr(hfac)$_3$ is energetically unfavorable in the case of triplet acridine. Thus for triplet acridine it is likely that $k_q = {}^2k_q^{en}$, in which case ${}^2\kappa_{en} = 5 \times 10^{-3}$ since substitution of this value into eq 6, 5, and 2 gives ${}^2k_q^{en} = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1}, i.e., equal to the experimental quenching constant for acridine. Note that ${}^2\kappa_{en} = 6.3 \times 10^{-3}$ and 2.4×10^{-2} for Cr(acac)$_3$ and Cr(bzac)$_3$, and for these complexes ${}^4\kappa_{en}$ values are somewhat higher, being 7.3×10^{-3} and 4.9×10^{-2}, respectively.[6] This suggests that in the case of Cr(hfac)$_3$ a likely value for ${}^4\kappa_{en}$ will be $\sim 1.0 \times 10^{-2}$. As we shall see later, the value assumed for ${}^4\kappa_{en}$ only markedly affects the rate constants predictions for quenching by triplet benzophenone in all other cases either energy transfer to produce the quartet excited state is energetically prohibitive or charge-transfer quenching dominates the prediction for ${}^4k_q$. In the case of quenching of triplet states of carotene, pentacene, and 2,3-benzanthracene, quenching by energy transfer to produce the ${}^2\mathrm{E_g}$ state of Cr(hfac)$_3$ will also be negligible, and for triplet perylene the contribution from energy transfer will be small (cf. quenching behavior by Cr(acac)$_3$ shown in Figure 3).

In order to compare the experimental quenching constants with expectations based on Scheme III, we need to consider four further constants, namely, ${}^4k_{bt}$, ${}^6k_{bt}$ (see Scheme III), κ_{el}, and $\Delta G^{\ominus\ddagger}_{el}(0)$. The rate constants ${}^4k_{bt}$ and ${}^6k_{bt}$ are for processes which involve exoergic electron transfer and are therefore expected to be rapid processes. Spin effects and previous work concerning these processes have already been discussed in the Introduction (see also ref 12–18). Since no transient species were observed in these laser flash photolysis studies, this indicates that both ${}^4k_{bt}$ and ${}^6k_{bt}$ have values greater than 10^8 s^{-1}. In fact, calculations based on a range of values from 10^8 to 10^{14} s^{-1} for ${}^4k_{bt}$ and ${}^6k_{bt}$ demonstrate that the rate constants predicted on the basis of Scheme III are affected by less that 1% for the triplet donors studied here. It is apparent therefore that the values of ${}^4k_{bt}$ and ${}^6k_{bt}$ are not critical and from experiment we can say these are both $>10^8$ s^{-1}.

Since $\Delta G^{\ominus}_{el}$ is the same for quartet and sextet exciplexes and as written in Scheme III the electron transfer step to Cr(hfac)$_3$ does not involve any change of spin or electron rearrangement, the following equalities are expected to exist:

$$\Delta G^{\ominus\ddagger}_{el}(0) = {}^4\Delta G^{\ominus\ddagger}_{el}(0) = {}^6\Delta G^{\ominus\ddagger}_{el}(0) \tag{19}$$

and

$$\kappa_{el} = {}^4\kappa_{el} = {}^6\kappa_{el} \tag{20}$$

The value of κ_{el} determines the plateau values expected for electron transfer when $\Delta G^{\ominus}_{el} << 0$. After allowance is made for energy transfer, a value of $\kappa_{el} = 1.6 \times 10^{-2}$ was found to give best agreement with our experimental limiting rate constant of 8.2×10^9 dm^3 mol^{-1} s^{-1}. $\Delta G^{\ominus\ddagger}_{el}(0)$ values only markedly affect the quenching constants expected when $\Delta G^{\ominus}_{el}$ is close to zero, for example, in the range $\Delta G^{\ominus}_{el} = -3\Delta G^{\ominus\ddagger}_{el}(0)$ to $+3\Delta G^{\ominus\ddagger}(0)$. The values obtained using $\Delta G^{\ominus\ddagger}_{el}(0) = 0.16$ eV are shown in Table IV where the agreement with the experimental values is very good, confirming the suggestion that quenching by Cr(hfac)$_3$ can be accounted for by combined expectations for quenching by energy and electron transfer. This value for $\Delta G^{\ominus\ddagger}_{el}(0)$ is similar to that found by many other workers for quenching by mechanisms involving electron transfer in a variety of solvents.[9,15,16,20,45,46]

