

## References and Notes

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- Langehaar et al.<sup>31c</sup> have determined  $k_{GR} = 3 \times 10^6$  l. mol<sup>-1</sup> sec<sup>-1</sup> for A in ethanol at 298°K. We have estimated  $k_{GR} \approx 10^7 - 5 \times 10^8$  for DBA in 95% ethanol. Assuming these values the concentration quenching contributions to  $\alpha^0$  at room temperature could be as large as 240 sec<sup>-1</sup> and  $1.6 \times 10^4$  sec<sup>-1</sup> for A and DBA, respectively.
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## 9,10-Dibromoanthracene Excited State Interactions with Ethyl Iodide and Benzene in Fluid Solution<sup>1</sup>

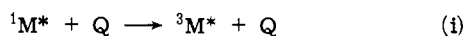
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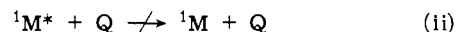
**Abstract:** The increase in the apparent molecular fluorescence of 9,10-dibromoanthracene (DBA) in fluid solution that results from the addition of ethyl iodide or benzene can be explained in terms of a collision-induced fluorescence process. Quantitative relative measurements of the fluorescence yield, triplet yield, and triplet quenching of DBA in cyclohexane solution as a function of ethyl iodide (and benzene) concentration have revealed a complex excited state relaxation distribution for the DBA-ethyl iodide interaction, while excited DBA interacts with benzene only to produce enhanced fluorescence. Bimolecular rate parameters appropriate to the mechanistic schemes invoked are given.

Ethanol solutions of 9,10-dibromoanthracene (DBA) increase their fluorescence in the presence of added ethyl iodide, bromobenzene, and benzene.<sup>2</sup>

For the heavy-atom components, ethyl iodide and bromobenzene, this behavior is in disharmony with that expected since these molecules are well known for quenching the fluorescence of aromatic hydrocarbons via a route which leads exclusively to the population of the molecular triplet state (normal heavy-atom quenching).<sup>1,3,4</sup> Normal heavy-atom quenching can therefore be described by the overall process



(where  ${}^1M^*$  and  ${}^3M^*$  are respectively the first singlet and triplet excited states of the aromatic, M, and Q is the quencher) and has been shown not to involve any interaction that does not lead to enhanced intersystem crossing of the  ${}^1M^*$  excitation

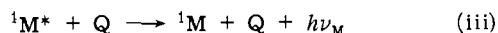


In fact the seemingly universal nature of the heavy-atom interaction i has established its role in an accurate method for determining triplet quantum yields which uses relative measurements of triplet absorbance (as determined by flash absorption spectroscopy) and fluorescence intensities in the presence and absence of heavy-atom quenchers.<sup>3a,5</sup>

The unusual fluorescence enhancement noted above cannot be solely attributed to the aromatic constituent, DBA, in that this molecule exhibits normal fluorescence quenching with potassium iodide in 95% ethanol.<sup>2</sup> Also, increased fluorescence in these systems is little influenced by solvent polarity since we have observed qualitatively similar behavior in cyclohexane solution.

To better assess the excitation-relaxation distribution resulting from the interaction of DBA with benzene and ethyl

iodide we have studied the concentration dependence ( $[Q] = [\text{benzene}], [\text{ethyl iodide}]$ ) of the relative fluorescence yield, relative triplet yield, and triplet state deactivation of DBA in cyclohexane solution. Our results are consistent with an interaction mode



common to both the DBA-ethyl iodide and DBA-benzene systems suggesting that the observed fluorescence enhancement can be explained in terms of collision-induced luminescence. For the DBA-ethyl iodide combination this process accounts for only 20% of the total  ${}^1M^*$ -Q interaction. We also find that ethyl iodide quenching of  ${}^3M^*$  contributes to the triplet decay of DBA in cyclohexane solution.

Our experimental study of the DBA-benzene, ethyl iodide systems has revealed the following additional characteristics. (a) No new fluorescence bands were found for the DBA-Q solution systems. In fact the shape and energy distribution of fluorescence spectra in the presence and absence of Q were essentially equivalent implying that the fluorescence component associated with process iii is structured and closely corresponds to the unperturbed molecular fluorescence of DBA. (b) No spectroscopic evidence could be found for ground state complexes. (c) A flash spectroscopic search revealed that triplet DBA was the only transient present with a lifetime greater than  $\sim 10 \mu\text{sec}$ .

### Experimental Section

Our experimental method consists of four basic measurements as outlined below.

(1) **Relative Triplet Yields, Triplet Quenching.** The triplet response,  $y_T(t)$ , for the solution systems DBA in cyclohexane as a function of  $[Q]$  ( $Q = \text{benzene, ethyl iodide}$ ) was measured by flash absorption spectroscopy. In these experiments  $y_T(t) = \epsilon_T(\lambda_a)[{}^3M^*]l$  is the transient absorbance corresponding to triplet-triplet absorption from the lowest triplet state ( ${}^3M^*$ ) of DBA at the analysis wavelength,  $\lambda_a = 425 \text{ nm}$ , with extinction coefficient,  $\epsilon_T$ , in an optical path length,  $l$ .  $y_T(t)$  was analyzed by nonlinear regression methods<sup>1</sup> to yield the triplet response extrapolated to  $t \equiv \text{time} = 0$ ,  $y_T(0)$ , and the first-order triplet decay parameter,  $\alpha$ . In the absence of Q these parameters are designated  $y_T^0(0)$ ,  $\alpha^0$ . The relative triplet yield and the triplet quenching functions are thus defined, respectively.

$$([Q], r_T), r_T = y_T(0)/y_T^0(0)$$

$$([Q], \alpha - \alpha^0)$$

Each sample solution corresponding to a different  $[Q]$  was simultaneously degassed with the corresponding  $Q = 0$  solution (lifetime blank)<sup>1</sup> to account for degassing variations among the DBA-Q samples comprising a given run. The degassing procedure consisted of exposing each frozen solution to a high vacuum ( $< 10^{-5}$  Torr) line for a 7-hr duration which was interrupted with repeated cycles of thawing, refluxing, and refreezing. No measurable solute or solvent loss was detected under these conditions. The parameter set  $y_T(0)$ ,  $\alpha$  (and  $y_T^0(0)$ ,  $\alpha^0$ ) corresponding to a given specimen solution was obtained from an average of five or more replicate decay curve samples.

The flash apparatus employed in this investigation has been described previously.<sup>1</sup> The flash energy is derived from a 125-J source and is delivered to an 8.5-cm linear Cajon<sup>7</sup> lamp filled with 30 Torr of pure argon. The half-peak width of the flash profile was 11  $\mu\text{sec}$ . The sample housing has provisions for flash filtering with planar glass filters and reproducible cell location, and it incorporates a flash lamp intensity monitor; these features are essential to ensure reliable comparative measurements as described above.

Appropriate filters were chosen to make certain that benzene and ethyl iodide did not absorb any light from the excitation flash or the steady state monitoring source. Uv and visible absorption spectra taken before and after flashing revealed no detectable decomposition in these systems. The relative triplet yield and quenching data are summarized in Table II.

Table I. Molecular Parameters for DBA

Solvent	$q_{FM}$	$\tau_M, \text{nsec}$	$k_{FM} \times 10^{-7}, \text{sec}^{-1}$	$q_{TM}$
Cyclohexane	0.094	1.56	6.03	
95% ethanol <sup>a</sup>	0.097	1.61	6.02	0.79

<sup>a</sup> From ref 1.

