

A FLASH PHOTOLYTIC STUDY OF *o*-NITROSOTOLUENE

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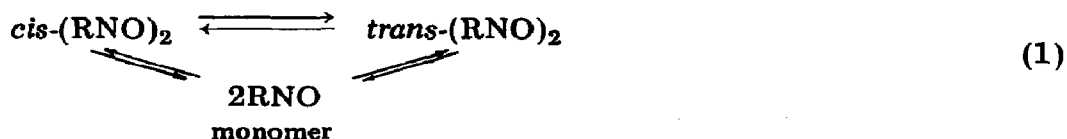
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Summary

When *o*-nitrosotoluene in ethanol solution is exposed to UV irradiation, a short lived species is formed which has a rather strong absorption band around the 385 nm region of the spectrum. The decay of this transient follows first order kinetics with $k = 3.27 \times 10^2 \text{ s}^{-1}$ at room temperature. If the methyl group is replaced by chlorine or bromine atoms, the transient is not observed. The transient is attributed to proton transfer from the methyl group to the nitroso group together with a change in the structure of the aromatic ring to a quinoid configuration.

1. Introduction

In the framework of studies on the aromatic C-nitroso compounds we decided to investigate by the flash photolysis technique the case of *o*-nitrosotoluene which is the first example of an aromatic C-nitroso compound to have been isolated in both the *cis* and *trans* dimeric forms [1]. The relations between the various species are shown in scheme (1) where $(\text{RNO})_2$ stands for the dimeric *o*-nitrosotoluene. The isomerization processes (*cis-trans* and internal rotation) occurring in the *o-o'*-azodioxytoluene have also been reported [2].



The flash photolysis technique was thought to be a suitable tool in this case for exploring possible monomer-dimer interchange, since such an interchange was not observed by steady state irradiation.

2. Experimental

The *trans*-*o,o'*-azodioxytoluene (the dimer of *o*-nitrosotoluene) was prepared as described previously [1]. *o*-Nitrosobromobenzene and *o*-nitroschlorobenzene were prepared by standard processes [3].

The flash photolysis apparatus (Hivotronic, Gt. Britain) consisted of two vertical photolysis lamps 200 mm long (between electrodes) of 10 mm diameter. The monitoring source was a quartz-iodine lamp suitable for wavelengths above 300 nm. The photolytic flash had a half-height width of about 30 μ s at full power. All the experiments were carried out in degassed solutions (flushing for 30 min with pre-purified nitrogen) in a 20 cm optical cell. A vertical quartz Dewar vessel with quartz windows was used for measurements at low temperatures using liquid nitrogen.

Absorption spectra were recorded on a Cary Model 17 spectrophotometer. Steady state irradiations were carried out with a 200 W high pressure mercury lamp.

3. Results

After flashing a 10^{-3} M solution of *o*-nitrosotoluene in ethanol a rather strong transient develops which decays following first order kinetics with $k = 3.27 \times 10^2 \text{ s}^{-1}$ at room temperature. The absorption spectrum of the transient could be calculated from plots of $\log \log (I_{\infty}/I)$ versus time at different wavelengths and is given in Fig. 1. Measurements of the decay rates at different temperatures results in the Arrhenius plot shown in Fig. 2 which yields $E = 0.26 \text{ kcal mol}^{-1}$ for the activation energy of the decay at 385 nm. Over the wavelength region investigated the permanent (irreversible) increase in optical density (OD) on exposure to a flash was less than 1% of the reversible change and therefore the overall process is essentially reversible. Thus

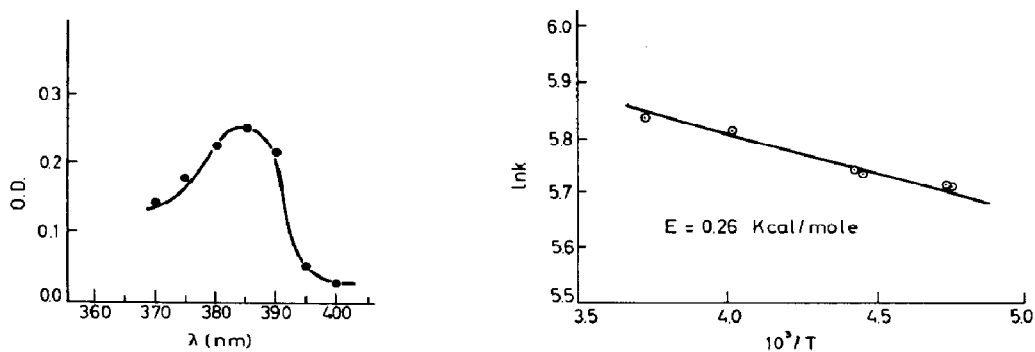


Fig. 1. Absorption spectrum of the transient produced on flash photolysis of 10^{-3} M *o*-nitrosotoluene in ethanol. The OD was read at 500 μ s after the start of the flash.

