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Energy Transfer from Triplet Acetophenones to 9,10-Dibromoanthracene (S_1): Role of Its T_n State

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Abstract: The efficiency of energy transfer to 9,10-dibromoanthracene (S_1) (DBA, $0.5–5 \times 10^{-4}$ M) from triplet acetophenone, methyl-substituted acetophenones, and indanone (**1**) (0.02 M, $E_T = 71.5–75.8$ kcal) was measured as a function of temperature (1–57 °C) in acetonitrile. The decay of DBA fluorescence follows double-exponential functions, with a ca. 2-ns component (direct DBA excitation) and a ca. 0.1–3-μs component (sensitization by triplet ketone). The rate parameters are the same for all ketones, but the amplitude of the slow component depends on the triplet energy of the ketone. With Φ_{TS} defined as k_{TS}/k_{ET}, $\Phi_{TS} = 0.3$ for **1** ($E_T = 75.8$ kcal) and 0.004 for 3,5-dimethylacetophenone ($E_T = 71.5$ kcal) at 20 °C; DBA deactivates all triplet ketones with $k_{ET} = 1.15 \times 10^{10}$ M^{-1} s^{-1}. The temperature dependence of Φ_{TS} shows the involvement of DBA (T_n), ca. 4 kcal above S_1, in a two-step exchange process: TT transfer to T_n (k_{TT_n}) and then isc $T_n \rightarrow S_1$. The E^a of k_{TT_n} matches the gap between E_T and DBA (T_n). Φ_{TS} of **1** is close to the limit set by the isc efficiency in DBA (ca. 0.3–0.4); thus, the 35-kcal exothermic triplet transfer to DBA (T_1) is unimportant compared with the near-isothermic transfer to T_n.

Many studies have addressed the role of higher excited states of anthracenes in intersystem-crossing (isc) and energy-transfer processes.[1,2] For example, the effect of temperature and of meso substituents on the fluorescence quantum yield can be readily understood on the basis of the position of higher triplet states relative to S_1 in these compounds.[3-7] A case in point is 9,10-dibromoanthracene (DBA). Its fluorescence efficiency Φ_F decreases from unity at 77 K[4,7] to ca. 0.1 at room temperature in ethanol,[6] because fluorescence competes with intersystem crossing to a higher triplet manifold; this mediated isc process[2] depends on temperature, according to an Arrhenius equation (eq 1), where

$$k_{isc} = A_{isc} \exp(-E_{isc}/RT) \qquad (1)$$

$E_{isc} \approx 4 \pm 1$ kcal.[7] Thus, in DBA at least one (and possibly several) higher triplet state(s) is estimated to be located ca. 4 ± 1 kcal above S_1.[8,9] Solvents shift S_1 and T_n ($n \geq 2$) to different extents and therefore E_{isc} and Φ_F are solvent dependent.[6] Recent experiments of Amirav and Jortner with jet-cooled isolated DBA, prepared in the S_1 state with excess vibrational energy, have refined the understanding of mediated isc.[2]

This T_n state may also be important in exothermic energy transfer from triplet donors to DBA, a process known to result in part in DBA (S_1).[10] With some triplet donors, such as acetophenone, this spin-forbidden process has a remarkably high efficiency, $\Phi_{TS} \approx 0.1$,[11] defined here by eq 2, where k_{TS} and k_{ET} are the rate constants of reactions 3 and 4. Equation 3 is the

$$\Phi_{TS} = k_{TS}/k_{ET} \qquad (2)$$

$$^3K^* + DBA \xrightarrow{k_{TS}} K + DBA\ (S_1) \qquad (3)$$

$$^3K^* + DBA \xrightarrow{k_{ET}} K + DBA \qquad (4)$$

overall process leading to the formation of DBA (S_1), while eq 4 represents all processes of deactivation of the triplet donor $^3K^*$ by DBA, which result mostly in the formation of DBA (T_1). Such high values of Φ_{TS} as 0.1 allow DBA (or a water-soluble sulfonated derivative[12b]) to serve as a fluorescence probe for the generation of triplet excited molecules in chemical or biochemical reactions.[12a] This property, which has been widely exploited, adds a practical interest to the study of energy transfer to DBA. Yet the exact mechanism of this process has not been definitely established, and significant differences in values of Φ_{TS} between triplet carbonyl donors, for example, remain unexplained. The present paper addresses, and answers, some of these questions.

Both long-range (Forster) and collisional (exchange) interactions could in principle be at play in eq 3; arguments in support of both have indeed been offered. A major contribution from Forster energy transfer can, however, be safely ruled out, since the efficiency of such a process should not be affected by the presence of heavy atoms in the acceptor.[13] Yet chemiluminescence and time-resolved fluorescence studies have established, for example, that Φ_{TS} is 1 order of magnitude higher with DBA than with 9,10-dichloroanthracene, although these two anthracenes have almost identical absorption spectra.[15,16]

If, on the other hand, the energy-transfer process is collisional and requires prior formation of an encounter complex (eq 5), two

$$^3K^* + DBA \underset{k_{-diff}}{\overset{k_{diff}}{\rightleftharpoons}} (^3K^*DBA) \qquad (5)$$

distinct mechanisms need be considered. In the first, eq 3 may be viewed as representing two consecutive processes, shown in Figure 1, a triplet–triplet energy transfer resulting in excitation of DBA (T_n) (eq 6) followed by isc from this higher triplet to DBA (S_1) (eq 7). The rate of the latter process is enhanced by the

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[1] Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970; pp 142–192.