(2) **Relative Fluorescence Yields.** The ratio of the unnormalized fluorescence yield in the absence ( $F^0$ ) and presence ( $F$ ) of Q is given by the following expression

$$r_F = F^0/F = (A^0/A)(f/f^0)((n^0)^2/n^2)$$

where  $A$  is the integrated area under the corrected fluorescence spectrum corresponding to  $F$ , and  $f$  is the fraction of light absorbed by the specimen solution of refractive index  $n$  at the exciting wavelength  $\lambda_x$  ( $= 391 \text{ nm}$ ). The superscribed quantities  $A^0$ ,  $f^0$ , and  $n^0$  are defined identically but with reference to  $F^0$ .  $r_F$  as defined above specifies the relative fluorescence quantum yield as used in this study.

The fluorescence spectra corresponding to  $F^0$  and  $F$  (fully corrected for emission monochromator-photomultiplier response) were collected in one experiment under identical excitation-emission conditions for the same solution systems used in the flash photolysis experiments. A small bathochromic shift of the 0-0 fluorescence transition due to added  $Q = \text{benzene, ethyl iodide}$  was observed; this shift was not greater than 3 nm for either case at  $[Q]_{\text{max}}$ .

Fluorescence spectra were recorded (ratio recording) on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter and were observed at  $90^\circ$  to the excitation beam. The refractive index of each DBA-cyclohexane-Q solution was measured with an Abbé refractometer. The values of  $r_F$  obtained are reported in Table II.

(3) **Fluorescence Quantum Yield.** The fluorescence quantum efficiency  $q_{FM}$  of DBA in dilute cyclohexane solution (absorbance in a 1 cm path length at  $\lambda_x$  was less than 0.015) was determined by the same method as described above by employing quinine bisulfate in 1.0  $N$   $\text{H}_2\text{SO}_4$  as a quantum standard.<sup>8</sup> The value of  $q_{FM}$  obtained ( $q_{FM} = 0.094 \pm 0.006$ ) was derived from an average of four replicate determinations.

(4) **Fluorescence Lifetime.** The fluorescence response function<sup>9</sup>

$$f_M(t) = \int_0^t e^{-(t-x)} i_M(x) dx$$

was collected for DBA in cyclohexane solution by the single photon counting technique. Analysis of  $f_M(t)$  by the method of moments<sup>10</sup> revealed a single exponential decay curve giving a fluorescence lifetime  $\tau_M = 1.56 \text{ nsec}$ . The photon counting fluorometer constructed by Brand and coworkers has been described elsewhere.<sup>11</sup> The molecular parameters  $\tau_M$  and  $q_{FM}$  determined in this work are compared with those obtained in 95% ethanol in Table I.

All fluorescence solutions were degassed by purging them with solvent saturated argon for 10 min. This technique proved quite satisfactory when tested against the more rigorous method previously described for the flash photolysis solutions; no discernible difference was discovered. All measurements were made at room temperature.

**Chemicals.** DBA, obtained from Eastman Kodak, was chromatographed on alumina in three cycles. The final fraction was vacuum sublimed ( $< 10^{-3}$  Torr) twice. Spectroscopic grade cyclohexane and benzene were used without further purification. Ethyl iodide, reagent grade, was carefully distilled on an efficient, packed fractionating column.

### Results and Discussion

The relative fluorescence intensity of DBA in cyclohexane as a function of  $[Q]$  for Q equal to ethyl iodide and benzene is plotted in the normal Stern-Volmer fluorescence quenching representation

$$([Q], r_F), r_F = F^0/F$$

in Figure 1. It is observed that these plots manifest definite curvature and are characterized by a negative slope the

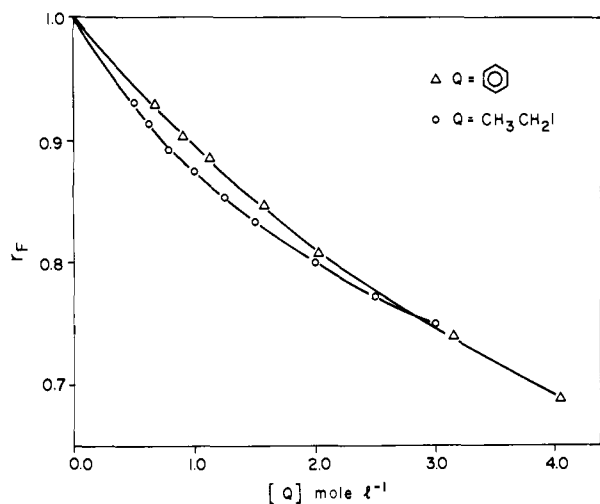


Figure 1. Relative fluorescence yield of DBA in cyclohexane with added ( $\Delta$ ) benzene and (O) ethyl iodide.

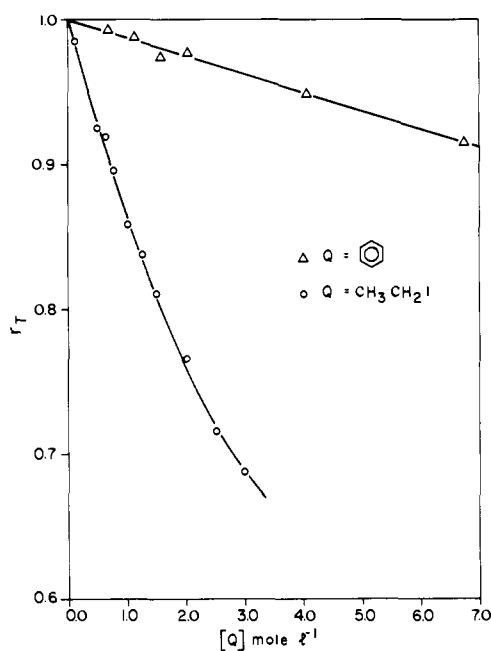


Figure 2. Relative triplet yield of DBA in cyclohexane with added ( $\Delta$ ) benzene and (O) ethyl iodide.

magnitude of which is similar for both ethyl iodide and benzene "quenching" in the data range examined. Although the fluorescence of DBA in the presence of added Q has increased the designation "quenching" will be retained to describe this behavior.<sup>12</sup>

The relative triplet formation,  $r_T = y_T(0)/y_T^0(0)$ , of cyclohexane solutions of DBA with added Q (ethyl iodide, benzene) is displayed in Figure 2. Both plots show that the addition of Q causes a decrease in the molecular triplet state population. This decrease is much greater for the ethyl iodide perturbation than it is for the benzene perturbation.

Triplet quenching of DBA by ethyl iodide and benzene is represented in the linear plot of Figure 3. A small contribution to the first-order triplet decay due to ethyl iodide quenching was found. No correlation of triplet decay with benzene concentration was observed.

A simple transformation of the fluorescence data in Figure 1

$$([Q], r_F) \rightarrow ([Q]^{-1}, [r_F - 1]^{-1})$$

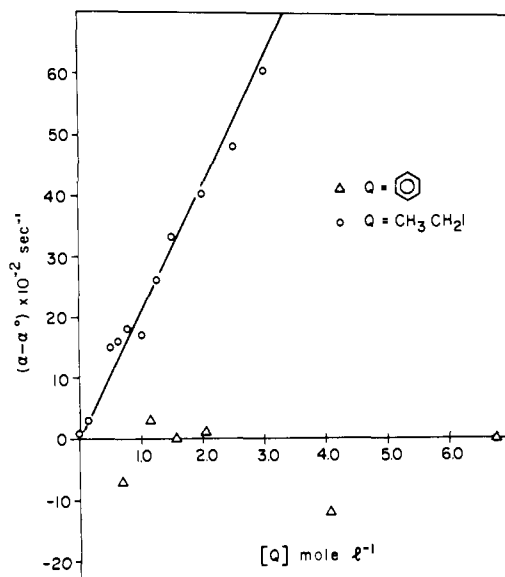


Figure 3. Triplet quenching of DBA in cyclohexane by ( $\Delta$ ) benzene and (O) ethyl iodide.

