EXCIPLEX QUENCHING AS A METHOD OF INVESTIGATING PHOTOCHEMICAL REACTION MECHANISMS

M. G. KUZMIN, N. A. SADOVSKII and I. V. SOBOLEVA

Chemistry Department, Moscow State University, 117234 Moscow (U.S.S.R.)

Summary

The application of exciplex quenching to the investigation of photochemical reaction mechanisms is investigated. Kinetic analyses of exciplex fluorescence quenching and photochemical reaction quenching are presented. The product of a photochemical reaction is generally formed by one of the following three routes: (a) the product is formed in parallel with the exciplex; (b) the product and the exciplex are both formed from a common non-relaxed charge transfer state; (c) the product is formed from the fluorescent (relaxed) state of the exciplex or the reaction proceeds via the exciplex as an intermediate. Expressions enabling the partial quantum yields of routes (a), (b) and (c) to be determined are obtained.

The quenching method is used to analyse the mechanism of halogen photoelimination in 9,10-dichloroanthracene in the presence of diethylaniline. The reaction is shown to proceed via both the non-relaxed and relaxed states of the exciplex.

1. Introduction

Excited state quenching is widely used to investigate photochemical reaction mechanisms [1]. The role of exciplexes in some photochemical reactions has been studied using this method [2 - 10]. The effect of quenching on exciplex formation and reaction may be rather complicated. In this paper kinetic analyses of exciplex fluorescence quenching and photochemical reaction quenching are presented.
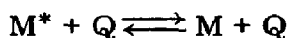
The quenching method is used to analyse the mechanism of halogen photoelimination in 9,10-dichloroanthracene in the presence of diethylaniline.

2. Kinetics of exciplex quenching

Exciplex fluorescence quenching can proceed by one of three routes:

$$M^* + X \rightleftharpoons (M^{\pm}X^{\mp})^{\tilde{*}} \rightleftharpoons (M^{\pm}X^{\mp})^* \tag{1}$$

$$Q\downarrow \qquad\qquad Q\downarrow \qquad\qquad Q\downarrow$$
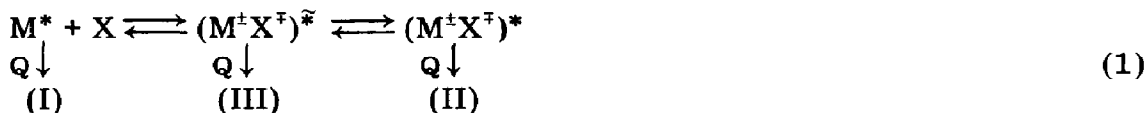
$$(I) \qquad\qquad (III) \qquad\qquad (II)$$

where route (I) is the quenching of the excited molecules

$$M^* + Q \rightleftharpoons M + Q$$

route (II) is the quenching of the exciplex emissive state

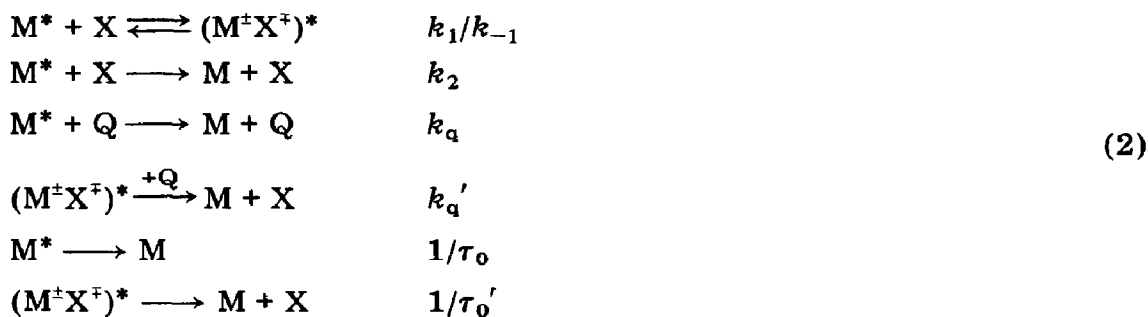$$(M^{\pm}X^{\mp})^* + Q \longrightarrow M + Q + X$$

and route (III) is the decrease in the yield of formation of the exciplex emissive state.

