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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)

$$A^* + DBA \xrightarrow{\phi_{TS}k_{ET}} DBA^* + A \qquad (1)$$

$$A^* + DBA \xrightarrow{\phi_{TT}k_{ET}} DBA + A \qquad (2)$$

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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.

(3) Loufty. R. O.; Yip, R. W. *Can. J. Chem.* **1973**, *51*, 1881.

(4) Wilson, T.: Halpern. A. M.: preceding paper in this issue.

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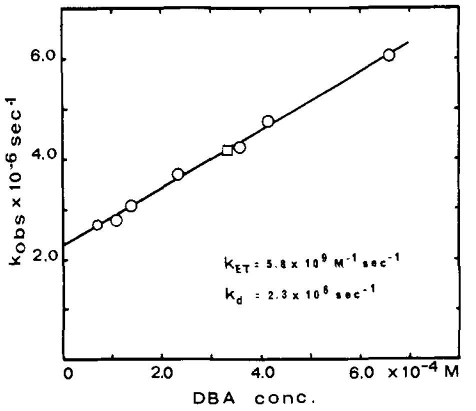

Figure 1. Rate of "slow" decay of DBA, k_{obs}, as a function of the concentration of DBA, in degassed cyclohexane solution at 20 °C: (○) acetone concentration 0.109 M, λ_{exc} = 302.5 nm; (□) acetone concentration 0.027 M in one experiment and 0.218 M in another experiment, λ_{exc} = 305 nm (no detectable effect of acetone concentration on k_{obs}).

with

$$\phi_{TS} + \phi_{TT} = 1 \tag{3}$$

or according to reactions 4 and 5, which assume the intermediacy of a higher triplet state (T_n) of DBA:

$$\begin{tikzcd} A^* + DBA \arrow[r, "\phi_{TTn}k_{ET}"] & A + DBA\,(T_n) \arrow[r, "\phi_{isc}k_C"] \arrow[d, "(1-\phi_{isc})k_C"] & DBA^* \\ & {} & \end{tikzcd} \tag{4}$$

$$A^* + DBA \xrightarrow{(1-\phi_{TT})k_{ET}} A + DBA\,(T_1) \tag{5}$$

with

$$\phi_{TS} = \phi_{TT}\phi_{isc(T_n-S_1)} \tag{6}$$

Although no direct evidence was obtained in support of reactions 4 and 5, this alternative seems conceptually more likely.[4] In any event, reactions 1 and 4 are kinetically indistinguishable here.

Results[5]

A. Fluorescence Decay and Energy-Transfer Rates and TS Transfer Efficiency. 1. Cyclohexane and Acetonitrile as Solvents. In these two solvents, the results obtained with triplet acetone parallel those obtained with triplet acetophenone. The rate of the "slow" decay of DBA fluorescence, emitted by those DBA molecules which received their excitation energy from triplet acetone, is always at least 2 orders of magnitude slower than the "prompt" decay, which results from light absorbed by DBA directly. The decay curves are well described by the sum of two exponentials, according to eq 7 (eq 17 in preceding paper).

$$I_t = (k_F[DBA^*] - c)\phi_F \exp(-k_Ft) + c \exp(-k_{obs}t) \tag{7}$$

$$c = (k_F\phi_{TS}k_{ET}[A^*]_0)/(k_F - k_{obs}) \tag{8}$$

k_F is the rate of decay of the prompt fluorescence of DBA* (in the conditions of the experiments) and

$$k_{obs} = k_d + k_{ET}[DBA] \tag{9}$$

k_d is the rate of decay of triplet acetone by all pseudo-first-order processes in which DBA does not take part.

Excellent linear plots of k_{obs} vs. DBA concentration were obtained in these two solvents; Figure 1 is an example. The values of k_d and k_{ET}, the intercepts and slopes of these plots (eq 9), are presented in Table I. Note that two direct determinations of k_d in cyclohexane, without DBA, gave k_d = 2.13 and 2.66 × 10^6 s^{-1}.

