

Fe porphyrin species. Linear relationships were also obtained when the logarithm of the formation constants were plotted vs. the Hammett-Taft substituent constant for each substituted pyridine.

Battioni et al.<sup>9</sup> have shown that the C=S stretching frequency for (TPP)FeCS[L] complexes (measured in a KBr pellet) was dependent upon the identity of L. Buchler and co-workers<sup>36</sup> have previously investigated trans effects on the mixed CO-L complexes for Fe, Ru, and Os porphyrins. They observed that the trans effects in the C=O stretching frequencies were explicable by the basicity of the ligand trans to C=O in the case of Fe. However, this explanation was not applicable to Os porphyrins, in which both  $\sigma$  and  $\pi$  donor and acceptor properties had to be considered.

The results presented in Table I concur with the findings of both Battioni and Buchler. A linear relationship between the C=S stretching frequency and the  $pK_{BH^+}$  of the ligand trans to the C=S moiety was obtained and is consistent with expectations. The ligand series of substituted pyridines was selected to provide a means for evaluating the trans effect operative in the (TPP)FeCS[L] system over the widest range of  $pK_{BH^+}$  values available. The C=S stretching frequency decreased as the  $\pi$  donor ability of the Fe center increased. The  $pK_{BH^+}$  of the amine trans to the C=S moiety is a measure of the amine to Fe  $\sigma$  interaction and, by induction, controls the  $\pi$  donor ability of the Fe center.

The observation of two chemically reversible oxidations for the thiocarbonyl Fe(II) porphyrin is particularly intriguing when compared with the analogous carbon monoxide adducts of Fe(II) porphyrins. Brown et al.<sup>15</sup> reported that (Etio)FeCO(ImH) was irreversibly oxidized at  $E_p = 0.32$  V in  $CH_2Cl_2$ . Buchler and co-workers<sup>11</sup> observed similar behavior for (OEP)FeCOpy at  $E_p = 0.43$  V. Gurira and Jordan<sup>16</sup> have investigated the oxidation of (protoporphyrin IX)Fe<sup>II</sup>CO in aqueous media. In all cases reported to date, oxidation of the carbon monoxide bound Fe(II) porphyrin proceeds concomitantly with the loss of CO. In nonaqueous media, the dissociation appears to occur very rapidly after the electron transfer.<sup>37</sup> These observations are in marked contrast with

the behavior of the thiocarbonyl Fe porphyrins. Scheidt and Geiger<sup>38</sup> have utilized (OEP)FeCS as a stereochemical equivalent for the analogous five-coordinate complex (OEP)FeCO. Clearly, this analogy does not extend to either the redox or coordination chemistry of these two carbene Fe porphyrin complexes.

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**Registry No.** (TPP)FeCS, 67583-11-3; {(TPP)FeCS}<sup>+</sup>, 92054-41-6; {(TPP)FeCS}<sup>2+</sup>, 92054-46-1; (TPP)FeCS[L] (L = 3,5-dichloropyridine), 92054-29-0; {(TPP)FeCS[L]}<sup>+</sup> (L = 3,5-dichloropyridine), 92054-42-7; {(TPP)FeCS[L]}<sup>2+</sup> (L = 3,5-dichloropyridine), 92054-55-2; (TPP)FeCS[L] (L = 3-cyanopyridine), 92054-30-3; {(TPP)FeCS[L]}<sup>+</sup> (L = 3-cyanopyridine), 92054-48-3; {(TPP)FeCS[L]}<sup>2+</sup> (L = 3-cyanopyridine), 92054-56-3; (TPP)FeCS[L] (L = 4-cyanopyridine), 92054-31-4; {(TPP)FeCS[L]}<sup>+</sup> (L = 4-cyanopyridine), 92054-49-4; {(TPP)FeCS[L]}<sup>2+</sup> (L = 4-cyanopyridine), 92054-57-4; (TPP)FeCS[L] (L = 3-chloropyridine), 92054-32-5; {(TPP)FeCS[L]}<sup>+</sup> (L = 3-chloropyridine), 92054-43-8; {(TPP)FeCS[L]}<sup>2+</sup> (L = 3-chloropyridine), 92054-58-5; (TPP)FeCS[L] (L = 3-bromopyridine), 92054-33-6; {(TPP)FeCS[L]}<sup>+</sup> (L = 3-bromopyridine), 92054-50-7; {(TPP)FeCS[L]}<sup>2+</sup> (L = 3-bromopyridine), 92054-59-6; (TPP)FeCS[L] (L = 3-acetylpyridine), 92054-34-7; (TPP)FeCS[L] (L = 4-acetylpyridine), 92054-35-8; {(TPP)FeCS[L]}<sup>+</sup> (L = 4-acetylpyridine), 92054-51-8; {(TPP)FeCS[L]}<sup>2+</sup> (L = 4-acetylpyridine), 92054-60-9; (TPP)FeCS[py], 67670-43-3; {(TPP)FeCS[py]}<sup>+</sup>, 92054-44-9; {(TPP)FeCS[py]}<sup>2+</sup>, 92054-61-0; (TPP)FeCS[3-pic], 92054-37-0; {(TPP)FeCS[3-pic]}<sup>+</sup>, 92054-45-0; {(TPP)FeCS[3-pic]}<sup>2+</sup>, 92054-47-2; (TPP)FeCS[4-pic], 92054-38-1; {(TPP)FeCS[4-pic]}<sup>+</sup>, 92054-52-9; {(TPP)FeCS[4-pic]}<sup>2+</sup>, 92054-62-1; (TPP)FeCS[L] (L = 3,4-dimethylpyridine), 92054-39-2; {(TPP)FeCS[L]}<sup>+</sup> (L = 3,4-dimethylpyridine), 92054-53-0; {(TPP)FeCS[L]}<sup>2+</sup> (L = 3,4-dimethylpyridine), 92054-63-2; (TPP)FeCS[L] (L = imidazole), 92054-40-5; {(TPP)FeCS[L]}<sup>+</sup> (L = imidazole), 92054-54-1; {(TPP)FeCS[L]}<sup>2+</sup> (L = imidazole), 92054-64-3; (TPP)FeCS[L] (L = methylimidazole), 80697-79-6; (TPP)FeCS[L] (L = piperidine), 92078-13-2; (TPP)FeCS[L] (L = aniline), 92054-36-9.

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Contribution from the Department of Chemistry,  
University of Technology, Loughborough, Leicestershire, United Kingdom

## Quenching of the Triplet States of Organic Compounds by Iron(III) Complexes of $\beta$ -Diketones due to Reversible Electron Transfer

F. WILKINSON\* and C. TSIAMIS

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The rate constants,  $k_q$ , for quenching of the triplet states of 15 different organic molecules by iron(III) tris(1,1,1-trifluoro-2,4-pentanedionate), Fe(tfac)<sub>3</sub>, and by iron(III) tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate), Fe(hfac)<sub>3</sub>, in benzene solution have been measured by using the technique of nanosecond laser flash photolysis. Limiting high  $k_q$  values of  $(6.3 \pm 0.2) \times 10^9$  and  $(7.9 \pm 0.2) \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> were obtained for quenching of several triplet states by Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub>, respectively. The quenching efficiencies are compared with those of Fe(acac)<sub>3</sub>, which has been previously shown to quench by the mechanism of electronic energy transfer, and the marked increase in the efficiency of quenching especially for low-energy triplet donors by these iron(III) complexes containing the fluorinated ligands is shown to be due to the occurrence of the additional mechanism of reversible electron-transfer quenching. Correlations of the quenching rate constants with the standard Gibbs free energy change for electron transfer to the iron(III) complexes allow an intrinsic barrier of 0.26 eV for both quenchers and transmission coefficients of 0.007 and 0.014 to be evaluated for electron transfer from electronically excited triplet states to Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub>, respectively.

