

Xanthene-dye Photo-sensitized Decomposition of a Diazonium Salt

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Summary Monochromatic light absorbed only by a dye leads to the decomposition of a diazonium salt which is thought to involve an ion-pair-excimer mechanism.

THE sensitization to visible light of the decomposition of diazonium systems is of considerable interest in reprography.¹ Inoue *et al.* have discussed the indirect spectral sensitization of a diazonium salt decomposition, by dyes through an intermediate activator.² We report here the direct sensitization of diazonium salt decomposition in solution by xanthene dyes.

A mixture of the zinc chloride double salt of 4-*NN*-diethylaminobenzenediazonium chloride (*ca.* 1×10^{-2} M) and a xanthene dye (*ca.* 3×10^{-3} M) in a suitable solvent (*e.g.* EtOH, HCONMe₂) was irradiated with monochromatic light absorbed by the dye only. Decomposition of the diazonium salt was followed by absorption spectrometry using a 0.06 mm path length spectrophotometer cell. Comparison of the initial rate (proportional to quantum yield) of this sensitized decomposition with the initial rate of direct photolysis of the diazonium salt at 380 nm, enabled sensitization efficiencies for four dyes to be obtained (Table 1).

The observed sensitization cannot be due to energy transfer. Both the singlet and triplet states of the dye are well below the corresponding states of the diazonium salt

TABLE 1. Xanthene dye experimental data in ethanol

Xanthene dye	Sensitization efficiency	$10^{11} k_q /$	E_{ox}/V^a
	%	$1 \text{ mol}^{-1} \text{ s}^{-1}$	
Disodium Eosin	58	2.0	0.80
Disodium Erythrosin	102	1.5	0.77
Disodium Rose Bengal	51	1.2	0.80
Rhodamine B	1.2	0.6	>1.00

^a Using a pyrolytic graphite electrode against saturated Ag-AgCl.

(E_S *ca.* 82 kcal mol⁻¹, E_T *ca.* 70 kcal mol⁻¹ for benzenediazonium fluoroborate;³ E_S *ca.* 53 kcal mol⁻¹ for the dyes). Despite this, it is found that the diazonium salt quenches the fluorescence of the dyes with high efficiency (see rate constants, k_q in Table 1). It is thus suggested that the sensitization is due to electron transfer from the singlet excited state of the dye to the ground state of the diazonium

salt, similar to the electron-transfer processes studied by Weller.⁴ This interpretation is supported by the parallel between the oxidation potentials of the dyes (E_{ox}) and the sensitization efficiencies (Table 1), and also by the controlling effect of the dielectric constant (ϵ) of the solvent (Table 2). The addition of an electron to a diazonium ion induces decomposition.⁵

TABLE 2. Effect of solvent on efficiencies

Solvent	ϵ	Efficiency %		
		Erythrosin	Eosin	
EtOH	24.55	102	58.0	
HCONMe ₂	36.71	191	89.6	
Me ₂ SO	46.68	185	—	
HCONH ₂	111.00	31	21.1	
Mixtures				
EtOH	HCONH ₂			
100	0	24.55	102	58.0
95	5	27.0 ^a	136	72.0
90	10	29.7 ^a	169	87.0
85	15	32.5 ^a	178	96.2
80	20	35.5 ^a	224	116
75	25	38.7 ^a	208	116
70	30	42.0 ^a	177	107
0	100	111.00	31	21.1

^a Calculated from the equation quoted by H. Looyenga, *Mol. Phys.*, 1965, **9**, 501.

¹ J. Kosar, 'Light Sensitive Systems,' Wiley, New York, 1965, p. 194.

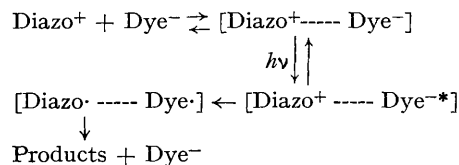
² E. Inoue, T. Ikawa, H. Kokado, and T. Yamase, *Phot. Sci. Eng.*, 1973, **17**, 28, 268; 1974, **18**, 25.

³ M. Sukigara and S. Kikuchi, *Bull. Chem. Soc. Japan*, 1967, **40**, 461; M. Sukigara, K. Honda, and S. Kikuchi, *J. Phot. Sci.*, 1970, **18**, 38.

⁴ A. Weller, *Pure Appl. Chem.*, 1968, **16**, 115.

⁵ R. M. Eloffson and F. F. Gadallah, *J. Org. Chem.*, 1969, **34**, 854.

Assuming Stern-Volmer kinetics, the rate constant for fluorescence quenching is higher than the diffusional rate constant for ethanol ($k_{diff} = 5.5 \times 10^9$ l mol⁻¹ s⁻¹), although no spectroscopic evidence for a ground-state complex has been found. The high rate constant and an observed deviation from Stern-Volmer kinetics can be attributed to the formation of an ion-pair between the ground-state diazonium and dye ions. The involvement of ion-pairs is further suggested by the fact that the efficiency of sensitization passes through a maximum as the dielectric constant of the solvent is increased, for both individual and mixed solvents. With the increase in dielectric constant, ion-pair formation and excited-state electron transfer are assisted, but at higher values the single ions are solvated so that ion-pair formation is now decreased. The proposed mechanism is summarised in the Scheme.



SCHEME

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