

## QUENCHING OF EXCIMERS BY ELECTRON DONORS

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### Summary

The quenching of excimers of pyrene and 9,10-dichloroanthracene by electron donors in toluene, ethanol and acetonitrile has been investigated. The excimer quenching rate constants are substantially lower than those of the parent excited molecules. The decrease in the reactivity of the excited molecules arising from excimer formation is related to the enthalpy of formation of the excimer. The rate constants for quenching of the excimers were found to be affected only slightly by the polarity of the medium.

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### 1. Introduction

It has been suggested that excited state complexes (excimers and exciplexes) are important intermediates in some photochemical reactions [1]. The quenching of such complexes provides a method of studying reaction mechanisms [2, 3]. Furthermore, by comparing the rate constants for quenching of excited molecules and complexes one is able to investigate the effect of excited state complexing processes on reactivity. Previous results [3 - 6] give only a few examples of rate constants for quenching of both excimers and excited molecules by the same quencher. We have already proposed some rules that govern the quenching of excited complexes by electron donors and acceptors and have studied the quenching of some exciplexes by electron acceptors [7 - 9].

The present paper is concerned with the quenching of excimers by electron donors. Since the solvent polarity only slightly affects the processes of excimer formation and deactivation, the role of the solvent in excimer quenching was also studied.

### 2. Experimental details

The fluorescence decay rates were measured by means of a time-correlated single-photon counting instrument with an exciting light pulse

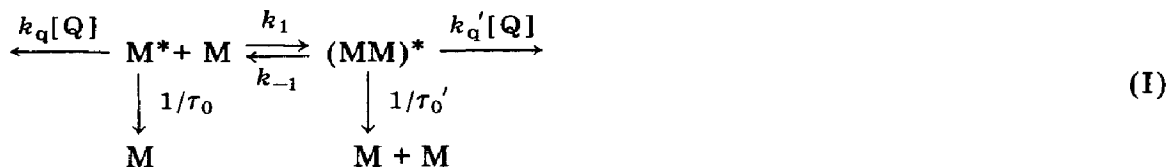
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decay time of about 1 ns [10]. The fluorescence spectra were obtained using a Jobin-Yvon spectrofluorometer. Pyrene was zone refined and 9,10-dichloroanthracene was recrystallized twice from alcohol. *p*-Dimethoxybenzene, 2,6-dimethoxyphenol, 2-aminopyridine, diphenylamine, *p*-toluidine, *p*-anisidine and *p*-phenylenediamine were sublimed twice *in vacuo*. Diethylamine, triethylamine, aniline and *N*-methylpiperidine were refluxed and distilled over sodium *in vacuo*. Toluene (scintillational grade) was used without further purification. Ethanol and acetonitrile were purified according to standard procedures [11]. The solutions were degassed by repeated pump-freeze-thaw cycles.

### 3. Results

The processes of excimer formation in the presence of a quencher (Q) are described by the following kinetics scheme.



where  $\text{M}^*$  is the excited molecule,  $(\text{MM})^*$  is the excimer,  $\tau_0$  and  $\tau_0'$  are their lifetimes,  $k_1$  and  $k_{-1}$  are the rate constants for the formation and dissociation of the excimer and  $k_q$  and  $k_q'$  are the quenching rate constants for the excited molecule and the excimer.

The method for determining the rate constants  $k_1$ ,  $k_{-1}$ ,  $1/\tau_0$  and  $1/\tau_0'$  is well known and is described elsewhere [10, 12, 13]. The values obtained in the present work are given in Table 1. For excimers of pyrene in toluene and 9,10-dichloroanthracene in ethanol the values of the rate constants  $k_1$ ,  $k_{-1}$ ,  $1/\tau_0$  and  $1/\tau_0'$  reported earlier [12, 14] are close to those obtained here.

The rate constants  $k_q$  were obtained at low concentrations of M (about  $10^{-5}$  mol l<sup>-1</sup>) by means of lifetime measurements:

TABLE 1

Pyrene and 9,10-dichloroanthracene: lifetimes  $\tau_0$ , excimer lifetimes  $\tau_0'$ , formation and dissociation rate constants  $k_1$  and  $k_{-1}$  and the enthalpy  $\Delta H$  of formation of the excimer (293 K; degassed)

Fluorophore	Solvent	$\tau_0$ (ns)	$\tau_0'$ (ns)	$k_1$ (mol <sup>-1</sup> l s <sup>-1</sup> )	$k_{-1}$ (s <sup>-1</sup> )	$\Delta H$ (eV)
Pyrene	Toluene	270	56	$4.7 \times 10^9$	$5.5 \times 10^6$	-0.4
Pyrene	Ethanol	330	55	$6.6 \times 10^9$	$4.9 \times 10^6$	-0.4
Pyrene	Acetonitrile	335	54	$12.3 \times 10^9$	$5.4 \times 10^6$	-0.4
9,10-Dichloroanthracene	Toluene	11.9	60	$6.7 \times 10^9$	$1.0 \times 10^6$	-0.2

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] \quad (1)$$

where  $\tau_0$  and  $\tau$  are the lifetimes of  $M^*$  in the absence and presence of  $Q$  respectively. The  $k_q$  values obtained are given in Tables 2 and 3.

