exceed the contraction due to the bond formation. This anomaly in $\Delta V_1^{\ddagger}$ is also consistent with the anomalously high $\Delta S_1^{\ddagger}$ found in the same reaction.[17] More extensive volumetric studies of anionic complexes of polynitroaromatics, for example, with multivalent nucleophilic ions and with a series of lyate ions may support this explanation.

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A Kinetic Study of Sensitized 9,10-Dibromoanthracene Fluorescence Produced by Energy Transfer from Triplet Ketones. 1. Acetophenone as Donor

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Abstract: The decay of the fluorescence intensity of degassed solutions of 9,10-dibromoanthracene (DBA) and acetophenone, upon excitation in the absorption band of the ketone, was studied by the time-correlated single-photon-counting method. The decay curves are described by double-exponential functions. For each solution, the prompt intensity component is due to direct excitation of DBA, and the slow component is the result of energy transfer from triplet acetophenone. The rate constant k_{ET} of this energy-transfer process is obtained from linear plots of the rate of the slow decay component vs. DBA concentration; the values of k_{ET} are 7.0×10^9 M^{-1} s^{-1} in benzene and in cyclohexane and 1.1×10^{10} M^{-1} s^{-1} in acetonitrile. Extrapolation of the same plots gives the rate of decay of triplet acetophenone in the absence of DBA in the particular solvent. The results agree well with the literature values. Knowing k_{ET}, the efficiency ϕ_{TS} of the overall triplet-singlet energy-transfer process is obtained from the analysis of each double-exponential decay curve, using the prompt component as internal standard. The values of ϕ_{TS}, 0.118, 0.102, and 0.126 in benzene, cyclohexane, and acetonitrile, respectively, show that ϕ_{TS} is quite insensitive to the solvent, with triplet acetophenone as donor. The value of ϕ_{TS} in benzene is consistent with the result of photostatic experiments in that solvent. The mechanism of this TS energy transfer to DBA is discussed, mainly in terms of a collisional triplet-triplet transfer to a higher triplet of DBA, followed by isc (isc = intersystem crossing) to the (lower) S_1 state. If this interpretation is correct, the efficiency of isc T_2 (or T_3) to S_1 is high, $\gtrsim 0.12$. DBA is shown to be a sensitive probe for triplet ketones.

Introduction

The population of the excited singlet state of 9,10-dibromoanthracene (DBA) via energy transfer from triplet ketones is an example of an overall spin-forbidden (T-S) process. It may, however, involve the intermediacy of a higher excited state of DBA, resulting from a triplet-triplet transfer, followed by intersystem crossing to populate S_1. This is one of many interesting aspects of a process which is surprisingly efficient and lends itself well to quantitative kinetic study.

Attention was first called to DBA as an acceptor of triplet energy by Vassil'ev[2] in the course of his studies of the chemiluminescence accompanying autoxidation processes. He observed that the addition of DBA to solutions presumed to contain chemically excited triplet carbonyls produced an intense emission which matched spectroscopically the fluorescence of DBA. This emission could be dramatically brighter than the very weak luminescence emitted by the triplet carbonyls themselves. Vassil'ev interpreted this phenomenon as the result of a T-S energy-transfer process rendered more efficient—i.e., less spin forbidden—by the presence of the bromine atoms in the acceptor molecule.

If the efficiency of this T-S process were known with some accuracy and if it were independent of the nature of the carbonyl donor and solvent, a useful tool would be at hand for the investigation of reactions suspected of generating triplet state products.[3] Unfortunately, however, there is a discrepancy of more than an order of magnitude between the two reported values of ϕ_{TS}, defined as $\phi_{TS} = k_{TS}/k_{ET}$ (where k_{TS} is the rate constant for the process resulting in the formation of excited singlet DBA and k_{ET} is the sum of the rate constants for all the bimolecular quenching processes involving DBA). With triplet acetophenone as the donor in benzene solution, Vassil'ev et al. reported $k_{TS} = 3.8 \times 10^8$ M^{-1} s^{-1} and $\phi_{TS} = 0.027$, assuming $k_{ET} = 1.4 \times 10^{10}$ M^{-1} s^{-1}. For the same donor, but with 9,10-diphenylanthracene as the acceptor, these authors reported values of ϕ_{TS} 2 orders of magnitude smaller.[2]

However, from an almost contemporary but independent photophysical study of the same acetophenone-DBA system, Berenfel'd et al.[4] reported the much higher value of $\phi_{TS} = 0.3$. These authors excited acetophenone in degassed benzene solution containing DBA and measured the effect of DBA on (1) the rate of decay of the sensitized fluorescence of DBA following 10^{-7}-s pulsed excitation and (2) the efficiency of this sensitized fluorescence of DBA under photostationary conditions. The first set of experiments gave $k_{ET} = (5 \pm 0.5) \times 10^9$ M^{-1} s^{-1}; from the second set, they obtained $\phi_{TS} = 0.3$, hence $k_{TS} = 1.5 \times 10^9$ M^{-1} s^{-1}, thus a significantly higher value than that of Vassil'ev et al. Unfortunately this paper presented only scant experimental information, in spite of the problems attached to quantitative fluorescence measurements in highly absorbing solutions. Selective photoexcitation of acetophenone in the presence of DBA is very difficult to achieve. Thus in static photosensitization experiments,

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(1) (a) Harvard University. (b) Northeastern University.

(2) Vassil'ev, R. F. *Nature (London)* **1963**, *200*, 773. Belyakov, V. A.: Vassil'ev, R. F. *Photochem. Photobiol.* **1970**, *11*, 179.

(3) See, for example: Wilson, T. *Int. Rev. Sci.*; *Phys. Chem.*, *Ser. Two* **1976**, *9*, 265. Turro, N. J.; Lechten, P.; Schore, N. E.; Schuster, G. B.; Steinmetzer, H.-C.; Yekta, A. *Acc. Chem. Res.* **1974**, *7*, 97 and references therein.

(4) Berenfel'd, V. M.; Chumaevskii, E. V.; Grinev, M. P.; Kuratnikov, Yu. I.; Artem'ev, E. T.; Dzhagatspanyan, R. V. *Bull. Acad. Sci. USSR, Phys. Ser. (Engl. Transl.)* **1970**, *3*, 597.

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the fluorescence emission always comprises an undesirable component resulting from direct absorption by DBA itself, in addition to the delayed emission.

It can be shown, however, that the analysis of fluorescence decay curves on the nanosecond time scale can turn this difficulty into an advantage. This is because the intensity of the prompt emission, resolved according to its decay constant, can serve as an internal standard to calibrate the intensity of the delayed emission. With lifetimes of prompt and delayed emissions differing by as much as 3 orders of magnitude, such as is the case in some experiments reported here, the time-correlated photon-counting method is ideal. Thus one can easily obtain not only the values of k_{ET}, k_{TS}, and ϕ_{TS} from a few experiments at different concentrations of DBA, but also the lifetime of the triplet ketone donor.

The motivation for this work was threefold: (1) to obtain a reliable value of the efficiency ϕ_{TS}; (2) to elucidate the mechanism of this overall T–S transfer (i.e., whether it involves a collisional process and whether a higher triplet of DBA participates); and (3) to evaluate the usefulness of this technique as a probe for investigating the properties of triplet donors. This paper describes the method and its applications to the case of triplet acetophenone at 20 °C in three solvents. Supporting evidence from earlier photostatic experiments will also be summarized. An accompanying paper extends the method to the study of triplet acetone, where interesting complications were observed in benzene solutions.