This table also lists the values of ϕ_{TS} obtained in these two solvents. These values were calculated according to eq 10. Here,

$$\phi_{TS} = \frac{N_s}{N_p}\,\frac{k_{obs}}{k_{ET}[DBA]}\,\frac{\epsilon_{DBA}[DBA]}{\epsilon_A[A]} \tag{10}$$

Table I. Values of k_d, k_{ET} and ϕ_{TS} with Triplet Acetone as Energy Donor at 20 °C

solvent	k_d, s^{-1}	k_{ET}, M^{-1} s^{-1}	ϕ_{TS}	σ[a]
cyclohexane[b]	(2.2 ± 0.1) × 10^6	(5.8 ± 0.2) × 10^9	0.049	0.007
acetonitrile[c]	(1.7 ± 0.1) × 10^4	(6.8 ± 0.2) × 10^9	0.083	0.002

[a] 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. [b] Acetone concentration = 0.027–0.218 M, see Figure 1. [c] Acetone concentration = 0.054 M (lit. value, k_d = 2.2 × 10^4 s^{-1} [2a]).

Table II. Decay Rates and Values of ϕ_{TS} in Benzene at 20 °C

acetone concn, M	DBA concn, M	k_{obs}, M^{-1} s^{-1}	ϕ_{TS}
0.054	2.4 × 10^{-3}	6.7 × 10^7	0.15
0.064	3.5 × 10^{-5}	8.3 × 10^7	0.25
0.109	1.1 × 10^{-3}	7.1 × 10^7	0.35
0.109	1.9 × 10^{-4}	5.9 × 10^7	0.30
0.120	7.5 × 10^{-4}	6.7 × 10^7	0.30
			av 0.27

Table III. Values of k_{ET}, the Rate of "Quenching" of Triplet Acetone by DBA in Mixed Cyclohexane-Benzene Solutions at 20 °C[a]

benzene concn, M	$10^{-9}k_{ET}$, M^{-1} s^{-1}	benzene concn, M	$10^{-9}k_{ET}$, M^{-1} s^{-1}
0	5.8	4.5	7.3
2.2	7.0	6.3	8.1
3.4	7.0		

[a] Acetone concentration = 0.109 M.

N_s/N_p is the ratio of the total number of "slow" photons and "prompt" photons emitted by DBA as a result of the pulse excitation (taking into account an experimental correction factor F which is 0.99 in these two solvents; see Kinetic Scheme and Treatment of Data in the preceding paper). ϵ_A and ϵ_{DBA} are the respective extinction coefficients of acetone and DBA at the excitation wavelength.

2. Benzene as Solvent. In neat benzene, the "slow" rate of decay is nearly as fast as the "prompt" decay, as illustrated in Figure 2, where the two rates differ by less than a factor of 6. A computer convolution of the data with the lamp pulse profile gives a good fit for a double exponential decay (eq 7) with k_F = 3.3 × 10^8 s^{-1} and k_{obs} = 5.9 × 10^7 s^{-1}. Surprisingly, this "best-fitting" decay function corresponds to an efficiency of energy transfer $\phi_{TS} \approx 0.3$, which is 6 times higher than that in cyclohexane (if a value of $k_{ET} \approx 10^{10}$ M^{-1} s^{-1} is assumed, see Discussion; a lower value of k_{ET} would result in an even higher value of ϕ_{TS}). As shown in Table III, other experiments in benzene at various concentrations of acetone and DBA gave similarly high values of k_{obs} and ϕ_{TS}.[6] Good double-exponential fits were obtained in all cases; nevertheless, because k_{obs} and k_F are so close, larger uncertainties enter into the identification of the best-fit curves, by the "convolute and compare" method.[4]

3. Mixed Benzene–Cyclohexane as Solvent. Four series of experiments were carried out in mixed cyclohexane–benzene solutions of different compositions (from 20 to 56% benzene per volume). All the "slow" decay components were exponential (Figure 3, curve B) and the plots of their rate constants, k_{obs}, vs. DBA concentration were linear, according to eq 9. The slopes of these plots, k_{ET}, are listed in Table III. Figures 4 and 5 show the increase in k_d, the rate of decay of the triplet donor, and ϕ_{TS}

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(5) Acetone (Baker Instra-Analyzed) was used as received. All other materials and methods have been described in the companion paper. All experiments were performed at 20.0 °C.