Fig. 2. Temperature dependence of the decay rates (s^{-1}) at 385 nm in the flash photolysis of *o*-nitrosotoluene in ethanol.

after six flashes the solution is practically unchanged. However, on prolonged steady state irradiation the spectrum is changed and a permanent product is formed. Figure 3 shows the spectrum of a 10^{-3} M solution of *o*-nitrosotoluene in ethanol after six flashes and after 2 h of steady state irradiation. In the same figure the spectrum of a 2×10^{-5} M solution of *o*-nitrotoluene in ethanol is displayed for comparison. This suggests that *o*-nitrotoluene may be the result of photo-oxidation of *o*-nitrosotoluene as has been reported for nitrosobenzene [4, 5]. It should be noted that during the steady state irradiation the 780 nm weak band ($n-\pi^*(N)$) which belongs to the monomer drops because the nitro group absorbs less strongly in this region [6].

Flashing 10^{-3} M solutions of *o*-nitrosochlorobenzene and *o*-nitrosobromobenzene in ethanol does not produce the transient observed for *o*-nitrosotoluene at 385 nm, but a much weaker transient 50 times slower with a maximum absorption at about 510 nm is observed. Figure 4 shows the transient absorption spectra of these two compounds together with the original spectra. After repeated flashing or on long steady state irradiation a yellow product is formed, the spectrum of which, for the case of *o*-nitrosochlorobenzene, is included in Fig. 4 for comparison.

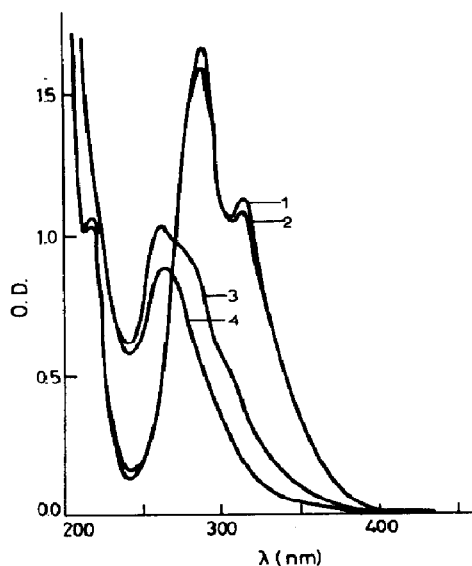


Fig. 3. Comparison between spectrum of *o*-nitrosotoluene in 10^{-3} M ethanol (curve 1), after six flashes (curve 2) and after 2 h steady state irradiation (curve 3). Curve 4 is the spectrum of 2×10^{-5} M nitrotoluene in ethanol.

4. Discussion

The photochemical reaction responsible for the formation of the coloured transient species appears, in the case of *o*-nitrosotoluene, to involve hydrogen abstraction by the nitroso group. Because of the proximity of the

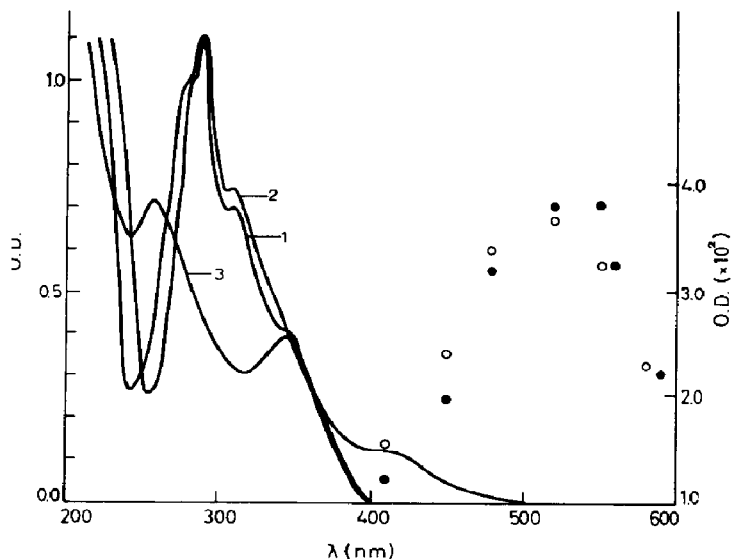
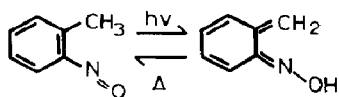


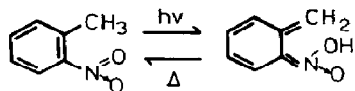
Fig. 4. Spectral changes produced on flash photolysis of 10^{-3} M *o*-nitrosobenzene and *o*-nitrosobromobenzene in ethanol: • transient absorption spectrum of *o*-nitrosobenzene (OD read at 5 ms after the start of the flash); ○ transient absorption spectrum of *o*-nitrosobromobenzene (OD read at 5 ms after the start of the flash); curves 1 and 2, absorption spectra of 10^{-3} M *o*-nitrosobenzene and *o*-nitrosobromobenzene in ethanol; curve 3, absorption spectrum of the yellow product formed after steady state irradiation of *o*-nitrosobenzene for 2 h.

methyl group the abstraction proceeds intramolecularly leading to a change in the structure of the aromatic ring to a quinoid configuration



The above explanation is supported by a number of arguments.