Kinetic Scheme and Treatment of Data

Consider the photoexcitation of a solution of DBA and a ketone A (here acetophenone) by monochromatic light. The competitive processes to take into account are reactions 1–4, where A* represents the donor *triplet* A (T_1) and DBA* represents DBA (S_1), the excited acceptor.

$$\mathrm{A} + h\nu \rightarrow \mathrm{A^*} \tag{1a}$$

$$\mathrm{DBA} + h\nu \rightarrow \mathrm{DBA^*} \tag{1b}$$

$$\mathrm{A^*} \xrightarrow{k_{\mathrm{d}}} \mathrm{A} \tag{2}$$

$$\mathrm{A^*} + \mathrm{DBA} \xrightarrow{\phi_{\mathrm{TS}}k_{\mathrm{ET}}} \mathrm{DBA^*} + \mathrm{A} \tag{3a}$$

$$\mathrm{A^*} + \mathrm{DBA} \xrightarrow{\phi_{\mathrm{TT}}k_{\mathrm{ET}}} \mathrm{DBA} + \mathrm{A} \tag{3b}$$

$$\mathrm{DBA^*} \xrightarrow{\phi_{\mathrm{F}}k_{\mathrm{F}}} \mathrm{DBA} + h\nu \tag{4a}$$

$$\mathrm{DBA^*} \xrightarrow{(1-\phi_{\mathrm{F}})k_{\mathrm{F}}} \mathrm{DBA} \tag{4b}$$

Reaction 1a shows direct production of triplet ketone, without the intermediacy of the excited singlet; since intersystem crossing is extremely fast and efficient in acetophenone[5] (as well as in acetone, see following paper in this issue), this simplification is adequate here. Reaction 2 represents the sum of all the (pseudo)-first-order processes, radiative and nonradiative, which deactivate A* without the participation of DBA. Reaction 3b represents all processes of deactivation of A* by DBA which do not result in DBA(S_1), here DBA*, and which probably yield mainly DBA(T_1) instead; therefore

$$\phi_{\mathrm{TS}} + \phi_{\mathrm{TT}} = 1 \tag{5}$$

ϕ_{F} is the fluorescence efficiency of DBA, in the experimental conditions. Reaction 4b is mainly intersystem crossing to T_1, which plays no role here.

Note that reactions 3a and 3b could be replaced by (3a′) and (3b′), in which the hypothetical intermediacy of a higher triplet

$$\begin{tikzcd}
\mathrm{A^*} + \mathrm{DBA} \arrow[r, "\phi_{\mathrm{TT}_n}k_{\mathrm{ET}}"] & \mathrm{A} + \mathrm{DBA}(\mathrm{T}_n) \arrow[r, "\phi_{\mathrm{isc}}k_{\mathrm{c}}"] \arrow[d, "(1-\phi_{\mathrm{isc}})k_{\mathrm{c}}"] & \mathrm{DBA^*} \quad (3\mathrm{a}') \\
\mathrm{A^*} + \mathrm{DBA} \arrow[r, "(1-\phi_{\mathrm{TT}_n})k_{\mathrm{ET}}"] & \mathrm{A} + \mathrm{DBA}(\mathrm{T}_1) & \quad (3\mathrm{b}')
\end{tikzcd}$$

T_n of DBA is expressed. In this case

$$\phi_{\mathrm{TS}} = \phi_{\mathrm{TT}_n}\phi_{\mathrm{isc}(\mathrm{T}_n\text{-}\mathrm{S}_1)} \tag{6}$$

Since T_n has a very short lifetime (estimated at ~0.2 ns),[6] this mechanism would be undistinguishable from the simpler scheme (eq 3a and 3b) bypassing T_n. The simpler scheme will be adopted now. The possible role of T_n will be considered in the Discussion.

Pulse Excitation. First, consider excitation at time $t = 0$ by a monochromatic flash of very short duration, which produces *only* an initial concentration of excited ketone, $[\mathrm{A^*}]_0$. At later times, the rate expressions are:

$$-\frac{\mathrm{d}[\mathrm{A^*}]}{\mathrm{d}t} = k_{\mathrm{ET}}[\mathrm{A^*}][\mathrm{DBA}] + k_{\mathrm{d}}[\mathrm{A^*}]$$

$$[\mathrm{A^*}] = [\mathrm{A^*}]_0 e^{-k_{\mathrm{obs}}t}$$

with

$$k_{\mathrm{obs}} = k_{\mathrm{d}} + k_{\mathrm{ET}}[\mathrm{DBA}] \tag{7}$$

$$-\frac{\mathrm{d}[\mathrm{DBA^*}]}{\mathrm{d}t} = k_{\mathrm{F}}[\mathrm{DBA^*}] - \phi_{\mathrm{TS}}k_{\mathrm{ET}}[\mathrm{A^*}][\mathrm{DBA}]$$
$$= k_{\mathrm{F}}[\mathrm{DBA^*}] - \phi_{\mathrm{TS}}k_{\mathrm{ET}}[\mathrm{DBA}][\mathrm{A^*}]_0 e^{-k_{\mathrm{obs}}t}$$

or

$$-\frac{\mathrm{d}[\mathrm{DBA^*}]}{\mathrm{d}t} = k_{\mathrm{F}}[\mathrm{DBA^*}] - re^{-k_{\mathrm{obs}}t} \tag{8}$$

with

$$r = \phi_{\mathrm{TS}}k_{\mathrm{ET}}[\mathrm{DBA}][\mathrm{A^*}]_0 \tag{9}$$

The solution of eq 8 is

$$[\mathrm{DBA^*}] = \frac{r}{k_{\mathrm{F}} - k_{\mathrm{obs}}}(e^{-k_{\mathrm{obs}}t} - e^{-k_{\mathrm{F}}t}) \tag{10}$$

Now, consider that some DBA is also excited by the flash at $t = 0$, producing $[\mathrm{DBA^*}]_0$ via reaction 1b:

$$[\mathrm{DBA^*}] = \frac{r}{k_{\mathrm{F}} - k_{\mathrm{obs}}}(e^{-k_{\mathrm{obs}}t} - e^{-k_{\mathrm{F}}t}) + [\mathrm{DBA^*}]_0 e^{-k_{\mathrm{F}}t} \tag{11}$$

The intensity of DBA fluorescence is

$$I = \phi_{\mathrm{F}}k_{\mathrm{F}}[\mathrm{DBA^*}] \tag{12}$$

Hence, at time t after the light pulse, the intensity is

$$I_t = \frac{k_{\mathrm{F}}\phi_{\mathrm{F}}r}{k_{\mathrm{F}} - k_{\mathrm{obs}}}(e^{-k_{\mathrm{obs}}t} - e^{-k_{\mathrm{F}}t}) + \phi_{\mathrm{F}}k_{\mathrm{F}}[\mathrm{DBA^*}]_0 e^{-k_{\mathrm{F}}t} \tag{13}$$

The first term in eq 13 is the "slow" component of the total fluorescence intensity I_t expressed here in $h\nu$/s; this slow component results from energy transfer from the triplet ketone. The second term is the "prompt" component, arising from direct absorption by DBA.

Integrating separately each term of eq 13 between $t = 0$ and $t = \infty$ gives the total number of prompt and slow photons of fluorescence, N_{s} and N_{p}, emitted as the result of excitation by the light pulse.

$$N_{\mathrm{s}} = \frac{\phi_{\mathrm{F}}r}{k_{\mathrm{obs}}} \qquad N_{\mathrm{p}} = \phi_{\mathrm{F}}[\mathrm{DBA^*}]_0 \tag{14}$$

Thus the ratio of slow to prompt intensities is given by

$$\frac{N_{\mathrm{s}}}{N_{\mathrm{p}}} = \frac{r}{k_{\mathrm{obs}}[\mathrm{DBA^*}]_0} \tag{15}$$

Replacing r by its value in eq 9 gives

$$\phi_{\mathrm{TS}} = \frac{N_{\mathrm{s}}}{N_{\mathrm{p}}}\,\frac{k_{\mathrm{obs}}}{k_{\mathrm{ET}}[\mathrm{DBA}]}\,\frac{[\mathrm{DBA^*}]_0}{[\mathrm{A^*}]_0} \tag{16}$$

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[5] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

[6] (a) Liu, R. S.; Edman, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 1492. (b) In eq 3a′, for simplicity's sake, an arrow in opposite direction, i.e., from DBA* to DBA(T_n), has been omitted. The reversibility of the formation of DBA* from T_n is of no consequence in the kinetic treatment; since the emitter DBA* is the same in the direct and sensitized emission, factors which affect the quantum yield of DBA fluorescence cancel out.