### Introduction

The photochemistry and photophysics of coordination compounds is a topic of current interest. Information concerning

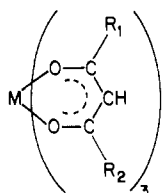
excited states obtainable from absorption and emission spectra can be greatly amplified and extended by making sensitization and quenching studies. In fluid solution, transition-metal

complexes often quench electronically excited states with high efficiency, and when spin restrictions are taken into account, diffusion is often rate determining. The two most prevalent quenching mechanisms have been shown to be electron<sup>1,2</sup> and energy transfer.<sup>2,3</sup> The existence of closely spaced excited states and the wide range of redox potentials make transition-metal complexes particularly suitable for quenching studies. Spin effects can also be probed by changing the electronic configuration of the central atom.

Many studies have been carried out to establish the parameters that determine the quenching efficiency, usually on systems chosen so that either exchange energy transfer or electron transfer is the only quenching mechanism. However, not many studies have been undertaken in which the two mechanisms are competing against each other. Recently experimental evidence with organic and inorganic systems is accumulating concerning competition between these and possibly other mechanisms.<sup>4</sup> With organic molecules, substituent effects on the spectral and redox properties of donor and acceptor can be predicted and exploited in a systematic way. Change of ligands, on the other hand, usually results in more drastic changes in the stereochemistry, energy levels, redox potentials, overall charge of the coordination complex, etc., so that discrimination of the relative importance of each parameter in the quenching efficiency is difficult to assess. However, these inherent difficulties can be reduced significantly by selecting a series of closely related coordination compounds in which minor modifications result in substantial changes of only one parameter.

A great deal of knowledge has accumulated on coordination complexes of substituted  $\beta$ -diketonates.<sup>5-7</sup> Thus, structural changes,<sup>5</sup> changes in energy levels,<sup>6</sup> and changes in redox potentials<sup>7</sup> have all been studied, the latter being particularly large. This makes the coordination compounds of  $\beta$ -diketonates eminently suitable for systematic studies aimed at establishing the factors that determine the quenching efficiency of transition-metal complexes.

For convenience metal(III)  $\beta$ -diketonates with the general formula



will be abbreviated as  $M(\text{acac})_3$  ( $R_1 = R_2 = \text{CH}_3$ ),  $M(\text{tfac})_3$  ( $R_1 = \text{CH}_3$ ,  $R_2 = \text{CF}_3$ ),  $M(\text{hfac})_3$  ( $R_1 = R_2 = \text{CF}_3$ ), and  $M(\text{dpm})_3$  ( $R_1 = R_2 = t\text{-Bu}$ ).

Several years ago we investigated<sup>8</sup> quenching of excited organic triplet states by  $\text{Fe}(\text{acac})_3$  and by  $\text{Fe}(\text{dpm})_3$ , and we

established that quenching occurs by exchange energy transfer. More recently we have exploited knowledge of the energy levels and redox potentials of Cr(III) complexes with substituted  $\beta$ -diketonates to quantify spinstatistical<sup>9a</sup> and steric factors<sup>9b</sup> and in the case of quenching of organic triplet states by Cr(hfac)<sub>3</sub> in benzene solution to demonstrate that quenching results from a combination of energy transfer and reversible electron transfer.<sup>10</sup> In this paper we examine triplet quenching by  $\text{Fe}(\text{tfac})_3$  and  $\text{Fe}(\text{hfac})_3$  in benzene solution and show that in these cases reversible electron-transfer quenching is the predominant mechanism of quenching for all but one of the 15 triplet states studied.

## Experimental Section

**Materials.** Tris(2,4-pentanedionato)iron(III),  $\text{Fe}(\text{acac})_3$ , was purchased from Aldrich and was recrystallized several times from ethanol-water. Finally, it was sublimed under vacuum. The tris-(fluorinated  $\beta$ -diketonato)iron(III) complexes,  $\text{Fe}(\text{hfac})_3$  and  $\text{Fe}(\text{tfac})_3$ , were prepared by refluxing under continuous magnetic stirring a suspension of anhydrous  $\text{FeCl}_3$  in  $\text{CCl}_4$  with an excess of the corresponding fluorinated  $\beta$ -diketone, a modification of the method reported in the literature for  $\text{Fe}(\text{hfac})_3$ .<sup>11</sup> Purification was effected by repeated washing with distilled water, evaporation of the solvent, and recrystallization from  $\text{CCl}_4$ . Finally, the products were sublimed under vacuum ( $\sim 3$  torr). Elemental analyses and melting points were in agreement with values given in the literature.<sup>6</sup>

The donors and sensitizers used in this work were of high purity in order to eliminate or minimize quenching by impurities. Thus, triphenylene, chrysene, and pyrene, obtained from Koch-Light, were zone refined as was perylene obtained from Sigma. Anthracene (BDH) was scintillation grade, and phenanthrene, purchased from Kodak, was fluorescence grade. Coronene, supplied by Koch-Light, was purified by chromatography. 2,3-Benzanthracene and pentacene were obtained from K and K. 1,2,3,4-Dibenzanthracene was purchased from Aldrich. Xanthone (Aldrich) and 2-acetylnaphthalene (Kodak) were recrystallized several times as were benzophenone and acridine obtained from BDH.  $\beta, \beta$ -Carotene, supplied by Fisons, was stored under nitrogen and was kept in the dark in a refrigerator. The purity of the organic molecules was checked by obtaining their absorption and emission spectra in specially purified ethanol and comparing them with the spectra of pure compounds reported in the literature. In the quenching experiments Fisons spectrograde benzene was used as solvent.

**Instruments.** The excitation source was a frequency-doubled Q-switched ruby laser that gives a pulse of  $\sim 25$  mJ at 347 nm with a half-peak duration of  $\sim 20$  ns. The decay of the triplet state within a 10-mm fluorimeter cell was monitored at right angles to the unfocused excitation beam by using as analyzing source part of the light of the flash lamp that pumped the ruby laser. Details of the laser instrumentation and the transient signal-monitoring system have been given previously.<sup>12</sup> The data capture and processing arrangement has also been described elsewhere.<sup>9</sup>

Absorption spectra in the range 190–900 nm were measured on a Pye-Unicam SP8-250 double-monochromator spectrophotometer employing a 0.5–1 nm slit width. Spectra in the near-IR region were recorded on a Perkin-Elmer EPS-3T spectrophotometer. Corrected emission spectra were measured on a Perkin-Elmer 44B spectrofluorimeter.