(6) In these experiments, the correction factor F which enters in the determination of N_s/N_p in eq 10 is large, 0.75; therefore ϕ_{TS} was calculated directly from the following equation (eq 23 in the preceding paper):

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

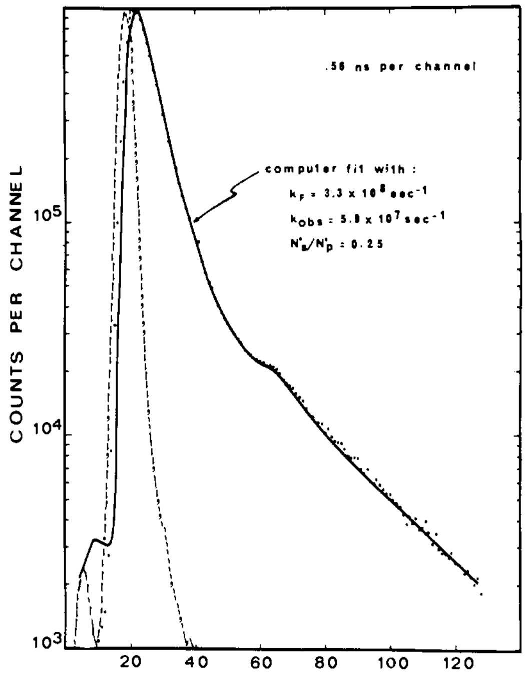

Figure 2. Fluorescence decay curve of a degassed benzene solution of acetone (0.109 M) and DBA (1.9×10^{-4} M), at 20 °C and with λ_{exc} = 305 nm. The dashed line is the lamp profile, and the full line is the convoluted "best-fit" double-exponential function.

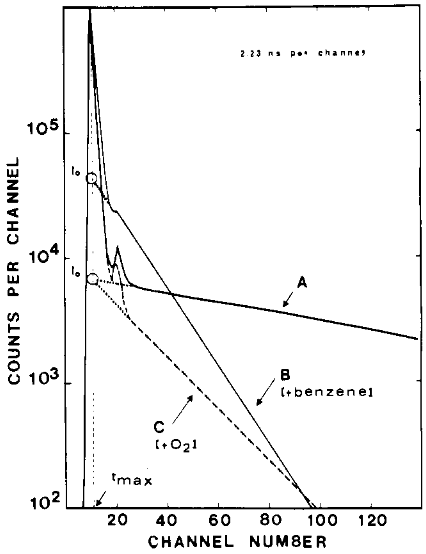

Figure 3. Effect of benzene and of oxygen on the fluorescence decay curves. Solutions: A, degassed cyclohexane; B, degassed cyclohexane–benzene (2.2/2.8, v/v); C, solution A, aerated (λ_{exc} = 305 nm, acetone concentration = 0.109 M, DBA concentration 2.35×10^{-4} M). The curves were normalized at channel no. 11.

Table IV. Effect of Acetone Concentration on k_d and k_{ET} in a Mixed Benzene-Cyclohexane Solution[a]

acetone concn, M	$10^{-7}k_d$, s^{-1}	$10^{-9}k_{ET}$, $M^{-1}\,s^{-1}$
0.054	3.4	8.4
0.109	3.1	8.1
0.218	2.7	7.7

[a] Benzene concentration = 6.3 M.

with increasing benzene concentration. By extrapolating those two curves to neat benzene (11.2 M), one obtains values of k_d and ϕ_{TS} of $\sim 6 \times 10^7$ s^{-1} and ~0.3, respectively, which are compatible with the results of Table II.

