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A Study of Quenching of Triplets by Ferrocene

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Rate constants for quenching of several triplets by ferrocene have been determined in ethanol. Most triplets have been found to be deactivated by ferrocene, yielding no observable transient absorption. The rate constant increases with increasing triplet energy in the range 8000—17000 cm^{-1}. The quenching mechanism has been discussed, the lowest triplet level of ferrocene being estimated to be 15000±1000 cm^{-1}.

It is well-known that ferrocene is an excellent quencher for many triplets of organic compounds.[1-3] Fry *et al.*[1] investigated the quenching of typical triplets by ferrocene and found that all triplets whose levels are located between 14000 and 23800 cm^{-1} are quenched by ferrocene at about a diffusion-controlled rate. However, they found no evidence for the formation of excited states of ferrocene, and could not account for the quenching mechanism.

Scott and Becker[4] observed an S→T absorption of ferrocene at 18940 cm^{-1} and a long-lived emission interpreted to be phosphorescence in EPA at 77 K, since the location corresponds to the band assigned to S→T absorption. Armstrong *et al.*[5] observed S→T absorption bands of ferrocene at 14000, 16500 and 18500 cm^{-1}, but no emission in EPA at 77 K. Smith and Meyer[6] observed phosphorescence at 20 K which has an emission peak at 21500 cm^{-1} in argon and at 20000 cm^{-1} in methane matrix. Information on the triplet of ferrocene is very conflicting and the lowest triplet level of ferrocene cannot be estimated exactly. However, it seems certain that the triplet level is higher than 14000 cm^{-1}.

All the triplet levels of the compounds studied by Fry *et al.* are higher than 14000 cm^{-1}. Thus a study of quenching by ferrocene for triplets having energy levels lower than 14000 cm^{-1} is expected to clarify, whether it is a triplet energy transfer or not. A triplet with energy level lower than 14000 cm^{-1} can not be quenched if the quenching is due to triplet energy transfer, but can be quenched if it is due to another mechanism. We have determined accurately the rate constants of quenching of several triplets whose levels are located between 8000 and 23800 cm^{-1}.

Experimental

Materials. Ferrocene (G. R. grade, Tokyo Kasei) was purified by recrystallization from benzene, zone refining twice, and sublimation twice. Pentacene and tetracene (G. R. grade, Tokyo Kasei) were used without further purification, but confirmed by measuring absorption and fluorescence spectra. Ethanol (G. R. grade, Wako Junyaku) was used without further purification. All other reagents were purified by standard methods.

Apparatus and Procedure. The flash energy was usually about 130 J, its half duration being about 10 μs. A Hoya-U2 or Toshiba V-051 filter was used for excitation. All measurements were made at room temperature. Ethanol solutions were degassed by repeating bulb to trap distillation in vacuum. Benzene solutions were degassed by freeze-pump-thaw method.

Results and Discussion

The dependence of decay curves of triplets upon the concentration of ferrocene has been studied. The observed first-order rate constants, k_{obs}, of perylene and anthracene are plotted against the ferrocene concentration in Fig. 1 as a typical example. From the plots the quenching rate constant k_q is obtained, since the observed first-order rate constant is given by

$$k_{\text{obs}} = k_t + k_q\,[\text{Ferrocene}] \qquad (1)$$

where k_t is the pseudo-first order rate constant of triplet deactivation in the absence of ferrocene.

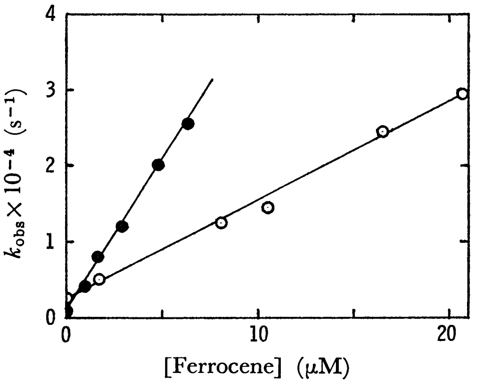

Fig. 1. The dependence of the decay rate of triplet upon the concentration of ferrocene.
○: Perylene, 8×10^{-5} M
●: Anthracene, 1×10^{-4} M