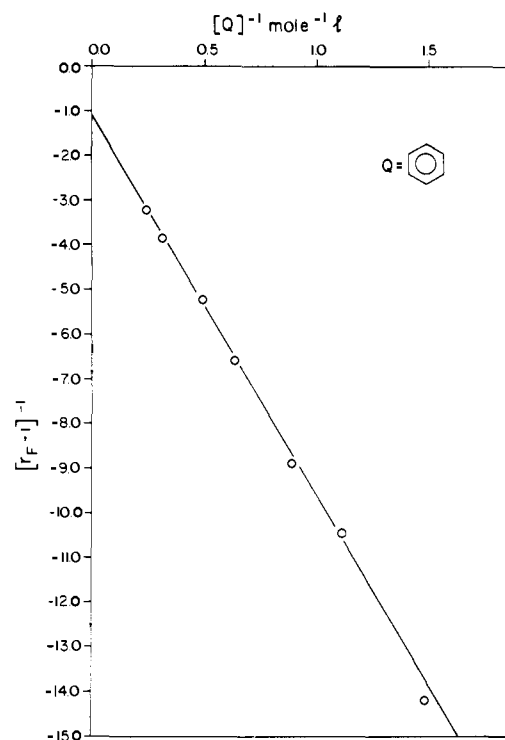


Figure 4.  $([Q]^{-1}, [r_F - 1]^{-1})$  relative yield representation of DBA fluorescence in cyclohexane for Q = benzene.

results in a linear representation for both Q = benzene (Figure 4) and Q = ethyl iodide (Figure 5). This result suggests that the parameterization in the original Stern-Volmer metric defines a hyperbola of the general form

$$r_F = \frac{1 + a_F[Q]}{1 + b_F[Q]} \quad a_F, b_F > 0 \quad (1)$$

For nonzero  $b_F$  the total fluorescence quantum yield ( $\phi_F = q_{FM}/r_F$ ) is a sum of two terms indicating that the observed fluorescence in the presence of Q (benzene or ethyl iodide) is derived from two sources. And, the concentration dependence of the total fluorescence quantum yield as expressed in eq 1 clearly points to a mechanism involving collisional interaction and subsequent photoassociation of singlet ex-

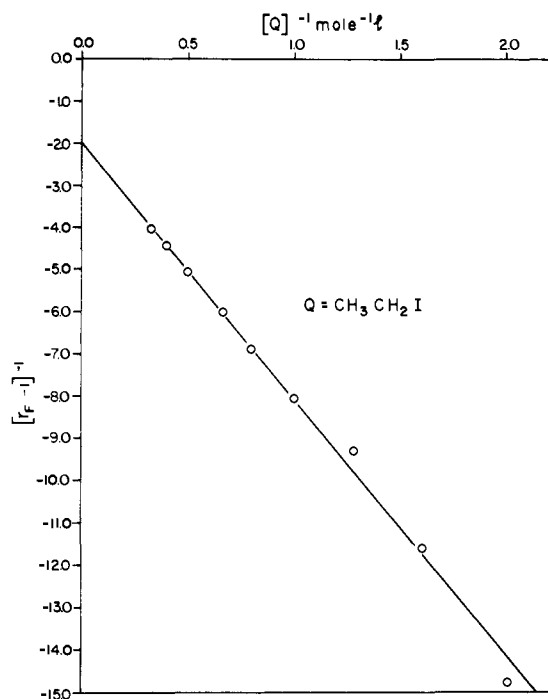
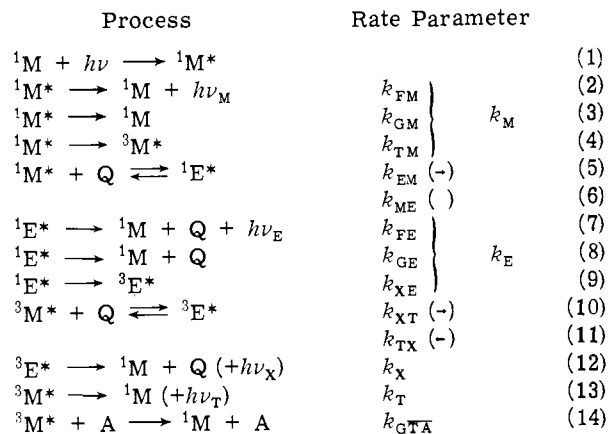


Figure 5.  $([Q]^{-1}, [r_F - 1]^{-1})$  relative yield representation of DBA fluorescence in cyclohexane for  $Q = \text{ethyl iodide}$ .

cited DBA with  $Q$ . Qualitative observations of the relative triplet yield and triplet quenching of DBA as a function of  $[Q]$  are not so instructive and a full kinetic analysis is necessary to explain the observed behavior.

In Scheme I a general reaction mechanism is presented

Scheme I



$$k_M = k_{FM} + k_{TM} + k_{GM} = 1/\tau_M$$

$$k_E = k_{FE} + k_{XE} + k_{GE} = 1/\tau_E$$

$$k_T = k_{PT} + k_{GT}$$

$$k_X = k_{PX} + k_{GX}$$

which involves reversible photoassociation in both the molecular singlet,  $^1M^*$ , and triplet,  $^3M^*$ , manifolds of DBA.<sup>13</sup>  $^1E^*$  and  $^3E^*$  represent the singlet and triplet exciplex populations derived from  $^1M^*-Q$  and  $^3M^*-Q$  photoassociation, respectively.  $Q$  stands for either benzene or ethyl iodide and  $A$  represents adventitious triplet quenchers (including  $^1M$ ). We now investigate the implications of this mechanism and test them against the fluorescence quenching, triplet quenching, and triplet formation observations under study.

**Kinetic Relations and Consequences.** Photostationary reaction kinetics based on Scheme I imply the following fluorescence relations:

molecular fluorescence quantum efficiency

$$q_{FM} = k_{FM}/k_M = \tau_M/\tau_{FM}$$

exciplex fluorescence quantum efficiency

$$q_{FE} = k_{FE}/k_E$$

molecular fluorescence quantum yield

$$\phi_{FM} = k_{FM}/(k_M + K_e k_E [Q])$$

exciplex fluorescence quantum yield

$$\phi_{FE} = K_e k_{FE} [Q]/(k_M + K_e k_E [Q])$$

total fluorescence quantum yield

$$\phi_F = \phi_{FM} + \phi_{FE} =$$

$$(k_{FM} + K_e k_{FE} [Q]) / (k_M + K_e k_E [Q]) \quad (2)$$

where

$$K_e = \frac{k_{EM}}{k_E + k_{ME}}$$

Transient reaction kinetics determines the triplet quantum yield, in the absence of  $Q$

$$q_{TM} = k_{TM}/k_M$$

and in the presence of  $Q$  (see Appendix)

$$\phi_T = \frac{k_{TM} + [k_{TX} k_{XE} K_e [Q] / (k_X + k_{TX})]}{k_M + k_E K_e [Q]} \quad (3)$$

The relative fluorescence yield,  $r_F$ , and the relative triplet yield,  $r_T$ , may now be expressed in terms of the rate parameters of Scheme I.

$$r_j = \frac{1 + a_j [Q]}{1 + b_j [Q]} = \begin{cases} r_F = \frac{F^0}{F} = \frac{q_{FM}}{\phi_F} \text{ for } j = F & (4) \\ r_T = \frac{y_T(0)}{y_T^0(0)} = \frac{\phi_T}{q_{TM}} \text{ for } j = T & (5) \end{cases}$$

$$a_F = b_T = \tau_M K_e k_E \quad (6)$$

$$b_F = \tau_{FM} K_e k_{FE} \quad (7)$$

$$a_T = k_{TM}^{-1} (k_{TX} k_{XE} K_e) / (k_X + k_{TX}) \quad (8)$$

The experimental observations  $\partial r_F / \partial [Q] < 0$ ,  $\partial r_T / \partial [Q] < 0$  impose the following conditions on the molecular parameters

$$a_F < b_F, q_{FM} < q_{FE} \quad (9a)$$

$$a_T < b_T, q_{TM} > (k_{TX} / (k_X + k_{TX})) q_{XE} \quad (9b)$$

where  $q_{XE} = k_{XE}/k_E$  is the  $^3E^*$  formation efficiency originating from  $^1E^*$ .

