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Registry No. (\pm)-1a, 89908-35-0; (-)-1a, 69515-17-9; (\pm)-1b, 89908-41-8; (R)-1b-(S)- α -methyl-*p*-nitrobenzylamine, 90024-32-1; (S)-1b-(S)- α -methyl-*p*-nitrobenzylamine, 90024-31-0; (\pm)-3, 89908-36-1; (\pm)-18, 89908-37-2; 19, 22047-88-7; (\pm)-20a, 89908-38-3; (\pm)-20b,

89908-39-4; (\pm)-21, 89908-40-7; (\pm)-22, 89955-26-0; (-)-22, 89955-27-1; (\pm)-23, 89908-42-9; (\pm)-24, 89908-43-0; (\pm)-25, 89908-44-1; (\pm)-28a, 89908-46-3; (\pm)-28a (acid), 89908-45-2; (\pm)-28b, 89908-47-4; (\pm)-29a, 89908-48-5; (\pm)-29b, 89908-49-6; (\pm)-31, 89908-50-9; 34, 89908-56-5; 35, 89908-57-6; 36, 86728-17-8; 37, 89908-51-0; 38a, 89908-52-1; 38b, 89908-54-3; 39a, 89908-53-2; 39b, 89908-55-4; 42, 89955-28-2; 43, 89908-58-7; 44a, 89908-59-8; 44b, 89908-61-2; 45a, 89955-29-3; 45b, 89955-30-6; 46, 89908-60-1; 47, 89908-62-3; PhSeCl, 5707-04-0; cyclohexanone, 108-94-1; 4-methylcyclohexanone, 589-92-4; (S)-(-)- α -methyl-*p*-nitrobenzylamine, 4187-53-5.

Energy-Transfer Study of a Triplet Exciplex of Cyclohexanone and Mesitylene

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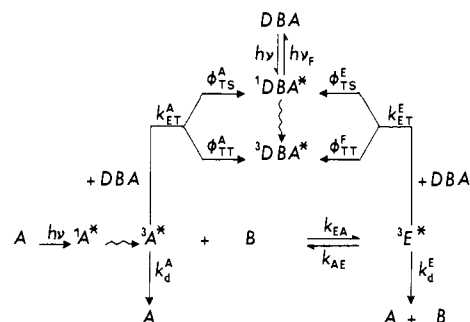
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Abstract: Triplet cyclohexanone associates ($k_{EA} \sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$) with mesitylene to form a triplet exciplex, E^* , with a lifetime of $\sim 0.3 \mu\text{s}$ in cyclohexane at 20 °C, i.e. half that of the uncomplexed triplet ketone. This conclusion rests on evidence obtained from energy-transfer experiments with 9,10-dibromoanthracene (DBA) as energy acceptor in a formal triplet-singlet energy-transfer process which populates DBA (S_1). In degassed cyclohexane solutions of cyclohexanone (0.077 M), DBA ($0.5\text{--}5.0 \times 10^{-4}$ M), and mesitylene (0.07–1.0 M), both E^* and the uncomplexed triplet alkanone sensitize the fluorescence of DBA; its intensity decay is studied by the time-correlated single-photon counting method following pulse excitation at 305 nm where both cyclohexanone and DBA absorb. In the presence of mesitylene, the DBA fluorescence decay profiles reveal the buildup of an excited transient, which is postulated to be the triplet exciplex. The decay curves can be fitted to triple-exponential functions, as predicted by a kinetic scheme based on the reversible formation of E^* . Kinetic expressions derived from this scheme allow the calculation of *all* the rate constants of the scheme. At 20 °C, the equilibrium constant favors the exciplex ($K_E \sim 13$). The efficiency ϕ_{TS}^E of the overall triplet-singlet energy transfer from E^* to DBA is ~ 7 times higher than from the triplet alkanone; this result is in line with an earlier finding in the case of the less stable triplet exciplex of acetone and benzene. Work is in progress to ascertain the origin of the low k_{EA} , to investigate the effects of solvent and substitution on this rate and on K_E , and to investigate the mechanism of TS transfer to DBA.

In contrast to singlet exciplexes, triplet exciplexes in fluid solution have remained largely elusive.¹ Like any other triplet species, they can be expected to be poor emitters at best; thus, only indirect arguments are, by and large, available for proposing their likely intermediacy in reactions.² It has recently been shown³ that exciplexes of triplet alkanones and benzene or methyl-substituted derivatives can be intercepted by 9,10-dibromoanthracene (DBA), which acts as a unique fluorescence probe.⁴ Energy transfer from the triplet donors populates DBA (S_1) of 2-ns lifetime, possibly via a higher triplet state of DBA. Consequently, the intensity decay profile of the resulting fluorescence of DBA contains information on the triplet donors. The fluorescence of DBA has a maximum at ~ 430 nm and is easily monitored as a function of time by the single-photon counting technique.^{4b} This DBA method first revealed the presence of an exciplex of triplet acetone in benzene in dynamic equilibrium with its components, in solutions irradiated at 305 nm.^{3a} This result showed conclusively that the much reduced lifetime of triplet acetone in benzene, which is 10 times shorter than in cyclohexane and 1000 times shorter than in acetonitrile, can be regarded as the result of weak complexation. The triplet exciplex which results from the association of a more substituted alkanone such as cyclohexanone with *o*-xylene, for example, was shown to be significantly more stable at room temperature, judging by the three-component fluorescence decay of DBA in this system.^{3b}

The present paper describes a study of the cyclohexanone/mesitylene system, in cyclohexane at 20 °C. As in the previous

Scheme I



work, solutions of the ketone, the aromatic, and DBA were submitted to pulse excitation at a wavelength absorbed by both the

(1) Triplet exciplexes of metalloporphyrins and anthracene (but see ref 1c) with nitro aromatics or chloro compounds have been reported from flash spectroscopy data: (a) Roy, J. K.; Carroll, F. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 6349. (b) Kapinus, E. I.; Aleksankina, M. M.; Dilung, I. I. *J. Photochem.* **1983**, *21*, 125. (c) Kuzmin, V. A.; Renge, I. V.; Borisevich, Yu. E. *Chem. Phys. Lett.* **1980**, *70*, 257.

(2) See, for example: Gupta, A.; Hammond, G. S. *J. Am. Chem. Soc.* **1976**, *98*, 1218. Farid, S.; Hartman, S. E.; Doty, J. C.; Williams, J. L. R. *Ibid.* **1975**, *97*, 3697. Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45. Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141. Loufty, R. O.; Yip, R. W. *Can. J. Chem.* **1973**, *51*, 1881. Scaiano, J. C.; Perkins, M. J.; Sheppard, J. W. *J. Photochem.* **1983**, *21*, 137. Ulrich, T.; Steiner, U. E.; Föll, R. E. *J. Phys. Chem.* **1983**, *87*, 1873 and references therein.