The increase in ϕ_{TS} due to benzene is strikingly demonstrated by a pair of experiments in cyclohexane, with and without 6.3 M benzene. In these two solutions, the concentrations of acetone and DBA are the same, as were all other experimental conditions such as excitation wavelength, temperature, and time scale. The only difference, therefore, was the presence of benzene. The two decay curves shown in Figure 3 were normalized at t_{max}. This normalization corrects for the difference in the efficiencies of DBA fluorescence between the two solutions, as well as for the difference in the acquisition times. Two features of the results are striking: (1) the "slow" decay is much faster in the mixed cyclohexane–benzene solution than in pure cyclohexane, and (2) the slow decay component intersects the prompt decay curve at a much higher intensity, i.e., the initial intensity, I_0, of the slow decay (extrapolated to t_{max}) is 6 times higher with benzene than without benzene. Since the extinction coefficient of acetone is about the same in pure cyclohexane as in the mixed solvent, the same number of acetone molecules are excited by the light pulse. Immediately after the flash, these excited acetone molecules undergo roughly the same number of collisions with DBA in the two solvents. Therefore, if the probability, ϕ_{TS}, that a collision between A* and DBA resulted in DBA* was the same in the two solvents, the intensity of the "slow" fluorescence of DBA right after the flash should be the same. Therefore ϕ_{TS} must be ~6 times larger in the benzene–cyclohexane solution than in pure cyclohexane, since I is ~6 times higher.

B. Effect of Acetone Concentration on k_d, k_{ET}, and ϕ_{TS} in Mixed Benzene–Cyclohexane Solutions. As shown in Table IV, the triplet donor appears to decay more slowly when the concentration of acetone is increased. These results were obtained from plots of k_{obs} vs. [DBA] in mixed benzene–cyclohexane (2.8/2.2, v/v), at three different concentrations of acetone. Also, the rate of quenching of the triplet donor by DBA, k_{ET}, is somewhat higher at lower concentration of acetone. ϕ_{TS} appears to be independent of the concentration of acetone, within the limits of errors.

C. Quenching by Oxygen. The introduction of a quencher of triplet acetone to this system should increase k_{obs}. With oxygen, for example

$$k_{obs} = k_d + k_Q[O_2] + k_{ET}[DBA] \qquad (11)$$

The results of a few experiments in air-equilibrated solutions (in cyclohexane and in mixed cyclohexane–benzene solutions) are given in Table V. The values of k_Q were calculated from eq 11 with $[O_2] = 2.3 \times 10^{-3}$ M in cyclohexane and 2.1×10^{-3} M in the mixed solvent. The presence of oxygen does not change the value of ϕ_{TS} (see Figure 3, curve C). For comparison, Table V includes also the results of an experiment with acetophenone.

Discussion

Comparison with Triplet Acetophenone as Donor. The results obtained previously[4] with triplet acetophenone as energy donor provide useful points of comparison for the acetone data, as seen in Table VI. First, for both acetone and acetophenone, the rates of triplet decay are lowest in acetonitrile. But whereas the value of k_d for triplet acetophenone is smaller in benzene than in cyclohexane (as expected, if hydrogen abstraction is the quenching process), k_d for triplet acetone is ~30 times *larger* in benzene than in cyclohexane. The comparison between the ϕ_{TS} values for these two ketones is also noteworthy. In the case of acetophenone, the nature of the solvent has little effect on ϕ_{TS}; similarly, there is no great difference between the ϕ_{TS} values of triplet acetone in acetonitrile and in cyclohexane, despite the different polarities of these two solvents. By way of contrast, triplet acetone in *benzene* is a much more efficient energy donor to DBA. If this higher ϕ_{TS} was a direct effect of benzene on DBA itself, one would expect ϕ_{TS} of triplet acetophenone to be also larger in benzene; this is in fact not observed. Clearly benzene seems to play a very specific role in the *acetone*–DBA system.

As discussed previously,[4] the most straightforward way to rationalize the triplet–singlet energy transfer to DBA is in terms of a two-step process (eq 4) in which excitation of a higher triplet level,[7] T_n, of DBA precedes intersystem crossing to DBA (S_1). It would be expected, then, that ϕ_{TS} may depend critically on the relative energies of the T_1 level of the ketone and the T_n level of DBA—or even of specific vibrational levels thereof. Thus, in a