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**Table I.** Triplet-Triplet Analyzing Wavelength ( $\lambda_{TT}$ ), Wavenumbers of the O-O Phosphorescence Transition ( $\bar{\nu}_{00}(T)$ ), Oxidation Potentials ( $E_D^{ox}$ ), and the Concentration of the Donors ([D]) Used in Laser Flash Photolysis Experiments

	$\bar{\nu}_{00}(T)^a / \mu\text{m}^{-1}$	$\lambda_{TT}^a / \text{nm}$	$E_D^{ox} b / \text{V}$	[D] / $\text{mmol dm}^{-3}$
xanthone	2.58	610		0.2
benzophenone	2.43	535	2.46 <sup>g</sup>	10.0
triphenylene	2.33	415	1.55	6.1
phenanthrene	2.16	481	1.50	4.0
2-acetylnaphthalene	2.06	425	1.69 <sup>g</sup>	1.0
chrysene	1.98	570	1.35	2.0
coronene	1.94	465	1.23	0.08
1,2,5,6-dibenz-anthracene	1.83	532	1.19	1.0
1,2,3,4-dibenz-anthracene	1.78	454	1.25	1.0
pyrene	1.68	416	1.16	0.5
acridine	1.58 <sup>c</sup>	438	1.58	0.15
anthracene	1.47	425	1.09	0.3
perylene	1.24 <sup>d</sup>	488	0.85	0.8
methylene blue	1.20	440		0.01
anthranthrene	1.19	573		0.1
2,3-benzanthracene	1.03	459	0.77	0.1
pentacene	0.80 <sup>e</sup>	498	0.54 <sup>g</sup>	0.01
$\beta,\beta$ -carotene	0.63 <sup>f</sup>	520	0.35 <sup>g</sup>	0.03

<sup>a</sup> Reference 13. <sup>b</sup> Reference 14. <sup>c</sup> Singlet-triplet oxygen-enhanced absorption. <sup>d</sup> Singlet-triplet absorption in crystal. <sup>e</sup> Theoretical value. <sup>f</sup> Reference 18. <sup>g</sup> From ionization potentials correlation in ref 14 (see ref 10).

**Technique.** The standard procedure for carrying out quenching experiments was to prepare benzene stock solutions of the various donors in light-protected flasks. Aliquots were then taken and diluted in volumetric flasks so that the absorbance with a 10-mm path length of each donor solution at 347 nm was in the range 0.9–1.2. There were a few exceptions to this procedure when it was either not applicable or not desirable. Thus, no transient absorption of  $\beta,\beta$ -carotene is observed upon direct laser photolysis; its production was therefore sensitized with anthracene. Sensitization techniques were also employed in several other cases, e.g. triphenylene, perylene, and 2,3-benzanthracene. Perylene, in addition to a low extinction coefficient at the laser excitation wavelength, has a low quantum yield of triplet-state production in benzene. As a result, direct observation of triplet perylene is difficult. Therefore, sensitization was essential, and in this case benzophenone was selected as sensitizer. Triphenylene and 2,3-benzanthracene do not normally require sensitization. However, in a number of experiments sensitizers were used as a means of comparing quenching results obtained by direct excitation with those obtained with sensitization by xanthone and benzophenone, respectively. It was found that the results obtained with and without sensitizer were equal within experimental error. Triphenylene has a low absorbance at 347 nm; therefore, it was necessary to use high concentrations of triphenylene to obtain the preferred absorbance. However, large amounts of organic donors might have resulted in nonideal behavior. Consequently, lower concentrations were preferred, employing at the same time a sensitizer, and in the case of most quenching experiments involving triplet triphenylene, xanthone was selected as the sensitizer. Pentacene has a low solubility, and in this case the concentration used was the highest possible value. The actual concentrations of donors and sensitizers used are listed in Table I, together with the triplet-triplet analyzing wavelengths and other parameters.

The stability of the donor solutions varied considerably. Anthracene solutions stored in the dark remained unchanged for more than 2 weeks. Chrysene, on the other hand, showed signs of deterioration after 36 h. Pentacene and 2,3-benzanthracene are readily photo-oxidized. They were therefore dissolved in deoxygenated benzene in light-protected graduated flasks under nitrogen and were used within hours. All other solutions were used within 24 h.

## Results

Mixtures of the organic molecules employed in this work and the coordination compounds of iron(III) studied were examined spectroscopically for any signs of ground-state as-

sociation or reaction. For the pairs Fe(hfac)<sub>3</sub>-acridine the intensities of the charge-transfer bands of the Fe(hfac)<sub>3</sub> diminish with increasing acridine concentration, whereas in the pair Fe(hfac)<sub>3</sub>- $\beta,\beta$ -carotene addition of Fe(hfac)<sub>3</sub> induced a hypsochromic shift in the  $\beta,\beta$ -carotene absorption bands, which was enhanced upon further addition of Fe(hfac)<sub>3</sub>. No quenching studies were made with these systems; for all the other pairs of compounds the electronic absorption spectra of photolysis mixtures of each donor with each iron(III)  $\beta$ -diketonate were found to be the sum of the separate spectra of the donor and acceptor. In addition, spectra were measured in which the concentration of the organic compound was, when feasible, increased at least 10-fold, i.e. to  $\sim 10^{-2}$  mol dm<sup>-3</sup> with the concentration of the iron(III)  $\beta$ -diketonate at  $\sim 5 \times 10^{-3}$  mol dm<sup>-3</sup>. Most of these organic donors do not absorb in the region of the first charge-transfer band of the iron(III)  $\beta$ -diketonates so the shape of this band and the absorbance (at the band maximum) could be examined. No changes in absorbance were detected within experimental error, which was  $\pm 3\%$ . Thus, the association constants,  $K_{as}$ , are estimated to be  $< 3$  mol<sup>-1</sup> dm<sup>3</sup>.

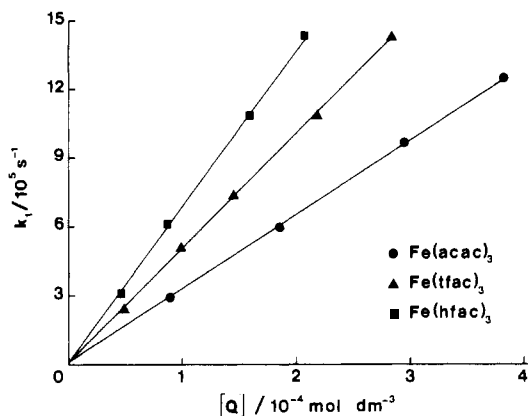
Decay constants were measured from deoxygenated fresh samples. During the experiments, no sample was exposed to the laser beam more than twice. Nevertheless, the photostability of donor-acceptor mixtures was examined by exposing them to 20 laser flashes. The absorption spectra of the photolyzed samples were also found to undergo no significant changes, indicating that product formation was absent or negligible and that there was no concentration change due to product formation. Oxygen, which might have effected photooxidation, was excluded from the photolysis cell by continuous purging with oxygen-free nitrogen. Solvent losses were avoided by saturating the nitrogen stream with benzene vapor. Nitrogen flushing was established to be an efficient means of minimizing the amount of dissolved oxygen to acceptable levels so that the quenching results were identical with those obtained employing as an alternative the usual repetitive freeze-pump-thaw method with a vacuum system. The decay of triplet states was studied by monitoring the triplet-triplet absorption at the wavelength of maximum absorbance listed in Table I. In the absence of quencher, the decay of the triplet is usually the sum of first- and second-order contributions. Upon addition of sufficient quencher to the solution, the decay becomes pseudo first order. The first-order decay constant  $k_1$  showed a linear dependence on the quencher concentration [Q], i.e.

