# The Electronic Spectrum and Photolysis of S-Nitrosotoluene-α-thiol

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S-Nitrosotoluene-α-thiol, $C_6H_5 \cdot CH_2 \cdot SNO$, was prepared by the method reported by Saville.[1] The compound in dilute (4×10^{-2}M) hexane solution was found to be thermally stable at 25° over a period of weeks. 3650Å-radiation caused the decomposition of the compound, the only products being nitric oxide and dibenzyl disulphide.

The electronic spectrum of S-nitrosotoluene-α-thiol in hexane solution was measured and is shown in the Figure. The absorption at $\lambda_{max} =$
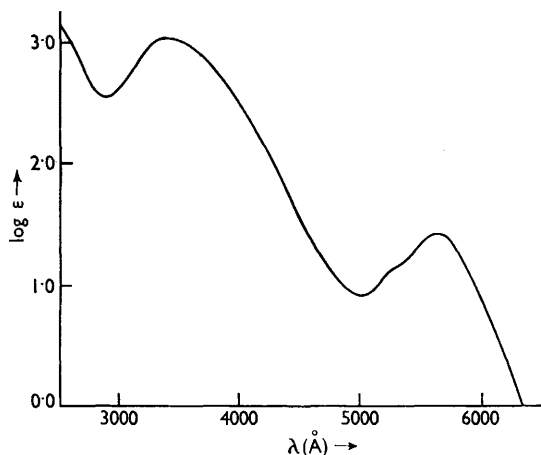

The electronic spectrum of S-nitrosotoluene-α-thiol in hexane solution

5600 Å (ϵ, 26) for which the oscillator strength, f, is 2×10^{-4}, may be assigned to an $n_N \to \pi^*$ transition. A similar assignment has been made[2] for the absorption at 5988 Å of S-nitroso-2-methyl-propane-2-thiol. The shoulder at 5300 Å can be attributed to the existence of two rotational isomers of the molecule as have been shown to exist in the analogous alkyl nitrite.[3] The band is not photochemically active.

The absorption at $\lambda_{max} = 3400$ Å (ϵ, 1030) with $f = 2 \cdot 7 \times 10^{-2}$, is responsible for the photo-activity of the molecule. It is assigned to an $n_O \to \pi^*$ transition. The $\pi \to \pi^*$ transition is in the benzenoid region at 2200 Å ($\epsilon \sim 10^4$).

The result of the irradiation of S-nitrosotoluene-α-thiol at 3650 Å would be the excitation of an electron from the pure p-lone-pair orbital on the oxygen atom to a π-orbital which would be anti-bonding with respect to the nitrogen and oxygen atoms. The absorption of 3650 Å-radiation causes excitation to the extent of 79 kcal. mole^{-1}, this being in excess of the calculated sulphur–nitrogen bond dissociation energy of 52 kcal. mole^{-1} and sufficient to cause the fission of this bond. By the homolytic fission of the sulphur–nitrogen bond the orbital on the nitrogen atom containing a single electron can be used, together with the p-orbital on the oxygen atom which also contains one electron, to form a second π-bond between the nitrogen and oxygen atoms. Thus formed, the nitric oxide would be in its electronic ground state. These processes can be formulated as:

$$\text{RSNO (R = Benzyl)} \xrightarrow{h\nu} \text{RSNO*} \qquad (1)$$

$$\text{RSNO*} \to \text{RS} + \text{NO} \qquad (2)$$
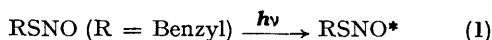
Evidence for thiyl radical production is that the monomers acrylonitrile and methyl methacrylate reduce the quantum yield for RSNO disappearance from 0·8 to a limiting value of 0·4 and in doing so become polymerised. These observations are consistent with the mechanism for the photolysis of reactions (1) and (2) followed by:

$$\text{RS} + \text{RSNO} \to \text{RSSR} + \text{NO} \qquad (3)$$

Thiyl radicals are known to react rapidly with sulphur–sulphur bonds[4] and there seems to be no reason to expect their reaction with sulphur–nitrogen bonds to be very different.

S-Nitroso-derivatives of the following thiols have been prepared and undergo similar photolysis: n-hexanethiol, 2-methylpentane-4-thiol, 2-methyl-propanethiol, cyclohex-3-enethiol, 2-methyl-pentane-2-thiol and 2-methylpropane-2-thiol.

Some support for the argument that the electronic changes occurring subsequently to an $n_O \to \pi^*$ transition, which so conveniently result in a thiyl radical and the electronic ground state of nitric oxide, are a major factor in producing

[1] B. Saville, Analyst, 1958, 83, 660.
[2] G. Kreze and U. Uhlich, Chem. Ber., 1959, 92, 1048.
[3] L. H. Piette and W. A. Anderson, J. Chem. Phys., 1959, 30, 899.
[4] W. A. Pryor, "Mechanisms of Sulphur Reactions," McGraw-Hill series in Advanced Chemistry, 1962, p. 51.

high quantum yields in these photolyses comes from a study of the photochemistry of the analogous nitrites and N-nitroso-compounds. Bamford[5] reports that N-nitrosodimethylamine and N-nitrosodiethylamine have quantum yields for decomposition at 3650 Å of only 0·01. It is known[6] that 3650 Å-radiation has no effect on N-nitrosodibenzylamine. In these cases the radiation would cause $n_N \rightarrow \pi^*$ transitions[7] and in spite of the fact that there would be ample energy to break the nitrogen–nitrogen bond there would have to be a major electronic rearrangement in order to produce nitric oxide in its electronic ground state. This limitation also applies to the photolysis of nitrites at 3650 Å and these do involve very low quantum yields, e.g. for the photolysis of t-butyl nitrite[8] $\phi = 0·08$. There are, however, some exceptions in the case of nitrite photolyses, these being those instances where the alkoxy-radical can undergo the Barton reaction[9] effectively or can abstract a hydrogen atom from a solvent molecule.

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[5] C. H. Bamford, *J. Chem. Soc.*, 1939, 12.
[6] J. Barrett, L. H. Fitzgibbons, and P. J. N. Young, unpublished observations.
[7] S. F. Mason, *Quart. Rev.*, 1961, **15**, 287.
[8] H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.*, 1937, **33**, 1546.
[9] M. Akhtar, *Adv. Photochem.*, 1964, **2**, 263.