[2] Amirav, A.; Jortner, J. *Chem. Phys. Lett.* **1986**, *132*, 335.

[3] Bennett, R. G.; McCartin, P. J. *J. Chem. Phys.* **1966**, *44*, 1969.

[4] Lim, E. C.; Laposa, J. D.; Yu, J. M. H. *J. Mol. Spectrosc.* **1966**, *19*, 412.

[5] Dreescamp, H.; Pabst, J. *Chem. Phys. Lett.* **1979**, *61*, 262.

[6] Wu, K.-C.; Ware, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 5906.

[7] Kearvell, A.; Wilkinson, F. *Transitions Non Radiatives dans les Molecules*; Paris, 1969; *J. Chim. Phys.* **1970**, *20*, 125.

[8] Gillispie, G. D.; Lim, E. C. *J. Chem. Phys.* **1976**, *65*, 2022; *Chem. Phys. Lett.* **1979**, *63*, 355.

[9] Tanaka, M.; Tanaka, I.; Tai, S.; Hamanoue, K.; Sumitani, K.; Yoshihara, K. *J. Phys. Chem.* **1983**, *87*, 813.

[10] Vasil'ev, R. F. *Nature (London)* **1963**, *200*, 773. Belyakov, V. A.; Vassil'ev, R. F. *Photochem. Photobiol.* **1970**, *11*, 179.

[11] Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7272.

[12] (a) Wilson, T. *Int. Rev. Sci.: Phys. Chem., Ser. Two* **1976**, *9*, 265. Turro, N. J.; Lechtken, P.; Schore, N. E.; Schuster, G.; Steinmetzer, H.-C.; Yekta, A. *Acc. Chem. Res.* **1974**, *7*, 97. Cilento, G. *Pure Appl. Chem.* **1984**, *56*, 1179. (b) Catalani, L. H.; Wilson, T.; Bechara, E. J. H. *Photochem. Photobiol.* **1987**, *45*, 273.

[13] The experiments of Turro et al.[14] with chemically generated triplet acetone (from tetramethyldioxetane) and DBA in polystyrene matrix were interpreted as suggesting an important contribution from long-range TS transfer. But the possibility of energy migration along the phenyl groups of the polymer and also of some SS transfer in these fluorescence intensity measurements complicates the analysis, as does the possible role of exciplexes of triplet acetone with the phenyl groups[15] of the polymer.

[14] Turro, N. J.; Steinmetzer, H.-C. *J. Am. Chem. Soc.* **1974**, *96*, 4677, 4679. Turro, N. J.; Kochevar, I. E.; Nogochi, Y.; Chow, M.-F. *Ibid.* **1978**, *100*, 3170.

[15] Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7279.

[16] Schmidt, R.; Kelm, H.; Brauer, H.-D. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81*, 402. *J. Photochem.* **1979**, *11*, 145.

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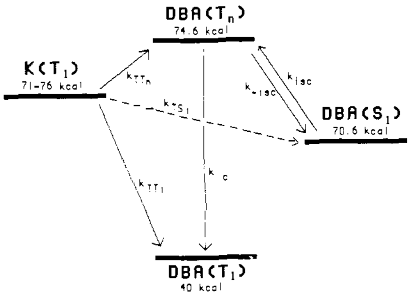


Figure 1. Diagram of excited states of an acetophenone (K) and 9,10-dibromoanthracene (DBA) illustrating the energy-transfer processes considered here.

bromine substituents and therefore able to compete with internal conversion (eq 8). This two-step mechanism was first proposed

$$({}^3K^*DBA) \xrightarrow{k_{TT_n}} K + DBA\ (T_n) \tag{6}$$

$$DBA\ (T_n) \xrightarrow{k_{-isc}} DBA\ (S_1) \tag{7}$$

$$DBA\ (T_n) \xrightarrow{k_{ic}} DBA\ (T_1) \tag{8}$$

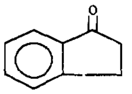
$$({}^3K^*DBA) \xrightarrow{k_{TT_1}} K + DBA\ (T_1) \tag{9}$$

by Schmidt et al.[16] on the basis of high-pressure experiments with chemically generated triplet acetone.[17] The conclusions of this study, designed primarily to evaluate the role of a long-range mechanism, were questioned by Wu, who proposed an alternative pathway, still within the framework of an exchange energy-transfer mechanism.[18] He argued that the bromine atoms introduce considerable triplet character in the singlet wave functions of DBA, and vice versa. Because of this mixing of states, reaction 3 is not truly "spin-forbidden". Therefore, within an encounter complex of $^3K^*$ and DBA, direct energy transfer to form DBA (S$_1$) takes place in competition with triplet-triplet transfer to form T$_1$ and T$_n$. Thus, Φ_{TS} now reflects the efficiency of formation of the encounter complex (eq 5) and the partition within the complex between reaction 10 and reactions 6 and 9.