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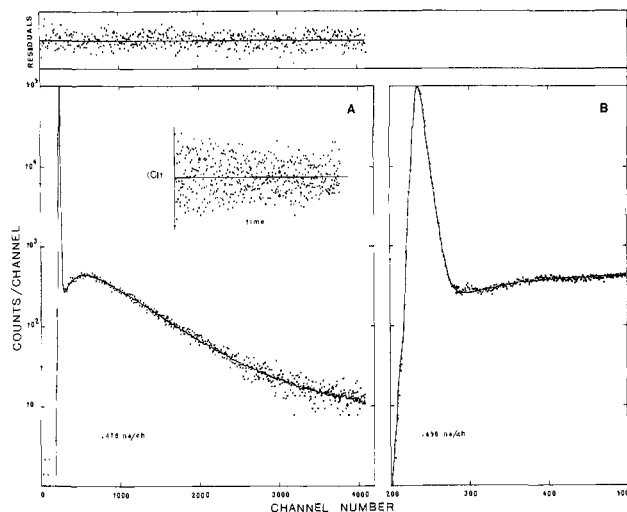


Figure 1. Fluorescence decay curve of a degassed cyclohexanone solution of cyclohexanone (0.077 M), mesitylene (0.96 M), and 9,10-dibromoanthracene (1.05×10^{-4} M) at 20 °C; $\lambda_{\text{exc}} = 305$ nm, fluorescence monitored in 420–500 nm spectral region; see text. The time scale is 0.416 ns per channel. In (A), the plot shows only one data point in eight, with even spacing between points. The weighted residuals are plotted at the top; the insert shows the autocorrelation function $C(t)$ of these residuals. In (B), all data points are plotted between channels 200 and 600. The full-line is the convoluted “best-fit” triple-exponential function, with the following parameters: $k_F = 4.61 \times 10^8 \text{ s}^{-1}$, $\lambda_a = 4.06 \times 10^6 \text{ s}^{-1}$, $\lambda_b = 1.28 \times 10^7 \text{ s}^{-1}$, $\alpha = 221$, $\beta = -0.938$ (eq 1). The value of χ^2 is 1.59, in the range 200–4096 channel numbers.

ketone and DBA. Figure 1 is a typical triple-exponential decay curve of DBA fluorescence in a degassed solution of mesitylene, cyclohexanone, and DBA; the buildup of an excited transient is evident. A series of such curves obtained at different concentrations of the reactants contains a wealth of information from which all the rate constants pertaining to the formation and dissociation of the exciplex can be extracted.

Kinetic Scheme and Method

The general Scheme I, where A stands for the alkanone, here cyclohexanone, and B for the benzene derivative, here mesitylene, accounts for all the experimental observations. For simplicity, all unimolecular or bimolecular reactions of triplet alkanone or exciplex not involving DBA, such as the photoreduction of cyclohexanone by the solvent, are lumped together in the pseudo-first-order rate constants k_d^A and k_d^E . Furthermore, eventual reactions of, and emission from, $^3\text{DBA}^*$ are of no consequence here and thus need not be considered.

At each concentration of DBA and the aromatic, Scheme I predicts that the experimental decay curve of DBA fluorescence intensity, I_t vs. t , can be fitted to a function of the form (see Appendix for complete derivation):

$$I_t \propto \alpha e^{-k_F t} + \beta e^{-\lambda_a t} + e^{-\lambda_b t} \quad (1)$$

The three rate parameters k_F , λ_a , and λ_b and the two amplitude ratios α and β (β has a negative value) are thus accessible experimentally. The parameter k_F is the rate constant of DBA fluorescence decay ($\sim 5 \times 10^8 \text{ s}^{-1}$), and λ_a and λ_b are given by

$$\lambda_{a,b} = (1/2)(k_1 + k_2) \pm (1/2)\sqrt{(k_1 - k_2)^2 + 4k_{EA}k_{AE}[B]} \quad (2)$$

In this equation, k_{EA} and k_{AE} are the two important rate constants concerning the exciplex formation and dissociation, and k_1 and k_2 are the rates of decay of the uncomplexed triplet ketone and of the exciplex, respectively:

$$k_1 = k_{EA}[B] + k_{ET}^A[\text{DBA}] + k_d^A \quad (3)$$

$$k_2 = k_{AE} + k_{ET}^E[\text{DBA}] + k_d^E \quad (4)$$

Equation 2 can be rearranged to give k_1 and k_2 :

$$k_{1,2} = (1/2)(\lambda_a + \lambda_b) \pm (1/2)\sqrt{(\lambda_a - \lambda_b)^2 - 4k_{EA}k_{AE}[B]} \quad (5)$$

It can easily be shown that in a series of experiments at a given concentration of DBA, the product $\lambda_a \lambda_b$ and the sum $(\lambda_a + \lambda_b)$ should both be linear functions of $[B]$, the concentration of mesitylene, whereas if $[B]$ is kept constant, the plot of $(\lambda_a + \lambda_b)$ vs. $[\text{DBA}]$ should be linear. Different combinations of rate constants are thus immediately accessible from the slopes and intercepts of these plots (see eq A31, A32 in Appendix).

Because both A and DBA absorb at λ_{exc} , i.e., $[\text{DBA}^*]_0 \neq 0$, the values of the amplitude ratios α and β provide a way of determining the efficiencies, ϕ_{TS}^A and ϕ_{TS}^E , of triplet-singlet energy transfer, i.e., the fractions of the collisions of DBA and either A^* or E^* which result in quenching of the donor and concomitant singlet excitation of DBA. If one defines

$$k_A = \phi_{\text{TS}}^A k_{ET}^A[\text{DBA}] \quad (6)$$

$$k_E = \phi_{\text{TS}}^E k_{ET}^E[\text{DBA}] \quad (7)$$

$$Z = (k_E/k_A)k_{EA}[B] \quad (8)$$

then, with two simplifying assumptions, $k_F \gg \lambda_a$ and $\alpha \gg 1$ (see below), expressions for Z and for k_A can be derived

$$Z = \frac{(k_2 - \lambda_a) + \beta(k_2 - \lambda_b)}{1 + \beta} \quad (9)$$

$$k_A = \frac{\beta k_F R (\lambda_b - \lambda_a)}{\alpha(k_2 - \lambda_a + Z)} \quad (10)$$

where R is the ratio of absorbances of DBA and the ketone

$$R = \frac{\epsilon_{\text{DBA}}[\text{DBA}]}{\epsilon_A[A]} \quad (11)$$

Thus, if k_2 has been determined from the experimentally measured λ_a and λ_b , then Z can be calculated by eq 9 and a plot of Z vs. $[B]$ should be linear, according to eq 8. Note, however, that since β is negative, the error on Z becomes prohibitively large as β tends to -1 , at high values of $[B]$.