A useful linear expression relating  $r_F$  and  $r_T$  is obtained by eliminating  $[Q]$  in eq 4 and 5

$$r_F - 1 = m_h (h - 1) \quad (10)$$

with  $h = r_F r_T$  and gradient  $= m_h = (a_F - b_F) / (a_T - b_F)$ . The function  $(h - 1, r_F - 1)$  is independent of  $[Q]$  and therefore independent of kinetic activity factors which may be necessary to describe the effective value of  $[Q]$  in these experiments. Equation 10 will therefore serve as a control to determine whether parameters obtained from eq 4 and 5 need be modified by activity factors.

The pseudo-first-order triplet decay parameters,  $\alpha^0$ , in the absence of  $Q$  and,  $\alpha$ , in the presence of  $Q$  were derived from the transient components of the triplet response functions  $y_T^0(t)$  and  $y_T(t)$  (see Appendix). The triplet quenching parameter,  $K_X k_X$  is therefore obtained as the gradient of the function  $([Q], \alpha - \alpha^0)$ .

Table II. Relative Yield, Triplet Quenching Data

Q-[DBA]	[Q], mol l. <sup>-1</sup>	r <sub>F</sub>	r <sub>T</sub>	(α - α <sup>0</sup> ) × 10 <sup>-2</sup> sec <sup>-1</sup>
Ethyl iodide 7.82 × 10 <sup>-5</sup> mol l. <sup>-1</sup>	0	1.000	1.000	1.0
	0.125		0.9848	3.0
	0.500	0.9323	0.9250	15
	0.625	0.9140	0.9196	16
	0.780	0.8927	0.8962	18
	1.00	0.8759	0.8592	17
	1.25	0.8546	0.8375	26
	1.50	0.8340	0.8114	33
	2.00	0.8021	0.7659	40
	2.50	0.7738	0.7152	48
	3.00	0.7507	0.6875	60
Benzene 3.91 × 10 <sup>-5</sup> mol l. <sup>-1</sup>	0	1.000	1.000	0.0
	0.675	0.9296	0.9931	-7.0
	0.900	0.9043		
	1.125	0.8875	0.9884	3.0
	1.575	0.8482	0.9727	0.0 <sup>a</sup>
	2.025	0.8077	0.9770	1.0
	3.150	0.7400		
	4.050	0.6883	0.9485	-12.0 <sup>a</sup>
	6.750		0.9160	0.0

<sup>a</sup> A triplet "lifetime blank" was not run with this data sample.

**Data Analysis.** The functions  $r_j = r_j([Q])$  ( $j = F, T$ ) define hyperbolas and may be linearized by the following transformation

$$r_j \longrightarrow (r_j - 1)^{-1}$$

resulting in

$$(r_j - 1)^{-1} = (a_j - b_j)^{-1}[Q]^{-1} + b_j(a_j - b_j)^{-1} \quad (11)$$

The reciprocal functions  $(r_j - 1)^{-1}$  are linear in  $[Q]^{-1}$  with

$$\text{slope} = m_j = (a_j - b_j)^{-1}$$

and

$$\text{intercept} = n_j = b_j(a_j - b_j)^{-1}$$

giving  $b_j = n_j/m_j$  and  $a_j = (1 + n_j)m_j$  which may be obtained by linear regression analysis (LRA) of the reciprocal data with eq 11 properly weighted for the specified metric transformation.

Alternatively the yield parameters  $a_j$  and  $b_j$  may be recovered from eq 4 and 5 directly by using nonlinear regression analysis (NLRA).<sup>1</sup> This method is more precise than the approximate linearization technique described above. The yield parameters that were used to generate rate parameters were always taken from NLRA when appropriate.

The functions  $(h - 1, r_F - 1)$  and  $([Q], \alpha - \alpha^0)$  as well

Table III. Parameter Estimates

Function	Graphical representation	Type of analysis	$n_j$	$m_j$ , mol l. <sup>-1</sup>	$a_j$ , l. mol <sup>-1</sup>	$b_j$ , l. mol <sup>-1</sup>
DBA-Benzene						
([Q], r <sub>F</sub> )	Figure 1	NLRA			0.0118 ± 0.001	0.127 ± 0.011
([Q] <sup>-1</sup> , [r <sub>F</sub> - 1] <sup>-1</sup> )	Figure 4	LRA	-1.10 ± 0.053	-8.51 ± 0.26	0.0117 ± 0.006	0.129 ± 0.007
(h - 1, r <sub>F</sub> - 1) <sup>a</sup>	Figure 7	LRA	0.002 ± 0.0005	0.904 ± 0.042 <sup>b</sup>		
([Q], r <sub>T</sub> )	Figure 2					
([Q], r <sub>T</sub> <sup>-1</sup> )	Figure 6	LRA	0.997 ± 0.04	0.0132 ± 0.0018 <sup>c</sup>		0.0132 ± 0.0018
([Q], α - α <sup>0</sup> )	Figure 3					
DBA-Ethyl Iodide						
([Q], r <sub>F</sub> )	Figure 1	NLRA			0.168 ± 0.008	0.334 ± 0.019
([Q] <sup>-1</sup> , [r <sub>F</sub> - 1] <sup>-1</sup> )	Figure 5	LRA	-2.00 ± 0.077	-6.10 ± 0.18	0.164 ± 0.013	0.328 ± 0.016
(h - 1, r <sub>F</sub> - 1) <sup>a</sup>	Figure 9	LRA	0.001 ± 0.0004	0.516 ± 0.018 <sup>b</sup>		
([Q], r <sub>T</sub> )	Figure 2	NLRA			0.0098 ± 0.004	0.165 ± 0.01
([Q] <sup>-1</sup> , [r <sub>T</sub> - 1] <sup>-1</sup> )	Figure 8	LRA	-1.05 ± 0.20	-6.46 ± 0.32	0.008 ± 0.03	0.163 ± 0.03
([Q], α - α <sup>0</sup> )	Figure 3	LRA	0.075	2.03 ± 0.48 × 10 <sup>3d</sup>		

<sup>a</sup> See footnote 15. <sup>b</sup> Dimensionless. <sup>c</sup> Units of l. mol<sup>-1</sup>. <sup>d</sup> Units of l. mol<sup>-1</sup> sec<sup>-1</sup>.