$$k_1 = k_1^0 + k_q[Q]$$

where  $k_1^0$  represents the first-order decay constant in the absence of quencher. The bimolecular quenching constant  $k_q$  was obtained graphically by constructing plots of  $k_1$  against quencher concentration.  $k_1$  values were obtained for four to six different concentrations in addition to that obtained in the absence of quencher. A typical series of plots is shown in Figure 1. For each concentration three to five samples were photolyzed. As the iron(III)  $\beta$ -diketonates absorb strongly at the excitation wavelength, the number of samples analyzed increased whenever the quencher concentration was high enough to influence the accuracy of the results. The results are summarized in Table II. Previous results<sup>8</sup> on Fe(acac)<sub>3</sub> are included in the same table for comparison purposes.

## Discussion

Table III summarizes the spectral transitions for Fe(acac)<sub>3</sub>, Fe(tfac)<sub>3</sub>, and Fe(hfac)<sub>3</sub> and serves to demonstrate that there are only small changes in the absorption band maxima for all three complexes. Thus, if quenching by Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub> were only due to energy transfer as is the case for Fe(acac)<sub>3</sub>, one would expect the same kind of correlation of



**Figure 1.** Dependence of the first-order rate constant  $k_1$  of the triplet state decay of 2-acetylnaphthalene on the concentration of quencher in deoxygenated solution.

**Table II.** Rate Constants for Quenching of the Triplet States of Organic Donors by the Tris( $\beta$ -diketonato)iron(III) Complexes Fe(acac)<sub>3</sub>, Fe(tfac)<sub>3</sub>, and Fe(hfac)<sub>3</sub> in Deoxygenated Benzene Solution at 22 ± 2 °C

	$k_q/10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		
	Fe(acac) <sub>3</sub> <sup>a</sup>	Fe(tfac) <sub>3</sub>	Fe(hfac) <sub>3</sub>
xanthone	5.0 ± 0.5		
benzophenone	3.2 ± 0.3	4.3 ± 0.5	7.5 ± 0.1
triphenylene <sup>c</sup>			7.9 ± 0.1
phenanthrene		6.5 ± 0.2	7.8 ± 0.1
2-acetylnaphthalene	3.2 ± 0.3	5.7 ± 0.4	7.7 ± 0.1
chrysene	3.2 ± 0.2	6.4 ± 0.2	7.8 ± 0.1
coronene	2.2 ± 0.2 <sup>b</sup>	6.5 ± 0.2	7.8 ± 0.1
1,2,5,6-dibenzanthracene	3.2 ± 0.2		
1,2,3,4-dibenzanthracene	2.5 ± 0.2 <sup>b</sup>	6.0 ± 0.4	7.9 ± 0.1
pyrene	2.5 ± 0.3	5.8 ± 0.4	7.8 ± 0.1
acridine	0.73 ± 0.05	1.7 ± 0.5	reacts
anthracene	0.76 ± 0.05	3.9 ± 0.8	7.5 ± 0.1
perylene <sup>d</sup>	0.40 ± 0.03 <sup>b</sup>	3.3 ± 0.8	7.3 ± 0.1
methylene blue	0.54 ± 0.12		
anthranthrene	0.55 ± 0.05		
2,3-benzanthracene <sup>d</sup>	0.53 ± 0.03		
pentacene	0.055 ± 0.02	0.9 ± 0.08	6.4 ± 0.3
$\beta,\beta$ -carotene <sup>e</sup>	<0.01	0.6 ± 0.04	reacts

<sup>a</sup> From ref 8. <sup>b</sup> This work. <sup>c</sup> Sensitized with xanthone. <sup>d</sup> Sensitized with benzophenone. <sup>e</sup> Sensitized with anthracene.

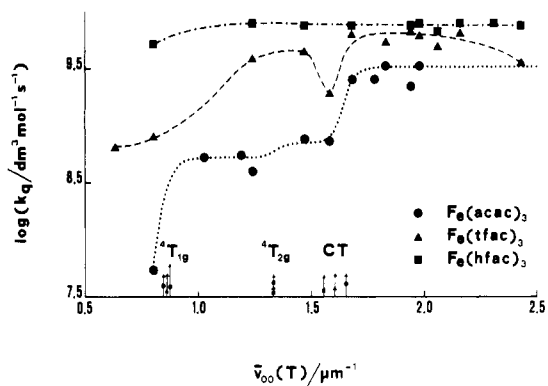
**Table III.** Spectral Transitions, Band Maxima ( $\bar{\nu}_{\text{max}}$ ), Wavenumbers at 5% of Band Maxima Absorbance ( $\bar{\nu}_{0.05}$ ), and Reduction Potentials ( $E_Q^{\text{red}}$ ) for the Tris( $\beta$ -diketonato)iron(III) Complexes

	Fe(acac) <sub>3</sub>	Fe(tfac) <sub>3</sub>	Fe(hfac) <sub>3</sub>
<sup>4</sup> T <sub>1g</sub> ← <sup>6</sup> A <sub>1g</sub> $\bar{\nu}_{\text{max}}/\mu\text{m}^{-1}$	0.979 <sup>b</sup>	0.993 <sup>b</sup>	1.010 <sup>b</sup>
<sup>4</sup> T <sub>2g</sub> ← <sup>6</sup> A <sub>1g</sub> $\bar{\nu}_{\text{max}}/\mu\text{m}^{-1}$	1.333 <sup>b</sup>	1.333 <sup>b</sup>	1.333 <sup>b</sup>
<sup>4</sup> E <sub>g</sub> , <sup>4</sup> A <sub>1g</sub> ← <sup>6</sup> A <sub>1g</sub> $\bar{\nu}/\mu\text{m}^{-1}$	2.166 <sup>c</sup>	2.158 <sup>c</sup>	2.158 <sup>c</sup>
<sup>6</sup> CT ← <sup>6</sup> A <sub>1g</sub> ( $e_g \leftarrow \pi$ )			
$\bar{\nu}_{\text{max}}/\mu\text{m}^{-1}$	2.30	2.28	2.21
$\bar{\nu}_{0.05}/\mu\text{m}^{-1}$	1.81	1.76	1.66
<sup>6</sup> CT ← <sup>6</sup> A <sub>1g</sub> ( $\pi^* \leftarrow t_{1g}$ )	2.83	2.72	2.58
$\bar{\nu}_{\text{max}}/\mu\text{m}^{-1}$			
$E_Q^{\text{red}}/\text{V}$	-0.63 <sup>d</sup>	0.07 <sup>d</sup>	0.59 <sup>d</sup>

<sup>a</sup> Band assignments taken from ref 6, but see also ref 22 and 23. <sup>b</sup> Band maxima taken from ref 6. <sup>c</sup> Calculated from the corresponding Tanabe-Sugano matrices.<sup>19</sup> <sup>d</sup> Calculated values from ref 7c (see text); vs. SCE.