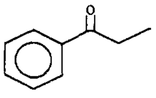
$$({}^3K^*DBA) \xrightarrow{k_{TS_1}} K + DBA\ (S_1) \tag{10}$$

As Wu pointed out, these alternative mechanisms (eq 5–7 or 5 and 10) lead to the same kinetic expression for Φ_{TS}. Neither can be dismissed a priori on the basis of unreasonable demand on the magnitude of the rate constants involved. Thus, whether or not T$_n$ is involved cannot be decided on the basis of the available experimental data.

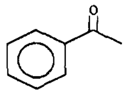
We have designed an experiment that provides a clear-cut answer to this question. Consider a series of energy donors of similar structures: indanone, acetophenone, and three methyl-substituted acetophenones (listed with their corresponding triplet energies, in kilocalories).[19a] Their triplet states are all above DBA (S$_1$) at ca. 70.6 kcal; therefore, TS energy transfer is exothermic in all cases. But some of these donors have their triplet above and some below DBA (T$_n$),[20] so that TT$_n$ energy transfer is either slightly exothermic, isothermic, or endothermic by up to 3 kcal. If T$_n$ is not involved, then eq 10 predicts that the relative Φ_{TS} values of these donors will be determined by the spectral overlap between the phosphorescence spectra of the donors and the absorption spectrum of DBA (eq 11).[21]



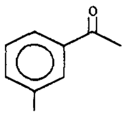
1 (75.8)



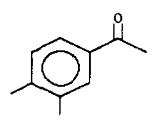
2 (74.6)



3 (74.1)



4 (72.5)



5 (71.5)

$$k_{TS} \propto \int_0^\infty P_D(\bar{\nu})\, \epsilon_{DBA}(\bar{\nu})\, d\bar{\nu} \tag{11}$$

On the other hand, if eq 6 and 7 represents the dominant mechanism, then one expects the energy-transfer process to be temperature dependent when the donor's triplet energy is below DBA (T$_n$), with a corresponding activation energy predictable on the basis of the energy gap between the donor triplet and DBA (T$_n$). This, in fact, is what we found.

Note that our analysis is simplified by the very short lifetime (ca. 2 ns) of the singlet excited state of DBA, the energy acceptor. The observed rates of forward TS energy transfer do not require correction for the rate of back-transfer, as is normally the case in triplet–triplet transfer studies when the process is near isothermicity and both triplets have long lifetimes.[21b]

The values of Φ_{TS}, k_{ET}, and therefore k_{TS} (eq 2) were determined by the time-correlated single-photon counting method, which has previously been shown to be ideally suited to the determination of these parameters in the case of acetophenone and two alkanones as triplet donors.[11,15] Pulsed UV excitation of solutions of ketones and DBA generates both direct and sensitized fluorescence of DBA. Consequently, the fluorescence of DBA decays as the sum of two exponentials of very different rate parameters (eq 12). DBA (S$_1$) is the emitter of the prompt as

$$I_t \propto \alpha \exp(-k_F t) + \exp(-k_{obsd} t) \tag{12}$$

well as the delayed fluorescence; thus, factors such as temperature that affect its rate of deactivation cancel out here. All necessary information on rates and yields can be extracted from eq 12, notably k_{ET} and Φ_{TS}.

The same method was also applied to the quenching of triplet ketones **1**, **3–5** by another brominated anthracene, 1,5-dibromo-9,10-bis(phenylethynyl)anthracene (DBPEA), also an efficient TS fluorescence probe.[22] Here Φ_{TS} was found to be the same for these four ketones, the differences in their triplet energies notwithstanding.

The implications of our results will be discussed in the context of the photophysics of DBA and DBPEA and of their use as triplet probes in chemiluminescence studies.

Experimental Section

Indanone (**1**), propiophenone (**2**), acetophenone (**3**), 3-methylacetophenone (**4**), and 3,4-dimethylacetophenone (**5**) were obtained from Aldrich and distilled before use. 9,10-Dibromoanthracene (DBA, Aldrich) was vacuum sublimed. 1,5-Dibromo-9,10-bis(phenylethynyl)anthracene (DBPEA) was a gift from Dr. A. P. Schaap, Wayne State

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[17] The solvent was toluene, which like benzene and methyl derivatives is known to form triplet exciplexes with acetone; these exciplexes are efficient energy donors to DBA.[15] This adds a complication to an already complex system.

[18] (a) Wu, K.-C. *J. Photochem.* **1980**, *12*, 363. (b) See, however: Schmidt, R.; Kelm, H.; Brauer, H.-D.; *Ibid.* **1980**, *14*, 261.

[19] (a) E_T values from the O–O band of phosphorescence emission in a polar solvent at 77 K determined by: S. L. Murov Ph.D. Thesis, University of Chicago, 1966. Listed in: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973. (b) In parentheses, net energies of the triplet states, i.e., the energy differences between relaxed T$_1$ and S$_0$, not the energies associated with vertical transitions. For justification, see: Kiri, A.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 196. Gessner, F.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7206. These net triplet energies were obtained from the E_T values of Murov[19a] by adding half of the Stokes shifts (1.1 ± 0.3 kcal for **1–3** with n,π^* lowest triplet; 0.7 ± 0.3 kcal for **4** and **5** with lowest triplet of π,π^* configuration; see ref 26). We also corrected for the relaxation of n,π^* (but not $^3\pi,\pi^*$) ketone triplets in fluid solutions, by substracting 2 kcal from the rigid solution values as recommended by Wagner.[26] Note that our conclusions are the same whether we adopt the E_T values from Murov or the revised net triplet energies, because the energy of the S$_1$ of DBA is always below the E_T of **1–5**.