Table V. Effect of Oxygen on k_{obs} at 20 °C[a]

solvent	DBA concn, M	$10^{-7}k_{\mathrm{obs}}$(aerated), s^{-1}	k_{obs}(degassed), s^{-1}	$10^{-9}k_Q$,[b] $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$
cyclohexane	0	2.2	2.6×10^6	8.4
cyclohexane	5.36×10^{-5}	2.1	2.6×10^6 [c]	8.5
cyclohexane	3.57×10^{-4}	2.2	4.2×10^6	7.7
cyclohexane	7.14×10^{-4}	2.5	6.4×10^6 [c]	8.1
benzene–cyclohexane[d]	5.43×10^{-4}	5.0	3.5×10^7	7.2
acetophenone, in cyclohexane[e]	3.33×10^{-4}	1.8	6.8×10^6	4.7[f]

[a] Acetone concentration = 0.109 M. [b] The oxygen concentrations assumed in these air-equilibrated solutions were 2.3×10^{-3} M in cyclohexane and 2.1×10^{-3} M in the mixed benzene-cyclohexane solution (an average of the O_2 concentration in cyclohexane and in benzene (1.9×10^{-3} M); these are taken from: Murov, S. "Handbook of Photochemistry", Marcel Dekker: New York, 1973. [c] These values of k_{obs} were taken from the plot of Figure 1. [d] Benzene–cyclohexane (2.8/2.2, v/v), i.e., benzene, 6.3 M. [e] Acetophenone concn 1.05×10^{-2} M. [f] Lit. value: $k_d = 4.0 \times 10^9$ in benzene.[12a]

given solvent, it is not too surprising that two ketones of different triplet energies should have different values of ϕ_{TS}. In cyclohexane, for example, ϕ_{TS} of acetone is only half of the ϕ_{TS} for acetophenone, even though—or perhaps because—the triplet level of acetone is 4 kcal *above* that of acetophenone.

Possible Role of an Exciplex. These considerations suggest a possible explanation for the effect of benzene, namely that triplet acetone forms an exciplex with benzene. This exciplex would be a more efficient triplet energy donor to DBA, because its triplet energy would be lower than that of uncomplexed acetone. For the sake of discussion, an exciplex with an approximately 4 kcal binding energy and a triplet level assumed accordingly to be also 4 kcal below that of acetone might well resemble acetophenone in several respects, including greater delocalization of the excitation energy.

The hypothesis of a short-lived triplet exciplex of acetone and benzene helps to rationalize not only the higher values of ϕ_{TS} in benzene but also the higher decay rates of the excited donor (Figures 4 and 5). The formation of such an exciplex has been proposed before. Loufty and Yip[3] have interpreted the quenching of triplet acetone by benzene in terms of "enhanced coupling of the locally excited triplet ketone and quencher states, as a result of interaction with the charge-transfer state", concluding that their interpretation "neither requires nor excludes the possibility that $E_{\mathrm{binding}} > RT$ for the complex". Reversible formation of an exciplex has been postulated by Giering et al.[8] in the case of triplet benzaldehyde, which is quenched by benzene much more rapidly than either acetophenone or benzophenone.

Additional information bearing on the assumption of a benzene–acetone exciplex is contained in the intensity decay curves: in all the experiments with acetone in mixed benzene–cyclohexane solutions, as well as in neat benzene, the "slow" decay component is always exponential. Therefore, the formation of the assumed exciplex E^* must be a fast, reversible process, eq 12, where B is benzene.

$$\begin{tikzcd} A^* + B \arrow[r, shift left, "k_{EA}"] \arrow[d, "k_A"] & E^* \arrow[l, shift left, "k_{AE}"] \arrow[d, "k_E"] \\ A & A + B \end{tikzcd} \qquad (12)$$

$$K_E = \frac{k_{EA}}{k_{AE}} = \frac{[E^*]}{[A^*][B]} \qquad (13)$$

Under conditions of dynamic equilibrium,[9] A* and E* decay at the same rate, k_d, given by

$$k_d = \frac{k_A + k_E K_E[B]}{1 + K_E[B]} \qquad (14)$$

and k_A is the decay rate of triplet acetone in pure cyclohexane. Qualitatively, it is immediately evident that eq 14, although accounting for an increase in k_d with the benzene concentration, will not represent the upward curvature of Figure 4. At high concentration of benzene (>2 M), k_d is observed to increase more sharply, suggesting that the exciplex itself may well be quenched by benzene

$$E^* + B \xrightarrow{k_B} A + 2B \qquad (15)$$

This would introduce a quadratic term in expression 16 for k_d.