A small increase in the polarity of the medium (from $\epsilon \approx 2$ to $\epsilon \approx 4$) by the addition of polar compounds markedly reduces the quantum yield of exciplex fluorescence; however, the fluorescence lifetime is almost unchanged [11]. The reduction in the exciplex yield from the primary non-relaxed charge transfer state is due to radiationless deactivation induced by the quencher and the polar medium [12]:

$$(M^{\pm}X^{\mp})^{\tilde{*}} + Q \longrightarrow M + X + Q$$

The tilde denotes the non-relaxed state of the exciplex.

The kinetics of exciplex quenching can be described by the following general formal scheme:

$$M^* + X \rightleftharpoons (M^{\pm}X^{\mp})^* \qquad k_1/k_{-1}$$

$$M^* + X \longrightarrow M + X \qquad k_2$$

$$M^* + Q \longrightarrow M + Q \qquad k_q \tag{2}$$

$$(M^{\pm}X^{\mp})^* \xrightarrow{+Q} M + X \qquad k_q'$$

$$M^* \longrightarrow M \qquad 1/\tau_0$$

$$(M^{\pm}X^{\mp})^* \longrightarrow M + X \qquad 1/\tau_0'$$

where k_1 and k_{-1} are the rate constants of exciplex formation and backward dissociation respectively, k_2 is the rate constant of induced radiationless deactivation and τ_0 and τ_0' are the lifetimes of the excited molecule M^* and the exciplex $(M^{\pm}X^{\mp})^*$ respectively. It has been reported [13] that the quenching of the exciplex fluorescence by polar substances obeys the Stern–Volmer quenching law. Therefore k_2/k_1 is proportional to the concentration of the polar substance, i.e. $k_2/k_1 \approx \alpha[Q]$.

A kinetic analysis of scheme (2) results in rather complicated expressions for the relations between the fluorescence quantum yield, the exciplex lifetime and the quencher concentration. However, if backward dissociation

of the exciplex to the excited molecule M* and the complexing agent X is neglected $(k_{-1} \ll k_1[X]$ and $k_{-1} \ll 1/\tau_0')$ we obtain the following quite simple expressions for the fluorescence quantum yields and lifetimes:

$$\frac{\varphi}{\varphi_q} = \frac{\tau}{\tau_q} = 1 + k_q \tau [Q]$$

$$= 1 + \chi_q[Q]$$

$$= 1 + \frac{k_q \tau_0}{1 + (k_1 + k_2)\tau_0[X]}[Q] \tag{3}$$

$$\frac{\varphi'}{\varphi_q'} = (1 + k_q \tau[Q])(1 + k_q'\tau'[Q])(1 + \alpha[Q])$$

$$= (1 + \chi_q[Q])(1 + \chi_q'[Q])(1 + \alpha[Q])$$

$$= \frac{\varphi}{\varphi_q}(1 + \chi_q'[Q])(1 + \alpha[Q]) \tag{4}$$

$$\frac{\tau'}{\tau_q'} = 1 + k_q'\tau'[Q] = 1 + \chi_q'[Q] \tag{5}$$

where φ and τ are the fluorescence quantum yield and fluorescence lifetime respectively of M* in the presence of a specific concentration of X and in the absence of Q, φ_q, τ_q and φ_q', τ_q' are the fluorescence quantum yields and fluorescence lifetimes respectively of M* and $(M^{\mp}X^{\mp})^*$ in the presence of Q, τ_0 is the lifetime of M* in the absence of X and Q, and χ_q and χ_q' are the Stern−Volmer constants. If Q specifically quenches an exciplex, $\varphi/\varphi_q = 1$ and

$$\frac{\varphi'}{\varphi_q'} = (1 + \alpha[Q])(1 + k_q'\tau'[Q])$$

$$= (1 + \alpha[Q])(1 + \chi_q'[Q])$$

$$= \frac{\tau'}{\tau_q'}(1 + \alpha[Q]) \tag{6}$$

At small concentrations of Q

$$\frac{\varphi'}{\varphi_q'} \approx 1 + (\alpha + \chi_q')[Q] = 1 + \chi_{qE}[Q] \tag{7}$$

