

III

which was first proposed by Badger and Buttery [4], whereas Squire and Jaffé [5] propose a rapid protonation in the first excited state prior to the rearrangement. Both an ionic mechanism involving the nucleophilic attack of an oxyanion via a π, π^* state [3] and an electrophilic substitution by oxygen via an n, π^* state [2] have been proposed for the formation of the excited singlet state. The ionic mechanism is based on the catalysis of the photorearrangement by polar protic solvents, whereas the electrophilic role of oxygen is supported by the observation of higher quantum yields when oxygen migrates into the ring containing more electron-donating substituents.

In the present work the temperature dependence of the quantum yields of the photorearrangement of azoxybenzene in polar protic solvents and of 6,2'-dimethylazoxybenzene in polar protic and non-polar solvents was studied in the range from room temperature to liquid nitrogen temperature in order to obtain further information on the mechanism of the photorearrangement.

2. Experimental details

2.1. Materials

Azoxybenzene (Aldrich) was recrystallized successively from ethanol, petroleum ether (30 - 60 °C) and ethanol. 6,2'-dimethylazoxybenzene (melting point, 58 °C) was synthesized as described in ref. 6 and was recrystallized from ethanol. 2-hydroxyazobenzene (melting point, 78.5 °C; ϵ^{375} , 9700 (ethanol) and 9800 (heptane)) was synthesized according to the method given in ref. 7. 2-hydroxy-6,2'-dimethylazobenzene was prepared as follows. A solution of 0.34 g of 6,2'-dimethylazoxybenzene in 400 ml of ethanol was irradiated for 4 h using an immersion medium pressure mercury lamp (125 W). The photoproduct (melting point, 95 °C [6, 8]; ϵ^{395} , 9540 (ethanol) and 8860 (heptane)) was isolated on a silica gel column (5 g) by elution with petroleum ether (30 - 60 °C). All the solvents used in the spectroscopic measurements were commercial spectroscopic grade materials.

2.2. Quantum yield measurements

Azoxybenzene and 6,2'-dimethylazoxybenzene solutions and a ferrioxalate actinometer [9] were irradiated in a carousel (Baird and Tatlock Ltd., London). The formation of 2-hydroxyazobenzene and 2-hydroxy-6,2'-dimethylazobenzene was monitored at 410 nm and 395 nm respectively. The ratio of the initial slopes of the plots of ferrous phenanthroline (510 nm)

and 2-hydroxy product concentration *versus* time gave the quantum yields in each case. The samples were irradiated using an Osram HBO 200 W high pressure mercury lamp; the spectral mercury lines at 313 nm, 365 nm and 436 nm were isolated using a Schott 313 nm interference filter, a combination of Corning 7-60 and 0-52 filters and a Corning 5-74 filter respectively. The absorption spectra were recorded in thermostatted Dewar-type cells using a Cary model 17 spectrophotometer or a Varian Techtron 635 instrument [10].

3. Results and discussion

Solutions of I and of 6,2'-dimethylazoxybenzene in ethanol, heptane and benzene were irradiated with UV light, and the quantum yields of the photorearrangement to II and 2-hydroxy-6,2'-dimethylazobenzene respectively were measured.

When a solution of I in ethanol is irradiated at 313 nm and room temperature for 200 min conversion to II is practically complete. The *trans* → *cis* isomerization is initially observed by the decrease in the first absorption band. The quantum yields measured at different concentrations and at wavelengths of 313 and 365 nm are shown in Table 1. At higher concentrations the light is absorbed totally by the system which is a basic requirement for measuring the quantum yield by the method used here. There is no wavelength dependence of the quantum yields, contrary to what was found previously [11]. The yield of II is 3.5% when solutions of I in heptane and benzene are irradiated. The quantum yields in heptane and benzene are also included in Table 1 and are about a factor of 4 less than those in ethanol.