[7] With the assumption that k_{d} is determined by self-quenching ($k_{\mathrm{SQ}} = 8 \times 10^5\ \mathrm{s^{-1}}$, see: Giering, L.; Berger, M.; Steel, C. *J. Am. Chem. Soc.* **1974**, *96*, 953) and that $k_{\mathrm{ET}} \simeq 5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$.

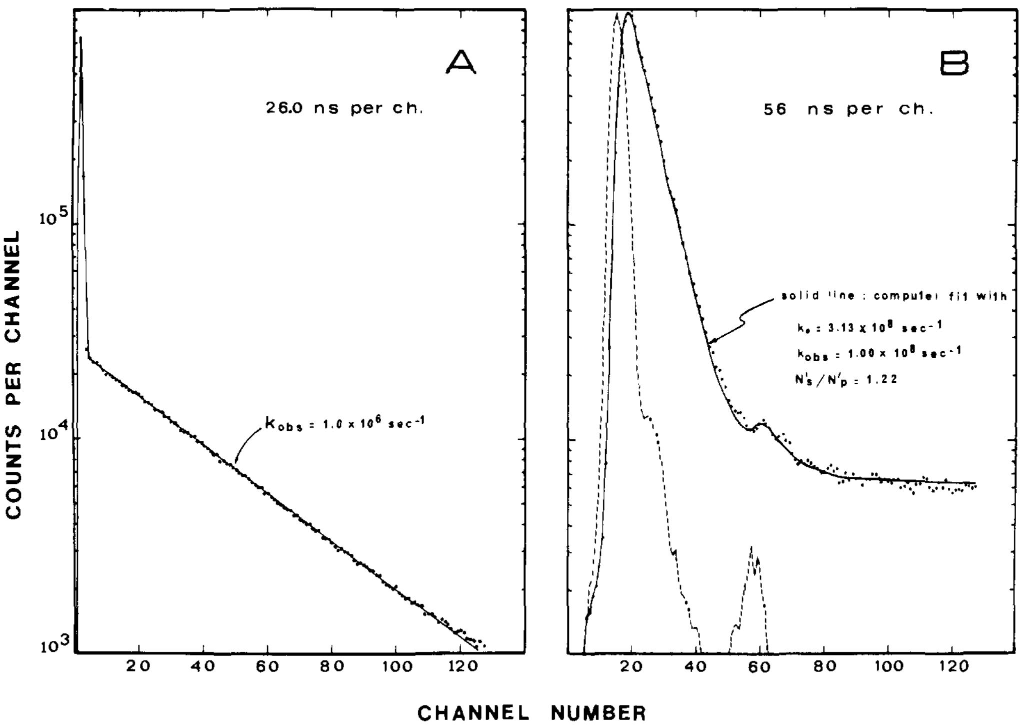

Figure 1. Fluorescence decay curves of a degassed benzene solution of acetophenone (7.4×10^{-3} M) and 9,10-dibromoanthracene (1.20×10^{-4} M) at 20 °C and with $\lambda_{exc} = 305$ nm. Data obtained on two different time scales: A, 26.0 ns per channel; B, 0.56 ns per channel. The dashed line is the lamp profile and the full line is the convoluted "best-fit" double-exponential function.

Note that since DBA* is the emitter in both the prompt and the sensitized components of this emission, ϕ_{TS} is independent of ϕ_F, the quantum efficiency of DBA*. For the same reason, no correction is needed for fluorescence reabsorption.

Equation 13 can be rearranged as the sum of two exponentials:

$$I_t = \left\{k_F[\mathrm{DBA}^*]_0 - \frac{k_F r}{k_F - k_{obs}}\right\}\phi_F e^{-k_F t} + \frac{k_F r}{k_F - k_{obs}}\phi_F e^{-k_{obs} t} \qquad (17)$$

The experimental decay curve is most easily analyzed according to eq 17. Its two exponential terms can be integrated separately and will be called N_p' and N_s'; their ratio is given by

$$\frac{N_s'}{N_p'} = \frac{r}{k_{obs}[\mathrm{DBA}^*]_0}\,\frac{k_F}{k_F - k_{obs} - \dfrac{r}{[\mathrm{DBA}^*]_0}} \qquad (18)$$

Combining eq 15 and 18 and replacing r by its value (eq 9) gives the ratio N_s/N_p in terms of the experimental ratio N_s'/N_p' as

$$\frac{N_s}{N_p} = \frac{N_s'}{N_p'}F \qquad (19)$$

where

$$F = 1 - \frac{k_{obs}}{k_F} - \frac{\phi_{TS}k_{ET}[\mathrm{DBA}][\mathrm{A}^*]_0}{k_F[\mathrm{DBA}^*]_0} \qquad (20)$$

From eq 16 and 19, one gets an expression for ϕ_{TS} accessible to measurements:

$$\phi_{TS} = F\frac{N_s'}{N_p'}\,\frac{k_{obs}}{k_{ET}[\mathrm{DBA}]}\,\frac{[\mathrm{DBA}^*]_0}{[\mathrm{A}^*]_0} \qquad (21)$$

Figure 1 shows representative decay curves for a solution of acetophenone and DBA in benzene, acquired on two different time scales. The prompt and slow decay rates differ by several orders of magnitude, and this is always the case when triplet acetophenone is the donor. The slope of the slow component is $-k_{obs}$ on the log plot. From a series of similar experiments at different concentrations of DBA but identical concentration of acetophenone, k_d and k_{ET} are, then, the intercept and the slope, respectively, of a plot of k_{obs} vs. DBA, according to eq 7. k_F is the fluorescence decay constant of DBA.

Since acetophenone and DBA are in a homogeneous mixed solution, they absorb the incident light in any small volume element in this solution in proportion to their extinction coefficient and partial concentration. Thus the ratio of $[\mathrm{A}^*]_0$ and $[\mathrm{DBA}^*]_0$ is simply the ratio of their absorbances, at the excitation wavelength

$$\frac{[\mathrm{DBA}^*]_0}{[\mathrm{A}^*]_0} = \frac{\epsilon_{\mathrm{DBA}}[\mathrm{DBA}]}{\epsilon_{\mathrm{A}}[\mathrm{A}]} \qquad (22)$$

and is irrespective of the geometry of the system. The ratio N_s'/N_p' can be obtained either by computer-fitting the experimental decay curve or by a combination of numerical and graphical analyses (see Experimental Section).

In the first approximation and for each DBA concentration at which a decay curve was obtained, a value of ϕ_{TS} can be calculated according to eq 21, with $F = 1$. This approximate value of ϕ_{TS} is then used to estimate F (eq 20), following which ϕ_{TS} is recalculated. In all the experiments with acetophenone as donor, $F \geq 0.98$ and therefore F is a negligible correction factor in this system. However, smaller values of F ($\sim$0.75) are obtained in systems where the decay rate of the ketone k_d is faster (such as with triplet acetone in benzene, see companion paper) and closer to the fluorescence decay rate k_F. The correction F is then no longer negligible, and a closed form for ϕ_{TS} was used:

$$\phi_{TS} = \left(1 - \frac{k_{obs}}{k_F}\right)\left[\frac{k_{ET}\epsilon_{\mathrm{A}}[\mathrm{A}]}{\epsilon_{\mathrm{DBA}}}\left(\frac{N_p'}{N_s'}\,\frac{1}{k_{obs}} + \frac{1}{k_F}\right)\right]^{-1} \qquad (23)$$

The kinetic derivations above were based on the assumption of a light pulse of very short duration. The experimental pulse width is, of course, finite, and the instrumental decay curve consists of a main peak followed by one or two smaller peaks. The treatment of the data is outlined in the Experimental Section; in any case, the lamp width and distortions are of little consequence here, in view of the very long decay time of the processes studied.