3. Kinetics of the quenching of the photochemical reaction

In the photochemical reaction

$$M^* + X \xrightarrow{k_R} P \tag{8}$$

which accompanies exciplex formation the product P is generally formed via one of the following three routes (Fig. 1): (a) the product is formed in
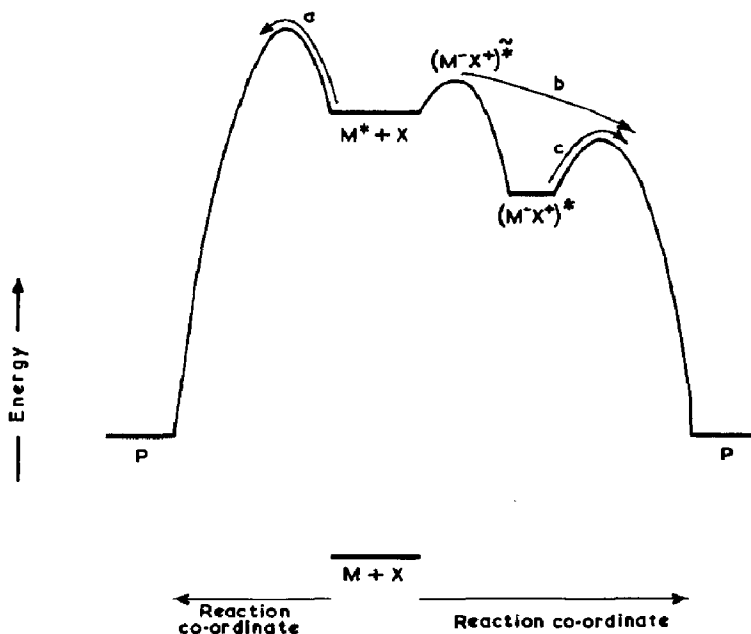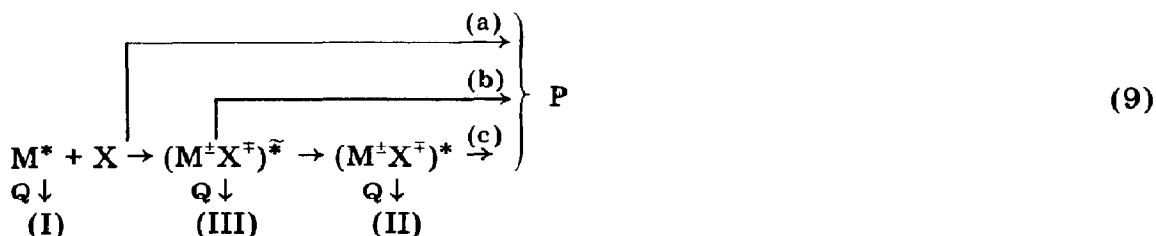
Fig. 1. Scheme showing the possible routes for the photochemical reaction.

parallel with the exciplex; (b) the product and the exciplex are both formed from a common non-relaxed charge transfer state; (c) the product is formed from the fluorescent (relaxed) state of the exciplex or the reaction proceeds via the exciplex as an intermediate.

A kinetic analysis of scheme (1) shows that these pathways cannot be distinguished using stationary excitation. The reaction should be investigated by either the pulse method or the quenching method. The latter method needs no complex and costly facilities and in many cases gives a more reliable result.

