

PHOTOREARRANGEMENT OF AZOXYBENZENE TO 2-HYDROXYAZOBENZENE. A FLASH PHOTOLYSIS STUDY[†]

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Several mechanisms were proposed for the photorearrangement of azoxybenzene to 2-hydroxyazobenzene¹. Among them a mechanism involving a rapid protonation in the first ($^1\pi-\pi^*$) excited state prior to the rearrangement², an intramolecular mechanism involving a $^1\pi-\pi^*$ state and nucleophilic attack by oxygen on the ortho position of the more distant aryl substituent and resulting in the formation of a cyclic intermediate^{3,4} and a third mechanism involving a low-lying $^1n-\pi^*$ state and electrophilic attack at the aromatic ring⁵.

We studied the photochemistry of azoxybenzene by flash photolysis. Azoxybenzene and some methyl substituted azoxybenzenes were investigated in a number of solvents, a wide temperature range and degassed and non degassed solutions.

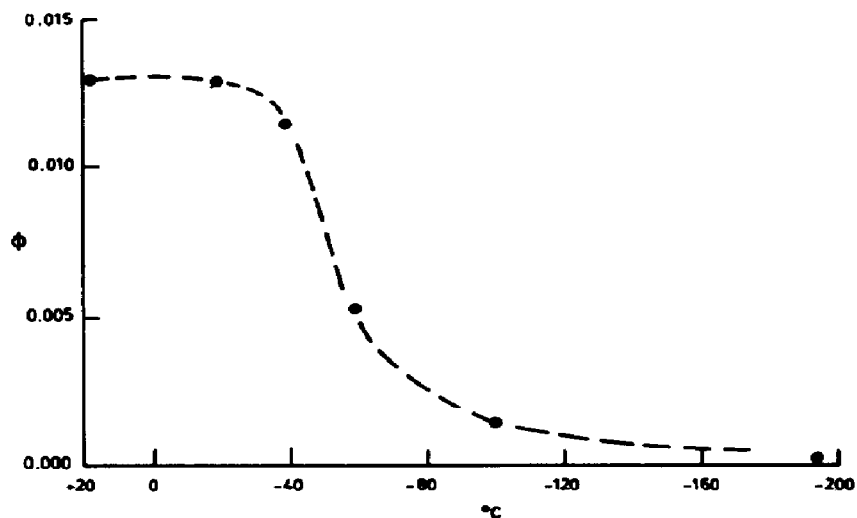
Three transient species were observed with most compounds and solvents used, both in degassed and non degassed solutions, which could be described generally as follows: a) A relatively fast transient species in the region around 380nm with a lifetime in the msec region, depending on solvent and compound investigated. The decay of this transient was independent of temperature. b) In the same region another relatively slow transient was observed with both its formation and decay dependent on temperature. The lifetime of this transient, being in the sec region in non polar solvents, showed also a strong solvent dependence. c) The third

[†]Preliminary results were presented at the VIII International Conference on Photochemistry, 7-13 August, Edmonton, Canada (1975)

transient with a spectrum centered at 510nm and a lifetime (msec) dependent on temperature showed an appreciable solvent dependence mostly in formation.

All the transients followed first order kinetics. Rate constants in all cases were calculated and energies of activation were measured.

The photorearrangement was also studied by steady state irradiation. Indicatively, the energy of activation of the reaction of azoxybenzene to 2-hydroxyazobenzene in ethanol was found to be $E_a = 5.7$ Kcal mole. The temperature dependence of the quantum yields of azoxybenzene in ethanol is shown in the graph below:



In the light of the above results a reexamination of the mechanism will be attempted.

1. H.M. Knipscheer, *Rec. Trav. Chim., Pays Bas*, 22, 1 (1903)
2. R.H. Squire, H.H. Jaffé, *J. Am. Chem. Soc.*, 95, 8188 (1973).
3. G.M. Badger and R.G. Buttery, *J. Chem. Soc.*, 2243 (1954).
4. R. Tanigaka, *Bull. Chem. Soc. Jap.*, 41, 2151 (1968).
5. N.J. Bunce, J.P. Schock and M.C. Zerner, *J. Am. Chem. Soc.*, 99, 7986 (1977).