Photostationary Conditions. Under constant illumination, the reaction scheme comprises reactions 1–4 and, in the presence of a quencher of triplet ketone, reaction 24 also.

$$\mathrm{A}^* + \mathrm{Q} \xrightarrow{k_Q} \mathrm{A} + \mathrm{Q} \qquad (24)$$

Consider three solutions in the same solvent: (1) solution AB, containing acetophenone and DBA; (2) solution B, containing only DBA; (3) solution ABQ, which is solution AB with an added quencher (which does not absorb the exciting light). The concentration of DBA in solution B is such that solutions B and AB have the same optical densities at the exciting wavelength. Therefore all the DBA molecules, whether in solutions AB, ABQ, or B, "see" the same intensity of exciting light at a given geometrical position in identical cuvettes. Similarly, each molecule of ketone A in solution AB sees the same light intensity as its neighboring DBA molecules.

The concentration of DBA in solution B is higher than the concentration of DBA in solution AB, by an amount of extra DBA. Imagine that these extra molecules of DBA in solution B could somehow be labeled DBA_x and distinguished from the other molecules of DBA, which would be labeled DBA_0. Thus the concentration of DBA in solution B is

$$[DBA] = [DBA_o] + [DBA_x]$$

with

$$\epsilon_{DBA}[DBA_x] = \epsilon_A[A] \tag{25}$$

$\epsilon_A[A]$ = the absorbance of acetophenone in solution AB.

Consider now the fluorescence intensities of these three solutions, I_B, I_{AB}, and I_{ABQ}, when all three solutions are excited by the same monochromatic light. All three solutions are under equal irradiation at any specific location within the cell. Thus I_B consists of the direct fluorescence of the DBA_o molecules plus the direct fluorescence of the DBA_x molecules. I_{AB} consists of the direct fluorescence of its own DBA_o molecules plus the indirect fluorescence coming from DBA molecules which received their excitation energy from triplet ketones.

With the assumption of steady-state concentrations of A* and DBA*, these fluorescence intensities can be expressed as follows:

$$I_B = \phi_F(I_{abs} \text{ by } DBA_o) + \phi_F(I_{abs} \text{ by } DBA_x)$$

$$I_{AB} = \phi_F(I_{abs} \text{ by } DBA_o) + \phi_F\phi_{TS}(I_{abs} \text{ by } A)\frac{k_{ET}[DBA]}{k_d + k_{ET}[DBA]}$$

Finally

$$I_{ABQ} = \phi_F(I_{abs} \text{ by } DBA_o) + \phi_F\phi_{TS}(I_{abs} \text{ by } A)\frac{k_{ET}[DBA]}{k_d + k_{ET}[DBA] + k_Q[Q]}$$

or, at high concentration of quencher

$$I_{ABQ} = \phi_F(I_{abs} \text{ by } DBA_o)$$

Consequently and with

$$\frac{k_{ET}[DBA]}{k_d + k_{ET}[DBA]} = \phi_{ET} \tag{26}$$

$$I_{AB} - I_{ABQ} = \phi_F\phi_{TS}\phi_{ET}(I_{abs} \text{ by } A)$$

Similarly

$$I_B - I_{ABQ} = \phi_F(I_{abs} \text{ by } DBA_x)$$

But by definition (eq 25), I_{abs} by DBA_x = I_{abs} by A. Therefore

$$\phi_{ET}\phi_{TS} = (I_{AB} - I_{ABQ})/(I_B - I_{ABQ})$$

and since $k_d < 6 \times 10^5\ s^{-1}$ and $\phi_{ET} > 0.9^7$ at $[DBA] \geq 10^{-3}$ M, therefore ϕ_{ET} can be replaced by unity at high [DBA] and

$$\phi_{TS} \simeq \frac{I_{AB} - I_{ABQ}}{I_B - I_{ABQ}} \tag{27}$$

Results

Emission Spectra. The luminescence spectra of degassed solutions of acetophenone and DBA overlap as shown in Figure 2 (Figure 3 shows the absorption spectra, for reference). However, the luminescence intensity of a solution of acetophenone (1.5×10^{-2} M) containing in addition a low concentration of DBA (2.4×10^{-5} M) is about 20 times more intense than that of a solution of pure acetophenone, and the emission spectrum is practically undistinguishable from that of a solution of pure DBA at the same concentration, except for an overall reduction of intensity due to the inner filter effect of acetophenone (Figure 2). If no energy transfer took place between acetophenone and DBA and yet double-exponential decay was observed, such as in the case of the mixed solution above, then the prompt emission would have to be attributed to the direct fluorescence of DBA, whereas the slow emission could only be the phosphorescence of acetophenone. In this hypothetical case of no energy transfer, the expected ratio N_s/N_p would then be 1/20; in the experiment cited above, however, the observed value is $N_s/N_p \simeq 1.0$. Thus there is no question that even at such a low concentration of DBA, the emitter of both prompt and slow emissions is indeed DBA*, and the contribution from acetophenone phosphorescence is negligible.

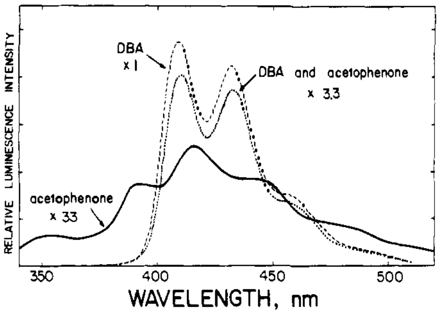

Figure 2. Luminescence spectra of degassed benzene solution of acetophenone and DBA: full line, phosphorescence of acetophenone = 1.5×10^{-2} M; dashed line, [DBA] = 2.4×10^{-5} M. Dotted line, [acetophenone] = 1.5×10^{-2} M, [DBA] = 2.4×10^{-5} M. Instrument sensitivity settings are indicated on the figure (λ_{exc} = 320 nm). (Note that the fluorescence of acetophenone may include a component from delayed fluorescence at the short wavelengths, see: Saltiel, J. et al. *J. Am. Chem. Soc.*, **1970**, 92, 410 and Discussion.)

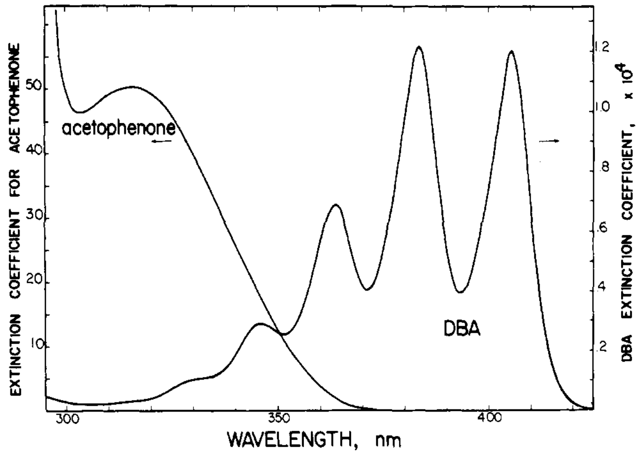

Figure 3. Absorption spectra of benzene solutions of acetophenone and of DBA.