The addition of the quencher Q into the system where the photochemical reaction takes place may result in a reduction in the quantum yield owing to the presence of various quenching processes as discussed earlier:

$$
\begin{array}{ll}
& \quad\quad\quad\quad\quad\quad\quad (a) \\
& \quad\quad\quad\quad\quad (b) \\
M^* + X \rightarrow (M^{\pm}X^{\mp})^{\tilde{*}} \rightarrow (M^{\pm}X^{\mp})^* \xrightarrow{(c)} \\
Q\downarrow \quad\quad\quad Q\downarrow \quad\quad\quad Q\downarrow \\
(I) \quad\quad\quad (III) \quad\quad\quad (II)
\end{array} \Bigg\} \; P \quad\quad\quad (9)
$$

A kinetic analysis of this scheme gives the following expression for the ratio of the quantum yield Φ of the photochemical reaction in the absence of Q to the quantum yield Φ_q of the reaction in the presence of Q:

$$
\frac{\Phi_q}{\Phi} = \frac{\varphi_q}{\varphi} a + \frac{\varphi_q' \tau'}{\varphi' \tau_q'} b + \frac{\varphi_q'}{\varphi'} c \quad\quad\quad (10)
$$

which can be rewritten

$$\frac{\Phi_q \varphi}{\Phi \varphi_q} = a + \frac{\varphi \varphi_q'}{\varphi_q \varphi'} \left(b \frac{\tau'}{\tau_q'} + c \right) \tag{11}$$

where a, b and c are the partial rates of the reaction via routes (a), (b) and (c) respectively in the absence of Q. To determine the value of a it is necessary to use a specific exciplex quencher of type (III). In this case $\varphi_q/\varphi = 1$, $\tau'/\tau_q' = 1$ and

$$\frac{\Phi_q}{\Phi} = a + (b + c) \frac{\varphi_q'}{\varphi'} \tag{12}$$

and hence the intercept on the Φ_q/Φ axis in a plot of Φ_q/Φ against φ_q'/φ' will give a. In the presence of a specific exciplex quencher of type II or of mixed type

$$\frac{\Phi_q}{\Phi} - a = b \frac{\varphi_q' \tau'}{\varphi' \tau_q'} + c \frac{\varphi_q'}{\varphi'} \tag{13}$$

or

$$\left(\frac{\Phi_q}{\Phi} - a \right) \frac{\varphi'}{\varphi_q'} = c + b \frac{\tau'}{\tau_q'} \tag{14}$$

The reaction quenching constant χ_{qR} obtained from the conventional Stern–Volmer relation (at low concentrations of the quencher)

$$\frac{\Phi}{\Phi_q} \approx 1 + \chi_{qR}[Q] \tag{15}$$

for specific exciplex quenchers must be equal to the exciplex emission quenching constant χ_{qE} which is approximately equal to $\alpha + \chi_q'$ for the reaction from the exciplex emissive state (pathway (c)) and to α for the reaction from the non-relaxed state (pathway (b)).

The above analysis is valid when (1) the reaction processes are described by scheme (9), (2) the quencher does not change the nature of the reaction products and (3) the exciplex formation and quenching processes are irreversible (if the quencher forms exciplexes with M or X the kinetic analysis is complicated). The most explicit results are obtained when Q specifically quenches the $(M^{\pm}X^{\mp})^*$ exciplex but does not quench M*, *i.e.* k_q' is much greater than k_q (or, more precisely, $k_q'\tau_0'$ is much greater than $k_q\tau_0$).