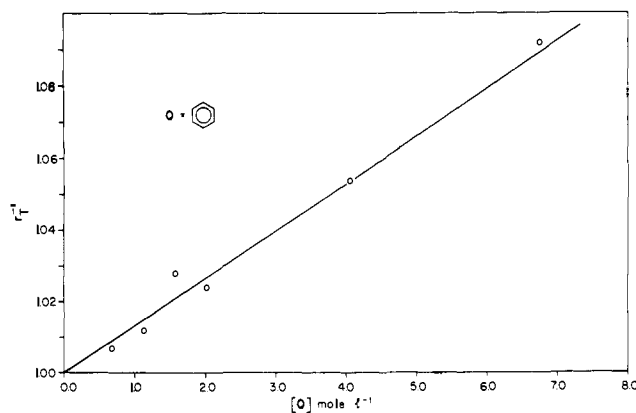


Figure 6.  $([Q], r_T^{-1})$  relative yield representation of DBA triplet state production in cyclohexane for Q = benzene.

as the other linear representations described above were analyzed by LRA.

The data corresponding to the relative yield and triplet quenching measurements as a function of  $[Q]$  are summarized in Table II and graphically displayed in Figures 1-9. Table III contains the parameter estimates  $m_j$ ,  $n_j$ ,  $a_j$ ,  $b_j$ ,  $k_X K_X$  obtained from both LRA and NLRA for comparison. Finally in Table IV are collected the derived rate parameters predicted by Scheme I.

**DBA-Benzene Interaction.** As noted previously the reciprocal fluorescence yield representation (Figure 4) for Q = benzene is linear. The fluorescence yield parameters obtained by NLRA (Table III) with eq 4 generate the solid line fit in Figure 1. The ratio  $a_F/b_F = q_{FM}/q_{FE} = 0.093$  is within experimental error equivalent to the measured value of  $q_{FM} = 0.094$  (Table I) and we may immediately conclude that  $q_{FE} \sim 1$ .

This result predicts that  $k_{XE} + k_{GE} \sim 0$  and establishes the condition  $a_T \sim 0$  in eq 5 which suggests a new linear relative triplet yield representation for this system viz.

$$r_T^{-1} = 1 + b_T[Q]$$

This function is plotted in Figure 6 and LRA determines  $b_T = 0.0132 \pm 0.0018$  l. mol<sup>-1</sup> which is within the estimated uncertainty equivalent to  $a_F$ .

The concentration independent representation (eq 10) for the DBA-benzene system is plotted in Figure 7 and is noticeably linear with a gradient equal to (Table III)

$$m_h = 0.904 = \frac{a_F - b_F}{-b_F} = 1 - (q_{FM}/q_{FE})$$

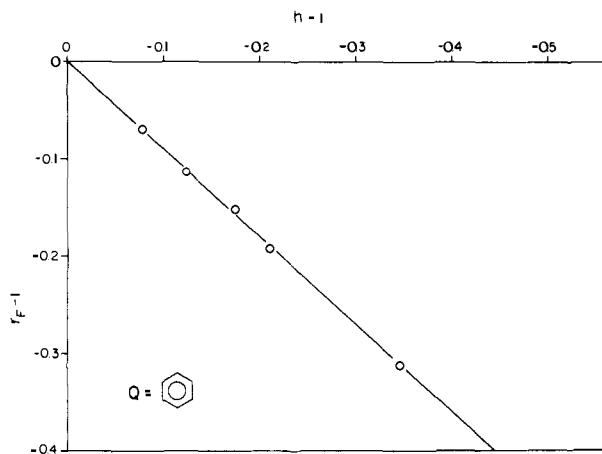
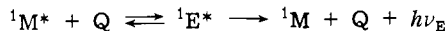


Figure 7.  $(h - 1, r_F - 1) Q =$  benzene concentration independent representation for DBA in cyclohexane solution.

which implies  $q_{FM} = 0.096$ , and the molecular fluorescence quantum efficiency is again generated. This result confirms that concentration dependent activity factors play a minor role in describing the benzene concentration for the concentration range employed.

As mentioned earlier no correlation was observed with the function  $([Q = \text{benzene}], \alpha - \alpha^0)$  which describes external triplet quenching according to step 10, Scheme I (Figure 3).

Our results for the DBA-benzene study reveal that processes 8-12 of Scheme I are absent.  $^1M^*$ -Q interaction is consistent with the overall process



with a bimolecular interaction rate parameter given by  $K_e k_{FE} = a_F / \tau_M = 7.6 \times 10^6 \text{ l. mol}^{-1} \text{ sec}^{-1}$ . While the collisional efficiency of this interaction is low the observation of a single energy dissipation channel for  $^1E^*$  (i.e., fluorescence only, confirmed by both the fluorescence and triplet yield measurements) unmasks a maximal fluorescence quantum efficiency ( $q_{FE} = 1$ ).

**DBA-Ethyl Iodide Interaction.** The concentration,  $[Q]$ , dependence of the  $r_F$  and  $r_T$  data is consistent with eq 4 and 5, respectively. The reciprocal plots Figures 5 and 8 are well behaved in each case and the yield parameters  $a_j$  and  $b_j$  obtained by NLRA with eq 4 and 5 (Table III) produce the solid line fits in Figures 1 and 2 for  $Q =$  ethyl iodide. From eq 4 and 5 the following identifications can be made with the experimental yield parameters (Table III)

$$K_e k_{FE} = a_F / \tau_M = 10.8 \times 10^7 \text{ l. mol}^{-1} \text{ sec}^{-1}$$

$$K_e k_{FE} = b_F / \tau_{FM} = 2.01 \times 10^7 \text{ l. mol}^{-1} \text{ sec}^{-1}$$

$$K_e k_{IE} = K_e k_{FE} - K_e k_{FE} = 8.79 \times 10^7 \text{ l. mol}^{-1} \text{ sec}^{-1}$$

$$K_e k_{XE} (k_{TX} / (k_X + k_{TX})) = a_T q_{TM} / \tau_M = 0.51 \times 10^7 \text{ l. mol}^{-1} \text{ sec}^{-1}$$

In the calculation of the triplet yield interaction parameter,  $K_e k_{XE} k_{TX} / (k_X + k_{TX})$ , the value of  $q_{TM}$  for DBA in ethanol<sup>1</sup> was used since  $q_{TM}$  was not available from the present analysis. The triplet formation efficiency,  $q_{TM}$ , has been determined for DBA in ethanol<sup>1</sup> (Table I) by correlating  $r_F$  and  $r_T$  as a function of potassium iodide concentration and this value is assumed in cyclohexane for the following reasons. (i) The fluorescence quantum yields and lifetimes of DBA determined in cyclohexane and in ethanol are equivalent within experimental accuracy (Table I) implying a similar solvent perturbation on the fluorescence ( $k_{FM}$ ) and in-

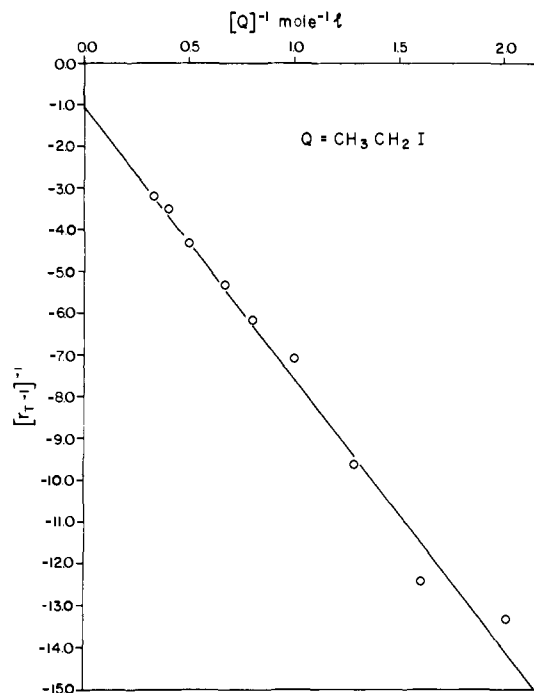


Figure 8.  $([Q]^{-1}, [r_T - 1]^{-1})$  relative yield representation of DBA triplet state production in cyclohexane for  $Q =$  ethyl iodide.

ternal quenching ( $k_{IM}$ ) probabilities for DBA in these two solvents. (ii) The fluorescence quenching of DBA by ethyl iodide in cyclohexane shows similar behavior in ethanol. (iii) We qualitatively observed  $\partial r_T / \partial [Q] < 0$  for DBA in ethanol for  $Q =$  ethyl iodide, and at  $[Q] = 3.0 \text{ mol l}^{-1}$   $r_T \sim 7.0$ , a value very similar to that obtained in cyclohexane.