In the absence of mesitylene and therefore of exciplex, the simplified reaction scheme^{3a} predicts that the DBA fluorescence decay curves will be double exponentials, of the form

$$I_t = \alpha e^{-k_F t} + e^{-k_{\text{obsd}} t} \quad (12)$$

where

$$k_{\text{obsd}} = k_d^A + k_{ET}^A[\text{DBA}] \quad (13)$$

The efficiency ϕ_{TS}^A is then given by

$$\phi_{\text{TS}}^A = \frac{R(k_F - k_{\text{obsd}})}{(1 + \alpha)k_{ET}^A[\text{DBA}]} \quad (14)$$

with R defined as in eq 11.⁷

Thus, the rate constants k_d^A and k_{ET}^A and the efficiency ϕ_{TS}^A can be independently obtained from a series of experiments with solutions of A and DBA only.

Experimental Section

The fluorescence decay curves were obtained by the time-correlated single-photon counting method. Preliminary work on this system was

(3) (a) Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7279. (b) *Ibid.* **1981**, *103*, 2412.

(4) (a) Vassil'ev, R. F. *Nature (London)* **1963**, *200*, 773. Belyakow, V. A.; Vassil'ev, R. F. *Photochem. Photobiol.* **1970**, *11*, 179. (b) Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7272 and references therein. (c) For a discussion of quenching experiments to reveal exciplex formation, see, for example: Kuzmin, M. G.; Sadowski, N. A.; Soboleva, I. V. *J. Photochem.* **1983**, *23*, 27 and references therein.

(5) Murov, S. L. “Handbook of Photochemistry”; Marcel Dekker: New York, 1973.

(6) For the details of the derivation of the equations below, see Appendix.

(7) Equation 14 is identical with eq 23 in ref 4b, since $N'_p/N'_s = k_{\text{obsd}}/k_F$.

done at Northeastern University, on an instrument previously described.^{4b,8} The results presented here were obtained at Harvard University with a setup consisting of a PRA lamp housing and deuterium-filled lamp, sample chamber and photomultiplier tubes, a Bausch and Lomb high intensity monochromator with adjustable entrance and exit slits on the exciting beam, Ortec electronics, and a Tracor-Northern TN-7200 multichannel analyzer. The vacuum-degassed samples were contained in 1-cm² quartz cells and their temperature (20 °C) controlled by a thermoelectric Peltier device (± 0.3 °C). The fluorescence emission was filtered through a combination of a wide-band interference filter and a cutoff filter (resulting $1/2$ bandwidth = 70 nm, centered at ~ 450 nm, 50% peak transmittance). Excitation was at 305 nm (15-nm band-pass) where $\epsilon_A = 12.2$ and $\epsilon_{DBA} = 180$ in cyclohexane, the solvent throughout. At least 90% of the exciting light was therefore absorbed by the ketone (concentration 0.077 M) and at most 10% by DBA (concentration range $0.5\text{--}5 \times 10^{-4}$ M). At 305 nm, the extinction coefficient of mesitylene is 3.5×10^2 M⁻¹; at its highest concentration (1 M), the partial absorbance of mesitylene is thus about 3.5% of that of cyclohexanone.

The full 4096-channel capability of the TN-7200 was used throughout. With such a large number of channels, it was necessary to acquire only one decay curve per sample, on one time scale, in order to determine accurately the slow decay components ($\tau \sim 0.5$ μ s; see Figure 1) and yet have completely adequate resolution of the first fast peak ($\tau \sim 2$ ns) as well as an unambiguous estimate of the amplitude ratios. In fact, a high resolution is a prerequisite for a meaningful analysis of the decay profiles obtained in this work.

The wide excitation band-pass (15 nm) was selected in order to minimize the necessary acquisition time; 1–2 h was standard. The width of the band-pass does not affect the determination of the three decay rates k_F , λ_a , and λ_b , hence of any of the rate constants of Scheme I, except k_A and k_E (eq 6, 7), although the ratio k_E/k_A is also independent of the excitation band-pass. In contrast, the ratio of absorbances (R) (eq 11) enters in the calculation of k_A (eq 10), hence of ϕ_{TS}^A ; here the 15-nm excitation band-pass may introduce an error of a factor of ≤ 2 , with the true value of ϕ_{TS}^A being higher than the experimental value. To obviate this difficulty, a narrow band-pass (1.6 nm) was used to determine ϕ_{TS}^A according to eq 14, in cyclohexane solutions of cyclohexanone and DBA only, without mesitylene.

A lamp profile was acquired either immediately before or after each fluorescence decay curve. The data (lamp and fluorescence curves) were stored on a PDP 11/10 prior to analysis on a VAX by an iterative reconvolution program developed at Northeastern University. The quality of the fit was judged by the values of χ^2 over the whole time range and by the standard deviations on each parameter of the three-exponential functions, the randomness of the residuals, and the autocorrelation function along the time axis⁹ as well as, importantly, by qualitative visual judgement on the CRT screen.

Absorption spectra and extinction coefficients were obtained with a Uvikon 820 (KONTRON) spectrophotometer, and the fluorescence spectra with a Perkin-Elmer MPF-44 spectrofluorimeter. Cyclohexane was from Burdick and Jackson ("distilled in glass"); 9,10-dibromanthracene (Aldrich) was recrystallized from xylene and vacuum sublimed; mesitylene (Fisher) and cyclohexanone (Eastman) were redistilled.

Results

1. Decay Rates. The kinetic scheme predicts that the formation of an exciplex of triplet cyclohexanone and mesitylene, in irradiated solutions containing DBA, will result in DBA fluorescence decay curves describable by the sum of three exponentials, of which one has a negative coefficient (β in eq 1), provided that the exciplex can sensitize DBA fluorescence and that its dissociation is slow compared to other modes of deactivation. The validity of this prediction was verified for all the cyclohexane solutions of cyclohexanone (0.076 M), DBA ($0.5\text{--}5.0 \times 10^{-4}$ M), and mesitylene (0.07–1.0 M) studied here. In all cases, the emission is DBA fluorescence, with only negligible contributions from cyclohexanone fluorescence and phosphorescence.

