

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

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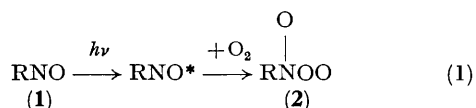
**Summary** The photo-oxidation of 2-methyl-2-nitrosopropane in the gas phase is shown to proceed by a dissociative mechanism *via* peroxy and alkoxy radicals and to provide a model system for the study of the oxidation of low levels of NO to NO<sub>2</sub>, which is of interest in studies of reactions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

THE photo-oxidation of nitrosoalkanes is reported to proceed *via* an intermediary diradical adduct (2) of O<sub>2</sub> to an excited state of the nitroso-compound leading either to quantitative formation of nitro-compounds in inert solvents<sup>1-3</sup> or to products explained by addition and abstraction reactions of (2)<sup>3,4</sup> in more reactive solvents. Recent

independent work appears to confirm a mechanism in which adducts (2) are formed.<sup>5</sup> On the other hand the photo-oxidation of *gem*-chloronitroso-compounds proceeds *via* photodissociation of (1) exclusively<sup>6</sup> 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.<sup>7</sup>

The results of a study of the photo-oxidation of 2-methyl-2-nitrosopropane (Bu<sup>t</sup>NO) in the gas phase reported here indicate that reaction (1) is unimportant.

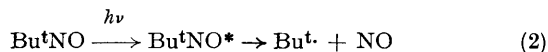
When 10–100 mTorr of gaseous Bu<sup>t</sup>NO were photolysed to completeness in the presence of a 10<sup>4</sup>–10<sup>5</sup>-fold excess of oxygen by brief exposure to intense 540–800 nm radiation† corresponding to the *n*\*→*π*\* absorption of the nitroso-chromophore, the main product (62%) was *t*-butyl nitrate as indicated by the i.r. bands of the product vapour at 1647 and 1309 cm<sup>-1</sup>. 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<sub>2</sub> and 750 Torr N<sub>2</sub>.

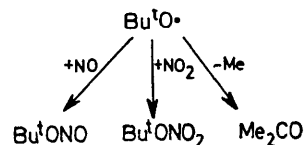
Mechanism (1)<sup>3</sup> requires that the nitro-compound be formed as the main product at sufficiently high [O<sub>2</sub>] to [Bu<sup>t</sup>NO] ratios. The complicated product pattern obtained in this work rules out mechanism (1), however, and can only be rationalised adequately by a mechanism based 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<sub>2</sub> virtually exclusively under the experimental conditions chosen, and will give rise to t-butoxyl radicals *via* the sequence (3).



The importance of alkoxy 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<sup>t</sup>NO in the presence of 5 Torr of O<sub>2</sub> and 750 Torr of N<sub>2</sub> containing 100 p.p.m. of NO. These conditions excluded significant conversion of NO into NO<sub>2</sub> by the usual slow thermal oxidation of NO and resulted in a twentyfold increase of the yield of Bu<sup>t</sup>ONO at the expense of all other products as predicted by the Scheme.

Reactions analogous to (3) are of importance in the con-

version of NO into NO<sub>2</sub> in photochemical smog.<sup>8,9</sup> The generally accepted view, that the important reaction of methylperoxy radicals with NO produces NO<sub>2</sub> and CH<sub>3</sub>O· has been questioned.<sup>10</sup> The effect of the small amounts of



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added NO found in this work, however, shows unambiguously that t-butylperoxy radicals react as in reaction (3) rather than by the proposed alternative combination,<sup>10</sup> a conclusion which is in agreement with the results of the most recent reinvestigation of the reaction of the methylperoxy radical with NO.<sup>11</sup> 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<sub>2</sub> by alkylperoxy radicals which is complementary to and in some aspects more advantageous than the photo-oxidation of azoalkanes,<sup>10,11</sup> both methods being based on the photochemical production of alkyl radicals in the presence of O<sub>2</sub>. The excited state mechanism proposed in the earlier work<sup>1–5</sup> for the photo-oxidation of nitrosoalkanes is ruled out by the present study.

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<sup>1</sup> A. Mackor and Th. J. de Boer, *Rec. Trav. chim.*, 1970, **89**, 164.

<sup>2</sup> R. Stammer, J. B. F. N. Engberts, and Th. J. de Boer, *Rec. Trav. chim.*, 1970, **89**, 169.

<sup>3</sup> J. A. Maassen and Th. J. de Boer, *Rec. Trav. chim.*, 1972, **91**, 1329.

<sup>4</sup> J. A. Maassen and Th. J. de Boer, *Rec. Trav. chim.*, 1973, **92**, 185.

<sup>5</sup> Y. L. Chow, J. N. S. Tam, and K. S. Pillay, *Canad. J. Chem.*, 1973, **51**, 2477.

<sup>6</sup> D. Hunter and J. Pfab, *Tetrahedron Letters*, submitted for publication.

<sup>7</sup> J. A. Maassen, Ph.D. Thesis, University of Amsterdam, 1972.

<sup>8</sup> J. N. Pitts, Jr., A. C. Lloyd, and J. L. Sprung, *Chem. Brit.*, 1975, **11**, 247.

<sup>9</sup> J. N. Pitts, Jr. and B. J. Finlayson, *Angew. Chem. Internat. Edn.*, 1975, **14**, 1.

<sup>10</sup> C. W. Spicer, A. Villa, H. A. Wiebe, and J. Hecklen, *J. Amer. Chem. Soc.*, 1973, **95**, 13.

<sup>11</sup> C. T. Pate, B. J. Finlayson, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, 1974, **96**, 6554.