$$k_d = \frac{k_A + k_E K_E[B] + k_B K_E[B]^2}{1 + K_E[B]} \qquad (16)$$

The exciplex assumption also provides an attractive, if qualitative, rationale for the increase in ϕ_{TS} with benzene concentration (Figure 5). Describing the triplet–singlet energy transfer by reactions 1 and 2, for simplicity

$$\phi_{TS} = k_{TS}/k_{ET} \qquad (17)$$

where k_{TS} is the weighted average of the rate constants for reaction 1 with either triplet acetone as donor ($k_{TS}{}^A$ or the triplet exciplex ($k_{TS}{}^E$); thus

$$k_{TS} = \frac{k_{TS}{}^A + k_{TS}{}^E K_E[B]}{1 + K_E[B]} \qquad (18)$$

In pure cyclohexane, $\phi_{TS} = 0.05$ and $k_{ET} = 5.9 \times 10^9$ M^{-1} s^{-1}, and therefore $k_{TS}{}^A = 3.0 \times 10^8$ M^{-1} s^{-1} from eq 17. If $k_{TS}{}^E$ is significantly larger than $k_{TS}{}^A$, eq 18 will account for the experimental results.

It is possible, therefore, to explain *qualitatively* the main features of the system triplet acetone–DBA–benzene on the basis of an assumed exciplex which would have a binding energy of a few kilocalories, a reasonable entropy of formation, and a shorter lifetime than triplet acetone itself.[10] In addition, this exciplex must have the following properties: (1) its rate of decay, k_E, must *increase* as the benzene concentration increases (eq 15) (by a factor of 2 between benzene (2 M) and neat benzene); (2) k_E must *decrease* as the concentration of acetone increases (Table IV). The latter effect is also small, since it requires a decrease in k_E of only 25% when the acetone concentration changes from 0.2

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[7] I.e., either T_2 or T_3 which are believed to be a few kilocalories above S_1. See. for example: Gillispie, G. D.: Lim, E. C. *Chem. Phys. Lett.* **1979**, *63*, 355.

[8] Giering. L.; Berger. M.; Steel. C. *J. Am. Chem. Soc.* **1974**, *96*, 953.

[9] (a) Where $k_{EA}[B] \gg k_A$, the sum of the rate constants for all deactivation processes of A* and $k_{AE} \gg k_E$, the rate constant for the decay of E* by all processes other than decomposition to triplet acetone and benzene. (b) By analogy with the excimer case; see, for example: Birks, J. B. "Photophysics of Aromatic Molecules": Wiley-Interscience: New York, 1970; p 309.

[10] (a) For example, an exciplex with $\Delta H \simeq -4$ kcal, as suggested earlier, and $\Delta S \simeq -18$ cal deg^{-1} mol^{-1} would have $K_E \simeq 0.08$. With this value of K_E, eq 16 and 18 fit the experimental data quite well. with the following chosen set of rate constants for the reactions of the exciplex: $k_E = 4 \times 10^7$ s^{-1}, $k_B = 8 \times 10^6$ M^{-1} s^{-1} and $k_{TS}{}^E = 5 \times 10^9$ M^{-1} s^{-1}. These rate constants all have reasonable values. The value of $K_E = 0.08$ would mean that about 30% of the triplet acetone molecules would be complexed with benzene in a 50% benzene–cyclohexane solvent and that the proportion of exciplex would rise to 50% in neat benzene. (b) In such an exciplex, the singlet–triplet splitting is expected to be small; therefore excitation of DBA could conceivably take place via singlet–singlet energy transfer, with singlet exciplex (resulting from thermal activation of the triplet exciplex) acting as donor. That this is not the case is demonstrated by an experiment with 9,10-dichloroanthracene instead of DBA but otherwise in conditions identical with that of the experiment of Figure 3, curve B. The rate of the "slow" decay is the same with 9,10-dichloroanthracene as with DBA, but I_0 and ϕ_{TS} are smaller (by at least 1 order of magnitude). If the energy donor had been a singlet species, the two anthracene derivatives should have been equally effective as acceptors. Since DBA is a better acceptor, the donor must be the triplet exciplex.