It is unfortunate that there is considerable uncertainty in the best estimates available for $\Delta G^{\ominus}_{el}$. These are at least ±0.1 eV and as is shown in Table IV this can affect the predicted rate constants by an order of magnitude when $\Delta G^{\ominus}_{el} \approx \Delta G^{\ominus\ddagger}_{el}(0)$. In view of this it is perhaps surprising that the fit of calculated and observed values is so good. However, we have been able to make calculations, variations in which are mainly based on a single set of experimental results obtained by Pysh and Yang.[35] This eliminates any differences due to systematic errors which probably accounts for the very good fit achieved.

In fact, the fit is so good that we suggest that, where other methods for determining the oxidation potential E_D^{ox} are not available, values can be estimated by measuring the quenching constants with an electron acceptor chosen to ensure k_q is critically dependent on E_D^{ox}. Better still, a series of acceptors of known E_Q^{red} values could be used and k_q measured, whence $E_{D\bullet}^{ox}$, in much the same way as has been developed in energy-transfer studies to give unknown excited-state energies (e.g., see ref 6, 47, and 48).

With the present results the application of eq 16, based on data referring solely to aromatic hydrocarbons, to the polyene β-carotene probably accounts for the poor fit obtained using the value of E_D^{ox} based on its measured ionization potential.

However, the experimental quenching constants can be used to estimate a value for E_D^{ox} as shown below. Rearrangement of eq 17 gives

$$k_q - {}^2k_q^{en} = {}^6k_q^{el} + {}^4k_q$$

and when ${}^4\kappa_{en}$ is small, i.e., for donors with $E_T < 2.2$ eV then

$$k_q - {}^2k_q^{en} = {}^6k_q^{el} + {}^4k_q^{el} = k_q^{el} \tag{21}$$

For several of the low-energy triplet donors, i.e., pentacene, 2,3-benzanthracene, and β-carotene itself, ${}^2k_q^{en}$ will be negligible. In the case of triplet perylene (see Figure 3) an estimated value of ${}^2k_q^{en} \approx 3 \times 10^8$ dm^3 mol^{-1} s^{-1} (i.e., only 10% of the experimental quenching constant) can be assumed. However, for the three donors anthracene, acridine, and pyrene for which 1.3 eV $< E_T$ $<$ 2.4 eV, ${}^2k_q^{en}$ is likely to equal the plateau value for energy transfer to produce the ${}^2\mathrm{E_g}$ state of Cr(hfac)$_3$. Within experimental error this will equal the quenching constant obtained for quenching of triplet acridine where k_q^{el} is expected to be negligible. Figure 4 shows that a plot of log $(k_q - {}^2k_q^{en}) \equiv$ log k_q^{el} vs. $\Delta G^{\ominus}_{el}$ gives

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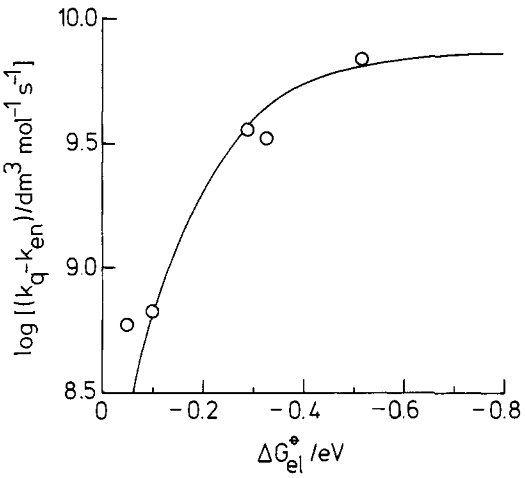

Figure 4. Dependence of $k_q - k_{en}$, where this is equal to the rate constant for quenching due to electron transfer on $\Delta G^{\ominus}_{el}$, the free-energy change for electron transfer from the triplet donor to Cr(hfac)$_3$.

a correlation as expected, and thus from the rate constant obtained for the quenching of triplet β-carotene and Figure 4 one obtains an estimate of E_D^{ox} for β-carotene equal to 0.35 ± 0.03 V (vs. SCE). This estimate for the half-wave oxidation potential of β-carotene agrees within experimental error with the value of 0.39 ± 0.04 V obtained from eq 15. This work demonstrates that charge-transfer quenching of excited states could occur in addition to energy-transfer quenching for carotenoids in many biological systems. It is worth noting that electrochemical measurements on β-carotene have revealed only two-electron oxidation for which the reported oxidation potentials are 0.51[49] and 0.74 V[50] in acetonitrile and benzene (2:1 vol) and in vigorously dried tetrahydrofuran, respectively.