Rates of Fluorescence Decay and of Energy Transfer. Solutions of acetophenone (~0.01 M) and DBA (concentration range = $(0.25\text{–}6.6) \times 10^{-4}$ M) were studied in three solvents: benzene, cyclohexane, and acetonitrile. In all cases, the decay curves were double exponentials, with at least a 100-fold difference in rate constants. Figure 1A is a representative example. The values of k_{obs} were directly obtained from the semilog plots. Figure 4 shows the values of k_{obs} for a series of experiments in benzene, plotted according to eq 7. The slope is k_{ET}, which represents the sum of all bimolecular quenching processes of A* involving DBA. The intercept is k_d, the rate of decay of triplet acetophenone by all pseudo-first-order processes in which DBA does not participate; in the benzene solution of Figure 4, least-squares analysis gave $k_d = (1.86 \pm 0.84) \times 10^5\ s^{-1}$.

Because of the fairly intense phosphorescence of acetophenone in fluid solution, the rate of decay of triplet acetophenone could

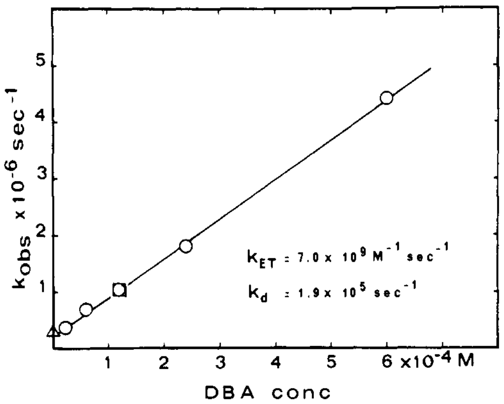

Figure 4. Rate of "slow" decay of DBA, k_{obs}, as a function of the concentration of DBA, in degassed benzene at 20 °C: (○) acetophenone concentration = 0.015 M, λ_{exc} = 320 nm, (□) acetophenone concentration = 7.4×10^{-3} M, λ_{exc} = 305 nm; (△) no DBA, acetophenone concentration = 0.015 M, λ_{exc} = 320 nm.

Table I. Rate Constants for the Decay of Triplet Acetophenone and the Quenching of Triplet Acetophenone by DBA in Three Solvents[a]

	acetonitrile	benzene	cyclohexane
$10^4 k_d$, s^{-1}	7 ± 2[b]	19 ± 6[c]	450 ± 20[d]
$10^{-9} k_{ET}$, M^{-1} s^{-1}	11.0 ± 0.2	7.00 ± 0.15	6.95 ± 0.15

[a] The concentration of acetophenone was 9.85×10^{-3} M, 1.50×10^{-2} M, and 1.05×10^{-2} M in the acetonitrile, benzene, and cyclohexane experiments, respectively. The solutions were degassed. [b] Literature value is 7.7×10^3 s^{-1}.[6] The literature value is lower because the concentration of acetophenone was lower, hence self-quenching was less important. [c] Literature value is 3.3×10^5 s^{-1}; Lutz, H.; Lindqvist, L. *Chem. Commun.* 1971, 493. [d] Literature value is 4.4×10^6 s^{-1}; ref *c* above.

Table II. Efficiency of Triplet-Singlet Energy Transfer, ϕ_{TS}, from Fluorescence Decay Curves (Donor – Acetophenone[a])

solvent[b]	10^4 [DBA] range, M	N_s'/N_p' min–max	ϕ_{TS}[c]	σ[d]
acetonitrile (4)	0.89–5.9	0.49–3.15	0.126	0.009
benzene (6)	0.24–6.0	0.34–1.98	0.118	0.011
cyclohexane (3)	1.7–6.7	0.17–6.7	0.102	0.002

[a] Acetophenone concentration as in Table I. Degassed solutions at 20 °C. [b] In parentheses, number of determinations. [c] The correction factor *F* (eq 21 and 22) was 0.99 in the acetonitrile and benzene experiments and 0.98 in cyclohexane. [d] Standard deviation σ of ϕ_{TS} was calculated from the range of ϕ_{TS} values multiplied by a factor taken from Table 9.4, p 244, in: Wilson, E. B. "An Introduction to Scientific Method"; McGraw Hill: New York, 1952.

also be measured directly in benzene, in the absence of DBA. A value of $k_d = 2.58 \times 10^5$ s^{-1} was obtained which is within the limits of errors of the value derived from the plot of k_{obs} vs. DBA concentration.

Similar experiments were carried out in acetonitrile and in cyclohexane. In all cases, the plots of k_{obs} vs. [DBA] were nicely linear. Table I summarizes the results.

Determination of ϕ_{TS} from the Fluorescence Decay Curves. Having determined the value of k_{ET} in each solvent, a value of ϕ_{TS} can now be estimated for each experiment. Only N_s'/N_p' is required, in addition to k_{ET}, k_{obs}, and ϵ at the excitation wavelength (eq 21). The results are listed in Table II. The average of ϕ_{TS} in the three solvents is 0.12 ± 0.02.

Rough Estimate of ϕ_{TS} from Fluorescence Intensities, in Static Conditions. In spite of the large errors attached to these intensity measurements (see Experimental Section), the data of Table III, acquired from eq 27, bring supporting evidence for $\phi_{TS} \simeq 0.14$ (±40%) in benzene. The agreement between these values is satisfying, particularly in view of the different approaches between the photostationary and the photokinetic methods.

Table III. Determination of ϕ_{TS} from Fluorescence Intensities in Degassed Benzene

acetophenone concn, M	10^3DBA concn, M	λ_{exc}, nm	ϕ_{TS}[a]
0.08	5.0	320	0.14
		320	0.16
0.21	6.6	320	0.17
		330	0.18
0.64	3.3	352	0.10
		320	0.07
			av 0.14 (±40%)

[a] Assuming $\phi_{ET} \approx 1.0$ (eq 20 and text).

Discussion

The results of Table I show clearly that the rate constant for energy transfer, k_{ET}, is high in all three solvents, where it approaches or equals the rate constant of a diffusion-controlled process. This is not surprising, since k_{ET} is defined as the sum of the rate constants for all the bimolecular quenching processes of A* by DBA. Since $E_T \approx 74$ kcal for acetophenone and only ~39 kcal for DBA(T_1), the overall quenching process is very exothermic and is expected to proceed at the diffusion-controlled rate by a collisional electron-exchange mechanism. The rate constant k_{ET} in acetonitrile is larger by a factor of 1.6 relative to benzene, which is consistent with the 1.75-fold difference in the viscosities of these two solvents. However, if this apparent dependence on viscosity was significant, one would then expect k_{ET} in cyclohexane to be smaller than in benzene by a factor of ~1.5. This is not observed, since k_{ET} is the same in these two solvents.

In any case, k_{ET} is never larger than k_{diff}. This is worth noting since a mechanism of energy transfer other than collisional, such as a long-range dipole–dipole Förster transfer or a triplet exciton process, could possibly apply to the T–S transfer between acetophenone and DBA and result in $k_{ET} > k_{diff}$. When k_{TS} is defined as the rate constant of reaction 3a, i.e., $k_{TS} = \phi_{TS} k_{ET}$, the values of k_{TS} calculated from the data of Tables I and II are as follows: 1.4×10^9 in acetonitrile, 8.3×10^8 in benzene, and 7.1×10^8 M^{-1} s^{-1} in cyclohexane. Thus k_{TS} is 7–10 times smaller than k_{ET} and about 1 order of magnitude smaller than k_{diff}.