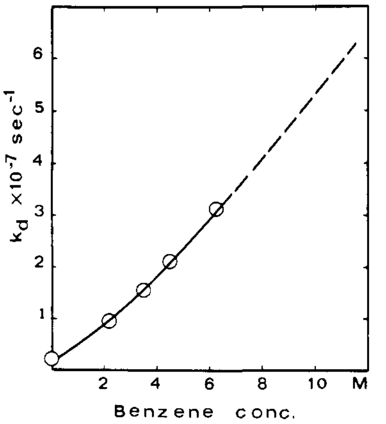

Figure 4. Effect of benzene concentration on the rate of decay of triplet acetone in mixed cyclohexane–benzene degassed solutions.

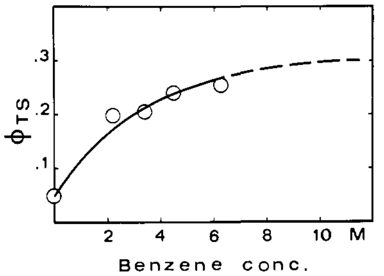

Figure 5. Effect of benzene concentration on the efficiency of triplet–singlet transfer to DBA from triplet acetone in mixed degassed cyclohexane.

Table VI. A Comparison between Acetone and Acetophenone as Triplet Energy Donors to DBA

	acetophenone		acetone	
solvent	k_d, s^{-1}	ϕ_{TS}	k_d, s^{-1}	ϕ_{TS}
acetonitrile	4.8×10^4	0.13	1.7×10^4	0.08
cyclohexane	4.5×10^6	0.10	2.2×10^6	0.05
benzene	1.9×10^5	0.12	$\sim 6 \times 10^7$	~ 0.3

to 0.02 M. It does not seem unreasonable that the proposed exciplex might be sensitive to interactions with its molecular components, and there are precedents in the literature for abrupt changes in decay rates at very high concentrations of one of the partners of an excimer, for example.[11]

Quenching by Oxygen. Oxygen was found to quench triplet acetone much more efficiently than expected, both in pure cyclohexane and in mixed benzene–cyclohexane solutions (the rate of quenching by oxygen was not measured in acetonitrile). Thus acetone joins the ranks of the few triplet compounds known to be quenched by oxygen at rates exceeding one-ninth of the diffusion-controlled rate, the limit dictated by the spin-statistical factor for the process[12a]

$$^3\mathrm{M}^* + {}^3\mathrm{O}_2 \xrightarrow{{}^1/_9 k_{\mathrm{diff}}} {}^1\mathrm{M} + {}^1\mathrm{O}_2^* \qquad (19)$$

which is thought to be the prevailing pathway for quenching of triplet states. Since k_{diff} in these solvents is $(2\text{–}3) \times 10^{10}$ M^{-1} s^{-1}, one would expect $k_Q \approx (2\text{–}3.3) \times 10^9$, instead of $k_Q \approx 8 \times 10^9$ M^{-1} s^{-1} as observed. This indicates that singlet oxygen is not formed in every quenching event (eq 19) and that a faster process dominates. Garner and Wilkinson[12b] have proposed that low-lying charge-transfer states of a complex with oxygen play an important part in the fast oxygen quenching of some aromatic ketones and amines which have high triplet states such as xanthone and methyl indole.[12c] A similar mode of quenching may take place in the case of aliphatic triplet ketones, and be so dominant that very little singlet oxygen is generated.[13] This could explain the results of Wu and Trozzolo,[14] who studied the photooxygenation of typical singlet oxygen acceptors, photosensitized by different aliphatic ketones, and concluded that the quantum yield of singlet oxygen production was only 0.03 in all cases. Two possible explanations were proposed by these authors, namely, (a) intrinsically low efficiency of production of singlet oxygen from the triplet state of an aliphatic ketone or (b) competition between quenching of these triplets by oxygen and by other deactivation processes not involving oxygen. The present results clearly favor the first of these possibilities.