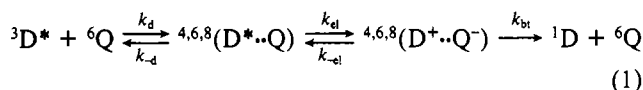
log  $k_q$  with  $E_T$ , the energy of the triplet state being quenched, as is the case for the Fe(dpm)<sub>3</sub>.<sup>8</sup> However, as can be seen in Figure 2, this correlation is not good in the case of Fe(tfac)<sub>3</sub>.

In view of our recent finding<sup>10</sup> that triplet quenching by Cr(hfac)<sub>3</sub> involves both energy and electron transfer, it is



**Figure 2.** Dependence of the bimolecular quenching constant  $k_q$  on the donor triplet energies and observed electronic transitions shown as arrows labeled <sup>4</sup>T<sub>1g</sub>, <sup>4</sup>T<sub>2g</sub>, and CT (charge transfer).

instructive to consider the possibility of reverse-electron-transfer quenching for Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub>, which may be represented as



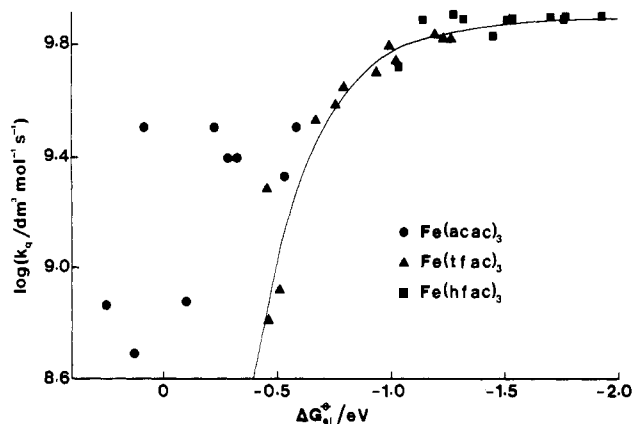
and to consider how log  $k_q$  correlates with  $\Delta G_{el}$  the standard free energy change for electron transfer to form the exciplex 4,6,8( $\text{D}^+\cdots\text{Q}^-$ ), a good estimate for which is given by

$$\Delta G_{el} = F(E_{\text{D}^{\text{ox}}} - E_{\text{Q}^{\text{red}}}) - E_T \quad (2)$$

where  $F$  is the Faraday constant and  $E_{\text{D}^{\text{ox}}}$  and  $E_{\text{Q}^{\text{red}}}$  are the oxidation and reduction potentials of the donor (of energy  $E_T$ ) and of the quencher, respectively. Equation 2 should contain a small extra term to allow for changes in interaction and solvation free energies when an electron is transferred from the excited donor to the coordination complex. However, Weller has shown<sup>20</sup> this term is small in hydrocarbon solutions, and we have shown that in benzene solution it is typically 0.1 ± 0.1 eV (see ref 10).  $E_{\text{Q}^{\text{red}}}$  for Fe(hfac)<sub>3</sub> and Fe(tfac)<sub>3</sub> has not been measured by many workers; however, in ref 7c cathodic and anodic peak potentials are given from cyclic voltammetric studies at scan rates of 100 mV s<sup>-1</sup> with dimethylformamide as solvent. A series of iron(III)  $\beta$ -diketonates were studied, and the peak separation varied from 0.06 to 0.22 V. The theoretical value of 0.06 V was obtained when the scan rate for one of the iron(III) complexes was increased to 500 mV s<sup>-1</sup>. The value of  $E_{\text{Q}^{\text{red}}}$  of -0.63 V (vs. SCE) for Fe(acac)<sub>3</sub> calculated from the mean of the cathodic and anodic peak potentials measured relative to the saturated Ag/AgCl electrode in ref 7c compares favorably with other literature values for  $E_{\text{Q}^{\text{red}}}$  for Fe(acac)<sub>3</sub>, which are -0.667 and -0.58 V (vs. SCE).<sup>21</sup> The  $E_{\text{Q}^{\text{red}}}$  values obtained for Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub>, given in Table III from ref 7c, are 0.07 and 0.59 V (vs. SCE), respectively. Even if these values are likely to yield  $\Delta G_{el}$  subject to some uncertainty (±0.1 eV), the relative values are likely to show few differences due to systematic errors. For similar reasons  $E_{\text{D}^{\text{ox}}}$  values were, where possible, taken from the same source.<sup>14</sup>

Figure 3 shows that there is quite a good correlation of log  $k_q$  with  $\Delta G_{el}$  in the case of Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub> but not in the case of Fe(acac)<sub>3</sub>, indicating as might be expected from the large change in  $E_{\text{Q}^{\text{red}}}$  for the fluorinated complexes that reversible electron-transfer quenching can predominate with

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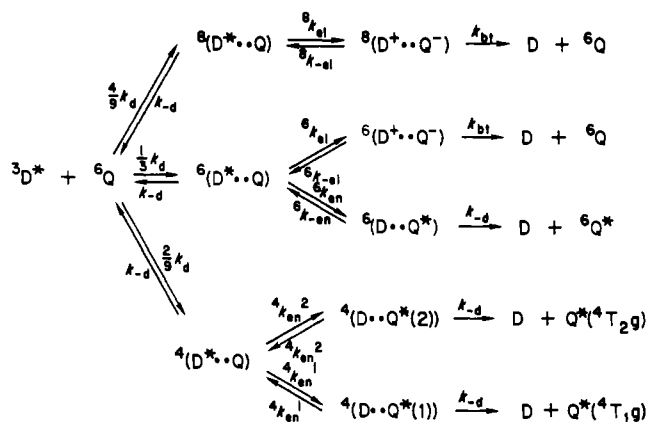
**Figure 3.** Dependence of the bimolecular quenching constants  $k_q$  on  $\Delta G_{ei}$ , the free energy change for electron transfer from the triplet donor to the triplet acceptor. The curve was fitted to quenching by  $\text{Fe}(\text{hfac})_3$  and  $\text{Fe}(\text{tfac})_3$  only (see text).

the fluorinated complexes. However, there seems no reason to suppose that quenching by electronic energy transfer cannot occur in the case of  $\text{Fe}(\text{tfac})_3$  and  $\text{Fe}(\text{hfac})_3$ , and in fact close examination of Figure 3 gives some indication of its occurrence. For example, quenching by  $\text{Fe}(\text{tfac})_3$  of the high-energy donor acridine is much higher than that of the low-energy triplet  $\beta, \beta$ -carotene for which energy transfer is not possible although the  $\Delta G_{ei}$  values for these two triplets are very similar, i.e.  $-0.49$  and  $-0.48$  eV, respectively.