[20] Estimated to be 74.5 kcal above S$_0$.[7]

[21] (a) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836. (b) Reference 1, pp 537–544.

[22] Schaap, A. P., private communication. Lampert, R. A.; Meech, S. R.; Metcalfe, J.; Phillips, D.; Schaap, A. P. *Chem. Phys. Lett.* **1983**, *94*, 137.

Table I. Efficiency and Temperature Dependence of Energy Transfer from Triplet Acetophenones to 9,10-Dibromoanthracene[a]

ketones	E_T[b]	Φ_{TS}[c]	spectral overlap[d] (rel)	$E_{TT_n}{}^{\mathrm{a}}$ [e]	$E_T + E_{TT_n}$[a,f] (rel)	Φ_{TS}[c] (rel)	$\exp(-E_{TT_n}{}^{\mathrm{a}}/RT)$[c]
1	75.8 (74.9)	0.30		(0)[g]	(75.8)[g] (74.9)[g]	2.3	4.6
2, 3	74.3_5 (73.4)	0.13	1.00	0.91 (0.34)	75.2 (74.3)	1.00	1.00
4	72.5 (73.2)	0.025	0.9	1.27 (0.41)	73.7 (74.5)	0.2	0.5
5	71.5 (72.2)	0.004	0.7	2.83 (0.47)	74.3 (75.0)	0.03	0.04
					av = 74.7 (74.7)		

[a] All energies in kilocalories/mole. [b] From Murov.[19a] In parentheses, net triplet energies estimated as in footnote 19b. All E_T ±0.3 kcal/mol. [c] At 20 °C. [d] See Figure 4 and the Results. [e] Standard errors calculated with the following numbers of data points: 31 for **2** and **3**, 13 for **4**, and 16 for **5**. [f] In parentheses, values based on net E_T. [g] Since Φ_{TS} is temperature independent, this is a guess; see Discussion.

University. Acetonitrile, benzene, and cyclohexane ("distilled in glass", Burdick and Jackson) were used as received. Absorption spectra and extinction coefficients were obtained with a Uvikon 820 (Kontron) spectrophotometer.

For the fluorescence decay measurements, the samples were deaerated by nitrogen purging following a standardized procedure. The experimental techniques and instrumentation for time-resolved single-photon counting have been described earlier.[23] In the experiments with DBA, fluorescence was monitored through a wide-band interference filter centered at 433 nm (MicroCoating, 50-nm fwhm). With DBPEA the filter was centered at 550 nm (Baird Associates, 100-nm fwhm).

Results

1. Energy Transfer to DBA. Effect of Temperature. Acetonitrile solutions of ketone (ca. 0.02 M) and DBA (ca. (0.5–5) × 10^{-4} M) were excited at 320 nm; the ratios of absorbances of ketone to DBA were >4 in all cases. All the decay curves of DBA fluorescence were strictly single exponentials in the absence of ketone: $\tau_F = 1/k_F = 2 \pm 0.1$ ns at 20 °C, $E_{isc} = 4.0$ kcal (±0.1 SD), eq 1. In acetonitrile, S_1 was determined to be 70.6 kcal above S_0, from the absorption and fluorescence spectra, which puts T_n at 74.6 kcal. In the presence of acetophenone, the decay curves were all strictly double exponentials (eq 12), as expected from the simplified reaction scheme presented in eq 13–17. Here eq

$$\mathrm{K} + h\nu \rightarrow {}^1\mathrm{K}^* \rightarrow {}^3\mathrm{K}^* \qquad (13)$$

$$\mathrm{DBA} + h\nu \rightarrow \mathrm{DBA}\ (\mathrm{S_1}) \qquad (14)$$

$${}^3\mathrm{K}^* + \mathrm{DBA} \xrightarrow{k_{\mathrm{TS}}} \mathrm{K} + \mathrm{DBA}\ (\mathrm{S_1}) \qquad (3)$$

$${}^3\mathrm{K}^* + \mathrm{DBA} \xrightarrow{k_{\mathrm{ET}}} \mathrm{K} + \mathrm{DBA} \qquad (4)$$

$${}^3\mathrm{K}^* \xrightarrow{k_d} \mathrm{K} \qquad (15)$$

$$\mathrm{DBA}\ (\mathrm{S_1}) \xrightarrow{k_r} \mathrm{DBA} + h\nu \qquad (16)$$

$$\mathrm{DBA}\ (\mathrm{S_1}) \rightarrow \mathrm{DBA} \qquad (17)$$

3 represents either eq 6, 7, or 10, as discussed in the introduction. The rate parameter of the slow-decay component depends linearly on the concentration of DBA,[11] according to eq 18. The plots

$$k_{\mathrm{obsd}} = k_d + k_{\mathrm{ET}}[\mathrm{DBA}] \qquad (18)$$

of k_{obsd} vs [DBA] with acetophenone at three temperatures (7, 20, and 40 °C) are linear. At 20 °C $k_{\mathrm{ET}} = 1.15 \times 10^{10}$ $\mathrm{M^{-1}\ s^{-1}}$, consistent with diffusion-controlled quenching of ${}^3\mathrm{K}^*$ by DBA. The temperature dependence of k_{ET} indicates an activation energy of 1.8 kcal/mol. All ketones have the same k_{ET}.