4. Mechanism of halogen photoelimination in 9,10-dichloroanthracene in the presence of diethylaniline

The halogen photoelimination reaction in 9,10-dichloroanthracene (DCA) in the presence of diethylaniline (DEA) has been thoroughly inves-

tigated [10, 14] and has been found to proceed through a singlet excited state of DCA:

$$\text{DCA (2 Cl)} \xrightarrow[C_6H_5N(C_2H_5)_2]{h\nu} \text{DCA (Cl, H)} \tag{16}$$
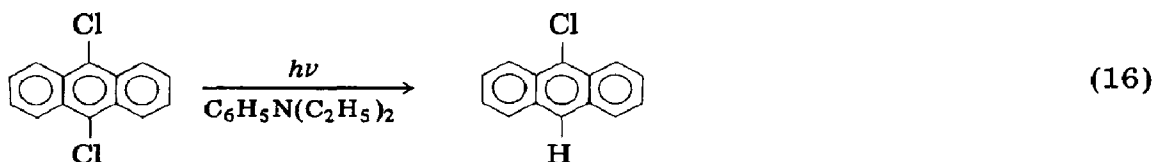
The addition of DEA to DCA results in both dynamic and static quenching of DCA fluorescence and exciplex emission.

Pyridine was used as a quencher [10, 14] to ascertain the role of the exciplex in the reaction. Pyridine quenches the exciplex fluorescence and the reaction; the DCA fluorescence intensity and the lifetime remain unchanged. Only the fluorescence quantum yields were measured to determine the rate constants of exciplex quenching; the quenching mechanism was ignored.

The mechanism of this reaction was established by studying the kinetics of the exciplex quenching and the change in the quantum yield of the reaction in the presence of azulene, acetonitrile, malondinitrile and dimethylformamide in heptane or toluene. All these substances have been found to be specific exciplex quenchers [15]: the exciplex fluorescence is reduced but the DCA fluorescence is unaffected (Fig. 2). The kinetic fluorescence decay curves remain single exponential throughout the quenching process. (The emission maximum of the DCA−DEA exciplex is shifted by less than 7 nm in the presence of acetonitrile, malondinitrile or dimethylformamide at the concentrations used in this work. The decrease in the exciplex emission rate constant produced by this shift is less than 10% [16].) This suggests that exciplex quenching is irreversible in all cases. The exciplex quenching constants χ_q' and α given in Table 1 were calculated using eqns. (5) and (6). In the estimation of the rate constant of quenching by azulene the absorption of azulene at the exciplex emission wavelength was taken into account. The same product is obtained in the presence of azulene and acetonitrile as in their absence (Fig. 3).

Azulene reduces the lifetime of the DCA−DEA exciplex and its fluorescence quantum yield at the same rate, *i.e.* quenching proceeds by route (II). Since azulene absorbs at the exciplex emission wavelength, the quenching mechanism is either energy transfer or electron transfer. The exciplex quenching mechanism is unimportant in investigations of the role of exciplexes in photochemical reactions. Comparison of the exciplex quenching rate constant with the electron affinity of the quencher [15, 17, 18] suggests that quenching by azulene proceeds mainly by the electron transfer mechanism.

In the presence of the other quenchers the fluorescence quantum yield of the DCA−DEA exciplex decreases much faster than the lifetime, *i.e.* the exciplex formation is quenched (scheme (1), path (III)). All these quenchers are polar compounds. Pyridine quenches exciplex formation almost exclusively. Acetonitrile quenches both exciplex formation and the exciplex emissive state.
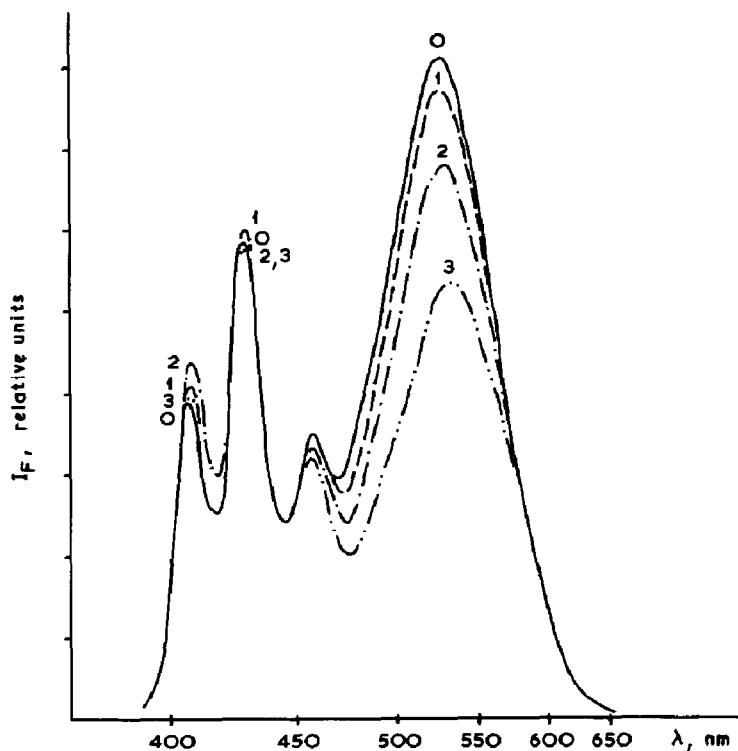
Fig. 2. Quenching of DCA–DEA exciplex fluorescence in outgassed heptane solutions by acetonitrile in various concentrations: curve 0, no quencher; curve 1, 0.06 mol l^{-1}; curve 2, 0.12 mol l^{-1}; curve 3, 0.24 mol l^{-1}.