Conclusions

By measuring DBA fluorescence decay rates under conditions where some of the DBA receives its excitation energy from triplet acetone, it has been possible to obtain a good estimate of the lifetime of triplet acetone in benzene, a value hitherto unavailable and remarkably short, ~17 ns. Benzene interacts very rapidly with triplet acetone, probably to form a triplet exciplex which is in dynamic equilibrium with its components. The increase in the decay rate of the triplet donor (to DBA) in the presence of increasing concentrations of benzene could be explained by an increase in the ratio of concentrations of exciplex to triplet acetone.[15] It is speculated that the exciplex is a very good triplet energy donor to DBA,[16] and in fact it is more efficient than triplet acetone itself. With this assumption, one can rationalize the increase in ϕ_{TS} as the concentration of benzene increases. In neat benzene, ϕ_{TS} is 0.3, which means that if a higher triplet of DBA is involved in the energy transfer, internal conversion $T_n \rightsquigarrow T_1$ is at most 2 times faster than intersystem crossing $T_n \rightsquigarrow S_1$, a surprising result.

It thus appears that when applying the DBA method to the determination of yields of triplet carbonyls in chemiluminescent reactions, one must be aware of the fact that ϕ_{TS} is *not* independent of the nature of the triplet donor nor of the solvent. Future experiments to evaluate the effect of substituents on the carbonyl and on benzene will help to assess reliability limits for this method and to further elucidate the role of the postulated exciplex.

Oxygen was found to quench triplet acetone with a rate constant $k_Q = 8 \times 10^9$ M^{-1} s^{-1}, more than twice the anticipated value. This result shows that formation of singlet oxygen is not the only mode of quenching of triplet aliphatic ketones by oxygen.

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(11) (a) Birks, J. B.; King, T. A. *Proc. R. Soc. London, Ser. A* **1966**, 291, 244. (b) Halpern, A. M.; Ravinet, P.; Sternfels, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 169. (c) Saltiel, J.; Townsend, D. E.; Watson, B. D.; Shannon, P. *Ibid.* **1975**, *97*, 5688.

(12) (a) Stevens, B.; Algar, B. E., *Ann. N.Y. Acad. Sci.* **1970**, *171*, 50. (b) Garner, A.; Wilkinson, F. *Chem. Phys. Lett.* **1977**, *45*, 432. (c) Even in the case of acetophenone, these authors found $k_Q = 4 \times 10^9$ M^{-1} s^{-1} (in agreement with two determinations reported here, Table V), which is already above the upper limit for the process generating singlet oxygen (eq 19).

(13) Addition of oxygen to the ketone to form a transient diradical is another possibility.

(14) Wu, K. C.; Trozzolo, A. M. *J. Photochem.* **1979**, *10*, 407.

(15) (a) Turro et al.[15b] have suggested that endothermic energy transfer from triplet acetone to the phenyl groups of polystyrene, followed by energy hopping from phenyl group to phenyl group, could be the mechanism of energy migration in some of their experiments with tetramethyldioxetane in polystyrene at 50 °C. A similar energy-transfer process could conceivably operate here, according to $A^* + B \rightarrow B^* + A$, and lead to an equation similar to eq 14, where K_E would be replaced by the equilibrium constant K of the reversible reaction above. However, with 6-kcal difference between the triplet states of acetone and benzene, one calculates $K = 4 \times 10^{-5}$ at 20 °C, assuming $k_{ET} = 5 \times 10^9$ M^{-1} s^{-1} for the isothermal process. Thus the concentration of B* would always be much too low to account for the observed increase in k_d and in ϕ_{TS} with benzene. (b) Turro, N. J.; Kochevar, I. E.; Noguchi, Y.; Chow, M.-F. *J. Am. Chem. Soc.* **1978**, *100*, 3170.

(16) Examples of energy transfer from exciplexes have been reported. See, for example: Heminway, R. E.; Park, S.-M.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 200; Tachikawa, H.; Faulkner, L. R. *Ibid.*, **1976**, *98*, 5569.