In contrast, there are striking differences between the ketones regarding the amplitudes α of the slow component of fluorescence decay (eq 12). This is illustrated in Figure 2, which compares the results obtained with three ketones in similar conditions of concentrations, temperature, and time scale; the curves are normalized at I_{max}. Triplet dimethylacetophenone (**5**), especially, is evidently a much poorer sensitizer of DBA fluorescence than acetophenone (**3**), for example. An expression for this efficiency, Φ_{TS} (eq 2), was previously derived[23] in terms of the experimentally available rate constants and the ratio R of absorbances of DBA and the ketone ($R = \epsilon_{\mathrm{DBA}}[\mathrm{DBA}]/\epsilon_K[\mathrm{K}]$):

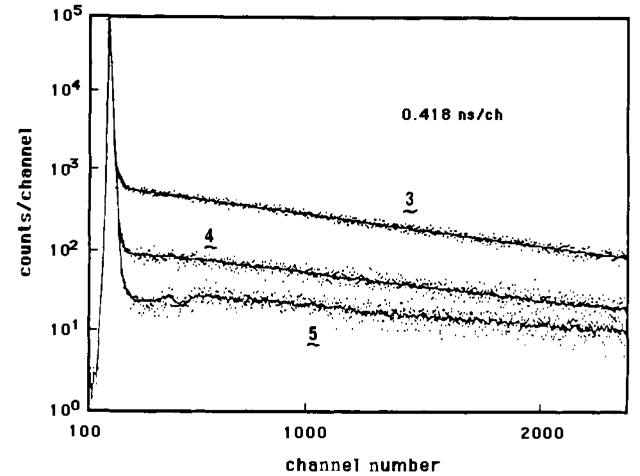

Figure 2. Fluorescence decay curves of acetonitrile solutions of 0.02 M ketones **3–5** and DBA (ca. 2 × 10^{-4} M) at 20 °C. λ_{ex} = 320 nm; fluorescence monitored in the 420–460-nm range.

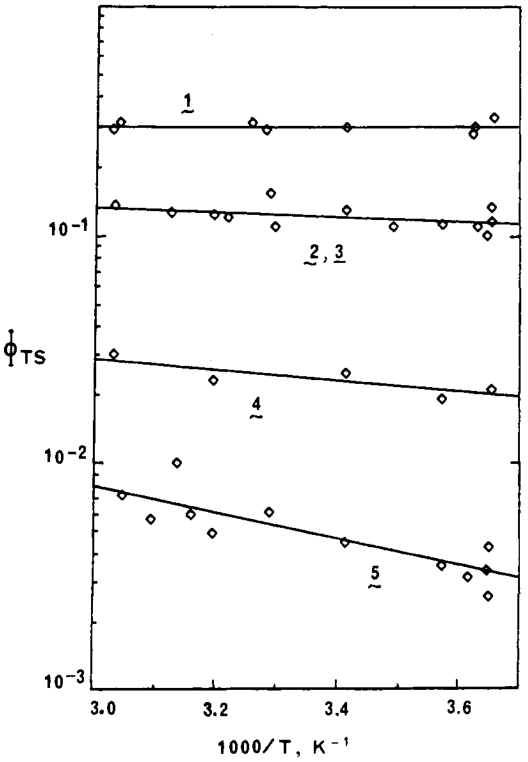

Figure 3. Temperature dependence of Φ_{TS} for ketones **1–5**. Some symbols represent the average of several data points.

$$\Phi_{TS}{}^{\mathrm{DBA}} = R(k_F - k_{\mathrm{obsd}})/(1 + \alpha)k_{\mathrm{ET}}[\mathrm{DBA}] \qquad (19)$$

Once k_{ET} has been determined at a given temperature, then every decay curve provides the information for a value of Φ_{TS}. We used

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(23) Wilson, T.; Frye, S. L.; Halpern, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 3600.

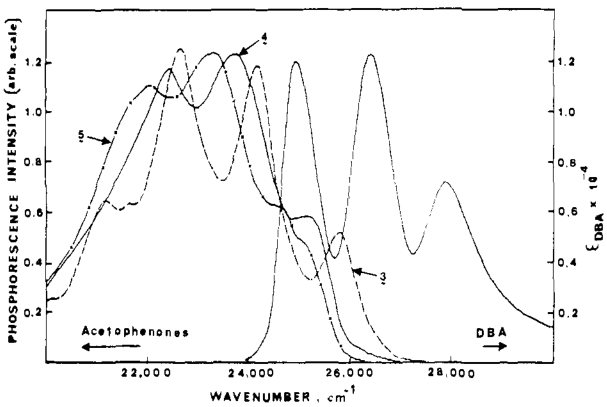

Figure 4. Phosphorescence spectra of acetophenones **3**–**5** (as labeled; data from ref 28) and absorption spectrum of DBA in acetonitrile.

the values of k_{ET} determined for acetophenone in the calculation of the Φ_{TS} of all ketones. The results at 20 °C are listed in Table I. Φ_{TS} was determined at several temperatures between 0 and 57 °C (Figure 3). It is independent of temperature in the case of **1** but increases with temperatures for the other ketones. The effect is largest with **5**; its Φ_{TS} doubles in this temperature range.