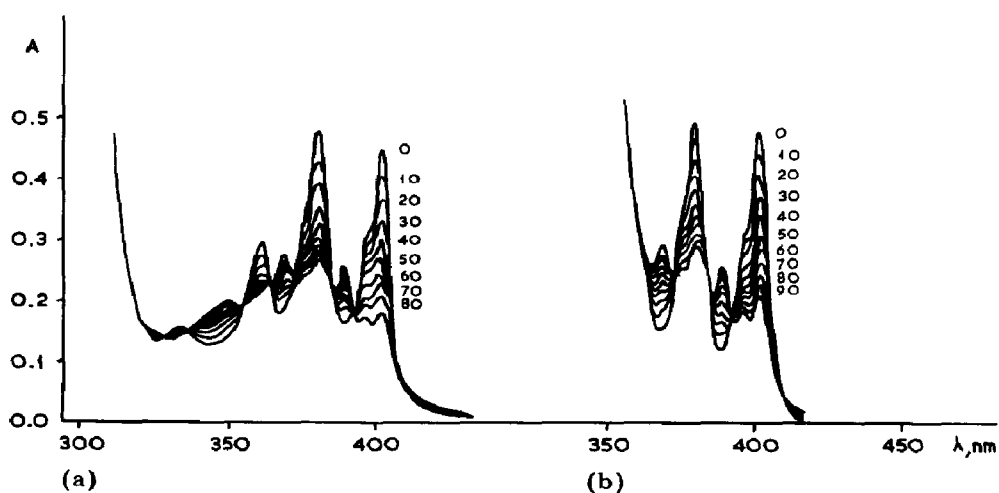(a)   (b)

Fig. 3. Variation in the absorption spectrum of DCA in heptane during photolysis in the presence of (a) a DEA concentration of 3×10^{-3} mol l^{-1} and (b) a DEA concentration of 3×10^{-3} mol l^{-1} and an azulene concentration of 2.10×10^{-3} mol l^{-1}. The numbers on the curves give the photolysis time in minutes.

TABLE 1

Quenching rate constants for the 9,10-dichloroanthracene–diethylaniline exciplex and the photoelimination reaction