There is a modest overlap between the absorption spectrum of DBA and the phosphorescence spectrum of acetophenone, which could allow a Förster-type energy transfer process between these molecules some distance apart. Using a dioxetane as the source of triplet acetophenone, Turro and his co-workers[8] have presented some evidence suggesting that when donor and acceptor are sequestered in polymer matrices, such a mechanism may obtain. It is difficult, however, to have a quantitative feeling for these results; one cannot appreciate, for example, how much more efficient DBA was at accepting triplet energy than another anthracene derivative without heavy-atom substituent and thus how much S–S energy transfer may contribute to the excitation of DBA. Vassil'ev[2] and others since[3] have shown that in fluid solution 9,10-diphenylanthracene (DPA) is far less successful than DBA (by ~2 orders of magnitude) at accepting the energy of triplet acetophenone chemically generated and converting it to singlet energy. In Förster transfer, relative rates of transfer between a given donor and two different acceptors equidistant from the donor are determined primarily by the spectral overlap between donor emission (here $T_1 \rightarrow S_0$) and acceptor absorption (here $S_0 \rightarrow S_1$). The absorption spectra and extinction coefficients of DBA and DPA are practically the same, and therefore one would expect that DPA would be as good an energy acceptor as DBA in a T–S

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[8] (a) Turro, N. J.; Kochevar, I. E.; Noguchi, Y.; Chow, M.-F. *J. Am. Chem. Soc.* **1978**, *100*, 3170. (b) The same argument can also be used to rule out a significant contribution from SS transfer between the very low concentration of acetophenone (S_1), resulting from thermal activation of T_1, and DBA. A photoexcitation experiment with acetophenone and 9,10-dichloroanthracene in acetonitrile gave a value of ϕ_{TS} ~25 times smaller than in a similar experiment with DBA at the same concentration.

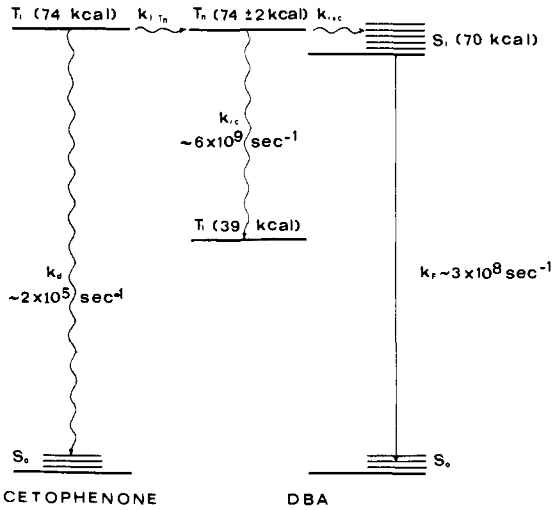

Figure 5. State diagram for DBA and acetophenone illustrating the possible T–T_n transfer.

Förster process. Since the type of transition involved in the distant acceptor is the spin-allowed $S_0 \rightarrow S_1$, there is no reason why the brominated species should have an advantage over the nonbrominated species.

In contrast, if there is contact between donor and acceptor during the lifetime of the donor, and electron-exchange processes are allowed to take place, one could see how the bromine atoms may confer an advantage to DBA in an overall spin-forbidden T–S process. Among collisional processes, the most attractive in the present context calls for the participation of the higher triplet(s) of DBA. It is well established that in DBA (as well as in several other anthracene derivatives) T_2 is higher than S_1 by only a few kilocalories (Figure 5).[9] The role of T_2 (or T_n) in thermally activated intersystem crossing $S_1 \rightsquigarrow T_2$ (or T_n) is well-documented and determines the effect of temperature and solvent on the efficiency of DBA fluorescence. There is, however, some degree of confusion about the symmetry assignments of these higher triplet states and their respective roles in the intersystem crossing for S_1. Recent observation[10] of emission bands in the far red attributed to $T_n \rightarrow T_1$ fluorescence locates the emissive state ~2.3 kcal above S_1, whereas the temperature dependence of $S_1 \rightarrow S_0$ fluorescence places the involved triplet level ~4.5–5 kcal above S_1.

Inasmuch as one or possibly two higher triplet states are located above S_1, but within a few kilocalories of it, and the solvent does not appear to reverse the order of S_1 and T_n, it seems very reasonable to assume that the transfer of triplet energy from acetophenone produces first DBA(T_n) via eq 3a′. Since E_{T_1} of acetophenone is ~74 kcal, the donor and acceptor triplet levels should be very close (Figure 5). DBA(S_1) would then be populated via isc from T_n, in competition with internal conversion to T_1, a process which has a rate constant estimated at $\sim 6 \times 10^9$ s^{-1}.[6] Note that this sequence of processes would then be the exact reverse of the very interesting T_2 photochemical reactions studied by Liu and co-workers,[6] where excitation of the S_1 state of anthracene derivatives was followed by isc to T_2 and then energy transfer from T_2 to quenchers or reactive acceptors.

In the system under discussion, ϕ_{TS} would then be expressed by eq 6 and the bromine substituents would have the obvious role

$$\phi_{TS} = \phi_{TT_n}\phi_{isc(T_n-S_1)} \qquad (6)$$

of facilitating T_n–S_1 intersystem crossing, i.e., increase $\phi_{isc(T_n-S_1)}$ compared to nonbrominated acceptors. From high-pressure studies of tetramethyldioxetane—a known source of triplet acetone[3]—Schmidt et al.[11] have reached the conclusion that DBA(T_2) was indeed involved in a first T–T energy-transfer process, but their arguments are somewhat indirect.

The recent studies of Wu and Ware[12] and of Dreeskamp and Pabst[13] show that solvents shift S_1 more than T_n. It is these relative effects on S_1 and T_n which account for the solvent dependence of the fluorescence efficiency of DBA, but since T_n remains above S_1 in all solvents, one does not expect $\phi_{isc(T_n-S_1)}$ to be much affected by the solvent, at least on an energy level basis. However, in the transfer process from triplet acetophenone to DBA(T_n), the donor and acceptor triplets are probably very close and the process may even be slightly endothermic. Therefore a small red shift of DBA(T_n) and a switch between n,π* and π,π* configurations of acetophenone T_1 may well have an effect on ϕ_{TT_n}.

If the interpretation of ϕ_{TS} according to eq 6 is valid, then a *lower limit* for $\phi_{isc(T_n-S_1)}$ can be derived from the data of Table II, which gave an average value $\phi_{TS} = 0.12$. (The static measurements in Table III, which are certainly subject to much larger errors, can be considered in rough agreement.) Thus

$$\phi_{isc(T_n-S_1)} \gtrsim 0.12$$

which means that, in DBA, the rate of internal conversion $T_n \rightsquigarrow T_1$ is *at most* ~8 times faster than isc rate $T_n \rightsquigarrow S_1$. The rates of these two processes may actually be much closer, since there is no reason to believe that the quenching of triplet acetophenone generates exclusively the higher triplet of DBA and no T_1.

Since the involvement of DBA(T_n) is likely, via a collisional process, it must be mentioned that the same T_n state also opens the way to a noncollisional, long-range mechanism of energy transfer in this system. Kasha[14] recently suggested a triplet exciton mechanism, in which he speculated a resonance interaction between the $T \rightarrow S_0$ transition of the ketone and the $S_0 \rightarrow T_n$ transition of DBA. Here the enhanced spin–orbit coupling due to the bromine atoms would have the effect of enhancing the $S_0 \rightarrow T_n$ transition probability (as well as enhancing the intersystem crossing $T_n \rightsquigarrow S_1$, not discussed in Kasha's brief note). This is a very interesting suggestion. Unfortunately, the results of the present work do not permit a distinction to be made between any of these mechanisms, although they certainly do not present any evidence for processes other than diffusion controlled. In actual fact, each of the various mechanisms mentioned (long-range T–S, collisional T–S, exciton T–T) may well play a role here, simultaneously.

Turning now to the use of DBA as a way of monitoring triplet ketones, it is clear that the kinetics of the sensitized fluorescence of DBA provides a sensitive method for the determination of the lifetime of the triplet ketone. Its use should be applicable to triplet donors which are difficult to study directly because of poor phosphorescence yields in fluid solutions. The time-correlated single-photon-counting method is an ideal technique for such a purpose. In addition, because it uses low-intensity light pulses, it avoids the complications due to photochemistry or photodegradation processes and to bimolecular reactions between triplets or between free radicals. Moreover, since DBA is present in relatively high concentration, its quenching of the ketone triplet becomes a dominant process which helps reduce the importance of undesirable side reactions. The very final product of energy transfer, namely, DBA(T_1), is of such low energy that it is probably inconsequential when no oxygen is present.

