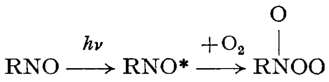
Photo-oxidation of Nitroso-compounds: Dissociative Mechanism for the Photo-oxidation of 2-Methyl-2-nitrosobutane

By JOSEF PFAB

(*Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh* EH14 4AS)

Summary The photo-oxidation of 2-methyl-2-nitrosopropane in the gas phase is shown to proceed by a dissociative mechanism *via* peroxyl and alkoxyl radicals and to provide a model system for the study of the oxidation of low levels of NO to NO_2, which is of interest in studies of reactions occurring in photochemical smog.

THE photo-oxidation of nitrosoalkanes is reported to proceed *via* an intermediary diradical adduct (**2**) of O_2 to an excited state of the nitroso-compound leading either to quantitative formation of nitro-compounds in inert solvents[1–3] or to products explained by addition and abstraction reactions of (**2**)[3,4] in more reactive solvents. Recent independent work appears to confirm a mechanism in which adducts (**2**) are formed.[5] On the other hand the photo-oxidation of *gem*-chloronitroso-compounds proceeds *via* photodissociation of (**1**) exclusively[6] and it is also known that the photo-oxidation of optically active (**1**) leads to formation of the racemic nitro-compound suggesting a dissociation–inversion–recombination sequence prior to formation of the oxidation product.[7]



$$\underset{(\mathbf{1})}{\text{RNO}} \xrightarrow{h\nu} \text{RNO*} \xrightarrow{+O_2} \underset{(\mathbf{2})}{\text{R}\overset{\overset{\text{O}}{|}}{\text{N}}\text{OO}} \qquad (1)$$

The results of a study of the photo-oxidation of 2-methyl-2-nitrosopropane (Bu^tNO) in the gas phase reported here indicate that reaction (1) is unimportant.

When 10—100 mTorr of gaseous Bu^tNO were photolysed to completeness in the presence of a 10^4—10^5-fold excess of oxygen by brief exposure to intense 540—800 nm radiation† corresponding to the $n^* \rightarrow \pi^*$ absorption of the nitroso-chromophore, the main product (62%) was t-butyl nitrate as indicated by the i.r. bands of the product vapour at 1647 and 1309 cm^{-1}. Direct g.l.c. analysis of the vapour

---

† The high intensities were achieved by operating a 400 W sodium lamp in the centre of a large silvered vessel in order to exploit multiple reflection of the emitted light.

revealed that the other products included acetone (18%), 2-methyl-2-nitropropane (14%), t-butyl nitrite (2%), and isobutylene (2%). Similar results were obtained in the presence of 5—10 Torr of O_2 and 750 of Torr N_2.

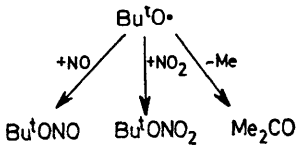
Mechanism (1)[3] requires that the nitro-compound be formed as the main product at sufficiently high $[O_2]$ to $[Bu^tNO]$ ratios. The complicated product pattern obtained in this work rules out mechanism (1), however, and can only be rationalised adequately by a mechanism based on an initial photodissociation of the C–N bond of (**1**) since 86% of the products do not contain this bond. The t-butyl radicals formed in the primary step (2) will react with O_2 virtually exclusively under the experimental conditions chosen, and will give rise to t-butoxyl radicals *via* the sequence (3).

$$Bu^tNO \xrightarrow{h\nu} Bu^tNO^* \rightarrow Bu^{t\cdot} + NO \qquad (2)$$

$$Bu^{t\cdot} \xrightarrow{+O_2} Bu^tO_2\cdot \xrightarrow{+NO} Bu^tO\cdot + NO_2 \qquad (3)$$

The importance of alkoxyl radical formation is evident from the fact that 82% of the products are directly derived from the combination and fragmentation reactions of this radical (Scheme). Confirmatory evidence was obtained from a study of the photo-oxidation of Bu^tNO in the presence of 5 Torr of O_2 and 750 Torr of N_2 containing 100 p.p.m. of NO. These conditions excluded significant conversion of NO into NO_2 by the usual slow thermal oxidation of NO and resulted in a twentyfold increase of the yield of Bu^tONO at the expense of all other products as predicted by the Scheme.

Reactions analogous to (3) are of importance in the conversion of NO into NO_2 in photochemical smog.[8,9] The generally accepted view, that the important reaction of methylperoxyl radicals with NO produces NO_2 and $CH_3O\cdot$ has been questioned.[10] The effect of the small amounts of added NO found in this work, however, shows unambiguously that t-butylperoxyl radicals react as in reaction (3) rather than by the proposed alternative combination,[10] a conclusion which is in agreement with the results of the most recent reinvestigation of the reaction of the methylperoxyl radical with NO.[11] It is thus apparent that the photo-oxidation of nitrosoalkanes provides a model system for the study of the oxidation of low levels of NO to NO_2 by alkylperoxyl radicals which is complementary to and in some aspects more advantageous than the photo-oxidation of azoalkanes,[10,11] both methods being based on the photochemical production of alkyl radicals in the presence of O_2. The excited state mechanism proposed in the earlier work[1–5] for the photo-oxidation of nitrosoalkanes is ruled out by the present study.



SCHEME

The author thanks Professor B. G. Gowenlock for his interest in this work.

(*Received*, 23*rd February* 1976; *Com.* 185.)

---

[1] A. Mackor and Th. J. de Boer, *Rec. Trav. chim.*, 1970, **89**, 164.
[2] R. Stammer, J. B. F. N. Engberts, and Th. J. de. Boer, *Rec. Trav. chim.*, 1970, **89**, 169.
[3] J. A. Maassen and Th. J. de Boer, *Rec. Trav. chim.*, 1972, **91**, 1329.
[4] J. A. Maassen and Th. J. de Boer, *Rec. Trav. chim.*, 1973, **92**, 185.
[5] Y. L. Chow, J. N. S. Tam, and K. S. Pillay, *Canad. J. Chem.*, 1973, **51**, 2477.
[6] D. Hunter and J. Pfab, *Tetrahedron Letters*, submitted for publication.
[7] J. A. Maassen, Ph.D. Thesis, University of Amsterdam, 1972.
[8] J. N. Pitts, Jr., A. C. Lloyd, and J. L. Sprung, *Chem. Brit.*, 1975, **11**, 247.
[9] J. N. Pitts, Jr. and B. J. Finlayson, *Angew. Chem. Internat. Edn.*, 1975, **14**, 1.
[10] C. W. Spicer, A. Villa, H. A. Wiebe, and J. Heicklen, *J. Amer. Chem. Soc.*, 1973, **95**, 13.
[11] C. T. Pate, B. J. Finlayson, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, 1974, **96**, 6554.