TABLE 1

Quantum yields $\Phi_{2\text{-OH}}$ of the photorearrangement of azoxybenzene to 2-hydroxyazobenzene

Solvent	Concentration (M)	Irradiation wavelength (nm)	$\Phi_{2\text{-OH}} \times 10^{-3}$
Ethanol	1×10^{-4}	313	11
Ethanol	1×10^{-4}	365	9
Ethanol	2×10^{-4}	313	13
Ethanol	2×10^{-4}	365	14
Ethanol	1×10^{-3}	313	22
Ethanol	1×10^{-3}	365	22
Ethanol	5×10^{-3}	313	22
Ethanol	5×10^{-3}	365	23
Heptane	5×10^{-3}	313	5
Heptane	5×10^{-3}	365	4
Benzene	5×10^{-3}	313	6
Benzene	5×10^{-3}	365	5

TABLE 2

Quantum yields $\Phi_{2\text{-OH}}$ of the photorearrangement of 6,2'-dimethylazoxybenzene to 2-hydroxy-6,2'-dimethylazobenzene

Solvent	Concentration (M)	Irradiation wavelength (nm)	$\Phi_{2\text{-OH}} \times 10^{-3}$
Ethanol	1×10^{-4}	313	9
Ethanol	1×10^{-4}	365	5
Ethanol	2×10^{-4}	313	10
Ethanol	2×10^{-4}	365	6
Ethanol	1×10^{-3}	313	20
Ethanol	1×10^{-3}	365	15
Ethanol	5×10^{-3}	313	20
Ethanol	5×10^{-3}	365	15
Heptane	5×10^{-3}	313	13
Benzene	5×10^{-3}	313	15

When a solution of 6,2'-dimethylazoxybenzene in ethanol is irradiated at 313 nm and room temperature, the yield of 2-hydroxy-6,2'-dimethylazobenzene is 56%. Previous results have shown that when concentrated solutions of 6,2'-dimethylazoxybenzene in ethanol are irradiated the following products are obtained: 2-hydroxy-6,2'-dimethylazobenzene (40% yield); 4-hydroxy-2,2'-dimethylazobenzene (5.5% yield); 2-hydroxy-4,2'-dimethylazobenzene (3.5% yield). The quantum yields measured in this case are shown in Table 2. These results suggest that the quantum yields depend on the wavelength probably because of the low value of ϵ for 6,2'-dimethylazoxybenzene at 365 nm (1300 in ethanol) which means that the irradiation is not totally absorbed even at concentrations of 5×10^{-3} M. The yield of 2-hydroxy-6,2'-dimethylazobenzene in non-polar solvents, which is 33%, and the quantum yields in heptane and benzene of the photorearrangement of 6,2'-dimethylazoxybenzene (Table 2) are much higher than the corresponding values obtained for I in heptane. These results show that the photorearrangement is not catalysed solely by the presence of proton-donating solvents. In this case the quantum yields in polar protic and non-polar solvents are comparable with those of azoxybenzene in ethanol solutions. The higher quantum yield of the rearrangement in the 6,2'-dimethylazoxybenzene-heptane system compared with that in the azoxybenzene-heptane system can be explained by the presence of the electron-donating *o*-methyl substituents which imply a mechanism with an intermediate in the ground state. Molecular orbital calculations of azoxybenzene show that the *o*-carbon atoms of the phenyl rings contribute to the electronegativity of the oxygen atom [12]. Consequently the methyl groups may act as *ortho* substituents and transfer negative charges to the oxygen, thus facilitating the nucleophilic attack of the oxyanion. $\text{p}K_{\text{a}}$ measurements in substituted azoxybenzenes have shown that 4,4'-dimethylazoxybenzene has a higher basicity by 1 pK unit compared with unsubstituted azoxybenzene [13]. In the case of *o*-methyl-substituted derivatives, the steric hindrance also has to be taken into

account. However, it is shown experimentally that even 2,2',4,4',6,6'-hexamethylazoxybenzene is a stronger base than azoxybenzene [14]. The foregoing discussion is justified by the lack of information about the excited state energies, crossings etc. of azoxy compounds in the different solvents. However, Squire and Jaffé [5], in their study of the H_0 dependence of the quantum yield of the photorearrangement of azoxybenzene, concluded that the H_0 behaviour of $n,\pi^* \rightarrow \pi,\pi^*$ state crossing is extremely unlikely to appear as is the acid-base reaction they observed [5].

The temperature dependence of the photorearrangement of azoxybenzene in polar protic solvents and of 6,2'-dimethylazoxybenzene in polar protic and non-polar solvents was studied in the range from room temperature to liquid nitrogen temperature for the first time. Figure 1 summarizes the temperature dependence of the quantum yields Φ_{2-OH} for both compounds. No photorearrangement takes place at liquid nitrogen temperature, but *trans* \rightarrow *cis* isomerization is observed.