For reasons to be discussed later, one experiment with **5** was carried out in benzene and one in cyclohexane instead of acetonitrile. This ketone remains a very poor energy donor in these other solvents ($\Phi_{TS} \leq 0.004$).

2. Energy Transfer to DBPEA at 20 °C. DBPEA was synthesized by Schaap for use as a fluorescence probe in the study of dioxetanes when the cleavage products have triplet energies too low (<70 kcal) to be monitored by DBA. DBPEA is intensely fluorescent ($E_s \approx 57$ kcal, $\Phi_F \approx 1$, $\lambda_{max_F} \approx 512$ nm in acetonitrile). Its fluorescence efficiency, in contrast to that of DBA, is practically temperature independent.[22]

Excitation at 330 nm of acetonitrile solutions of DBPEA (3.3×10^{-5} M) and ketones **1** and **3**–**5** (0.013–0.017 M) at 20 °C resulted in the emission of DBPEA fluorescence that exhibited double-exponential decay. The short-decay component indicates a fluorescence lifetime of ca. 6 ns, while the rate parameters of the long component were in keeping with the values of k_{obsd} calculated from eq 18 (substituting the concentration of DBPEA for [DBA]). But in sharp contrast to the decay curves obtained with these ketones and DBA, here the amplitudes α of the slow component were all roughly the same. This is reflected in the corresponding values of Φ_{TS}^{DBPEA}, which are identical for the four ketones, 0.08 ± 0.004.

Discussion

The experiments described here were designed to identify which of two possible pathways of collisional energy transfer is primarily responsible for the efficient sensitization of DBA fluorescence by triplet ketones. The two alternatives considered were (a) direct excitation of singlet DBA within an "encounter complex" (or possibly an exciplex) of DBA and the triplet donor (eq 10) or (b) excitation of a higher triplet of DBA followed by intersystem crossing to S_1 (eq 6 and 7). These two mechanisms are, of course, not mutually exclusive. Nevertheless, we believe that the evidence presented here demonstrates the major role of a T_n state of DBA.

If mechanism (a) was the dominant one, then the relative values of Φ_{TS} should be proportional to the extent of spectral overlap between the phosphorescence emission of the ketones and the absorption spectrum of DBA (eq 11). Figure 4 shows the relevant spectra,[24] from which the relative values of spectral overlaps, listed in Tables I for ketones **3**–**5**, were estimated. This comparison gives a clear answer: whereas the values of Φ_{TS} for **3** and **5**, for example, differ by nearly 2 orders of magnitude, the extent of spectral overlap accounts for a difference of less than a factor of 2. (The order of the relative values of Φ_{TS} and spectral overlaps is the same, since it reflects the triplet energies of the respective ketones.)

If this is a strong negative argument against direct population of DBA (S_1) (eq 10) as an important pathway, the effect of temperature on Φ_{TS} is a compelling argument in support of the intermediacy of T_n via mechanism (b) above. A look at Table I and Figure 3 immediately suggests this interpretation. The efficiency Φ_{TS} has the highest value and is temperature independent in the case of **1**, the ketone with the highest triplet energy. Φ_{TS} becomes increasingly temperature dependent as the triplet energy $E_T{}^K$ of the ketone decreases in the order **1**–**5**, even though $E_T{}^K$ is always above DBA (S_1). Table I shows that the uncertainties attached to the proper values of the ketones E_T do not alter this conclusion. These results are easily interpreted on the basis of reactions 6–8 and the quenching process (eq 9), as shown in Figure 1.

If deactivation of triplet donors proceeds exclusively via TT transfer to generate either the higher or the lower triplet of DBA, then the experimentally determined efficiency Φ_{TS} of TS transfer is given by eq 20, where $\Phi_{-isc} = k_{-isc}/(k_{-isc} + k_{ic})$.

$$\Phi_{TS} = \Phi_{-isc}k_{TT_n}/(k_{TT_n} + k_{TT_1}) \qquad (20)$$

Φ_{-isc}, the efficiency of intersystem crossing in DBA, is assumed to be independent of the ketone. A lower limit for this value is 0.3, since Φ_{TS} of indanone (**1**) is 0.3. (The Φ_{TS} of the triplet exciplex of acetone and benzene is also ca. 0.3.)[15] Using a double-excitation method to populate the T_n state of anthracenes in ethanol, Kokubun et al. found $\Phi_{-isc} = 0.27$ for DBA, later revising this value to 0.19.[25a] Importantly, they found Φ_{-isc} to be temperature independent, as expected since the two processes involved, ic and –isc, are exothermic. In this discussion we will *assume* $\Phi_{-isc} = 0.35 \pm 0.05$.[25b]

Rearrangement of eq 20 gives eq 21. Since k_{TT_1} can also be assumed to be independent of temperature, plots of ln $[\Phi_{TS}/(\Phi_{-isc} - \Phi_{TS})]$ vs $1/T$ should be linear, with slopes $E_{TT_n}{}^a/R$, where $E_{TT_n}{}^a$ is the activation energy of k_{TT_n} for each ketone. The values of $E_{TT_n}{}^a$ are listed in Table I.

$$\Phi_{TS}/(\Phi_{-isc} - \Phi_{TS}) = k_{TT_n}/k_{TT_1} \qquad (21)$$

In the case of **4** and **5**, since Φ_{TS} is small compared with Φ_{-isc}, the exact value of Φ_{-isc} has little effect on $E_{TT_n}{}^a$. With ketones **2** and **3**, the uncertainty attached to Φ_{-isc} introduces an uncertainty of about 10% on the values of $E_{TT_n}{}^a$.