Of the three decay parameters, one is larger than the others by 2 orders of magnitude; it is also independent of the concentrations of mesitylene and DBA. This is k_F ($\sim 4.7 \times 10^8$ s⁻¹). The two other decay parameters, λ_a and λ_b , increase with the concentrations of mesitylene and DBA, which means that neither λ_a nor λ_b can be identified with k_1 or k_2 , since k_2 , eq 4, should be

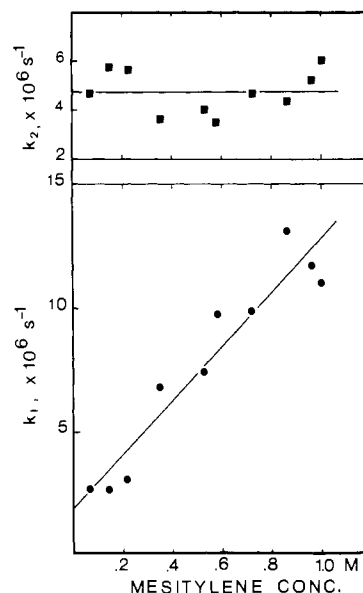


Figure 2. Plots of k_1 and k_2 , as defined by eq 3 and 4, as a function of the concentration of mesitylene in degassed cyclohexane at 20 °C. The concentrations of cyclohexanone and DBA were 0.077 M and 1.05×10^{-4} M, respectively. The values of k_1 and k_2 were calculated according to eq 25, with an arbitrary value of $k_{EA}k_{AE} = 9 \times 10^{12}$ M⁻¹ s⁻² (see text). The slope of k_1 vs. [B] is 1.09×10^7 M⁻¹ s⁻¹, and the intercept is 1.87×10^6 s⁻¹ (linear regression through all points, $\tau = 0.950$). The average value of k_2 is 4.7×10^6 s⁻¹.

independent of [B]. For a series of solutions at constant concentration of DBA and increasing concentrations of mesitylene, the values of k_1 and k_2 can, however, be derived from λ_a and λ_b on the basis of eq 5, as follows. Arbitrary values are assigned to the product $k_{EA}k_{AE}$ (with $k_{EA}k_{AE} < (\lambda_a - \lambda_b)^2/4[B]$) in eq 5 until a value of this product is found which renders one of $k_{1,2}$ independent of the concentration of mesitylene, i.e., k_2 , while the other, i.e., k_1 , becomes linearly dependent on [B]. A value of $k_{EA}k_{AE} \approx (9 \pm 2) \times 10^{12}$ M⁻¹ s⁻² is best (Figure 2). Note the apparent "crossing" of the rates: at low [B] λ_a is close to k_2 and λ_b to k_1 , while at high [B] the reverse is true. At a mesitylene concentration of 0.25 M, triplet cyclohexanone and its exciplex with mesitylene have nearly the same lifetimes.

According to eq 3, the slope of the plot k_1 vs. [B] (Figure 2) is k_{EA} , the association rate constant for exciplex formation. Least-squares analysis gave

$$k_{EA} = 1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

hence $k_{AE} = (8 \pm 2) \times 10^5$ s⁻¹, if $k_{EA}k_{AE} = (9 \pm 2) \times 10^{12}$ M⁻¹ s⁻². The intercept of this plot is

$$k_d^A + k_{ET}^A[\text{DBA}] = 1.9 \times 10^6 \text{ s}^{-1}$$

Figure 2 also shows that $k_2 = (4.7 \pm 1) \times 10^6$ s⁻¹ (eq 4). As will now be shown, further treatment of the data provide support for these results.

2. Estimate of All the Rate Constants of Scheme I. The values of λ_a and λ_b were determined for two series of solutions at constant cyclohexanone concentration (0.076 M), in which either the mesitylene or the DBA concentration was varied with the other kept constant. The data were analyzed according to eq A31 and A32 (Appendix), and the resulting plots are shown in Figures 3 and 4.

The slope of $(\lambda_a + \lambda_b)$ vs. [B] is $k_{EA} = 1.1 \times 10^7$ M⁻¹ s⁻¹, in agreement with the value obtained above from the plot of k_1 vs. [B]. A host of rate constants, or sums of constants, can immediately be derived from Figures 3 and 4, using eq A31 and 32. They are listed in Table I, along with their sources. For example, the ratio of the slopes of $\lambda_a\lambda_b$ and of $(\lambda_a + \lambda_b)$ vs. [B] is $k_d^E + k_{ET}^E[\text{DBA}] = 4.4 \times 10^6$ s⁻¹ (Figure 3 and eq A31, A32, Appendix). Combined with $k_2 = 4.7 \times 10^6$ s⁻¹, one gets $k_{AE} \sim 3 \times 10^5$ s⁻¹. This is lower than the value of $(8 \pm 2) \times 10^5$ s⁻¹ derived

(8) Halpern, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 7655.

(9) Grinvald, A.; Steinberg, I. *Z. Anal. Biochem.* **1974**, *59*, 583.

Table I. Rate Constants of Scheme I

rate constants	entry	estimated value	sources ^a
k_{EA}	1a	$1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	slope of k_1 vs. [B] with arb. $k_{EA}k_{AE} = 9 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ (eq 4, 5, Figure 2)
k_{AE}	1b	$1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	slope of $(\lambda_a + \lambda_b)$ vs. [B] (eq A32, Figure 3)
	2a	$8 \times 10^5 \text{ s}^{-1}$	from $k_{EA}k_{AE} = 9 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ with 1a
	2b	$3 \times 10^5 \text{ s}^{-1}$	from ratio of slopes of $\lambda_a\lambda_b$ and $(\lambda_a + \lambda_b)$ vs. [B], with 3a (eq A31, A32, and 4)
$k_2 = k_d^E + k_{AE} + k_{ET}^E[\text{DBA}]$	3a	$4.7 \times 10^6 \text{ s}^{-1}$	from eq 5 with $k_{EA}k_{AE} = 9 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ (Figure 2)
k_{ET}^A	3b	$4.4\text{--}4.8 \times 10^6 \text{ s}^{-1}$	from eq 4 with 2, 6, 9
	4	$4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	slope of k_{obsd} vs. [DBA] (eq 13)
$k_{ET}^E + k_{ET}^A$	5	$9.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	slope of $(\lambda_a + \lambda_b)$ vs. [DBA] (eq A31, Figure 4)
k_{ET}^E	6	$5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	from 4 and 5
k_d^A	7a	$1.7 \times 10^6 \text{ s}^{-1}$	intercept of k_{obsd} vs. [DBA] (eq 13)
	7b	$1.4 \times 10^6 \text{ s}^{-1}$	intercept of k_1 vs. [B] (eq 3) with 4
$k_d^A + k_{AE} + k_d^E$	8a	$5.5 \times 10^6 \text{ s}^{-1}$	intercept of $(\lambda_a + \lambda_b)$ vs. [B] (eq A32, Figure 3) with 5
	8b	$5.7 \times 10^6 \text{ s}^{-1}$	intercept of $(\lambda_a + \lambda_b)$ vs. [DBA] (eq A32, Figure 4) with 1
k_d^E	9a	$3.0 \times 10^6 \text{ s}^{-1}$	from 2, 7, and 8
	9b	$3.4 \times 10^6 \text{ s}^{-1}$	from 2, 3a, and 6
$k_{EA}(k_d^E + k_{ET}^E[\text{DBA}])$	10a	$4.9 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$	slope of $\lambda_a\lambda_b$ vs. [B] (eq A31, Figure 3)
	10b	$3.9 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$	from 1, 6, and 9
$k_{ET}^E\phi_{TS}^E k_{EA}/k_{ET}^A\phi_{TS}^A$	11	$8.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	slope of Z vs. [B] (eq 6, 7, 8, 9, Figure 5)
	12a	0.01	eq 6 and 10 with 4
ϕ_{TS}^E	12b	0.01–0.02	eq 14
	13	0.07–0.15	from 1, 4, 6, 11, 12 (6, 7, 8)