Quencher	ϵ^a	Solvent	Q_{max} (mol l^{-1})	χ_q' (mol l^{-1})	α (mol l^{-1})	χ_{qR} (mol l^{-1})	b	c
Azulene	—	Heptane	5×10^{-3}	180 ± 30	25 ± 11	95 ± 13	0.5 ± 0.1	0.6 ± 0.2
Acetonitrile[b]	38	Heptane	0.24	0.7 ± 0.1	1.2 ± 0.1	1.6 ± 0.3	0.5 ± 0.3	0.5 ± 0.3
Acetonitrile[c]	38	Heptane	0.24	0.7 ± 0.1	1.1 ± 0.1	1.1 ± 0.4	0.7 ± 0.5	0.1 ± 0.5
Malondinitrile	20	Toluene	0.4	0.9 ± 0.05	3.5 ± 0.4	—	—	—
Dimethylformamide	36	Toluene	0.65	0.34 ± 0.05	2.7 ± 0.3	—	—	—
Pyridine[d]	12.3	Toluene	0.5	<0.1	1.6 ± 0.8	2.5 ± 1.0	—	—
Pyridine	12.3	Toluene	0.5	<0.1	1.8 ± 1.0	4.0 ± 2.0	—	—

[a] Dielectric constant of the quencher.
[b] In an outgassed solution.
[c] In the presence of oxygen.
[d] Calculated from the data of ref. 10.

The addition of acetonitrile and azulene results in a reduction in the reaction quantum yield (Fig. 4). In the presence of azulene, which quenches only the exciplex emissive state, the reaction quenching constant χ_{qR} is a factor of 2 less than the exciplex quenching constant χ_q'. This indicates that only half of the reaction product is formed from the exciplex emissive state (via route (c)). Acetonitrile quenches exciplex formation and exciplex emission almost equally and hence the reaction quenching constant χ_{qR} is almost equal to the constants χ_q' and α. This means that the reaction product is formed via the emissive and non-relaxed states of the exciplex but not via route (a). Table 1 shows values of b and c for quenching by azulene and acetonitrile in the absence and presence of oxygen calculated using eqn. (16). It can be seen that in the outgassed solutions approximately half of the product is formed via the non-relaxed state of the exciplex and half is formed via the relaxed state. In the presence of oxygen, which quenches the relaxed state of the exciplex, the relation between b and c changes and most of the product is formed via route (b).

Pyridine quenches only exciplex formation. The quenching constants χ_{qR} and α calculated from the data of ref. 10 are almost equal within the limits of experimental error. (The values of χ_{qR}, χ_q' and α are calculated from the data of ref. 10 (in which the errors are greater than those for quenching by azulene and acetonitrile). Therefore the b and c values cannot be calculated accurately.) This confirms the formation of the reaction product via routes (b) and (c).
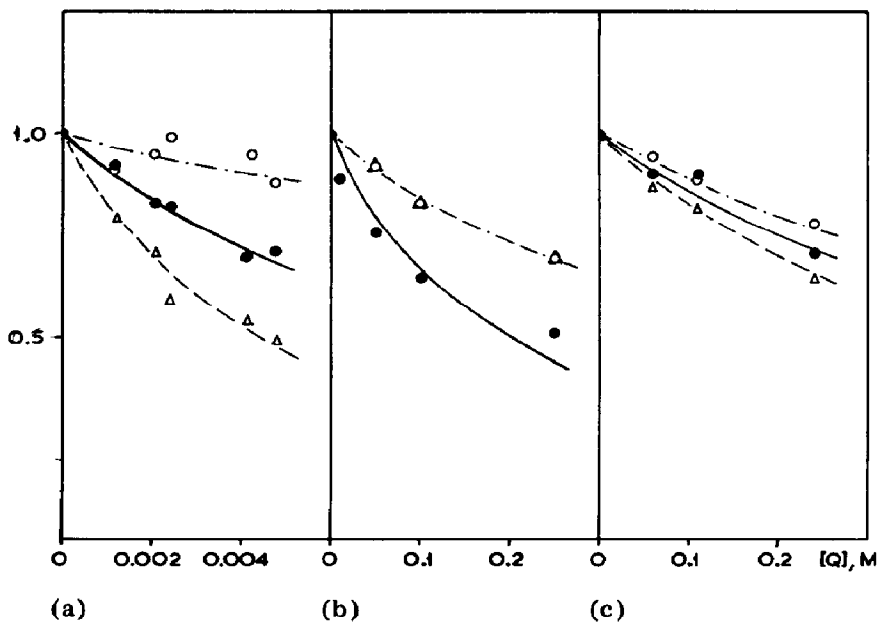

Fig. 4. Fluorescence quenching φ_q'/φ' (●), change in the value of $\varphi_q'\tau'/\varphi'\tau_q'$ (○) and quenching of the reaction quantum yield Φ_q/Φ (△) with the addition of (a) azulene, (b) pyridine and (c) acetonitrile to outgassed solutions.