Table I shows that for ketones **2**–**5**, the sum of the ketone triplet energy $E_T{}^K$ and $E_{TT_n}{}^a$ corresponds to an average energy of 74.7 ± 1 kcal. This is the total energy available for excitation of DBA; it matches well the level of the T_n state, which we located at 74.6 kcal (see Results). Given the uncertainties attached to the values of the triplet energies of the ketones,[19] our results are fully consistent with excitation of DBA (T_n) prior to DBA (S_1). Thus the "TS" transfer of energy from the triplet ketones is, in truth, a

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(24) Dusenbery, R. Ph.D. Thesis, University of Chicago, 1970. We thank Prof. N. C. Yang for providing us with this information.

(25) (a) Kikuchi, K.; Fukumura, H.; Kokubun, H. *Chem. Phys. Lett.* **1986**, *123*, 226. Kobayashi, S.; Kikuchi, K.; Kokubun, H. *Chem. Phys.* **1978**, *27*, 399. (b) A direct and reliable photophysical determination of Φ_{-isc} in acetonitrile would be highly desirable. If, as assumed here, only one higher triplet state T_n is involved in isc to and from S_1, then[6] $1/\tau_F = k_r + k_{isc}k_{ic}/(k_{ic} + k_{-isc})$, where τ_F is the measured lifetime of DBA (S_1) and k_r its radiative rate of decay ($k_r = \Phi_F/\tau_F \approx 8 \times 10^7$ s^{-1} at 20 °C). With these values, we have $k_{isc}(1 - \Phi_{-isc}) \approx 4.2 \times 10^8$ s^{-1}. It can reasonably be assumed[1,7,25a] that $k_{isc} = k_{-isc} \exp(E_{isc}/RT) = 1.3 \times 10^{-3}\, k_{-isc}$. Thus one can calculate k_{isc}, k_{-isc}, and k_{ic} for different values of Φ_{-isc}. For example, if $\Phi_{-isc} = 0.35$ as assumed here, then $k_{isc} \approx 7 \times 10^8$ s^{-1}, $k_{-isc} \approx 5 \times 10^{11}$ s^{-1}, and $k_{ic} \approx 10^{12}$ s^{-1}, which indicates a very short lifetime for T_n ($\tau_{T_n} = 1/[k_{ic} + k_{isc}k_r/(k_r + k_{-isc})] \approx 1$ ps), in contrast with the 200 ps estimated from chemical sensitization experiments. See: Liu, R. S. H.; Edman, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 1492. Other values of ϕ_{-isc} lead to similarly short T_n lifetimes. This difficulty, which has been perceived and discussed in different contexts by others,[8,9,25a] can be circumvented only by new assumptions. For example, there may be another triplet state slightly below T_n that gets populated very fast by internal conversion from T_n and has a longer lifetime, in keeping with the large energy gap between it and T_1. This triplet state, which we call T_2, would be responsible for the energy-transfer experiments of Liu and Edman and perhaps be the origin of the TT fluorescence emission at 840 nm; see footnote 27. Further speculation along these lines is outside the scope of this paper.

(26) Wagner, P. J.; Thomas, M. J.; Harris, E. *J. Am. Chem. Soc.* **1976**, *98*, 7675.

spin-allowed but temperature-activated TT process, followed by isc to give DBA (S_1).[27,28]

Our results lead to another interesting conclusion concerning the relative rates of energy transfer from the triplet ketones to the upper or to the lowest triplet of DBA. If $\Phi_{-\mathrm{isc}} \approx 0.35$, then $\Phi_{\mathrm{TS}} \approx \Phi_{-\mathrm{isc}}$ in the case of **1**, and k_{TT_1} must be small compared with k_{TT_n} (eq 21). Like k_{TT_1}, k_{TT_n} is likely to have no or a very small activation energy. The triplet energy of **1** may thus be entirely channeled into the upper triplet of DBA, because reaction 6, which is nearly isothermic, is faster than reaction 9, exothermic by ca. 35 kcal. Thus a large energy gap actually slows down an exothermic energy-transfer process.

With no preassumption regarding the relative Φ_{TS} from either n,π^* or π,π^* triplets, we ascertained that the inefficiency of ketones **4** and **5** as donors was not a consequence of the electronic configuration of their lowest triplet states, which are π,π^*, whereas the lowest triplets of **1**–**3** are n,π^* in acetonitrile. **4** and **5** have T_2 states of n,π^* configuration slightly above T_1. Going to a nonpolar solvent is expected to lower these T_2 (n,π^*) states without affecting T_1 (π,π^*), which remains the lowest triplet. This shift increases the mixing of these states and confers more n,π^* character to the lowest triplet.[28] Two experiments with **4**, one in cyclohexane and one in benzene, resulted in values of Φ_{TS} only minimally different from that in acetonitrile reported in Table I.