The observations ii and iii suggest that the differing solvent nature cyclohexane vs. ethanol is not significantly affecting the dissimilar "quenching" behavior experienced with ethyl iodide and KI but that this behavior is peculiar to specific DBA-Q interaction. The fact that  $q_{TM}$  cannot be determined from the DBA-ethyl iodide analysis reflects the complexity of interaction in this system and, therefore, exposes one limitation of the heavy-atom quenching method for determining  $q_{TM}$ .<sup>3a</sup>

With  $k_{GE} = 0$ ,<sup>16</sup> the total nonradiative component of  $k_E$  is quantitatively accounted for in the intersystem crossing process (XE) which populates  $^3E^*$ . The fraction of this excitation ( $^3E^*$ ) which relaxes to form  $^3M^*$  by dissociation is given by  $k_{TX} / (k_X + k_{TX}) \sim 0.06$  implying that  $k_X / k_{TX} \sim 16$ . The remaining leakage path for  $^3E^*$  relaxation is specified by the fraction  $k_X / (k_X + k_{TX}) = 0.94$  and appears as an overall internal conversion relative to the  $^1M^*$  relaxation scheme but which is really a process susceptible to heavy-atom perturbation ( $^3E^* \rightarrow ^1E$ ).<sup>18</sup> These conclusions are succinctly expressed by writing, for the total  $^1E^*$  relaxation parameter,

$$k_E = k_{FE} + k_{XE} = k_{FE} + k_{XE} \left( \frac{k_{TX}}{k_X + k_{TX}} \right) + k_{XE} \left( \frac{k_X}{k_X + k_{TX}} \right)$$

The  $(h - 1, r_F - 1)$  representation for this system is linear (Figure 9) giving  $m_h = 0.516 \pm 0.018$ . The component  $a_T$  may be calculated from the relation

$$a_T = \frac{a_F + b_F(m_h - 1)}{m_h} = 0.012$$

$a_F$  and  $b_F$  were taken from the NLRA. The value of  $m_h$  is consistent with the concentration dependent determinations

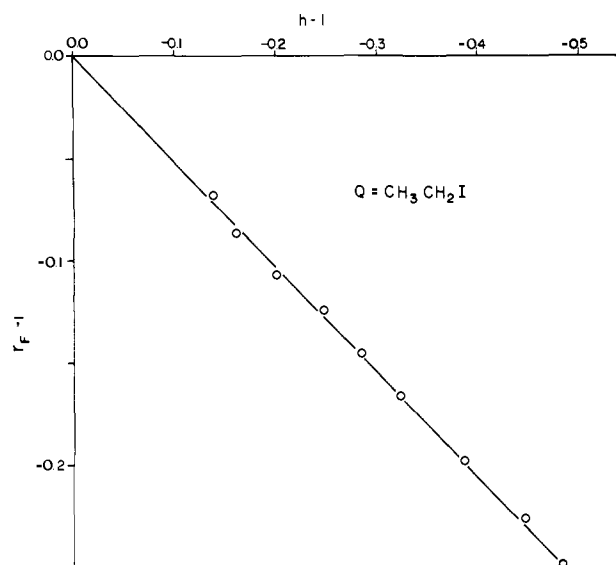
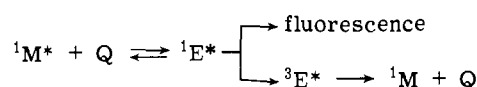


Figure 9.  $(h - 1, r_F - 1)$   $Q =$  ethyl iodide concentration independent representation for DBA in cyclohexane solution.

of  $a_F, b_F, a_T,$  and  $b_T$  again suggesting the insignificant role played by activity factors in describing  $[Q]$  for these interactions.

A measurable enhancement of the triplet decay rate of DBA in the presence of ethyl iodide consistent with steps 10–12 of Scheme I has been observed. The function  $([Q], \alpha - \alpha^0)$  describing this behavior is plotted in Figure 3. LRA extracts the triplet quenching parameter,  $K_X k_X = 2.0 \times 10^3$  l. mol<sup>-1</sup> sec<sup>-1</sup>.

The above analysis shows that DBA-Q interaction for  $Q =$  ethyl iodide is considerably more complex than for the  $Q =$  benzene case. The data for the DBA-ethyl iodide system are consistent with all the processes defined in Scheme I.<sup>16</sup> The dominant relaxation sequence resulting from  $^1M^*-Q$  interaction is as follows



The values of the derived interaction rate parameters for this system are summarized in Table IV.

### General Discussion and Conclusions

We have considered the interaction of benzene and ethyl iodide with DBA in terms of a general reaction mechanism involving the photoassociation products  $^1E^*$  and  $^3E^*$ . Scheme I defines a single  $^1M^*-Q$  interaction which specifies the formation step of a photoassociation process between the species  $^1M^*$  and  $Q$ . The observed quenching and fluorescence enhancement is attributed to the involvement of a new component,  $^1E^*$ , which undergoes its own characteristic photophysics. For the DBA-ethyl iodide system fluorescence competes favorably with internal quenching in  $^1E^*$  ( $q_{FE} \sim 0.2$ ). This internal quenching component is ascribed to the intersystem relaxation specified in  $k_{XE}$  which provides an internal pathway for populating  $^3E^*$ . Enhanced molecular triplet state production depends not only on the parameter  $k_{XE}$  but also on the fraction of the  $^3E^*$  excitation which dissociates ( $k_{TX}/(k_X + k_{TX})$ ) to form  $^3M^*$ . This fraction is small for the present case ( $\sim 0.06$ ) suggesting that the dominant mode of triplet excimer relaxation is  $^3E^* \rightarrow ^1E$  intersystem crossing. Both the triplet quenching data and the transient relative triplet yield data are consistent with reversible photoassociation in the triplet manifold. For

Table IV. Derived Rate Parameters for DBA in Cyclohexane Solution

Molecular Rate Parameters, sec <sup>-1</sup>		
$k_M$		$64.1 \times 10^7$
$k_{FM}$		$6.03 \times 10^7$
$k_{GM}$		$< 7.5 \times 10^7$
$k_{TM}^a$		$50.6 \times 10^7$
$\alpha^0$		$4.11 \times 10^4$
Interaction Rate Parameters, l. mol <sup>-1</sup> sec <sup>-1</sup>		
DBA-Q		
$Q =$ benzene ( $k_E = k_{FE}$ ),	$K_e k_{FE}$	$7.6 \times 10^6$
$q_{FE} = 1$		
$Q =$ ethyl iodide	$K_e k_E$	$10.8 \times 10^7$
( $k_E = k_{FE} + k_{XE}$ ),	$K_e k_{FE}$	$2.01 \times 10^7$
$k_X/k_{TX} = 16,$	$K_e k_{XE}$	$8.79 \times 10^7$
$q_{FE} = 0.19,$	$K_e \frac{k_{TX}}{k_X + k_{TX}} k_{XE}$	$0.51 \times 10^7$
$q_{XE} \leq 0.81$	$K_e \frac{k_X}{k_X + k_{TX}} k_{XE}$	$8.28 \times 10^7$
	$K_X k_X$	$2.03 \times 10^3$
	$k_{XT}$	$2.2 \times 10^3$

<sup>a</sup> $q_{TM}$  determined in 95% ethanol, ref 1.

the benzene system internal quenching in  $^1E^*$  is absent and enhanced fluorescence corresponds to an exciplex fluorescence quantum efficiency of unity.