These results show that the halogen photoelimination in DCA in the presence of DEA in a heptane solution proceeds via the non-relaxed and relaxed exciplex states. The product formation yields from these states are approximately equal. The large difference in the lifetimes suggests that the rate constant of process (b) is several orders of magnitude greater than that of process (c).

5. Experimental details

All substances were purified according to procedures described elsewhere [19]. The absorption and fluorescence spectra were obtained using a Unicam SP 8000 spectrophotometer and a Jobin–Yvon spectrofluorometer respectively. The fluorescence decay rates were measured using a time-correlated single-photon counting instrument with an exciting light pulse decay time of about 1 ns. The photoelimination reaction was performed using a high pressure mercury arc lamp equipped with a 405 nm glass filter. The quantum yield of the photochemical reaction was calculated using the method given in ref. 20. The solutions were outgassed by repeated freeze–pump–thaw cycles or by nitrogen bubbling; both methods gave similar results.

References

1 J. A. Barltrop and J. D. Coyle, *Excited States in Organic Chemistry*, Wiley, London, 1975, p. 148.
2 R. A. Caldwell, *J. Am. Chem. Soc.*, *95* (1973) 1690.
3 K. Mizumo, C. Pac and H. Sakurai, *J. Am. Chem. Soc.*, *96* (1974) 2993.
4 R. A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, *96* (1974) 2994.
5 D. Creed and R. A. Caldwell, *J. Am. Chem. Soc.*, *96* (1974) 7369.
6 R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, *100* (1978) 2905.
7 R. A. Caldwell, N. I. Ohali, C. K. Chien, D. De Marco and L. Smith, *J. Am. Chem. Soc.*, *100* (1978) 2857.
8 D. Creed, P. H. Wine, R. A. Caldwell and L. A. Melton, *J. Am. Chem. Soc.*, *98* (1976) 621.
9 M. Ohashi and K. Nakajima, *Chem. Lett.*, (1976) 1143.
10 O. M. Soloveichik, V. L. Ivanov and M. G. Kuzmin, *Zh. Org. Khim.*, *12* (1976) 859.
11 N. Mataga, in M. Gordon and W. R. Ware (eds.), *The Exciplex*, Academic Press, New York, 1975, p. 114.
12 M. G. Kuzmin and L. N. Guseva, *Dokl. Akad. Nauk S.S.S.R.*, *200* (1971) 375.
13 S. Basu, *J. Photochem.*, *11* (1979) 9.
14 O. M. Soloveichik, V. L. Ivanov and M. G. Kuzmin, *Khim. Vys. Energ.*, to be published.
15 I. V. Soboleva, N. A. Sadovskii and M. G. Kuzmin, *Khim. Vys. Energ.*, *14* (1980) 32.
16 F. D. Lewis and C. E. Hoyle, *J. Am. Chem. Soc.*, *98* (1976) 4338.
17 M. G. Kuzmin, N. A. Sadovskii and I. V. Soboleva, *Chem. Phys. Lett.*, *71* (1980) 232.
18 M. G. Kuzmin, N. A. Sadovskii and I. V. Soboleva, *Khim. Vys. Energ.*, *14* (1980) 38.
19 A. Weissberger (ed.), *Techniques of Organic Chemistry*, Vol. VII, *Organic Solvents*, Wiley-Interscience, New York, 1955, pp. 311, 318, 435, 445, 450.
20 O. M. Soloveichik and V. L. Ivanov, *Zh. Org. Khim.*, *10* (1974) 2404.