Our experiments with the second brominated anthracene, DBPEA, had the same broad objective of ruling out other possible photophysical or chemical interpretations of the low Φ_{TS} values observed with **4** and **5**, not solely resting on the level of their T_1 state. We find the results with DBPEA compelling in that regard, since energy transfer from ketones **1** and **3**–**5** all generated DBPEA (S_1) with the same efficiency, $\Phi_{\mathrm{TS}} \approx 0.08$. This is an interesting result in itself. Since the fluorescence quantum yield of this anthracene is reported to be near unity and temperature independent,[22] it is likely that its T_2 state is located relatively high above S_1, as in 9,10-diphenylanthracene for example,[3] but most probably well below even the triplet state of **5**. Thus one would not anticipate energy transfer to DBPEA from any of these ketones to require an activation energy.

The second concern of this paper was to elucidate the causes of the differences in Φ_{TS} between different triplet donors. Ketones **1**–**5** were purposefully selected for their structural similarity, all being substituted acetophenones, and for having T_1 levels critically located around DBA (T_n). Clearly, between these ketones the differences in Φ_{TS} can be entirely rationalized on the basis of their respective triplet energies. This is demonstrated in the last two columns of Table I, where the relative values of Φ_{TS}, normalized for acetophenone, are compared with the relative values of exp($-E_{\mathrm{TT}_n}/RT$) at room temperature. The agreement is good, considering the experimental errors. But this rationalization can probably not be extended to triplet donors unrelated to acetophenone, other than to predict the obvious: molecules with triplet energies much below DBA (T_n) will be poor donors. What are the factors that determine the preexponential factor in k_{TT_n}? Are ketones with T_1 much above DBA (T_n) as good donors as indanone, with $E_T{}^K = 75.8$ kcal? The answer is no, or not necessarily: ^{3}n,π^* acetone ($E_T{}^K = 78$ kcal) has a lower Φ_{TS} than acetophenone ($E_T{}^K = 74.6$ kcal). The fact that triplet exciplexes of acetone with benzene derivatives have higher Φ_{TS} than uncomplexed triplet acetone,[15,29] although their triplet energies are surely lower, is also significant. Further discussion would be too speculative at this point.

In view of the results presented here, a note of caution must be reiterated regarding the use of DBA for the determination of yields of chemically generated triplet carbonyl products, in the thermolysis of dioxetanes for example.[30] If the specific values of Φ_{TS} have not been predetermined by a reliable method, it is evidently unwarranted to assume that different carbonyl compounds, even closely related, have the same Φ_{TS}. The use of DBPEA in these systems would be a valuable check.

Conclusions

The well-known and relatively efficient sensitization of DBA fluorescence by triplet ketones, such as acetophenones, has been shown to involve the intermediacy of a higher triplet state of DBA. Thus the overall TS energy transfer is, in fact, a temperature-activated TT transfer followed by intersystem crossing to DBA (S_1), a process facilitated by the presence of the bromine substituents. It is noteworthy that the efficiency Φ_{TS} of indanone, with a T_1 state probably slightly above but close to DBA (T_n), must be equal or close to the limit set by the efficiency of intersystem crossing in DBA, assumed here to be ca. 0.35; a reliable value of $\Phi_{-\mathrm{isc}}$ in acetonitrile would evidently be very valuable. Of interest also is the implication of this result regarding the relative rates of energy transfer from triplet indanone to DBA (T_n) and to DBA (T_1), 35 kcal below. The latter rate is at least 6 times smaller than the first. Thus energy transfer becomes less efficient at large exothermicity (as does electron transfer in the "inverted region").[31] This result could be obtained only because the rate limitations imposed by diffusion are circumvented here, where we measure the relative rates of energy transfer either to a higher or to a lower triplet state of an acceptor already in an encounter complex with the donor. Since $k_{\mathrm{TT}_1} \geq 1.2 \times 10^{10}$ M^{-1} s^{-1}, $k_{\mathrm{TT}_n} \geq 7 \times 10^{10}$ M^{-1} s^{-1}, in keeping with previous estimates of energy transfer in an encounter complex.[32]

Within the substituted acetophenone family, the T_1 energy seems to be the sole determinant of Φ_{TS}. The factors other than triplet energy that determine the Φ_{TS} of unrelated triplet donors have not yet been identified.

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[27] We tried to establish the intermediacy of DBA (T_n) by a more incisive experiment. Gillispie and Lim[8] reported the observation of the fluorescence transition T_n–T_1 at ca. 840 nm, following excitation of DBA (S_1) in solution. Having confirmed this result, we had hoped to observe the sensitization of this extremely weak emission in conditions where acetophenone absorbs most of the exciting light (313 nm). Unfortunately, even with solutions only partially deaerated, a requirement for the detection of TT energy transfer to DBA, we only saw the well-known intense phosphorescence ($T_1 \rightarrow S_0$) of DBA, which unfortunately obscures the entire 700–900-nm region of interest. We thank Michel Bermane for performing these experiments.

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