Photochemical, Radiolytic, and Thermal Oxidation of 4-Dimethylamino-2′,4′-dinitroazobenzene—Model Experiments for the Degradation of Azo Dyes

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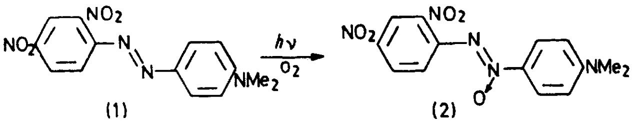
Summary 4-Dimethylamino-2′,4′-dinitroazobenzene (**1**) undergoes photo-oxidation in propan-2-ol giving 4-dimethylamino-2′,4′-dinitro-*NNO*-azoxybenzene (**2**) and other products; (**2**) is also formed by γ-radiolysis in presence of oxygen and by thermal reaction with hydrogen peroxide in the same solvent.

The formation of azoxy-compounds as a result of the action of light on azo-compounds in the presence of air has been suggested by a number of investigators,[1] but such a product has never been found. 1,4-Naphthaquinone was isolated as a major reaction product in photochemical oxidation of 4-arylazo-1-naphthols. No intermediate oxidation products were identified[3] in the photo-oxidation of 4-amino-4′-nitroazobenzene. We here report the isolation and characterization of an azoxy-compound generated by photo-oxidation.



(1) (2)

Compound (**1**) is representative of a large group of azo-dyes characterized by significant intramolecular charge-transfer interaction in the ground state. An azo-hydrazone tautomerism is absent in (**1**). On photolysing a $1{\cdot}5 \times 10^{-4}$M solution of (**1**) in propan-2-ol with a 700 W medium-pressure mercury lamp through Solidex glass in the presence of air and interrupting the reaction when *ca.* 35% of (**1**) had been consumed, (**2**) was separated from seven other coloured products by column chromatography on alumina with toluene–EtOAc (99:1). Typically a yield of 35—40% of (**2**) based on a 35% conversion of (**1**) was obtained. The photoreaction was followed spectrophotometrically and carried out at 30—35°.

The initial quantum yield for the disappearance of (**1**) is less than 1×10^{-4}. The concentration of hydrogen peroxide generated is too low to lead to (**2**) under these conditions. The same compound was obtained in 35—45% yield in the reaction of (**1**) with a 2·5% solution of H_2O_2 in propan-2-ol at 75° and by γ-radiolysis in oxygenated propan-2-ol at room temperature in 80—90% yield based on a 45% conversion of (**1**)

Compound (**2**) was isolated as orange crystals, m.p. 188—189°; it gave satisfactory elemental analyses, and showed $\lambda_{\max}$ (Me_2CHOH) 455 nm (ϵ 16,000 mol^{-1} cm^{-1}); $\nu_{\max}$ (KBr) 1180 and 1100 cm^{-1} [as distinct from (**1**)]; δ ($CDCl_3$) 3·12 (6H, s) and 6·6—8·9 (7H, m); *m/e* 331 (M^+; 52%), 211 (24), 150 (92), and 120 (100). The structure was assigned on the basis of elemental analysis, the characteristic nature of its mass spectrum which indicates the location of the oxygen on the N atom adjacent to the 4-dimethylamino group[4] and an *X*-ray analysis which confirms the assigned structure. Compound (**2**) absorbs at shorter wavelength in propan-2-ol than the azo-compound (**1**) (512 nm); this has an analogy in the 4′-dimethylaminoazobenzene series.[5] It is more stable towards attack by H_2O_2 than (**1**) but is photolysed initially faster than (**1**) when irradiated at 300—400 nm. 4-Dimethylamino-4′-nitroazobenzene also forms an azoxy-compound under our conditions of photochemical and thermal oxidation.

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