In order to consider competitive electron- and energy-transfer quenching further, we need to look at possible spin restrictions for these two processes. Iron(III)  $\beta$ -diketonates are high spin;<sup>22</sup> thus, on collision with triplet donors, the spin-allowed encounter complexes are, according to Wigner spin rule, only those with spin multiplicities 4, 6, and 8. Table III shows that the only low-lying ligand field states to which energy transfer is feasible are those with spin multiplicity 4. Thus, we need not concern ourselves with the position of the  ${}^2T_g$  states in these complexes. Transitions to the  ${}^4T_{1g}$  and  ${}^4T_{2g}$  states are very weak and are often only observed as shoulders on the trailing edge of the charge-transfer transitions, and thus the band maxima may not correspond too well with  $\bar{\nu}_{00}$ . Sextet charge-transfer states are tabulated in Table III. These are broad bands, and positioning  $\bar{\nu}_{00}$  is again difficult.  $\bar{\nu}_{0.05}$  values are also given in Table III. In fact four charge-transfer bands are expected, namely  $\pi^* \leftarrow t_{2g}$ ,  $t_{2g} \leftarrow \pi$ ,  $\pi^* \leftarrow e_g$ , and  $e_g \leftarrow \pi$ . The assignments given in Table II have been queried,<sup>23</sup> and if they are correct one would expect two further lower energy charge-transfer transitions that have not been observed. In addition, there are expected to be corresponding quartet charge-transfer states of similar or slightly higher energy associated with each sextet charge-transfer state. Thus, energy transfer can occur to quartet ligand field states and to sextet and possible quartet charge-transfer states. Evidence is accumulating that spin selection rules hold for electronic energy transfer to coordination complexes.<sup>9,10,24</sup>

By contrast intersystem crossing between degenerate charge-transfer encounter partners seems facile and occurs within the lifetime of such complexes.<sup>25,26</sup> The best evidence for this comes from the work of Ohno and Lichtin on forward

**Scheme I**



and reverse electron transfer from triplet methylene blue to organic reductants<sup>26a</sup> and to iron(II) complexes.<sup>26b</sup> In the case of electron transfer to high-spin iron(III) however, the three charge-transfer complexes  ${}^{4,6,8}(D^* \cdots Q^-)$  shown in eq 1 are unlikely to be degenerate. Thus, if we imagine the transferred electron entering a metal  $t_{2g}$  orbital, it must pair up with the electron already present and only charge-transfer complexes with spin multiplicities 4 and 6 are possible. Alternatively, if the electron enters the  $\pi^*$  orbital on the ligand, then spin multiplicities of 6 and 8 are possible as an almost degenerate pair of exciplexes. The relative energies of the orbitals in the complexes  $\text{Fe}(\text{tfac})_3$  and  $\text{Fe}(\text{hfac})_3$  are debatable.<sup>27</sup> The large dependence of the reduction potential of these iron(III) complexes on the nature of the substituents in the ligands demonstrates that the added electron enters an orbital that has a large amount of ligand character. For this reason we shall first consider competitive quenching by energy transfer and reverse electron transfer involving a degenerate sextet-octet pair of exciplexes as shown in Scheme I. According to this scheme

$$k_q = {}^8k_q + {}^6k_q + {}^4k_q$$

and applying the steady-state approximation gives

$${}^8k_q = ({}^4/9k_d) / \left[ 1 + \frac{k_d}{8k_{el}} \left( 1 + \frac{{}^8k_{el}}{k_{bt}} \right) \right] \quad (3)$$

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

$${}^4k_q = ({}^2/9k_d) / \left[ 1 + \frac{1}{\frac{{}^4k_{en}^2}{k_d + k_{en}^2} + \frac{{}^4k_{en}^1}{k_d + k_{en}^1}} \right] \quad (5)$$

The measured quenching rate constants for the triplet states of the eight aromatic hydrocarbons by  $\text{Fe}(\text{hfac})_3$  define a plateau value  $k_p = (7.9 \pm 0.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This is close to the diffusion-controlled rate constant expected for benzene<sup>28</sup> of  $1.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Thus, if there are any spin restrictions on the maximum quenching constants attainable for quenching by  $\text{Fe}(\text{hfac})_3$ , they must be small. The first two steps in Figure 2, for the correlation of  $\log k_q$  vs.  $E_T$

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for Fe(acac)<sub>3</sub>, are due to the <sup>4</sup>T<sub>1g</sub> and <sup>4</sup>T<sub>2g</sub> states accepting electronic energy, but assigning the third accepting state as a sextet charge-transfer state is questionable.<sup>8</sup> The rapid increase in quenching occurs well before the energy corresponding to the charge-transfer absorption band maxima although this rapid rise occurs reasonably close to the value of  $\bar{\nu}_{0.05}$  (see Table II).  $\bar{\nu}_{0.05}$  has been related by Adamson et al.<sup>29</sup> to the energy of the relaxed "thexi" state in some chromium ligand field transitions. The width of the charge-transfer transitions with  $\bar{\nu}_{\max} = 2.80 \mu\text{m}^{-1}$  in Fe(acac)<sub>3</sub> is so broad (half-band width  $0.5 \mu\text{m}^{-1}$ ) that it seems possible there may be another weaker hidden transition lying to lower energies than that responsible for the band maxima observed. The steep rise in quenching constant indicates a low intrinsic barrier, and the large plateau rate constant indicates a relatively large transmission coefficient, which would be compatible with the assignment of this state as a nonligand field state. In addition the next quartet ligand field states (<sup>4</sup>A<sub>g</sub>, <sup>4</sup>E<sub>g</sub>) from comparison with other complexes where it has been observed<sup>30</sup> and by prediction from the ligand field parameters given in ref 6 are expected to lie at considerably higher energies (see Table III). Thus, the simplest scheme for energy transfer is as shown in Scheme I, i.e. transfer can occur depending on the energy of the donor to give two quartets and a sextet state. There are no low-lying electronically excited octet states expected or found for these iron(III)  $\beta$ -diketonates (see Table III and ref 6 and 23). Thus, the maximum possible quenching constant expected from energy transfer to give quartet and sextet excited states of the quencher is  $(2/9 + 1/3)k_d$ , i.e.  $\sim 5.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

If reverse electron transfer competes with energy transfer and this only occurred via quartet and sextet encounter complexes, then the limiting quenching constant would still be  $5.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . In order to explain quenching constants as high as those given in Table II for Fe(hfac)<sub>3</sub>, it is essential to include considerable quenching via exciplexes with a spin multiplicity of 8. Thus, the simplest possible mechanism that explains quenching by Fe(acac)<sub>3</sub>, Fe(tfac)<sub>3</sub>, and Fe(hfac)<sub>3</sub> is that shown in Scheme I, which resembles closely that used by us recently to explain quenching by Cr(hfac)<sub>3</sub> in benzene as a result of competition between energy transfer and reverse electron transfer.<sup>10</sup>