^aThe boldface numbers refer to the entries in this table.

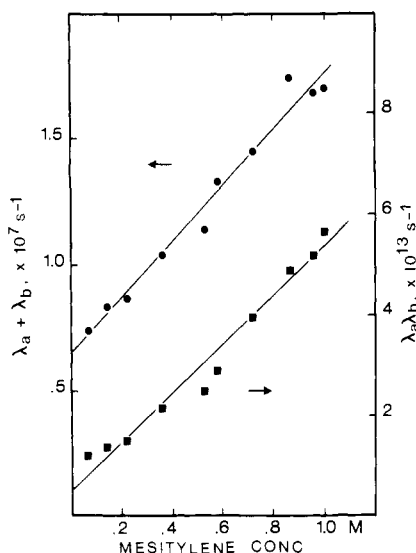


Figure 3. Plots of $(\lambda_a + \lambda_b)$ and of $\lambda_a\lambda_b$ (as defined in eq 1) as a function of the mesitylene concentration, according to eq A31 and A32, for a series of degassed cyclohexane solutions at 20 °C; cyclohexanone concentration = 0.077 M, DBA concentration = 1.05×10^{-4} M. Least-squares analysis through all points gave for $(\lambda_a + \lambda_b)$ vs. [B], slope = $(1.11 \pm 0.08) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, intercept = $(6.50 \pm 0.25) \times 10^6 \text{ s}^{-1}$, $r = 0.986$; for $\lambda_a\lambda_b$ vs. [B], slope = $(4.9 \pm 0.4) \times 10^{13} \text{ M}^{-1} \text{ s}^{-2}$, intercept = $(4.9 \pm 0.3) \times 10^{12} \text{ s}^{-1}$, $r = 0.984$.

above, but given the uncertainties attached to this type of calculations, a value of $k_{AE} \sim (6 \pm 4) \times 10^5 \text{ s}^{-1}$ can be accepted quite confidently.

To complete the analysis, a series of degassed solutions of cyclohexanone (0.09 M) and DBA ($0.5\text{--}7.2 \times 10^{-4}$ M), without mesitylene, was also studied under the same conditions of solvent and temperature (20 °C). The fluorescence decay curves were strictly double exponential, in accord with eq 12. The values of k_d^A and k_{ET}^A , obtained from the plot of k_{obsd} vs. [DBA] according to eq 13, are listed also in Table I.

3. Estimate of ϕ_{TS}^A from the Fluorescence Decay Curves. Only the values of λ_a and λ_b have been used thus far to estimate most of the rate constants of Scheme I. From the amplitude ratios α and β and the previously calculated values of k_2 (eq 4) for a series of solutions of cyclohexanone (0.076 M), DBA (1.06×10^{-4} M), and varying concentrations of mesitylene, one can use eq 8 and

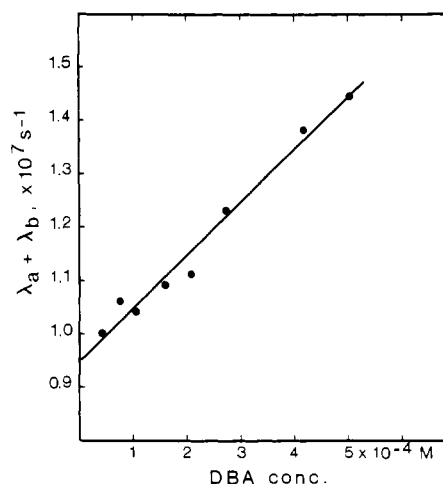


Figure 4. Plot of $(\lambda_a + \lambda_b)$ vs. DBA concentration, according to eq A32. Cyclohexanone concentration = 0.076 M, mesitylene concentration = 0.35 M, in cyclohexane at 20 °C. Slope is $(9.7 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, intercept is $(9.5 \pm 0.3) \times 10^6 \text{ s}^{-1}$ (linear regression through all points, $r = 0.988$).

9 to calculate the ratio, ϕ_{TS}^E/ϕ_{TS}^A , of the coefficients of energy transfer from triplet alkanone and exciplex to DBA (S_1), since k_{ET}^E , k_{ET}^A , and k_{EA} have been obtained before. Figure 5 is a plot of Z (eq 9) vs. [B]. The slope was obtained by least-square treatment of the data at [B] < 0.8 M, i.e., at values of $-\beta < 0.9$.¹⁰ From this slope one can calculate $\phi_{TS}^E/\phi_{TS}^A \simeq 7$. Furthermore k_A and thus ϕ_{TS}^A (eq 6) can now be derived from eq 10. On the basis of the results obtained at [B] ≤ 0.8 M, one gets $\phi_{TS}^A = 0.011 \pm 0.002$.

This result can be compared to a more direct and independent determination of ϕ_{TS}^A (eq 14) from the fluorescence decay curves of solutions of cyclohexanone and DBA ($0.5\text{--}7.2 \times 10^{-4}$ M) without mesitylene. These experiments gave $\phi_{TS}^A = 0.01\text{--}0.02$. The agreement is encouraging.

Discussion

The DBA method is uniquely able to reveal the formation of an excited transient during the decay of photoexcited cyclohexanone in the presence of mesitylene. The assignment of this

(10) With the straight line constrained to go through the origin.