The temperature dependence of the quantum yields shown in Fig. 1 shows that there is an energy barrier at some point in the photorearrangement. In order to find out where this energy barrier is situated, we performed several experiments. The results obtained with 6,2'-dimethylazoxybenzene are shown in Fig. 2. Thus when a solution of 6,2'-dimethylazoxybenzene in ethanol-methanol is cooled down to -70°C and irradiated for 1 h (the spectrum remains unchanged when the solution is kept at this temperature for a further 2 h) the new spectrum obtained is not that of 2-hydroxy-6,2'-dimethylazobenzene alone but also includes a contribution from an intermediate product which is converted to 2-hydroxy-6,2'-azobenzene when the irradiated solution is heated to room temperature. Con-

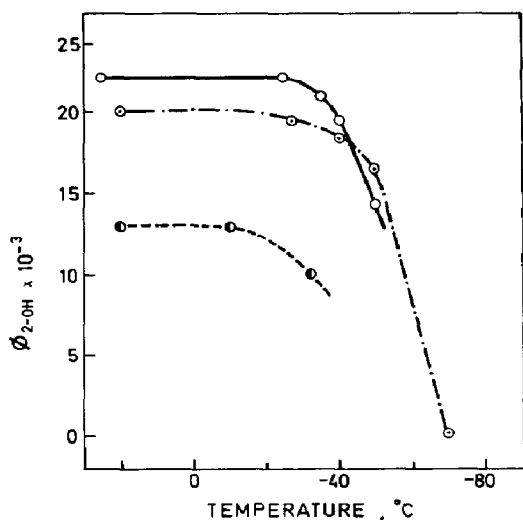


Fig. 1. Temperature dependence of the quantum yield Φ_{2-OH} of the photorearrangement: —, azoxybenzene in ethanol-methanol; - · -, 6,2'-dimethylazoxybenzene in ethanol-methanol; - - -, 6,2'-dimethylazoxybenzene in methylcyclohexane-isopentane.

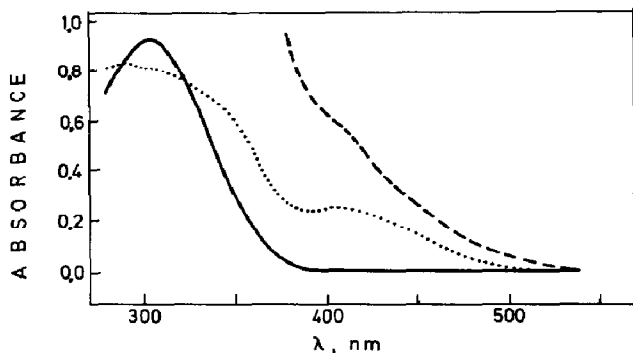


Fig. 2. Spectra of 6,2'-dimethylazoxybenzene (10^{-4} M) in ethanol-methanol: —, at room temperature; ···, at -70°C after irradiation at -70°C (the spectrum remains unchanged after leaving for 2 h); ---, after warming to room temperature.

version of the intermediate to 2-hydroxy-6,2'-dimethylazobenzene can also be achieved photochemically at -70°C by irradiation at 436 nm. This result proves that a ground state intermediate, which has to overcome a thermal barrier in order to be converted to the 2-hydroxy product, is involved in the photorearrangement mechanism. This is the first time to our knowledge that this intermediate, whose existence has previously been postulated, has been observed directly; a cyclic intermediate similar to III would be expected to absorb in this region. Similar results were obtained with I in ethanol-methanol and 6,2'-dimethylazoxybenzene in methylcyclohexane-isopentane. However, the spectrum obtained when I is irradiated at -62°C does not remain constant with time but undergoes a slow conversion to the spectrum of II. The following experiments were performed to estimate the height of the thermal barrier between the ground state intermediate and the photoproduct. Solutions of I (10^{-4} M) in ethanol-methanol were irradiated with light of wavelength 365 nm at -60 , -65 and -70°C for 30 min. The temperatures were accurate to $\pm 1^{\circ}\text{C}$. The increase in the absorbance at 395 nm with time was monitored from immediately after irradiation until equilibration. The working range of the temperature was limited by the fact that above -60°C the reaction was too fast to be followed and below -70°C the spectrum of an unstable red product interfered. The first-order rate constants of the thermal reaction were calculated by following the change in absorbance with time and were used to construct an Arrhenius plot from which an energy of activation of 12 kcal mol^{-1} was determined.

Finally, we report some preliminary results obtained at low temperature which are probably not directly related to the photorearrangement but might be helpful in explaining its low quantum yield. When a solution of I or 6,2'-dimethylazoxybenzene in a polar or a non-polar solvent is irradiated at -150°C , a possible new intermediate product I-150 is detected (Fig. 3) which converts to a red intermediate R which is detectable at temperatures of about -50°C when the solution is allowed to warm up. The final spectra recorded at room temperature are different from the initial spectra (Fig. 4).

