Aust. J. Chem., 1974, **27**, 425–7

The Photolysis of Rhodamine B in Solution

K. F. Langley

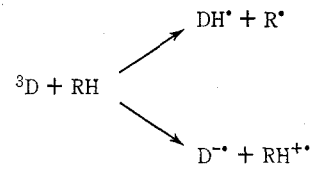
Division of Protein Chemistry, CSIRO,
Parkville, Vic. 3052.

Abstract

In the flash photolysis of aqueous alcoholic solutions of rhodamine B, the semiquinone radical of the dye is formed by absorption of light at wavelengths shorter than 300 nm. It is proposed that impurities in the alcohol sensitize the radical formation.

The flash photolysis technique has been used extensively to study the photochemical reactions of dye triplets and radicals with a variety of substrates. In the field of textile technology, the technique has been used in model systems to elucidate the mechanism of phototendering of cotton by anthraquinone dyes.[1] Because rhodamine B has an unacceptable low lightfastness on wool, it would be useful to study the reactivity of this dye towards substrates such as indole which can be regarded as models for the amino acid residues in wool.

Stevens *et al.*[2] have studied the decay of the semiquinone radical produced by flash photolysis of rhodamine B in deoxygenated aqueous alcoholic solutions. They were unable to obtain any transient species in the absence of an alcohol, from which it might be inferred that the role of the alcohol is to act as a reducing agent by hydrogen atom abstraction or electron transfer (^3D = dye triplet):



Such processes are known for fluorescein.[3] I have been able to reproduce the results of Stevens *et al.*,[2] using a 1250 J flash with photoelectric recording and a quartz cuvette. All solutions were flushed with nitrogen. Thus, no transients were observed from an aqueous solution of rhodamine B (10^{-5}M), but in an aqueous ethanol (1 : 1) solution a transient species was observed at 420 nm, persisting for several seconds, while the initial bleaching of the dye relaxed by 50%. However, no transients were

[1] Phillips, G. O., Worthington, N. W., McKellar, J. F. M., and Sharpe, R. R., *J. chem. Soc.* (*A*), 1969, 767.
[2] Stevens, B., Sharpe, R. R., and Bingham, W. S. W., *Photochem. Photobiol.*, 1967, **6**, 83.
[3] Lindquist, L., *Ark. Kemi*, 1960, **16**, 79.

observed when the aqueous ethanol solution was flashed in a Pyrex cuvette eliminating wavelengths below 300 nm. Furthermore, it was found that the transient species at 420 nm could only be detected in quartz cells provided that the ethanol used was unpurified (optical density 0·02 per cm at 280 nm); when the ethanol was carefully fractionated (optical density 0·005 per cm at 280 nm), the 420 nm transient absorption signal was greatly reduced. The addition of traces of acetone or acetaldehyde to the solutions with fractionated ethanol restored the transient signal, while repetitive flashing of a solution also led to an increase in the signal. It would seem therefore that the formation of the transient is sensitized by carbonyl compounds which may be present in ethanol, particularly in a sample that has aged. Stevens and Bingham[4] have shown that acetone sensitizes the photolysis of rhodamine B at wavelengths less than 300 nm, and they postulate a simple energy transfer process from triplet acetone to the dye, forming the dye triplet. In the present system, it is possible that the carbonyl triplet may react with the alcohol to form an $R_2C^{\cdot}OH$ radical, which in turn could react with the dye to form the $^{\cdot}DH$ radical. Thus 'sensitized' is used in a broader sense than simple triplet energy transfer between carbonyl compound and dye. Dempster *et al.*[5] have stressed the importance of the transmission of ethanol at wavelengths longer than 250 nm as a criterion for purity for flash photolysis experiments.