In the general case the  $k_q'$  values can be found by the equation

$$\theta_1 + \theta_2 = \theta_1^0 + \theta_2^0 + (k_q + k_q')[Q] \quad (2)$$

TABLE 2

Quenching rate constants  $k_q$  and  $k_q'$  for pyrene and its excimer (293 K; degassed)

Quencher	$E_{1/2}^{\text{ox a}}$	Solvent					
		Toluene		Ethanol		Acetonitrile	
		$k_q^b$	$k_q'^b$	$k_q^b$	$k_q'^b$	$k_q^b$	$k_q'^b$
<i>p</i> -Dimethoxybenzene	1.0	0.00071	—	—	—	—	—
2-Aminopyridine	0.93	0.046	0.0057	0.0051	—	0.033	—
Diethylamine	0.90	0.028 0.06 <sup>c</sup>	0.0016	0.014	0.00066	0.33	0.006
2,6-Dimethoxyphenol	0.84	—	—	—	—	0.10	0.001
<i>N</i> -Methylpiperidine	0.80	(0.074) <sup>d</sup>	(0.0073) <sup>d</sup>	0.057	0.0007	0.91	0.011
Aniline	0.65	0.81 1.7 <sup>c</sup>	0.016	3.04	0.0056	5.55	0.09
Diphenylamine	0.59	4.8 5.86 <sup>c</sup>	0.074	4.4	0.0046	10.2	0.23
<i>p</i> -Toluidine	0.52	5.58 5.67 <sup>c</sup>	0.055	4.69	0.13	9.80	0.19
<i>p</i> -Anisidine	0.34	8.24	0.57	5.09	0.88	13.6	0.91
<i>p</i> -Phenylendiamine	-0.08	11.1	—	—	—	—	—

<sup>a</sup>Reference electrode, Ag/0.1 N AgNO<sub>3</sub>.

<sup>b</sup>Units,  $\times 10^9 \text{ mol}^{-1} \text{ l s}^{-1}$ .

<sup>c</sup>Solvent, heptane.

<sup>d</sup>In this case, exciplex formation could decrease the value of the rate constant obtained.

TABLE 3

Rate constants  $k_q$  and  $k_q'$  for quenching of 9,10-dichloroanthracene and its excimer (293 K; degassed; solvent, toluene)

Quencher	$E_{1/2}^{\text{ox a}}$	$k_q$ ( $\times 10^9 \text{ mol}^{-1} \text{ l s}^{-1}$ )	$k_q'$ ( $\times 10^9 \text{ mol}^{-1} \text{ l s}^{-1}$ )
Diethylamine	0.90	2.38	0.025
Aniline	0.65	6.83	0.042
Triethylamine	0.63	4.93	0.03
<i>p</i> -Toluidine	0.52	16.5	1.16

<sup>a</sup>Reference electrode, Ag/0.1 N AgNO<sub>3</sub>.

where  $\theta_1 + \theta_2$  and  $\theta_1^0 + \theta_2^0$  are the sums of the exponents of the fluorescence decay curves  $F(t)$  and  $F'(t)$  for the excited molecule and the excited complex in the presence and absence of Q respectively:

$$F(t) = F_0\{\Theta \exp(-\theta_1 t) + \exp(-\theta_2 t)\} \quad (3)$$

$$F'(t) = F_0'\{\exp(-\theta_2 t) - \exp(-\theta_1 t)\}$$

If  $k_1[M] \gg k_{-1}$ , eqn. (2) reduces to a simple Stern-Volmer equation:

$$\frac{\tau_0'}{\tau'} = 1 + k_q' \tau_0' [Q] \quad (4)$$

If  $k_q \gg k_q'$  the accuracy of the results obtained from eqn. (2) is unsatisfactory and thus the rate constants were calculated using

$$k_q' [Q] = \frac{\theta_2 + k_{-1} + 1/\tau_0' + k_1 k_{-1} [M]}{\theta_2 + k_1 [M] - 1/\tau_0 + k_q [Q]} \quad (5)$$

The mean values of the rate constants for excimer quenching obtained at different quencher concentrations are given in Tables 2 and 3.

#### 4. Discussion

In earlier studies we have analysed the regularities of exciplex quenching by electron donors and acceptors [7, 9]. A good linear correlation exists between the rate constants for quenching of exciplexes and excited molecules and their donor-acceptor properties, given by the equation [8, 9]

$$\lg\left(\frac{k_{\text{diff}}}{k_q} - 1\right) = -\frac{\alpha C_0}{2.3RT} + \frac{\alpha(I - A)}{2.3RT} \quad (6)$$

where  $k_{\text{diff}} = 8RT/3000\eta$  is the diffusion rate constant,  $\alpha$  and  $C_0$  may be regarded as empirical constants,  $I$  is the ionization potential of the electron donor and  $A$  is the electron affinity of the acceptor. Equation (6) was derived in terms of a Polanyi-type expression  $\Delta G^\ddagger = \Delta G_0^\ddagger + \alpha\Delta G$  where  $\Delta G$  is the reaction free enthalpy and  $\Delta G^\ddagger$  is the activation free enthalpy.