The spectral features of the new emission from  $^1E^*$  (shape and energy distribution closely resembling that of the parent  $^1M^*$  fluorescence) indicate that the  $^1E^*$  fluorescent state is most likely weakly bound (e.g., a "contact exciplex"). The retention of parent structure in the  $^1E^*$  fluorescence spectrum can be rationalized by considering the enhanced fluorescence (i) to be derived from a locally excited configuration  $^1E^*_F \equiv ^1(M^*Q)$  which could arise directly upon formation, or from an electronic reorganization in  $^1E^*$ , or evolve in preequilibrium prior to  $^1E^*$  formation; (ii) to originate from a delocalized configuration which is strongly coupled to the molecular ground state; (iii) to emit to a weak, static ground state interaction. It is clear that our experiments cannot distinguish the above possibilities; however, it is expected that combined steady state and transient fluorescence measurements (including temperature dependence) will better define the nature of the  $^1E^*$  fluorescent state in these systems.<sup>19</sup> The fact that similar fluorescence behavior is observed for  $Q$  equal to both benzene and ethyl iodide supports the contention that the enhanced fluorescence of DBA in the presence of  $Q$  is interaction and not heavy-atom related.

It is of interest to compare the general quenching behavior of the DBA-ethyl iodide combination with that of normal systems<sup>1,3</sup> where fluorescence quenching by heavy atoms leads exclusively to populating the molecular triplet state. If an exciplex mechanism is invoked for normal heavy-atom quenching (as suggested by Stevens<sup>21</sup> and Birks<sup>9</sup>) which involves enhanced triplet production originating from  $^3E^*$  (TX) then the following additional restrictions to Scheme I must apply

$$k_{XE} \gg k_{FE}$$

$$k_{TX} \gg k_X$$

Furthermore, linear triplet quenching in fluid solution by heavy atoms has been reported for the normal systems anthracene-bromobenzene,<sup>1</sup> anthracene-ethyl iodide,<sup>1</sup> DBA-KI,<sup>1</sup> and molecular pyrene-ethyl iodide<sup>3b</sup> but there is no direct evidence implicating this interaction with  $^3E^*$  formation. However, if one admits to a fluorescence-heavy-atom

quenching mechanism involving the intermediary of  $^3E^*$  which was derived from an initial  $^1M^*-Q$  interaction, there is no good reason not to expect a parallel interaction ( $^3M^*-Q$ ) in the triplet manifold leading to  $^3E^*$  formation especially in view of the similar parallel which is believed to exist with singlet and triplet excimers of aromatic hydrocarbons in fluid solution.<sup>22</sup> It is likely that the low  $^3M^*-Q$  collisional efficiency that is observed in these systems including DBA-ethyl iodide reflects a low  $^3E^*$  formation efficiency relative to diffusion-controlled encounter.<sup>22</sup> Linear triplet heavy-atom quenching secures the validity of eq A4 and hence eq A5 in describing the triplet response under flash excitation conditions for both normal systems and DBA-ethyl iodide.

The above considerations establish the following important relations which characterize normal heavy-atom quenching behavior

$$\phi_F = \frac{k_{FM}}{k_M + K_e k_{XE}[Q]}$$

$$\phi_T = \frac{k_{TM} + K_e k_{XE}[Q]}{k_M + K_e k_{XE}[Q]}$$

$$\alpha - \alpha^0 = (k_X k_{XT} / k_{TX})[Q]$$

implying that the molecular triplet state quantum efficiency,  $q_{TM}$ , may be derived from the slope of the  $(h - 1, r_F)$  representation

$$r_F = (h - 1)q_{TM} + 1$$

According to Scheme I, then, the DBA-ethyl iodide system is distinguished from normal systems in two respects: (i) the DBA-ethyl iodide singlet exciplex,  $^1E^*$ , sustains substantial fluorescence, i.e.,  $k_{FE} \neq 0$ ; (ii) the DBA-ethyl iodide triplet exciplex,  $^3E^*$ , favors  $^3E^* \rightarrow ^1E$  intersystem crossing to  $^3E^* \rightarrow ^3M^* + Q$  dissociation. The tighter binding in  $^3E^*$  for this system  $k_{TX} < k_X$  takes advantage of the double heavy-atom perturbation that is available (bromine + iodine) for promoting the  $^3E^* \rightarrow ^1E$  intersystem relaxation.

Since the overall mode of  $M \rightarrow T$  intersystem crossing resulting from  $^1M^*-Q$  interaction represents several processes, and only one of these (XE) corresponds to a potentially strong singlet  $\rightarrow$  triplet intersystem crossing, it is not surprising to find an example system, viz. DBA-ethyl iodide, with somewhat different properties.

The interesting example of DBA and its interactions with ethyl iodide (and benzene) has provided a means whereby one could probe the photoassociation mechanism<sup>9,21</sup> of external heavy-atom interaction employing the combined studies of photostationary fluorescence and conventional microsecond flash photolysis techniques. These studies provide a semiquantitative description of the observed photophysical behavior in terms of bimolecular interaction rate parameters. To evaluate the individual rate parameters for a more complete description, fluorescence lifetime measurements are required.<sup>19</sup>

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## Appendix

From Scheme I it is observed that there are two routes available for populating the molecular triplet state (steps 4

and 11) and that including these processes defines the total triplet quantum yield

$$\phi_T = \phi_{TM} + \phi_{TX}$$

which is expressed as a sum of two components, originating from  $^1M^*$  and  $^3E^*$ , respectively.<sup>14</sup>

The parametric form of  $\phi_T$  is properly expressed under flash excitation conditions with a light flash of narrow width in the *initial triplet concentration*<sup>9</sup> which is obtained from the transient solution of the molecular triplet state decay extrapolated to time  $\equiv t = 0$ . The differential equation corresponding with Scheme I which describes the time dependence of  $[^3M^*]$  is conveniently represented in the complex frequency domain,  $s$ , by employing the right-handed Laplace transform operator,  $L$ , giving

$$\frac{[^3m^*]}{[^1M^*]_0} = \frac{k_{TM}(s + Y_E)(s + Y_X) + k_{TX}k_{XE}k_{EM}[Q]}{\prod_{n=1}^4 (s + \gamma_n)} = \sum_{n=1}^4 \frac{B_n}{(s + \gamma_n)} \quad (A1)$$

where  $[^3m^*] = L\{[^3M^*]\}$

$$\gamma_1, \gamma_2 = \frac{1}{2}[X_X + Y_X \mp \{(Y_X - X_X)^2 + 4k_{TX}k_{XT}[Q]\}^{1/2}]$$

$$\gamma_3, \gamma_4 = \frac{1}{2}[X_E + Y_E \mp \{(Y_E - X_E)^2 + 4k_{ME}k_{EM}[Q]\}^{1/2}]$$