I have also investigated a possible alternative mechanism for the formation of the transient at short wavelengths, namely that a more efficient primary process than the normal $S_1 \rightarrow T_1$ intersystem crossing might exist for rhodamine B photolysis below 300 nm. Evans[6] has noted that the quantum yield of rhodamine B photodegradation in aqueous solution increases as the photolysis wavelength decreases from 400 to 300 nm. I have extended Evans's results to wavelengths below 300 nm, and to aqueous ethanol solutions, using the Jasco spectro-irradiator for continuous photolyses. This instrument illuminates a series of 1 cm sample cells with near-monochromatic light (half-bandwidth 20 nm) obtained by dispersing the output of a 2 kW Xenon arc lamp with a grating. Samples were irradiated for up to 100 hr. Relative quantum yields for irradiation at two wavelength bands centred on λ_1 and λ_2 were determined by the formula

$$\phi_1\phi_2 = \{(\Delta D)_1/(\Delta D)_2\}(A_2/A_1)(I_2/I_1)$$

where ϕ_1 is the quantum yield at λ_1, $(\Delta D)_1$ the change in optical density of the sample caused by irradiation at λ_1, A_1 the average percentage absorption of the sample at λ_1 and I_1 the photon flux at λ_1. The absolute value for the quantum yield at λ_1 was

Table 1. Relative quantum yield (ϕ) for photodegradation of rhodamine B (10^{-5}M) in water and water–ethanol solutions

Photolysis wavelength (nm)	549	523	362	335	307	279	252	224
ϕ in water (this work)	1	1	22	26	33	120	220	10^3
ϕ in water (from ref.[6])	1	1	8	8	5	—	—	—
ϕ in water–ethanol (1 : 1)	*c.* 0	*c.* 0	*c.* 0	*c.* 0	*c.* 0	*c.* 10^4	*c.* 10^4	*c.* 10^4

estimated by using the manufacturer's calibration for the radiometer. Table 1 shows the quantum yield obtained for both an aqueous solution and an aqueous ethanol

[4] Stevens, B., and Bingham, W. S. W., *J. Soc. Dyers Colour.*, 1963, **79**, 632.
[5] Dempster, D. N., Morrow, T., Rankin, R., and Thompson, G. F., *Trans. Faraday Soc.*, 1972, **68**, 1479.
[6] Evans, N. A., *Text. Res. J.*, in press.

solution of rhodamine B relative to the quantum yield at $\lambda = 549$ nm for the aqueous solution ($\phi = 1$). The absolute value of $\phi = 1$ was found to be in the order of 10^{-6}. All solutions in these experiments were air-saturated.

It can be seen from Table 1 that although there are differences in magnitude between the two sets of results for water, which may be due to differing degrees of purity of the samples, the trend noted by Evans for aqueous solutions is continued to wavelengths below 300 nm. However, the results obtained for aqueous ethanol solutions are very different from those obtained for aqueous solutions.

Whatever the process is that produces the wavelength dependence of the photodegradation quantum yield for rhodamine B in aqueous solution,[6] there is no similar effect involved in the photodegradation of aqueous alcoholic solutions. The photodegradation of plain aqueous solutions of the dye is oxidative, while Koizumi and Usui[7] have shown that the reductive photodegradation of xanthene and thiazine dyes in ethanol is suppressed by oxygen. Presumably in the present case of aqueous alcohol solutions at wavelengths longer than 290 nm, the oxidative degradation is suppressed by ethanol while the reductive degradation is suppressed by oxygen. The onset of photodegradation below 290 nm indicates a mechanism initiated by a component of the system absorbing only at these wavelengths. Thus the spectro-irradiator results parallel the flash photolysis results.

I have concluded therefore that there is no unusual primary photolytic process involved in the formation of the transient, and that both the flash photolysis and the spectro-irradiator results for aqueous alcoholic solutions are explained by the effect of carbonyl impurities in the alcohol. There is no reason to doubt the assignment by Stevens *et al.*[2] of the 420 nm transient to the semiquinone species. However, because its formation involves absorption of light below 300 nm this is not a suitable system for studying the reactions of the radical with substrates which are themselves photolysed at these wavelengths. Work is continuing in this laboratory to establish a more suitable way of producing this radical by sensitization at longer wavelengths.

Manuscript received 6 September 1973

[7] Koizumi, M., and Usui, Y., *Molec. Photochem.*, 1972, **4**, 57.