Balzani et al.<sup>28</sup> have shown that energy and electron transfer from electronically excited states can be treated classically with the same formalism. Thus

$$\ln k_{\text{en}}/k_{-\text{en}} = -\Delta G_{\text{en}}/RT$$

and

$$\ln k_{\text{el}}/k_{-\text{el}} = -\Delta G_{\text{el}}/RT$$

where  $\Delta G_{\text{en}}$  the standard free energy change for the energy-transfer process can be obtained from the zero-zero transition wavenumber of the energy donor and acceptor  $\bar{\nu}_{00}({}^3\text{D}^*)$  and  $\bar{\nu}_{00}(\text{Q}^*)$ , respectively. It is usually assumed that

$$\Delta G_{\text{en}} = -hNc[\bar{\nu}_{00}({}^3\text{D}^*) - \bar{\nu}_{00}(\text{Q}^*)]$$

From transition-state theory

$$k_{\text{en}} = \kappa_{\text{en}}kT/h \exp(-\Delta G_{\text{en}}^*/RT)$$

and

$$k_{\text{el}} = \kappa_{\text{el}}kT/h \exp(-\Delta G_{\text{el}}^*/RT)$$

where  $\Delta G_{\text{en}}^*$  and  $\Delta G_{\text{el}}^*$  represent the free energies of activation and  $\kappa_{\text{en}}$  and  $\kappa_{\text{el}}$  the transmission coefficients for energy and

electron transfer, respectively. Several free energy relationships<sup>31-34</sup> have been and still are being used to relate  $\Delta G^*$  to  $\Delta G$ . We choose to use that of Agmon and Levine;<sup>33</sup> viz:

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

where  $\Delta G^*(0)$ , the free energy of activation when  $\Delta G = 0$ , is an adjustable parameter often referred to as the intrinsic barrier.

Applying the steady-state approximation to the mechanism given by eq 1 gives expression 3 with  $k_{\text{el}}$  and  $k_{-\text{el}}$  in place of  ${}^8k_{\text{el}}$  and  ${}^8k_{-\text{el}}$ . The curve drawn in Figure 3 correlating  $\log k_q$  with  $\Delta G_{\text{el}}$  for both Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub> was calculated with eq 3 by taking  $k_d = 1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $k_{-d} = 1.2 \times 10^{10} \text{ s}^{-1}$  (after Balzani et al.<sup>28</sup>),  $k_{\text{bt}} > 10^{10} \text{ s}^{-1}$  (see also ref 10),  $\kappa_{\text{el}} = 7.6 \times 10^{-3}$ , and  $\Delta G_{\text{el}}^*(0) = 0.26 \text{ eV}$ . These latter two values were varied to give a good fit to the data. This treatment assumes that the donors can be treated as a homogeneous series with constant intrinsic barriers and transmission coefficients as in the case of both Cr(acac)<sub>3</sub> and Cr(hfac)<sub>3</sub>.<sup>9,10</sup> In addition this curve is drawn on the assumption that quenching is only due to reversible electron transfer with no spin restrictions.

The curve drawn through the experimental points in Figure 2 for quenching by Fe(acac)<sub>3</sub> is based on Scheme I on the assumption that reversible charge-transfer quenching is negligible and with  $\bar{\nu}_{00}$  values of 0.84, 1.33, and  $1.65 \mu\text{m}^{-1}$  as well as  $\kappa_{\text{en}}$  values of  $5.9 \times 10^{-4}$ ,  $2.9 \times 10^{-4}$ , and  $5.4 \times 10^{-3}$  for the <sup>4</sup>T<sub>1g</sub>, <sup>4</sup>T<sub>2g</sub>, and <sup>6</sup>CT states, respectively. Although most of the experimental data on Fe(acac)<sub>3</sub> have already been published and discussed, a few comments are needed here. First, a value of  $8400 \pm 300 \text{ cm}^{-1}$  for  $\bar{\nu}_{00}({}^4\text{T}_{1g})$  is required mostly to fit the quenching constant of pentacene. Unfortunately  $\bar{\nu}_{00}({}^3\text{D}^*)$  for triplet pentacene is a theoretical value.<sup>17</sup> It could be out by  $\pm 1000 \text{ cm}^{-1}$ , implying that the fit requires  $\bar{\nu}_{00}({}^4\text{T}_{1g}) = 8400 \pm 1300 \text{ cm}^{-1}$ , which means that the value agrees within experimental error with the  $\bar{\nu}_{\max}$  value for the <sup>4</sup>T<sub>1g</sub> ← <sup>6</sup>A<sub>1g</sub> transition given in Table III. In order to explain quenching by exchange energy transfer,  $\bar{\nu}_{00}({}^4\text{T}_{2g}) = 13300 \pm 800 \text{ cm}^{-1}$ , which agrees very well with the spectroscopic value. In addition, the energy transfer correlation requires  $\bar{\nu}_{00}({}^6\text{CT}) = 16500 \pm 200 \text{ cm}^{-1}$ . In fact this value is, as mentioned earlier,  $1500 \text{ cm}^{-1}$  lower than the  $\bar{\nu}_{0.05}$  value for this transition.  $\Delta G_{\text{en}}^*(0)$  was taken as 0.03 eV for the first two ligand field states and 0.04 eV for the sextet charge-transfer state.

In order to compare the experimental quenching constants with expectations based on Scheme I for quenching by Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub>, we have used the energy-transfer parameters obtained above for Fe(acac)<sub>3</sub> allowing for the small shifts in  $\bar{\nu}_{00}({}^4\text{T}_{1g})$  and  $\bar{\nu}_{00}({}^6\text{CT})$  taken equal to the measured shifts given in Table III for  $\bar{\nu}_{\max}({}^4\text{T}_{1g})$  and  $\bar{\nu}_{0.05}({}^6\text{CT})$  for Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub>. Confirmation that such a treatment is justified is the fact that the quenching constant predicted for triplet acridine by Fe(tfac)<sub>3</sub>, which cannot be explained by reversible electron-transfer quenching alone, is within experimental error (see Table IV), and the overall fit of the experimental results to theory is invariably improved in the case of Fe(tfac)<sub>3</sub>. In the case of Fe(hfac)<sub>3</sub>, reversible electron transfer dominates virtually every value obtained. We have assumed since  $\Delta G_{\text{el}}$  is the same for sextet and octet exciplexes

$$\Delta G_{\text{el}}^*(0) = {}^6\Delta G_{\text{el}}^*(0) = {}^8\Delta G_{\text{el}}^*(0)$$

and

$$\kappa_{\text{el}} = {}^6\kappa_{\text{el}} = {}^8\kappa_{\text{el}}$$

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**Table IV.** Comparison of Calculated<sup>a</sup> Quenching Constants Based on Scheme I with Experimental Values (Given in Parentheses)