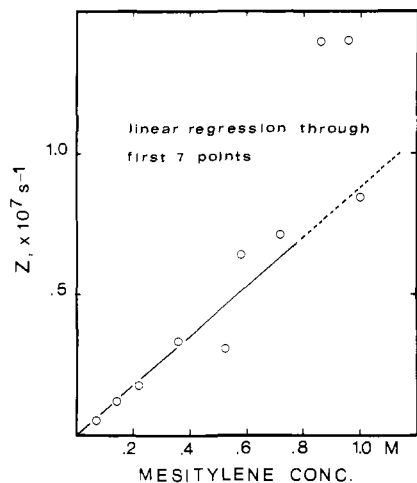


Figure 5. Dependence of Z , as defined by eq 8, on the concentration of mesitylene. Cyclohexanone concentration = 0.077 M, DBA concentration = 1.05×10^{-4} M, in degassed cyclohexane at 20 °C. The least-squares analysis was carried out on data points obtained at $[B] < 0.8$ M; see text; slope = $9.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

transient to a triplet exciplex of the ketone and the aromatic is the simplest hypothesis. The key observations which support it can be summarized as follow:

(a) DBA fluorescence slowly builds up to a second maximum after most of the prompt fluorescence has decayed. No second peak and no intensity anomalies are observed in the absence of a benzene derivative; on the other hand, in the absence of ketone the fluorescence of DBA decays always as a single exponential, with or without the aromatic.

(b) Delayed fluorescence has a higher integrated intensity when even low concentrations of an aromatic are present in the ketone/DBA solution. Thus the *transient* species generated is capable of transferring electronic energy to DBA.

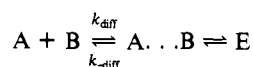
(c) Acetonitrile can replace cyclohexane as the solvent without seemingly affecting much the exciplex peak observed with cyclohexanone and mesitylene (one experiment at 0.28 M). Therefore the transient is not related to the photoreduction of the excited alkanone by cyclohexane, or to any other reaction involving this solvent.

(d) Singlet excited alkanone is obviously not directly involved; it undergoes intersystem crossing long before the exciplex peak appears.

The validity of the exciplex assumption is confirmed by the very good internal consistency between the predictions based on it (the kinetic expressions derived from Scheme I) and the experimental results. Figure 1 illustrates how well the decay of fluorescence intensity, followed over five decades, can be fitted to a triple exponential function, as the mechanism requires. Such a large dynamic range is indeed one of the major advantages of emission techniques compared to methods based on absorption spectroscopy. The use of a large number of channels, here 4096, in the time-to-pulse-height analysis allows for excellent time resolution. Table I shows convincingly that several of the rate constants of Scheme I can be obtained by different routes with very satisfactory agreement in most cases. Thus, the DBA method allows for the determination of all the rate constants of Scheme I.

Regarding the triplet exciplex dynamics, the following points are particularly significant:

(1) The rate of exciplex formation k_{EA} appears to be orders of magnitude slower than k_{diff} . This may indicate significant energy or entropy restrictions for the formation of the exciplex from a loose encounter complex



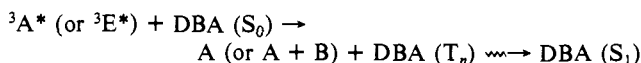
as suggested in the case of the proposed triplet excimers of naphthalene and of 1-chloronaphthalene, the phosphorescence of which was reported by Takemura et al.¹¹

(2) At 20 °C, the equilibrium constant, $K_E = k_{EA}/k_{AE} \approx 13$ (between ~ 10 and ~ 50), favors the exciplex.

(3) In the absence of DBA, the lifetime of the postulated exciplex of triplet cyclohexanone and mesitylene is half that of the uncomplexed triplet alkanone ($k_d^E \approx 2k_d^A$).

(4) The overall rate constants for energy transfer to DBA (k_{ET}^A and k_{ET}^E) are $\lesssim k_{diff}$, as expected for a collisional TT transfer (see below).

Turning now to the efficiency of the process of energy transfer from triplet donor to DBA which results in the population of the S_1 state of DBA, it is intriguing to find that, in this unusual TS sensitization, the exciplex is a significantly better donor than the uncomplexed ketone, since $\phi_{TS}^E \approx 7\phi_{TS}^A$. However, this result was not unexpected, having been obtained previously in the case of the more unstable triplet exciplex of acetone and benzene.^{3a} As proposed then, a possible interpretation invokes a better match of energy levels between the triplet exciplex and a higher triplet (T_n) of DBA. It is indeed likely, although still unproven, that one or several such T_n states of DBA, known to be located only a few kilocalories above DBA (S_1), play an important intermediary role in the overall TS energy transfer, as follow:

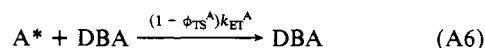
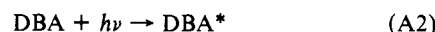
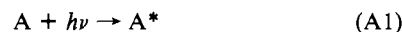


Evidently other factors besides energy levels may determine ϕ_{TS} , among them, for example, the size of the donor and the delocalization of its triplet energy.¹²

Extension of this work is under way along different directions. The effects of temperature and solvent may help ascertain the origin of the low rates of exciplex formation (enthalpy or entropy factors?) and the role of charge-transfer interactions in the binding of the exciplex. The effects of substitution on the alkanone and the aromatic are also being investigated.

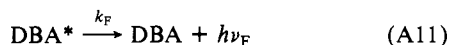
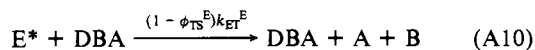
Appendix

Derivation of Eq 1–10. Pulse excitation at time $t = 0$ by monochromatic light absorbed by both A and DBA produces $[A^*]_0$ and $[\text{DBA}^*]_0$. The asterisks denote *triplet* excitation of the alkanone and of the exciplex and *singlet* excitation of DBA; i.e., A^* stands for ${}^3A^*$ (intersystem crossing is assumed to be fast and efficient⁵), E^* stands for ${}^3E^*$, and DBA^* for ${}^1\text{DBA}^*$. Only reactions A1 to A11 need be considered.



(11) (a) Takemura, T.; Aikawa, M.; Baba, H.; Shindo, Y. *J. Am. Chem. Soc.* **1976**, *98*, 2205. (b) For other examples of rates of triplet exciplex formation slower than k_{diff} , see for example: ref 1b and Caldwell, R. A., Sovocool, G. W.; Gajewski, R. P. *Ibid.* **1973**, *95*, 2549. (c) For a general discussion of k_{diff} and rate of exciplex formation, see: Lewis, C.; Ware, W. R. *Mol. Photochem.* **1973**, *5*, 261.

(12) In a personal communication (1982) Brian Stevens proposes an alternative mechanism for diffusional T–S energy transfer. It involves formation of a triplet exciplex of the ketone and DBA. Energy transfer would take place within this exciplex, with or without concomitant intersystem crossing in DBA to give $\text{DBA}(S_1)$, promoted by the bromine atoms. A decision regarding these alternative mechanisms must await new experimental evidence. We thank Prof. Stevens for this interesting suggestion.