Conclusions

The overall energy transfer from triplet acetophenone to excited singlet DBA is a relatively efficient process ($\phi_{TS} \approx 0.12$); this efficiency is nearly solvent independent. In the absence of compelling evidence to the contrary, this overall TS process can most easily be rationalized in terms of a T–T transfer to form a

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[9] For example, Kearvell, A.; Wilkinson, F. *J. Chim. Phys. Phys.-Chim. Biol.* **1970**, *20*, 1925.

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

[11] Schmidt, R.; Kelm, H.; Brauer, H.-D. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 402; *J. Photochem.* **1978**, *8*, 217.

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

[13] Dreeskamp, H.; Pabst, *J. Chem. Phys. Lett.* **1979**, *61*, 262.

[14] Kasha, M. *Photochem. Photobiol.* **1979**, *30*, 185.

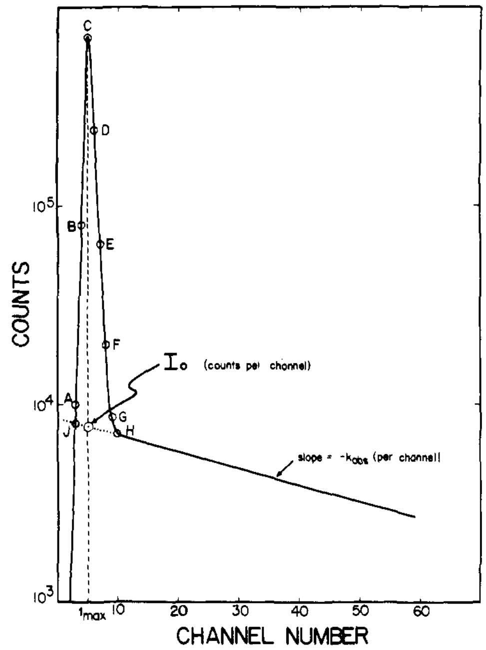

Figure 6. Schematic decay curve to illustrate the method used to calculate the ratio N_s'/N_p'—see Experimental Section.

short-lived higher triplet of DBA (not detected in the present work) followed by intersystem crossing to S_1 and finally DBA fluorescence.

The lifetime of triplet acetophenone, however, depends on the solvent and decreases in the order acetonitrile > benzene > cyclohexane, as expected from the relative hydrogen-donating ability of these solvents with respect to photoreductive quenching.

In the following paper, the method outlined here is applied to triplet acetone as the donor; the results of this study are quite different, in several respects, from those obtained here with acetophenone as donor.

Experimental Section

Materials and General Methods. Acetophenone (Fisher) was distilled at reduced pressure through a 35-cm Vigreux column. 9,10-Dibromoanthracene (Aldrich) was recrystallized from xylene and vacuum sublimed. Benzene, acetonitrile, and cyclohexane were from Burdick and Jackson ("Distilled in Glass"); benzene was purified according to the procedure of Wagner et al.,[15] and cyclohexane and acetonitrile were used as received. *cis*-1,3-Pentadiene (Columbia Organic) was also used as received, in the photostatic experiments. All solutions were degassed by four freeze-pump-thaw cycles and the cells sealed off at less than 10^{-4} torr, while being pumped. Absorption spectra and extinction coefficients were obtained with either a Cary 15 or a Cary 219 spectrophotometer and fluorescence spectra with a Perkin-Elmer MPF-44 spectrofluorimeter; these spectra were not corrected.

Fluorescence Decay Curves. Determination of ϕ_{TS}. The decay curves were obtained by the time-correlated single-photon-counting method, with an instrument previously described.[16] Monochromatic radiation was isolated from a D_2-filled flash lamp by a 0.25-m Jarrell Ash monochromator (1.6-nm band-pass). For experiments involving DBA, either an interference filter centered at 430 nm (Balzer, 12-nm 1/2 bandwidth) or a Corning 3-73 cut-off filter was employed. Right-angle excitation-detection geometry was used throughout. One- or two-hour acquisition times were typical. The temperature of the solution (20 °C) was controlled (±<0.5 °C) either by circulation of thermostated liquid through the cuvette block or by a thermoelectric device. The semilog fluorescence decay curves were analyzed in either of two ways. In the first, the experimental curves were graphically and mathematically compared with computer simulated curves (single exponential for solutions of pure DBA or sum of two exponentials for solutions of acetophenone and DBA), which were obtained via a convolution with the lamp profile. Because of the large difference in decay rates between the prompt and slow decays, such analyses were most prudently performed by collecting the data separately on two different time scales. The slow decay k_{obs} (see Figure 1a), which could easily be obtained graphically, was then used in fitting a theoretical curve to the data acquired on the expanded time scale, by the convolute-and-compare method. The ratio N_s'/N_p' was then obtained from the analyzed curve (Figure 1b). Alternatively, N_s'/N_s' was obtained from the decay curve acquired on a slow-time scale (as in Figure 1a), as follows. First the straight line corresponding to the slow decay was extrapolated to channel 0, as illustrated schematically in Figure 6. The value N_p' (in counts) was taken as the sum of the counts corresponding to the prompt emission, read from the computer printout, minus the sum of counts corresponding to the slow decay *in the same channels*, i.e., $\sum_A{}^H$(counts) − $\sum_J{}^H$(counts), in Figure 6. The value of N_s' is the integral of the slow exponential decay, I_0/k_{obs}, where I_0 is the intensity at t_{max} in counts per channel and k_{obs} is the rate of slow decay in units of channel^{-1}. The agreement between these two methods of estimating N_s'/N_p' was very good (within 3%).

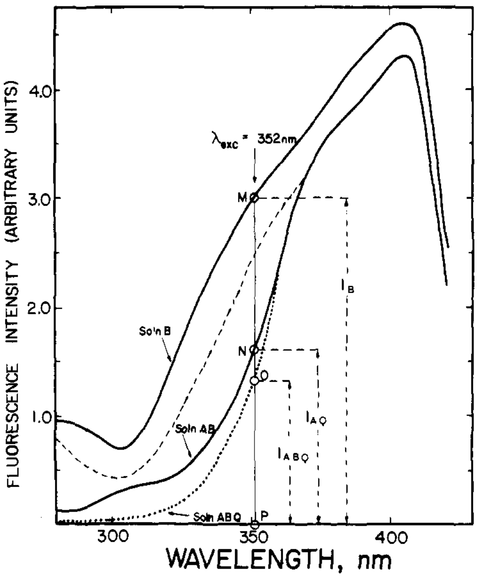

Figure 7. Fluorescence excitation spectra of solutions of DBA with or without acetophenone or *cis*-pentadiene. Fluorescence was monitored at 435 nm. Solution B: [DBA] = 6.6 × 10^{-3} M, degassed. Solution AB: [DBA] = 3.3 × 10^{-3} M; [acetophenone] = 6.4 × 10^{-1} M, degassed. Solution ABQ: Same as solution AB plus *cis*-pentadiene, 0.16 M, not degassed. For comparison, the dashed curve is the excitation of a solution of DBA, 3.3 × 10^{-3} M (same DBA concentration as solution AB but no acetophenone). This spectrum and those corresponding to solution AB and ABQ were normalized at 404 nm.