	$k_q/10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
	Fe(tfac) <sub>3</sub>	Fe(hfac) <sub>3</sub>
benzophenone triphenylene	4.3 ± 0.5 (3.5 ± 0.3)	7.5 ± 0.1 (7.5 ± 0.5)
phenanthrene	6.5 ± 0.2 (6.5 ± 0.4)	7.8 ± 0.1 (7.9 ± 0.5)
2-acetylnaphthalene	5.7 ± 0.4 (4.9 ± 0.4)	7.7 ± 0.1 (6.7 ± 0.4)
chrysene	6.4 ± 0.2 (6.1 ± 0.3)	7.8 ± 0.1 (7.9 ± 0.4)
coronene	6.5 ± 0.2 (6.4 ± 0.6)	7.8 ± 0.1 (7.8 ± 0.6)
1,2,3,4-dibenzanthracene	6.0 ± 0.4 (5.4 ± 0.3)	7.8 ± 0.1 (7.9 ± 0.4)
pyrene	5.8 ± 0.4 (6.3 ± 0.4)	7.8 ± 0.1 (7.8 ± 0.4)
acridine	1.7 $\begin{cases} +0.5 \\ -0.3 \end{cases}$ (1.9 ± 0.1)	reacts
anthracene	3.9 ± 0.8 (4.5 ± 0.2)	7.5 ± 0.1 (7.8 ± 0.4)
perylene	3.3 ± 0.8 (3.8 ± 0.2)	7.3 ± 0.1 (7.9 ± 0.4)
pentacene	0.9 $\begin{cases} +0.8 \\ -0.5 \end{cases}$ (0.8 ± 0.08)	6.4 ± 0.3 (5.1 ± 0.5)
β,β-carotene	0.6 $\begin{cases} +0.6 \\ -0.4 \end{cases}$ (0.65 ± 0.04)	reacts

<sup>a</sup> Best fit values with  $\kappa_{el} = 7.2 \times 10^{-3}$  and  $16 \times 10^{-3}$  for Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub>, respectively,  $\Delta G_{el}^{\ddagger}(0) = 0.26 \text{ eV}$  for both quenchers, and energy-transfer parameters based on best fit of quenching data of Fe(acac)<sub>3</sub> (see Figure 2 and text). Range of values was calculated with the assumption of an uncertainty in  $\Delta G_{el} = \pm 0.1 \text{ eV}$ .

The fits require  $\kappa_{el}$  values of  $7.2 \times 10^{-3}$  and  $16 \times 10^{-3}$ , respectively, and  $\Delta G_{el}^{\ddagger}(0)$  values of 0.26 eV for both Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub>. There is considerable uncertainty about the value of  $\Delta G_{el}^{\ddagger}(0)$  for Fe(hfac)<sub>3</sub> because most of the quenching constants for Fe(hfac)<sub>3</sub> have reached a plateau value of  $7.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . We have also fitted the experimental data to a scheme that eliminates spin restrictions for reversible electron transfer; i.e., reversible electron transfer is assumed possible for quartet, sextet, and octet exciplexes. The value of  $\Delta G_{el}^{\ddagger}(0)$  does not change, but as one would expect when another channel is opened up for reverse electron transfer, the value of  $\kappa_{el}$  drops slightly to  $5.4 \times 10^{-3}$  for Fe(tfac)<sub>3</sub> and it was

found that this fit is not as good as that from Scheme I. Thus, as well as being the simplest, Scheme I fits the experimental facts best. It is worth noting that all the different treatments give intrinsic barrier values of  $0.26 \pm 0.02 \text{ eV}$  and the transmission coefficient values for the various approaches for quenching by Fe(tfac)<sub>3</sub> and Fe(hfac)<sub>3</sub> only vary in the range  $(5.4-16) \times 10^{-3}$ .

It is of interest to compare the best fit parameters of  $\kappa_{el} = 0.016$  and  $\Delta G_{el}^{\ddagger}(0) = 0.26 \text{ eV}$  obtained in this work for reversible electron-transfer quenching by Fe(hfac)<sub>3</sub> of triplet states after making due allowance for energy-transfer quenching as in Scheme I, which gives the predicted values in Table IV with the best fit values obtained for triplet-state quenching by Cr(hfac)<sub>3</sub> where competitive energy and electron transfer were occurring. The best fit values of the transmission coefficients are the same, but an intrinsic barrier of  $\Delta G_{el}^{\ddagger}(0) = 0.16 \text{ eV}$  was obtained in the case of Cr(hfac)<sub>3</sub> where the Cr(II) produced is probably high spin.<sup>10</sup> According to outer-sphere electron-transfer theory, this difference would be attributed to higher intrinsic barrier for self-exchange in the Fe<sup>III</sup>/Fe<sup>II</sup> couple as opposed to the Cr<sup>III</sup>/Cr<sup>II</sup> couple, which can be interpreted in terms of the frequencies of critical promoting modes and the magnitude of the nuclear displacement associated with the individual vibrations. For a recent discussion see ref 35. It will be of interest to see whether this difference persists by comparison of reverse electron-transfer parameters for quenching by other ligands coordinated to Cr<sup>III</sup> and Fe<sup>III</sup> and to extend these studies to other central atoms. Such work is at present in progress.

**Registry No.** Fe(tfac)<sub>3</sub>, 14526-22-8; Fe(hfac)<sub>3</sub>, 17786-67-3; xanthone, 90-47-1; benzophenone, 119-61-9; triphenylene, 217-59-4; phenanthrene, 85-01-8; 2-acetylnaphthalene, 93-08-3; chrysene, 218-01-9; coronene, 191-07-1; 1,2,5,6-dibenzanthracene, 53-70-3; 1,2,3,4-dibenzanthracene, 215-58-7; pyrene, 129-00-0; acridine, 260-94-6; anthracene, 120-12-7; perylene, 198-55-0; methylene blue, 61-73-4; anthracene, 120-12-7; 2,3-benzanthracene, 92-24-0; pentacene, 135-48-8; β,β-carotene, 7235-40-7.

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Contribution from the Department of Chemistry,  
The University of Texas, Austin, Texas 78712

## The Nature of the S≡C Triple Bond

JAMES E. BOGGS

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The structures of SH<sub>3</sub>≡CH, SF<sub>3</sub>≡CH, SF<sub>3</sub>≡CF, and the staggered and eclipsed conformations of SF<sub>3</sub>≡C—CF<sub>3</sub> have been fully optimized by ab initio Hartree-Fock gradient calculations using a 3-3-21 basis set with added polarization functions for S and a 4-21 basis for C and F. The SH<sub>3</sub> and SF<sub>3</sub> groups are essentially in an octahedral configuration with XSC angles between 91 and 93° in every case. The remaining three sulfur orbitals make up the S≡C triple bond, which has a length of 1.41-1.45 Å, compared with a S=C double-bond length of 1.54 Å in SF<sub>4</sub>=CH<sub>2</sub>. Orbitals localized according to the Boys definition are used to assist in the interpretation of the geometric results. Tests are made with larger basis sets (d functions on all heavy atoms; d functions on all heavy atoms with two sets of d functions on S) to ensure basis set convergence in the computed angles in SF<sub>3</sub>≡CH. Comparisons are made with geometries in other compounds.

### Introduction

The hypervalent compounds of sulfur are currently attracting a great deal of attention both from preparative chemists and from theorists who are concerned with developing an understanding of the bonding involved. The known variety of such compounds has expanded in recent years as new compounds with multiple bonds to sulfur have been successfully synthesized. Especially interesting are the compounds

with S=C double bonds, such as SF<sub>4</sub>=CH<sub>2</sub>,<sup>1</sup> and the even more recently prepared triply bonded compound SF<sub>3</sub>≡C—CF<sub>3</sub>.<sup>2</sup> The electronic and geometric structures of SF<sub>4</sub>=CH<sub>2</sub> have been investigated previously<sup>3</sup> by ab initio gradient com-

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