$$X_X = \alpha^0 + k_{XT}[Q], \quad \alpha^0 = k_T + \sum_A k_{GTA}[A]$$

$$Y_X = k_X + k_{TX}$$

$$X_E = k_M + k_{EM}[Q]$$

$$Y_E = k_E + k_{ME}$$

$$B_n = \left[ (s + \gamma_n) \frac{[^3m^*]}{[^1M^*]_0} \right]_{s=-\gamma_n}, \quad n = 1, 4$$

and  $[^1M^*]_0$  is the initial concentration of excited molecules produced by the excitation flash at  $t = 0$ . Applying the inverse Laplace operator to eq A1 determines the time dependence of  $[^3M^*]$

$$[^3M^*] = [^1M^*]_0 \sum_{n=1}^4 B_n e^{-\gamma_n t} \quad (A2)$$

which is expressed as a sum of four exponential terms. The experimental triplet decay curves obtained in this study (microsecond resolution) were operationally characterized by a single exponential function implying that one of the terms in eq A2 must be dominant if Scheme I is to provide a consistent model for the observed triplet response. Under the assumption that the decay parameters which determine the relaxation of the excited singlet states involved ( $^1M^*$ ,  $^1E^*$ ) are significantly larger than those which govern the decay of the excited triplet states involved ( $^3M^*$ ,  $^3E^*$ ), i.e.  $\gamma_3, \gamma_4 \gg \gamma_1, \gamma_2$ , and utilizing the mathematical consequence that the decay parameters  $\gamma_1, \gamma_2$  and  $\gamma_3, \gamma_4$  must be real, i.e.,  $\gamma_2 > \gamma_1$  and  $\gamma_4 > \gamma_3$ , the following inequalities are valid

$$\gamma_1 < \gamma_2 < \gamma_3 < \gamma_4$$

$$B_1 > B_2, B_3, B_4$$

so that the first term in eq A2 is dominant, resulting in the single exponential triplet decay function

$$[^3M^*] \sim [^1M^*]_0 B_1 e^{-\gamma_1 t} \quad (A3)$$



From the exact relations

$$\gamma_2 = X_X + Y_X - \gamma_1$$

$$\gamma_1 = (X_X Y_X - k_{TX} k_{XT} [Q]) / \gamma_2$$

we have

$$\gamma_1 = \alpha \sim k_X K_X [Q] + \alpha^0, K_X = \frac{k_{XT}}{k_X + k_{TX}} \quad (\text{A4})$$

which was obtained by putting  $\gamma_2 \sim Y_X$ , a necessary approximation to ensure that triplet quenching by ethyl iodide (heavy atoms) sustains a linear concentration,  $[Q]$ , dependence as was observed experimentally (linear triplet quenching).

With the above restrictions, the initial triplet concentration  $[^3M^*]_0$ , and hence  $\phi_T$ , is now defined, from eq A3

$$\frac{[^3M^*]_0}{[^1M^*]_0} = \phi_T = B_1 \sim \frac{k_{TM} + (k_{TX} k_{XE} K_e [Q]) / (k_X + k_{TX})}{k_M + k_E K_e [Q]} \quad (\text{A5})$$

## References and Notes

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- (12) The fluorescence quenching observed in this investigation is more appropriately termed enhancement or negative quenching since  $\partial r_F / \partial [Q] < 0$ . We use the designation "quenching" to include both positive and negative quenching; its specific meaning will be revealed in context.
- (13) The rate parameter nomenclature we use follows closely with that of Birks<sup>9</sup> (see also ref 1).
- (14) A dissociative intersystem crossing process in  $^1E^*$  could provide an additional route for populating  $^3M^*$  which could be described by a lumped rate parameter,  $k_{TE}$ , to include such possibilities as
 
$$^1E^* \rightarrow ^3M^*$$

$$^1E^* \rightarrow ^3E^{**} \rightarrow ^3M^*$$

$$^1E^* \rightarrow ^3E^{**} \rightarrow ^3M^{**} \rightarrow ^3M^*$$

$$^1E^* \rightarrow ^3M^{**} \rightarrow ^3M^*$$
 where two asterisks implies a higher excited state. It is not necessary to incorporate this process into Scheme I to explain external heavy-atom quenching of aromatic hydrocarbons and we ignore it for the sake of seeking a marginal mechanism.
- (15) In the LRA of this function we treated  $h - 1$  as the dependent variable since the propagated error in the product  $r_F r_T$  makes this variable more uncertain than  $r_F$ .
- (16) Exciplex internal conversion ( $k_{CE}$ ) is unlikely to be efficient because of the large energy gap. Exciplex intersystem crossing ( $k_{XE}$ ) to the triplet exciplex state, however, is an important quenching process in many cases<sup>9</sup> even when Q is not a heavy-atom quencher.<sup>17</sup>
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- (18) We point out that the absolute magnitude of these rate ratios carries a significant uncertainty due to the 40% error in the determination of  $a_T$  for this system (Table III).
- (19) We have examined the fluorescence response functions for the system DBA-3.0 mol l.<sup>-1</sup> ethyl iodide in cyclohexane at three emission wavelengths 410, 435, and 490 nm and were unable to fit these data to a single exponential impulse response. Analysis of the data for double exponential decay secured a well-behaved fit in each case implying the presence of a two-component fluorescent system. The amplitude of the shorter component  $\tau \sim 0.3-0.5$  nsec was negative indicating the presence of an excited state reaction in the singlet manifold consistent with Scheme I. These results, although preliminary, offer direct support for  $^1M^*-Q$  photoassociation and demonstrate the presence of  $^1E^*$  in this system. We plan a systematic temperature and concentration study of this and related systems employing nanosecond fluorescence techniques and will report on our findings in a future publication. In such a study careful attention must be given to controlling excitation lamp drifts and wavelength dependent transit time effects in the detector photomultiplier<sup>20</sup> since the decay times involved are short.
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## An Investigation of Potassium Perchromate as a Source of Singlet Oxygen

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**Abstract:** Potassium perchromate undergoes aqueous decomposition with the concomitant generation of singlet oxygen. An upper limit for the yield of singlet oxygen, based on potassium perchromate, is estimated to be 6%. Use of the salt in a study of photodynamic reactions has demonstrated the occurrence of oxidative pathways other than those involving singlet oxygen and hence caution must be exercised in interpreting experiments employing the perchromate system as a source of singlet oxygen. In conjunction with this investigation the pH dependence of the rate of decomposition of  $CrO_8^{3-}$  in buffered solutions was investigated in the pH range from 10.0 to 12.5 using electron paramagnetic resonance (EPR) spectroscopy. The decomposition followed the approximate rate law  $k = k'[H^+]$ , with an order in hydrogen ion deviating slightly from unity, and  $k' = 7 \times 10^7 M^{-1} \text{ min}^{-1}$ . The thermal decomposition of solid  $K_3CrO_8$  resulted in conversion to potassium chromate, potassium superoxide, and oxygen. No singlet oxygen was observed by EPR during thermal decomposition of the solid salt, establishing an upper limit for singlet oxygen of 0.1% of the ground state oxygen evolved.

In a recent communication from this laboratory<sup>3</sup> it was reported that potassium perchromate ( $K_3CrO_8$ ) undergoes aqueous decomposition which, in the presence of singlet oxygen acceptors, results in the formation of typical singlet

oxygen products and product distributions. These results were submitted as evidence that the oxygen evolved during the aqueous decomposition of potassium perchromate was, at least in part, in the excited singlet state  $O_2(^1\Delta_g)$ .