

and the sum of the corresponding quantum yields of these processes is unity:  $\Phi_{ic} = 1 - \Phi_R - \Phi_F - \Phi_T$ .

In benzene and water there is no photochemical reaction from the singlet state, and in tert-BuOH the yield of the reaction is very low. Acridine does not fluoresce in non-polar solvents, in alcoholic solution its quantum yield is very low compared to a high yield in water [3]. The various data are summarized in the table:

Solvent	$\Phi_T$	$\Phi_R$	$\Phi_F$	$\Phi_{ic}$
Benzene	0.71	-	-	0.29
tert-BuOH	0.61	0.01	0.02	0.36
water	0.37	-	0.37	0.26

These data imply an internal conversion from the first excited singlet for acridine in these different solvents. It is significant that even in water where the fluorescence yield is important an internal conversion is present, contrary to the anthracene molecule where no internal conversion occurs. This different behaviour may be due to the lone pair of the nitrogen in the cycle. ISC quantum yields of aromatic heterocycles have not been extensively studied, Hadley [4], however stated similar observations between quinoline and naphthalene.

- 1 A. R. Horrocks, and F. Wilkinson, Proc. Roy. Soc. A, 206 (1968) 257.
- 2 A. Kellmann and L. Lindqvist, in A.B. Zahlan (ed.), The triplet State, Cambridge University Press, London, 1967, p. 439.
- 3 E. J. Bowen, N. J. Holder and G. B. Woodger, J. Phys. Chem., 66 (1962) 2491.
- 4 S. G. Hadley, J. Phys. Chem., 75 (1971) 2083.

#### O10

##### The Temperature and Viscosity Dependence of Energy Transfer from Triplet Aromatic Molecules

E. J. MARSHALL, N. A. PHILIPSON, M. J. PILLING, S. A. RICE and P. SPENCER

Physical Chemistry Laboratory, South Parks Road, Oxford (U.K.)

The deactivation of triplet aromatic molecules in alcohols was studied by laser flash photolysis, as a function of temper-

ature. Methanol/water and 2-methyl-2,4-pentanediol were used as solvents. Both form glasses, and a viscosity range of  $> 10^{12} \text{ kg m}^{-1} \text{ s}^{-1}$  was available. For exoergic transfer to other aromatic molecules, the reactions are diffusion-controlled, but the rate constant falls less rapidly with temperature than the solvent fluidity. This is in agreement with published results, but the present data cover a wider viscosity range than has previously been reported. For transfer to metal ions, the high temperature rate is less than the diffusion-controlled value, and the temperature dependence of the quenching process itself, exclusive of fluidity effects, may be determined. At lower temperatures the mechanism changes to one of diffusion-control. A theoretical analysis of the effect of an exchange interaction on a diffusion-controlled reaction shows that the encounter distance increases as the solvent fluidity is reduced. The implications of this to the present experimental results are discussed.

#### O12

##### Excited State Formation in *p*-Dioxane

AJIT SINGH, S. P. VAISH and M. J. QUINN

Research Chemistry Branch, Atomic Energy of Canada Limited and Whiteshell Nuclear Research Establishment, Pinawa, Manitoba ROE 1L0 (Canada)

Emission from purified liquid *p*-dioxane has been observed by photoexcitation and pulse radiolysis. Solute emission is observed on pulse radiolysis of solutions of naphthalene in *p*-dioxane. At a naphthalene concentration of  $10^{-3} \text{ M}$  the *p*-dioxane emission is reduced by  $\sim 75\%$ . However, at a naphthalene concentration of  $1 \text{ M}$ , the solute emission is  $\sim 10$  times greater than that at  $10^{-3} \text{ M}$ . This is attributable to energy transfer from higher excited states of the solvent to the solute, in the  $1 \text{ M}$  solution.

Evidence has been obtained for the formation of the triplet excited state of *p*-dioxane, by pulse radiolysis of solutions of  $\beta$ -carotene. Formation of the solute triplet has been studied as a function of naphthalene concentration ( $10^{-4}$  to  $1 \text{ M}$ ) in *p*-dioxane. The dependence of the naphthalene triplet formation on the naphthalene concentration is quite similar to that of the naphthalene emission.