The ratio of initial concentrations of excited ketone and excited DBA which enters in the determination of ϕ_{TS} (eq 22) was taken as

$$\frac{[\mathrm{DBA}^*]_0}{[\mathrm{A}^*]_0} = \frac{\epsilon_{\mathrm{DBA}}[\mathrm{DBA}]}{\epsilon_{\mathrm{A}}[\mathrm{A}]}$$

Fluorescence Intensity Measurements: Excitation Spectra and Estimate of ϕ_{TS}. The alternate determination of ϕ_{TS} was based on the excitation spectra of DBA fluorescence (monitored at 435 nm) obtained with and without acetophenone in degassed benzene solutions. High concentrations ((1–6) × 10^{-3} M) of DBA are necessary for efficient interception of triplet acetophenone. But even higher concentrations of acetophenone are needed to ensure appreciable partial absorption by the ketone. At these high concentrations frontal illumination is mandatory. Quartz cuvettes of 2-mm path length were positioned diagonally inside the cuvette compartment of an Aminco-Bowman spectrofluorimeter, by means of appropriate spacers; the angle of incidence was 30° and the fluorescence was viewed at 90° from the exciting beam. With this geometry, the excitation spectra retain the overall shape of the absorption spectrum, even at the higher concentration of DBA, and λ_{max} is not significantly shifted from 10^{-6}–10^{-3} M DBA. The presence of acetophenone modifies the excitation spectrum of DBA (Figure 7) because of two opposite effects: the inner-filter effect and the sensitization of the fluorescence of DBA. The first of these effects dominates. Acetophenone does not absorb above 375 nm and therefore does not affect the excitation spectrum of DBA above this wavelength. The determination of ϕ_{TS} required the measurement of the fluorescence intensities I_{AB}, I_B, and I_{ABQ} of three solutions (see kinetic scheme). I_{ABQ} is the fluorescence intensity of solution I_{AB} after admitting air and a high concentration of the quencher *cis*-1,3-pentadiene.[17] To illustrate the method, consider a

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[15] Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.

[16] Halpern, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 7655.

J. Am. Chem. Soc. **1980**, *102*, 7279-7283

solution of DBA and acetophenone such that at 352 nm the partial absorbances of DBA and A are equal. Upon excitation at 352 nm, I_{AB} corresponds to NP, I_{ABQ} to OP, and I_B to MP (see Figure 7). Therefore, from eq 27 which assumes $\phi_{ET} \approx 1$, one obtains

$$\phi_{TS} = NO/MO$$

This is a special case, since the partial absorbances of DBA and A were equal, in solution AB. In general, referring again to Figure 7, MP would be the fluorescence intensity of a DBA solution having a total absorbance equal to the sum of the partial absorbances of DBA and acetophenone in solution AB. The reproducibility of individual measurements of a given solution was only about 10%, because of errors due to lamp fluctuations, imprecisions in the position of the cuvette, etc. These errors add up, so that the realistic error in ϕ_{TS} is ~40%. Moreover, a systematic error, difficult to appreciate, is introduced by the 2 mm thickness of the cuvette, which causes reabsorption of an ill-defined and variable fraction of the fluorescence, in the frontal illumination geometry of these experiments.

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[17] *cis*-Pentadiene (PTD) was chosen as quencher for the following reasons: (1) it does not absorb above ~320 nm; (2) its triplet state (E_T = 58.8 kcal) is well below that of acetophenone (E_T = 74 kcal), which should make triplet-triplet quenching very efficient, and also below the singlet state of DBA (E_s = 72 kcal), hence there should be no TS transfer from the diene to ^{1}DBA*. A drawback of *cis*-pentadiene is that it is a weak quencher of DBA fluorescence: a Stern-Volmer plot of this quenching gives $k_q\tau$ = 0.35 M^{-1} (hence $k_q \approx 2 \times 10^8$ M^{-1} s^{-1}). However, since this quenching by PTD affects the fluorescence of DBA uniformly throughout the excitation spectrum, it can be corrected for by normalizing the "quenched" and unquenched spectra at 404 nm.

A Kinetic Study of Sensitized 9,10-Dibromoanthracene Fluorescence Produced by Energy Transfer from Triplet Ketones. 2. Acetone as Donor: Complications in Benzene

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Abstract: The kinetics of energy transfer from triplet acetone, A*, to DBA was studied by the single-photon-counting method, following pulse excitation of acetone and DBA. In keeping with results obtained with triplet acetophenone as donor, the rate of quenching of A* by DBA is close to the diffusion-controlled limit in acetonitrile and in cyclohexane ($k_{ET} = 5.8 \times 10^9$ and 6.8×10^9 M^{-1} s^{-1}, respectively); DBA (S_1) is formed with triplet-singlet transfer efficiencies, ϕ_{TS}, of 0.08 and 0.05. In benzene, the results are distinctly different. The addition of benzene to cyclohexane solutions increases both the rate of decay of triplet acetone and ϕ_{TS}. Studies in cyclohexane-benzene solutions provide extrapolated values of k_d and ϕ_{TS} of 6×10^7 s^{-1} and 0.3, respectively, in pure benzene, which are consistent with direct measurement in neat benzene. It is postulated that a triplet exciplex of acetone with benzene is formed. This exciplex must be in fast dynamic equilibrium with its components, since the decay curve of the sensitized fluorescence of DBA is a single exponential, and it must also have a higher efficiency of TS transfer to DBA than triplet acetone itself. Contrary to expectations, oxygen was found to quench triplet acetone with the unexpectedly high rate constant 8×10^9 M^{-1} s^{-1}; therefore processes other than generation of singlet oxygen must play an important role in the quenching.

Introduction

Benzene is a well-known quencher of the triplet state of aliphatic ketones;[2] however, even in the prototype case of acetone, questions remain regarding the mechanism of this process, which is believed to involve charge-transfer interactions.[3] Because the quenching by benzene is a fast process, the phosphorescence of acetone has not been measured in neat benzene, and the lifetime of triplet acetone in that solvent is not known. While specific interaction between triplet acetone and benzene may indeed be postulated, emission from a triplet exciplex of acetone and benzene has not been observed.

In the preceding paper,[4] it was shown that energy transfer from triplet acetophenone to form the excited singlet state of 9,10-dibromoanthracene (DBA) is a fast and apparently straightforward process. Moreover, the efficiency of the overall triplet-singlet transfer ϕ_{TS} was found to be 0.12 ± 0.02, irrespective of the solvent (acetonitrile, cyclohexane or benzene). Thus energy transfer to DBA provides an indirect but sensitive method for monitoring triplet carbonyls via photokinetic fluorescence studies, in which a pulse of light excites the ketone and also some of the DBA. Energy is transferred from the ketone to the DBA, whose emission is determined as a function of time.

The results obtained with triplet acetone as donor and benzene as solvent present a very different picture. Whereas in acetonitrile or in cyclohexane acetone and acetophenone behave quite similarly as donors of energy to DBA, benzene actually *increases* the efficiency of TS energy transfer from triplet acetone while decreasing the lifetime of the ketone triplets. The present paper describes the results of experiments carried out in acetonitrile, cyclohexane, and neat benzene as well as in mixed benzene-cyclohexane solutions, where it was hoped that the role of benzene could be elucidated. A reaction scheme involving the reversible formation of a short-lived triplet exciplex of acetone and benzene and the role of this exciplex as an energy donor will be shown to be compatible with the main observations.

The kinetic equations on which the analysis of the fluorescence decay curves is based have been derived previously. The energy-transfer step can be written as a direct TS transfer, according to eq 1 and 2, where A* is acetone (T_1) and DBA* is DBA (S_1)

$$A^* + DBA \xrightarrow{\phi_{TS}k_{ET}} DBA^* + A \tag{1}$$

$$A^* + DBA \xrightarrow{\phi_{TT}k_{ET}} DBA + A \tag{2}$$

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[1] (a) Harvard University. (b) Northeastern University.

[2] (a) Porter, G.; Dogra, S. K.; Loufty, R. O.; Sugamori, S. E.; Yip, R. W. *J. Chem. Soc., Faraday Trans. 1* **1973**, *1*, 69, 1462. (b) See also: Turro, N. J. "Modern Molecular Photochemistry", Benjamin Cummings: Menlo Park, CA, 1978; Wagner, P. J. *Top. Curr. Chem.* **1976**, 1-52 and references therein.

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[4] Wilson, T.; Halpern, A. M.; preceding paper in this issue.

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