The electron affinity  $A(M^*)$  of the excited molecule is given by the expression

$$A(M^*) = A(M) + E(M) \quad (7)$$

where  $A(M)$  is the electron affinity of the molecule M in the ground state and  $E(M)$  is the excitation energy of M. The electron affinity of the excimer can be calculated as [9]

$$A(MM^*) = A(M) + E(MM^*) = A(M^*) + \Delta H \quad (8)$$

where  $E(MM^*)$  is the excitation energy of the excimer and  $\Delta H$  is the enthalpy of formation of the excimer. If the electrochemical halfwave potentials are used, eqns. (6) - (8) can be written as

$$\lg\left(\frac{k_{\text{diff}}}{k_q} - 1\right) = \frac{\alpha C_0}{2.3RT} + \frac{\alpha(E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}})}{2.3RT} \quad (6a)$$

$$E_{1/2}^{\text{red}}(\text{M}^*) = E_{1/2}^{\text{red}}(\text{M}) + E(\text{M}) \quad (7a)$$

$$E_{1/2}^{\text{red}}(\text{MM}^*) = E_{1/2}^{\text{red}}(\text{M}) + E(\text{MM}^*) = E_{1/2}^{\text{red}}(\text{M}^*) + \Delta H \quad (8a)$$

Equations (8) and (8a) assume that on reduction  $\text{MM}^*$  produces  $\text{M}$  and  $\text{M}^-$  rather than a transient bound species.

Since the enthalpy of formation of the excited complex is negative, the electron affinity of the excimer is always lower than that of the parent excited molecule, and the rate constants for the quenching of the excimer must be much lower than those for the quenching of the parent excited molecules by the same quencher. Indeed, the excimer quenching rate constants are 10 - 100 times lower than those of the parent excited molecule (Tables 2 and 3).

The rate constants  $k_q$  and  $k_q'$  depend on the oxidation potentials of the donors. The experimental relationship for the components of eqn. (6a) seems to be linear both for excited molecules and excimers (Fig. 1). The points for  $k_q$  and  $k_q'$  seem to fall close to the same straight line. This means that the decrease in excimer reactivity is due to the decrease in its electron affinity.

The excimers are non-polar species, and the polarity of the solvent only slightly affects their spectra and lifetimes (Table 1). We have studied the quenching of excimers in solvents of various polarity. The quenching rate constants of excimers and excited molecules in polar solvents in some cases increase, but owing to the scatter in the data obtained all experimental points seem to fall on the same straight line (Fig. 1). The free energy change for electron transfer is expressed by

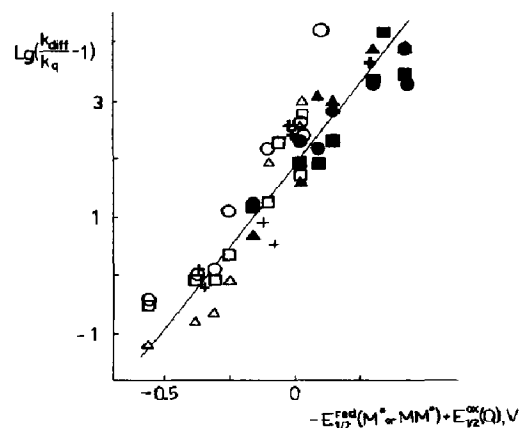


Fig. 1. Quenching of excimers and excited molecules: ○ and ●, pyrene and its excimer in toluene; □ and ■, in acetonitrile; △ and ▲, in ethanol; + and ⊕, 9,10-dichloroanthracene and its excimer in toluene.

$$\Delta G = I - A - C = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} - C$$

where  $C$  is the Coulomb term expressing the interaction between the ions formed:  $C = e^2/\epsilon r$ . If  $r = 7 \text{ \AA}$ , as is usually assumed [15],  $C = 0.8 \text{ eV}$  in toluene and  $C = 0.05 \text{ eV}$  in acetonitrile. To estimate the free energy change we used electrochemical potentials measured in acetonitrile, without taking the Coulomb term into account. As there is no systematic difference between the data obtained in the different solvents used, the change in  $C$  seems to be compensated by the change in  $E_{1/2}^{\text{ox}}$  and  $E_{1/2}^{\text{red}}$  from the solvation energy of the ions.

The results reported support the earlier suggestion [7, 9] that the rate constants for the quenching of excited complexes are related to the free energy change for the electron transfer in the same way as for the excited molecules.

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