Table 1. Rate constants for quenching of triplets by ferrocene and ΔG-values

Compound	Triplet level (cm^{-1})	Quenching rate constant (M^{-1} s^{-1})	ΔG (kcal/mol)
Triphenylene	23800	$(6.5\pm0.5)\times10^9$	−6.2
Naphthalene	21300	$(7.0\pm1.5)\times10^9$	2.1
β-Acetonaphthone	20700	$(6.0\pm0.5)\times10^9$	
1,2,5,6-Dibenzanthracene	18300	$(5.0\pm1.0)\times10^9$	
Pyrene	16800	$(6.0\pm0.5)\times10^9$	5.5
Phenazine	15250	$(4.6\pm0.5)\times10^9$	
Eosine	14800	$(3.5\pm0.5)\times10^9$	
Anthracene	14700	$(3.5\pm0.5)\times10^9$	8.2
Perylene	12600	$(1.3\pm0.1)\times10^9$	7.1
Tetracene	10250	$(4.6\pm0.5)\times10^7$	10.8
Pentacene[a)]	8000	$\ll10^7$	

a) In benzene.

The quenching rate constants in ethanol are summarized in Table 1. It is apparent that triplets having higher energy than 16000 cm^{-1} are quenched by ferrocene at about a diffusion-controlled rate* in accordance with the result of Fry *et al.*, but the quenching rate decreases with lowering triplet level between 8000 and 15000 cm^{-1}, and finally pentacene triplet, 8000 cm^{-1}, is scarcely quenched at all.

It is well-known that the rate of triplet energy transfer becomes slower owing to the reversible energy transfer when triplet levels of donor and acceptor are close to each other.[7–9] Sandros[8] studied the reversible energy transfer between biacetyl and many aromatic hydrocarbons, and found that the rate constant of energy transfer, k, is related to the difference of triplet levels of donor and acceptor, ΔE_T, as follows:

$$k = k_D \cdot \frac{1}{1+\exp(-\Delta E_T/RT)} \qquad (2)$$

where k_D is the diffusion-controlled rate constant, R is the gas constant and $\Delta E_T = E_T(\text{Donor}) - E_T(\text{Acceptor})$. Since $k \simeq k_D$ when $\Delta E_T \gg RT \simeq 200$ cm^{-1}, $k = \frac{1}{2} k_D$ when $\Delta E_T = 0$ cm^{-1}, and $k < k_D/140$ when $\Delta E_T < -1000$ cm^{-1}, the rate constant of the energy transfer decreases about two orders of magnitude as compared with the diffusion-controlled rate constant when the triplet level of acceptor (quencher) is higher than that of donor by 1000 cm^{-1}. Irrespective of the triplet level of ferrocene, it is obvious that the dependence of the quenching rate constant on the triplet level (Table 1) is too small as compared with the case of the energy transfer. Thus the results cannot be explained by energy transfer only.

It has been reported that the triplet level of ferrocene is higher than 14000 cm^{-1}, but it is necessary i) to confirm by kinetic study that triplet of tetracene is quenched not by energy transfer but by another mechanism, and ii) to clarify the reason why no transient absorption of ferrocene can be observed. We carried out the kinetic study of i) by examining the data given in Table 1. Assuming that tetracene triplet is quenched by energy transfer from tetracene triplet to ferrocene, we can calculate the triplet level of ferrocene by Eq. (2). From the values $k_D = 6 \times 10^9$ M^{-1} s^{-1} and $k = 4.6 \times 10^7$ M^{-1} s^{-1}, $\Delta E_T = E_T(\text{tetracene}) - E_T(\text{ferrocene}) = -990$ cm^{-1} was obtained. Thus the triplet level of ferrocene is estimated to be 11240 cm^{-1}. If this is the case, all the triplets having levels higher than about 12000 cm^{-1} should be quenched by ferrocene at the diffusion-controlled rate. However, this is inconsistent with the results (Table 1). Thus we could conclude that the quenching of tetracene triplet is not due to energy transfer, and that the triplet level of ferrocene is higher than 12000 cm^{-1}, which is in line with earlier reports.[4–6] For ii) we carried out an energy transfer experiment for a mixed system of eosin (D), tetracene (A) and ferrocene (F), in which eosin is at first irradiated selectively by a flash, the triplet eosin acting as an energy donor. The reaction scheme is described as follows.