Studies by flash photolysis of 2-nitrotoluene have yielded a transient with maximum absorption around 380 nm which fades in the dark following first order kinetics with a half-life in the millisecond region; this transient is attributed to intramolecular hydrogen abstraction by the nitro group, forming the aci-nitro derivative [7]



Thus the formation of the coloured species in the two systems is quite analogous to and resembles what has been observed with a number of aromatic ketones [7].

Other similar photo-induced hydrogen transfer reactions over a six-membered ring are known, *i.e.* with *o*-nitrobenzylideneaniline [8] and other Schiff bases having a hydroxyl group *ortho* to the C=N bond [9].

More recent work [10] has shown that there is hydrogen abstraction from the solvent during photolysis of nitrosobenzene, and internal hydrogen abstraction during photolysis of 2,4,6-tributylnitrosobenzene has been proposed [11] based on the analysis of the end products.

Two possibilities of explaining the observed transient are (i) dimerization (since it is a facile process [12]) and (ii) *cis-trans* isomerization. However, both these cases may be excluded on the grounds of the very low energy of activation observed and from the fact that the transient does not appear in *o*-nitrosobenzene and *o*-nitrosobromobenzene. Also the NMR data show that the *cis-trans* equilibrium is slow at -50°C and proceeds rapidly at higher temperatures [1], while in the present case the transient decays with very small differences in this range of temperature. A third possibility, the detection of a long lived excited state, was ruled out because the results were unaffected when oxygen-saturated solutions were photolysed.

A comment on the very weak transient observed in the case of *o*-chloronitrosobenzene and *o*-bromonitrosobenzene around 510 nm and the product formed after repeated flashing or steady state irradiation is necessary. The product might be a mixture of 2-2'-dichloroazoxybenzene and 2-2'-dichloro-6-hydroxyazobenzene since it has been reported that the photochemical decomposition of nitrosobenzene yields azoxybenzene and 2-hydroxyazobenzene [13]. The observed transient at 510 nm comes either from a 2-2'-dichloroazoxybenzene or from 2-2'-dichloro-6-hydroxyazobenzene since a transient at 510 nm has been observed in azoxybenzene [14] and in 2-hydroxy-5-methylazobenzene [15]. The first case is more probable because the decay times more or less coincide while the second is at least ten times slower. The same holds for *o*-nitrosobromobenzene.

Finally it must be pointed out that the transients were not connected with the free radicals which are produced from these nitrosobenzene derivatives first because their decay curve follows second order kinetics and second because in general they are, when they exist, long lived species [13, 5].

References

- 1 M. Azoulay, B. Stymne and G. Wettermark, *Tetrahedron*, **32** (1976) 2961.
- 2 M. Azoulay, T. Drakenberg and G. Wettermark, *Tetrahedron Lett.*, **26** (1974) 2243.
- 3 L. Gattermann, *Laboratory Methods of Organic Chemistry*, McMillan, London, 1952, p. 179.
- 4 E. Bamberger, *Chem. Ber.*, **35** (1902) 1606.
- 5 G. E. Russel and E. J. Geels, *J. Am. Chem. Soc.*, **87** (1965) 122.
- 6 B. G. Gowenlock and W. Lüttke, *Q. Rev.*, **12** (1958) 321.
- 7 G. Wettermark, E. Black and L. Dogliotti, *Photochem. Photobiol.*, **4** (1965) 229.
- 8 E. Hadjoudis and E. Hayon, *J. Phys. Chem.*, **74** (1970) 2224.
- 9 G. Wettermark and L. Dogliotti, *J. Chem. Phys.*, **40** (1964) 1486.
- 10 K. Pak and A. C. Testa, *J. Phys. Chem.*, **76** (1972) 1087.
- 11 L. R. C. Barclay and I. T. McMaster, *Tetrahedron Lett.*, **49** (1973) 4901.
- 12 R. Hoffmann, R. Gleiter and F. B. Mallory, *J. Am. Chem. Soc.*, **92** (1970) 1460.
- 13 K. Maruyama, R. Tanikaga and R. Goto, *Bull. Chem. Soc. Jpn*, **37** (1964) 1893.

- 14 D. Gegiou and E. Hadjoudis, in *Abstr. 8th Int. Conf. on Photochemistry*, Edmonton, Canada, 1975.
- 15 G. Wettermark, M. E. Langmuir and D. G. Anderson, *J. Am. Chem. Soc.*, 87 (1965) 476.