The rate expressions are

$$d[A^*]/dt = -k_1[A^*] + k_{AE}[E^*] \quad (A12)$$

$$d[E^*]/dt = k_{EA}[B][A^*] - k_2[E^*] \quad (A13)$$

$$d[DBA^*]/dt = k_A[A^*] + k_E[E^*] - k_F[DBA^*] \quad (A14)$$

where

$$k_1 = k_{EA}[B] + k_{ET}^A[DBA] + k_d^A \quad (3)$$

$$k_2 = k_{AE} + k_{ET}^E[DBA] + k_d^E \quad (4)$$

$$k_A = \phi_{TS}^A k_{ET}^A[DBA] \quad (6)$$

$$k_E = \phi_{TS}^E k_{ET}^E[DBA] \quad (7)$$

To find the solutions of the differential equations A12–A14, one tries the following solutions

$$[A^*] = a_1 e^{-\lambda t}$$

$$[E^*] = a_2 e^{-\lambda t}$$

$$[DBA^*] = a_3 e^{-\lambda t}$$

The time-dependent $e^{-\lambda t}$ factors out and one gets a set of homogeneous, linear, simultaneous, first-order algebraic equations in a_1, a_2, a_3 with parameter λ :

$$(\lambda - k_1)a_1 + k_{AE}a_2 = 0 \quad (A15)$$

$$k_{EA}[B]a_1 + (\lambda - k_2)a_2 = 0 \quad (A16)$$

$$k_A a_1 + k_E a_2 + (\lambda - k_F)a_3 = 0 \quad (A17)$$

Since these equations are homogeneous, one can only get the values of the ratios of variables, such as a_2/a_1 or a_3/a_1 , and therefore there is an extra equation. But one will get consistent solutions only for certain values of λ , such that the determinant A18

$$\begin{vmatrix} \lambda - k_1 & k_{AE} & 0 \\ k_{EA}[B] & \lambda - k_2 & 0 \\ k_A & k_E & \lambda - k_F \end{vmatrix} = 0 \quad (A18)$$

of the coefficients of the variables is zero. This is a cubic equation in λ , which has three roots, $\lambda_a, \lambda_b, \lambda_c$. The determinant A18 can also be written

$$(\lambda - k_F) \begin{vmatrix} \lambda - k_1 & k_{AE} \\ k_{EA}[B] & \lambda - k_2 \end{vmatrix} = 0 \quad (A19)$$

One solution is $\lambda - k_F = 0$, or

$$\lambda_c = k_F \quad (A20)$$

The other two solutions are the roots of the quadratic equation

$$\lambda^2 - (k_1 + k_2)\lambda + k_1 k_2 - k_{EA} k_{AE} [B] = 0 \quad (A21)$$

These two roots are

$\lambda_{a,b} =$

$$(1/2)(k_1 + k_2) \pm (1/2)\sqrt{(k_1 + k_2)^2 - 4k_1 k_2 + 4k_{EA} k_{AE} [B]} \quad (A22)$$

which rearranges to

$$\lambda_{a,b} = (1/2)(k_1 + k_2) \pm (1/2)\sqrt{(k_1 - k_2)^2 + 4k_{EA} k_{AE} [B]} \quad (2)$$

For each of the three values λ_a, λ_b , and λ_c of λ , a nontrivial solution of eq A15, A16, and A17 giving the ratios such as a_2/a_1 and a_3/a_1 can be obtained. One generates three sets of equations, A23a,b,c, A24a,b,c, and A25a,b,c, by substituting $\lambda = \lambda_a, \lambda = \lambda_b, \lambda = \lambda_c$, respectively, in eq A15, A16, and A17. In eq A23, where $\lambda = \lambda_a$, the coefficients will be called a_1, a_2 , and a_3 ; in eq A24, with $\lambda = \lambda_b$, the coefficients are b_1, b_2, b_3 , etc., as follow:

$$(\lambda_a - k_1)a_1 + k_{AE}a_2 = 0 \quad (A23a)$$

$$k_{EA}[B]a_1 + (\lambda_a - k_2)a_2 = 0 \quad (A23b)$$

$$k_A a_1 + k_E a_2 - (\lambda_a - k_F)a_3 = 0 \quad (A23c)$$

$$(\lambda_b - k_1)b_1 + k_{AE}b_2 = 0 \quad (A24a)$$

$$k_{EA}[B]b_1 + (\lambda_b - k_2)b_2 = 0 \quad (A24b)$$

$$k_A b_1 + k_E b_2 - (\lambda_b - k_F)b_3 = 0 \quad (A24c)$$

$$(\lambda_c - k_1)c_1 + k_{AE}c_2 = 0 \quad (A25a)$$

$$k_{EA}[B]c_1 + (\lambda_c - k_2)c_2 = 0 \quad (A25b)$$

$$k_A c_1 + k_E c_2 - (\lambda_c - k_F)c_3 = 0 \quad (A25c)$$

Thus, one has three sets of solutions for the original three differential eq A12–A14. Any linear combination of these three solutions with any coefficients is also a solution. The general solutions are the sums of three exponentials:

$$[A^*] = a_1 e^{-\lambda_a t} + b_1 e^{-\lambda_b t} + c_1 e^{-\lambda_c t} \quad (A26)$$

$$[E^*] = a_2 e^{-\lambda_a t} + b_2 e^{-\lambda_b t} + c_2 e^{-\lambda_c t} \quad (A27)$$

$$[DBA^*] = a_3 e^{-\lambda_a t} + b_3 e^{-\lambda_b t} + c_3 e^{-\lambda_c t} \quad (A28)$$

where $c_1 = c_2 = 0$ (no $[DBA^*]$ term in eq A12 and A13) and $\lambda_c = k_F$, the fastest of the three rates, of independently known value. Hence

$$I_t = \alpha e^{-k_F t} + \beta e^{-\lambda_a t} + e^{-\lambda_b t} \quad (1)$$

where

$$a_3/b_3 = \beta \quad (A29)$$

(which has a negative value)

$$c_3/b_3 = \alpha \quad (A30)$$

From the difference between λ_a and λ_b (eq 2), one obtains expressions for k_1 and k_2 (eq 5). The sum and product of λ_a and λ_b lead to two other useful expressions, eq A31 and A32:

$$\lambda_a \lambda_b = k_{ET}^A k_{ET}^E [DBA]^2 + (k_{ET}^A k_{AE} + k_{ET}^A k_d^E + k_d^A k_{ET}^E) [DBA] + k_{EA} k_d^E [B] + k_{EA} k_{ET}^E [B] [DBA] + k_d^A (k_{AE} + k_d^E) \quad (A31)$$