Figure 4 and Table IV demonstrate that the electron-transfer part of the quenching constant correlates well with $\Delta G^{\ominus}_{el}$, the free energy for electron transfer as estimated from oxidation and reduction potentials of the donors and Cr(hfac)$_3$, respectively. The best fit to the experimental data for the "intrinsic barrier", $\Delta G^{\ominus *}_{el}(0) = 0.16$ eV, lies between the values for the intrinsic barriers for energy transfer to Cr(III) β-diketonates which are ~0.03 and ~0.25 eV for energy transfer to the nondistorted ^2E_g state and the highly distorted $^4T_{2g}$ excited states, respectively. It is interesting to note that the transmission coefficient for electron transfer, $\kappa_{el} = 0.016$, is three times that for energy transfer to produce the ^2E_g state which reflects the more stringent orbital overlap requirements for exchange energy transfer to produce the metal-centered ^2E_g state.

Registry No. Cr(hfac)$_3$, 14592-80-4; benzophenone, 119-61-9; triphenylene, 217-59-4; naphthalene, 91-20-3; 2-acetonaphthone, 93-08-3; chrysene, 218-01-9; coronene, 191-07-1; pyrene, 129-00-0; acridine, 260-94-6; anthracene, 120-12-7; perylene, 198-55-0; 2,3-benzanthracene, 92-24-0; pentacene, 135-48-8; β-carotene, 7235-40-7.

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Correlation between Metal Stability, Charge Transfer, and Raman Frequencies in Metalloporphyrins and Their π–π Complexes[†]

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Abstract: The frequencies of the Raman core-size and oxidation-state marker lines of metalloporphyrins are found to be related to the electronegativity and ionic radius of the metal ion. The frequencies correlate with a stability index for the metalloporphyrins toward acid demetalation that is based on these properties. Higher electronegativity and smaller ionic radius of the metal increase conjugation of the $a_{2u}(\pi)$ orbital with the metal $4p_z$ orbital. The result is to lower the charge density and energy of the $a_{2u}(\pi)$ orbital. Stabilization of the $a_{2u}(\pi)$ orbital, which mainly affects charge density at the meso carbons and pyrrole nitrogens of the macrocycle, apparently increases the C_m–C_α stretching force constant and, therefore, accounts for the metal-dependent shifts in the Raman lines. The pattern of shifts in the core-size and oxidation-state marker lines observed when phenanthroline binds to metalloporphyrins is strikingly similar to the shifts induced by metal substitution. Raman difference spectroscopy shows that phenanthrolines form π–π donor/acceptor complexes with metallouroporphyrins in water. The $a_{2u}(\pi)$ orbital is the highest occupied molecular orbital of the macrocycle and is expected to be the principal donor orbital in a π–π charge-transfer complex. The Raman line shifts are entirely consistent with phenanthroline accepting charge density from the $a_{2u}(\pi)$ orbital. Moreover, these dissimilar phenomena affect the same porphyrin orbital, so the metal ion can easily modify the effect of π–π complexation, thus explaining both the similarity in the pattern of Raman line shifts and the effect of the metal on the shifts induced by complexation.

The mechanisms by which reactants are catalytically activated by metalloporphyrins are not well understood in either biological or other chemical reactions. A molecular basis of catalytic activation and control must include an understanding of the function of intermediate complexes in the activation process and, in particular, an understanding of the role of the various interactions that stabilize these molecular complexes.

Many of the reactions catalyzed by the metalloporphyrins are redox reactions, so an understanding of the role of charge transfer in these molecular complexes is paramount. In this regard the effects on ligation of cis electron-withdrawing substituents on the macrocycle and of trans axial ligands at the metal site have been examined.[1-4] Charge-donating groups at the porphyrin periphery

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