(0) $D \xrightarrow{\phi_{ST} I_{ab}} {}^3D$

(1) ${}^3D \longrightarrow D$

(2) ${}^3D + F \longrightarrow D + {}^3F$

(3) ${}^3D + A \longrightarrow D + {}^3A$

(4) ${}^3F + A \longrightarrow F + {}^3A$

(5) ${}^3F \longrightarrow F$

(6) ${}^3A \longrightarrow A$

(7) ${}^3A + F \longrightarrow A + {}^3F$

If the rate of deactivation of tetracene triplet is negligibly small in comparison with that of other triplets, the concentration of tetracene triplet immediately after flashing is given by

$$[{}^3A]_0 = \frac{1}{k_1+k_2[F]+k_3[A]} \cdot \left(k_3[A] + \frac{k_4[A]}{k_4[A]+k_5} \cdot k_2[F]\right) \cdot \phi_{ST} I_{ab} \,. \qquad (3)$$

When $[F]=0$, we have

$$[{}^3A]_0^0 = \frac{k_3[A]}{k_1+k_3[A]} \cdot \phi_{ST} I_{ab} \,. \qquad (4)$$

From Eqs. (3) and (4) we get

$$\frac{[{}^3A]_0^0}{[{}^3A]_0} = 1 + \frac{k_2[F]}{k_1+k_3[A]} - \frac{[{}^3A]_0^0}{[{}^3A]_0} \cdot \frac{k_4[A]}{k_4[A]+k_5} \cdot \frac{k_2[F]}{k_3[A]} \qquad (5)$$

Figure 2 shows the plot of $[{}^3A]_0^0/[{}^3A]_0$ *vs.* [F] for $[D] = 6.3 \times 10^{-6}$ M and $[A] = 5.0 \times 10^{-5}$ M. A straight line was obtained. This implies that the third term of the right-hand side of Eq. (5) is negligibly small as compared with the first and the second terms. Thus, $k_5 \gg k_4$ [A] or $k_4 \approx 0$. But it is obvious that $k_5 \gg k_4[A]$, because $k_4 \approx 0$ is very unlikely. Eq. (5) can thus be written as

$$\frac{[{}^3A]_0^0}{[{}^3A]_0} = 1 + \frac{k_2[F]}{k_1+k_3[A]} \,, \qquad (6)$$

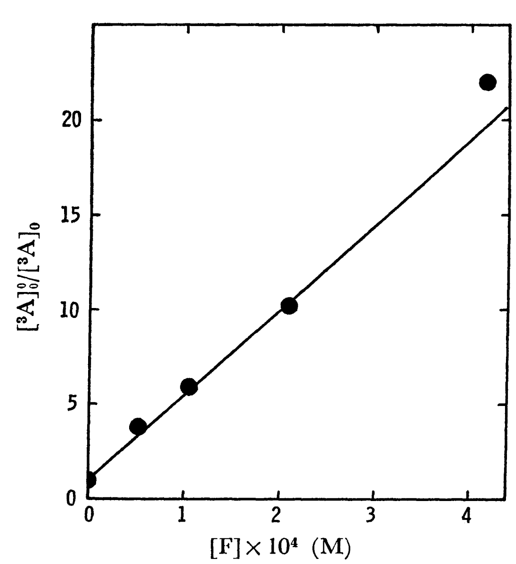

Fig. 2. The plot of $[{}^3A]_0^0/[{}^3A]_0$ *vs.* [F].
Straight line was calculated according to Eq. (6) by using independent data.

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* Most published rate constants for triplet quenching are about 5×10^9 M^{-1} s^{-1}.

where $[A]=5.0\times10^{-5}$ M**. The slope, $k_2/(k_1+k_3[A])$, agrees with the calculated value using $k_1=1.0\times10^3$ s^{-1}, $k_2=3.5\times10^9$ M^{-1} s^{-1}, and $k_3=1.5\times10^9$ M^{-1} s^{-1}, which have been obtained by other independent flash experiments. $k_5 \gg k_4[A]$ implies that the energy transfer from ferrocene triplet to tetracene is inefficient. This is attributable to the fast deactivation of ferrocene triplet, because $k_5 \gg 10^5$ s^{-1} if k_4 is of the order of the diffusion-controlled rate constant. This is consistent with the fact that no transient absorption owing to ferrocene has been observed by the conventional flash technique.