$\lambda_a + \lambda_b =$

$$(k_{ET}^A + k_{ET}^E) [DBA] + k_{EA} [B] + k_d^A + k_d^E + k_{AE} \quad (A32)$$

At $t = 0$, the boundary conditions of eq A26, A27, and A28 are

$$[A^*]_0 = a_1 + b_1 \quad (A33)$$

$$[E^*]_0 = a_2 + b_2 = 0 \quad (A34)$$

$$[DBA^*]_0 = a_3 + b_3 + c_3 \quad (A35)$$

Since the ketone and DBA are in a homogeneous solution, they absorb the light in any small volume element in this solution in proportion to their extinction coefficients and partial concentrations. Thus,

$$R = [DBA^*]_0/[A^*]_0 = \epsilon_{DBA}[DBA]/\epsilon_A[A] \quad (11)$$

Based on this definition of R , on the values of α and β (eq A29 and A30), and on the boundary conditions (eq A33–A35), two new expressions (eq 9 and 10) can be derived as follow, with

$$Z = k_E k_{EA} [B] / k_A \quad (8)$$

One can write

$$\frac{b_3}{a_3} = \frac{b_3 b_2 a_2}{b_2 a_2 a_3} \quad (A36)$$

and calculate each ratio separately.

From eq A23b:

$$\frac{a_1}{a_2} = \frac{k_2 - \lambda_a}{k_{EA}[B]} \quad (A37)$$

Dividing eq A23c by a_2 and replacing a_1/a_2 by its value above:

$$\frac{a_3}{a_2} = \left\{ k_A \frac{(k_2 - \lambda_a)}{k_{EA}[B]} + k_E \right\} \frac{1}{k_F - \lambda_a} \quad R \left(\frac{a_1}{a_3} + \frac{b_1}{a_3} \right) = 1 + \frac{1}{\beta} + \frac{c_3}{a_3} \quad (\text{A43})$$

With eq 8, this becomes

$$\frac{a_2}{a_3} = \frac{k_{EA}[B](k_F - \lambda_a)}{k_A(k_2 - \lambda_a + Z)} \quad (\text{A38})$$

The boundary condition (eq A34) gives

$$\frac{b_2}{a_2} = -1 \quad (\text{A39})$$

From eq A24b, one gets

$$\frac{b_1}{b_2} = \frac{k_2 - \lambda_b}{k_{EA}[B]} \quad (\text{A40})$$

Dividing eq A24c by b_2 , and replacing b_1/b_2 by its value above, one has

$$\frac{b_3}{b_2} = \left\{ k_A \frac{(k_2 - \lambda_b)}{k_{EA}[B]} + k_E \right\} \frac{1}{k_F - \lambda_b}$$

or

$$\frac{b_3}{b_2} = \frac{k_A(k_2 - \lambda_b + Z)}{k_{EA}[B](k_F - \lambda_b)} \quad (\text{A41})$$

Using eq A38, A39, and A41, eq A36 can now be rewritten

$$\frac{b_3}{a_3} = - \frac{(k_F - \lambda_a)(k_2 - \lambda_b + Z)}{(k_F - \lambda_b)(k_2 - \lambda_a + Z)} \quad (\text{A42})$$

In these experiments with cyclohexanone and mesitylene, $k_F \gg \lambda_{a,b}$. Thus, eq A42 can be further simplified to

$$Z = \frac{(k_2 - \lambda_a) + \beta(k_2 - \lambda_b)}{1 + \beta} \quad (9)$$

From the boundary conditions, eq A33 and A34, one calculates R , as defined by eq 11:

$$R = \frac{a_3 + b_3 + c_3}{a_1 + b_1}$$

which rearranges to

Since $b_2/a_2 = -1$ (eq A39)

$$\frac{a_1}{a_3} + \frac{b_1}{a_3} = \frac{a_1 a_2}{a_2 a_3} - \frac{b_1 b_2 a_2}{b_2 a_2 a_3} = \frac{a_2}{a_3} \left(\frac{a_1}{a_2} - \frac{b_1}{b_2} \right) \quad (\text{A44})$$

Using eq A37, A38, and A40, this equation becomes

$$\frac{a_1}{a_3} + \frac{b_1}{a_3} = \frac{(k_F - \lambda_a)(\lambda_b - \lambda_a)}{k_A(k_2 - \lambda_a + Z)} \quad (\text{A45})$$

The ratio c_3/a_3 in eq A43 can be written

$$\frac{c_3}{a_3} = \frac{c_3 b_3}{b_3 a_3}$$

or, from the definitions of α and β (eq A29 and A30)

$$\frac{c_3}{a_3} = \frac{\alpha}{\beta} \quad (\text{A46})$$

With eq A45 and A46, eq A43 becomes

$$\frac{R(k_F - \lambda_a)(\lambda_b - \lambda_a)}{k_A(k_2 - \lambda_a + Z)} = 1 + \frac{1 + \alpha}{\beta}$$

In these experiments $k_F \gg \lambda_a$ and $\alpha \gg 1$; therefore

$$\frac{k_F R(\lambda_b - \lambda_a)}{k_A(k_2 - \lambda_a + Z)} = \frac{\alpha}{\beta}$$

or

$$k_A = \frac{\beta k_F R(\lambda_b - \lambda_a)}{\alpha(k_2 - \lambda_a + Z)} \quad (10)$$

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Registry No. Cyclohexanone, 108-94-1; mesitylene, 108-67-8; 9,10-dibromoanthracene, 523-27-3; cyclohexanone-mesitylene complex, 89891-17-8.

The Use of Mixed Crystals for Engineering Organic Solid-State Reactions: Application to Benzylbenzylidenecyclopentanones

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Contribution from the Department of Physical Chemistry, University of Cambridge, Lensfield CB2 1EP, England, and the School of Chemistry, University of Hyderabad, P.O. Central University, Hyderabad 500 134, India. Received July 8, 1983

Abstract: The concept of chloro/methyl group interchange as a tool in crystal engineering is discussed with respect to derivatives of 2-benzyl-5-benzylidenecyclopentanone (1-4). A study of the mixed crystals containing either 1 and 2 (X) or 3 and 4 (Y) demonstrates that molecules which otherwise crystallize into photostable crystal structures may be incorporated into a light-sensitive form. Furthermore, such mixed crystals are demonstrated (using four-circle diffractometry) to undergo single-crystal \rightarrow single-crystal reaction with the formation of the product dimer molecules identified within the reactant lattice. The final R for X is 0.0418, for Y it is 0.0578, and for irradiated X it is 0.0394.

It is clear that the controlled variation of the substituent groups present on an organic molecule may allow subsequent crystalli-

zation into particular and desired packing arrangements². One particular strategy for this so-called crystal-engineering concept