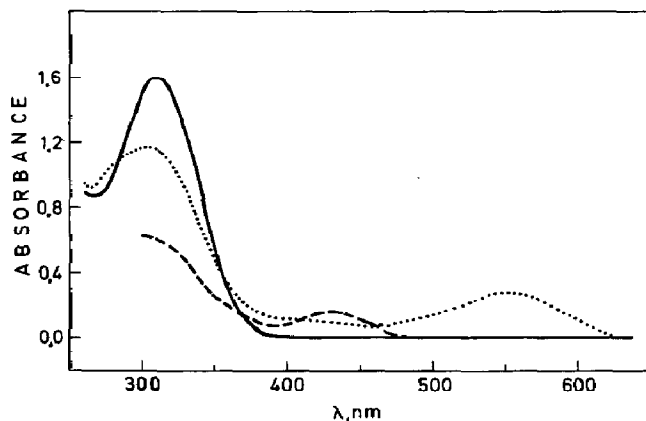


Fig. 3. Spectra of dimethylazoxybenzene (10^{-4} M) in ethanol-methanol: —, at -150 °C; ---, at -150 °C after irradiation at -150 °C; ..., after warming to -50 °C.

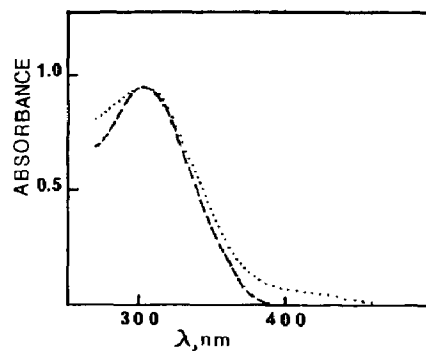
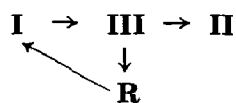


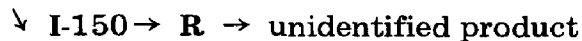
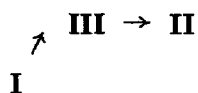
Fig. 4. Spectra of 6,2'-dimethylazoxybenzene in ethanol-methanol at room temperature before (---) and after (...) irradiation at -150 °C.

The red intermediate was also detected by flash photolysis in the millisecond region [1].

Thus this reaction is either reversible



and I-150 is the same as III or it is irreversible



and I-150 is different from III. We favour the second case, because if I-150 were the same as III some II should also be formed photochemically at -150 °C. A comparison of the rate constants obtained using flash photolysis supports this conclusion [15]. Of course the situation may be even more complex. In any case we can conclude that these results indicate that the photorearrangement does not compete only with the *trans* \rightarrow *cis* photoisomerization.

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References

- 1 D. Gegiou, A. Tsoka and E. Hadjoudis, *J. Photochem.*, **9** (1978) 216.
- 2 N. J. Bunce, J.-P. Schoch and M. C. Zerner, *J. Am. Chem. Soc.*, **99** (1977) 7986.
- 3 R. Tanikaga, *Bull. Chem. Soc. Jpn.*, **41** (1968) 2151.
- 4 G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, (1954) 2243.
- 5 R. H. Squire and H. H. Jaffé, *J. Am. Chem. Soc.*, **95** (1973) 8188.
- 6 D. J. Goon, N. G. Murray, J.-P. Schoch and N. J. Bunce, *Can. J. Chem.*, **51** (1973) 3827.
- 7 E. Bamberger, *Chem. Ber.*, **33** (1900) 3189.
- 8 G. E. Lewis and J. A. Reiss, *Aust. J. Chem.*, **19** (1966) 1887.
- 9 G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235** (1956) 518.
- 10 E. Fischer, *Mol. Photochem.*, **2** (1970) 99.
- 11 R. Squire, *Ph.D. Thesis*, 1973, University of Cincinnati microfilm 74-1706.
- 12 W. Maier, A. Saupe and A. Englert, *Z. Phys. Chem. N.F.*, **10** (1957) 273.
- 13 C. S. Hahn and H. H. Jaffé, *J. Am. Chem. Soc.*, **84** (1962) 949.
- 14 R. A. Cox and E. Buncel, *Can. J. Chem.*, **51** (1973) 3143.
- 15 D. Gegiou, A. Tsoka and E. Hadjoudis, to be published.