Communications

Dynamical Behaviour of Excimers

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Received 8 *June* 1977; *accepted* 20 *June* 1977

Dynamics of decay of aromatic excimers have been examined in different solvents employing pulsed nitrogen laser excitation. The results suggest solvent dependence of the rate constant for non-dadiative decay.

THE most characteristic feature of an aromatic excimer in solution phase is its fluorescence spectrum which occurs at a longer wavelength than the monomer fluorescence and is observed only when the concentration of the aromatic compound is sufficiently large[1]. There have been a few studies on the quantitative aspects of fluorescence quantum yields and decay of pyrene excimers[1]. The formation and decomposition processes of excimers can be described by the mechanism shown in Scheme 1.

$$D + h\nu \longrightarrow D^*$$
$$D^* \xrightarrow{k_1} D + h\nu_f$$
$$D^* \xrightarrow{k_2} D \text{ (Non-radiative)}$$
$$D^* + D \underset{k_4}{\overset{k_3}{\rightleftharpoons}} D_2^*$$
$$D_2^* \xrightarrow{k_5} D + D + h\nu'_f$$
$$D_2^* \xrightarrow{k_6} D + D \text{ (Non-radiative)}$$

Scheme 1

In the above scheme, k's are the rate constants with k_1 and k_2 representing the decay of the excited monomer molecule D*, while k_5 and k_6 represent the decay of the excimer D_2^*. Kinetics of formation of excimers can be investigated by the analysis of fluorescence decay curves. In this communication, we report preliminary results of such studies on the dynamical behaviour of excimers formed by aromatic molecules. The study was directed towards examining the solvent dependence of excimer decay.

A pulsed nitrogen gas laser with a pulse width of 7·5 nsec and peak intensity 3371 Å was employed for the study. The method of measurement of decay curves has been described elsewhere[2]. Spectroscopic grade solvents were used and solutions were degassed by the freeze-thaw technique under pure N_2-atmosphere.

In Table 1, the lifetimes of excimers, τ_e, of a few aromatic hydrocarbons are presented along with the monomer lifetimes, τ_A. The lifetimes τ_A directly give the rate constants k_1+k_2 while the

TABLE 1 — DECAY TIMES OF AROMATIC HYDROCARBON MONOMERS AND EXCIMERS[a]

$E(A^-/A)$ eV	τ_A nsec	τ_e nsec	$(k_1+k_2)\times10^{-7}$ sec^{-1}	$(k_5+k_6)\times10^{-7}$ sec^{-1}
		TEREPHTHALONITRILE		
1·8	25	23	4·0	4·34
		PYRENE		
2·1	94	71	1·06	1·40
		BENZOPYRENE		
2·1	56	18	1·78	5·55

(a) Toluene solvent, concentration of hydrocarbon for τ_A (monomer) $\sim10^{-5}M$ and $\geq10^{-3}M$ for τ Measurement of τ_e is at longer wavelength than τ_A. Thus, for pyrene monomer fluorescence maximum is at 425 nm and excimer fluorescence maximum is at 470 nm.

TABLE 2 — EFFECT OF SOLVENT ON EXCIMER DECAY

Solvent	ϵ[a]	Pyrene				Benzopyrene[b]	
		τ_A nsec	τ_e nsec	$(k_1+k_2)\times10^{-7}$ sec^{-1}	$(k_5+k_6)\times10^{-7}$ sec^{-1}	τ_e nsec	$(k_5+k_6)\times10^{-7}$ sec^{-1}
Toluene	2·38	94	71	1·06	1·40	18	5·5
Ethyl acetate	6·02	72	49	1·38	2·04	20	5·0
Dichloromethane	9·08	110	97	0·91	1·03	18	5·5
Isopropyl alcohol	18·31	—	—	—	—	28	3·6
Methanol	33·6	55	51	1·81	1·96	—	—
Acetonitrile	37·5	60	57	1·66	1·75	29	3·45

(a) Solvent dielectric constant.
(b) In cyclohexane τ_A and τ_e are 100 and 35 nsec respectively.

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τ_e values give k_5+k_6. The values of τ_A and τ_e are quite similar in terephthalonitrile and pyrene but not so in 1,2-benzopyrene.

Earlier studies[1,3] have shown that $k_1>k_2$ and $k_5>k_6$; also, $k_1>k_5$ and $k_2>k_6$. Furthermore, k_5 is reported to be independent of the nature of the solvent[4,5]. Thus, for pyrene, k_5 is $1{\cdot}16\times10^7$ sec^{-1} in cyclohexane and $1{\cdot}3\times10^7$ sec^{-1} in both acetone and ethanol. This implies that any solvent-dependence of τ_e of excimers should arise from the variation of k_6 with solvent. In Table 2, are listed the values of τ_A and τ_e of pyrene and 1,2-benzopyrene in different solvents. It is observed that τ_A and τ_e are comparable in the case of pyrene in solvents of varying degrees of polarity and both of them arise from single exponential decay. The lifetimes do not vary in any systematic manner with the solvent dielectric constant. If we take the value of k_5 to be constant ($1{\cdot}0$-$1{\cdot}3\times10^7$ sec^{-1}) based on earlier studies[1,4,5] it is found that k_6 varies significantly from solvent to solvent. The value of k_6 varies by $\sim$100% in the series of solvents studied. The results on benzopyrene are also similar; in this system, the value of (k_5+k_6) varies between $2{\cdot}9$ and $5{\cdot}5\times10^7$ sec^{-1} again suggesting solvent-dependence of k_6. The present study indicates the interesting possibility that the rate constant representing non-radiative decay of excimers is considerably more solvent-dependent than their radiative decay. It is indeed noteworthy that in a very recent report[6] on the photophysical processes in aromatic electron donor-acceptor complexes, the non-radiative rate constant has been found to increase with solvent polarity while the rate constant for inter-system crossing remains constant.

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