The triplet level of ferrocene can be estimated as 15000 ± 1000 cm^{-1} by the following considerations; 1) it has been reported that the triplet level of ferrocene is higher than 14000 cm^{-1}, 2) all triplets having a level higher than 16000 cm^{-1} are quenched with the diffusion-controlled rate, 3) the quenching rates of anthracene and eosin triplet are nearly one-half of the diffusion-controlled rate, 4) the quenching of tetracene triplet by energy transfer to ferrocene is highly improbable, 5) the rate constant of energy transfer decreases by about two orders of magnitude as compared with the diffusion-controlled rate constant when the triplet level of acceptor is higher than that of donor by 1000 cm^{-1}, and is practically the diffusion-controlled rate constant when the triplet level of donor is higher than that of acceptor by 500 cm^{-1}, 6) the reversible energy transfer is very inefficient because the lifetime of ferrocene triplet may be very short,7) as the rate of energy transfer depends on ΔE_T predominantly and other factors, it would be suitable to estimate the error as ±1000 cm^{-1}.

Rosenblum *et al.*[10] have reported that ferrocene forms a charge transfer complex with tetracyanoethylene owing to low ionization potential of ferrocene. The quenching of fluorescence due to charge transfer interaction between fluorescer and quencher is widely known.[11] Thus it is necessary to examine the possibility of triplet quenching by charge-transfer interaction, although quenching of triplet by charge transfer interaction has scarcely been reported at all. The changes of free enthalpy (ΔG) involved in the electron transfer reactions[11] are calculated approximately and listed in Table 1. It seems that a qualitative correlation between the rate constant and ΔG is satisfactory. This strongly suggests that charge transfer interaction is involved in the quenching.

If the triplet quenching by ferrocene is exclusively attributed to the electron transfer reaction, detection of anion originating in the triplet might be expected. However, no additional transient absorption was observed by the addition of ferrocene. Triphenylene which is most expected to produce anion was also examined in acetonitorile, but no additional transient absorption was observed. If the quenching is due to the charge transfer interaction, it seems most likely that the lifetime of charge transfer complex is extremely short.

Porter and Wright[12] studied the quenching action of various metal ions to naphthalene triplet in water and in ethylene glycol, and found that paramagnetic metal ions of first transition series deactivate the triplet at the rate constant, $k_q \approx 5\times10^7$ M^{-1} s^{-1}. As the rate constant of quenching for tetracene triplet is 4.6×10^7 M^{-1} s^{-1}, the quenching ability of ferrocene for tetracene triplet is similar to that of Fe^{2+} and Fe^{3+}. However, pentacene triplet has not been quenched by ferrocene in benzene, and paramagnetic quenching cannot be considered, since ferrocene is diamagnetic. It thus seems that the iron atom in ferrocene does not contribute directly to the quenching.

If several compounds with triplet levels between 8000 and 15000 cm^{-1} are contained simultaneously in ferrocene as impurities, the results might be interpreted as those given in Table 1. But quenching by such impurities is improbable since no emissoin due to impurities has been observed in concentrated solution of ferrocene. The result in Fig. 2 denies the existence of such impurities.

Consequently, it seems that the quenching of triplet by ferrocene might occur according to the following mechanisms. As the triplet level of ferrocene has been estimated as 15000 ± 1000 cm^{-1}, a triplet with a level higher than 15000 cm^{-1} would be quenched mainly by the energy transfer, but a triplet with a level lower than 13000 cm^{-1} would be quenched by another mechanism. The most probable mechanism would be the instantaneous formation of charge transfer complex with an extremely short lifetime.

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** Eq. (6) is also satisfied when $k_4[A]+k_5 \ll k_6+k_7[F]$, where $[A]=5\times10^{-5}$ M, $k_6=1.2\times10^3$ s^{-1} and $k_7=4.6\times10^7$ M^{-1} s^{-1}. However, this assumption is improbable, since the triplet level of ferrocene is higher than that of tetracene.