Photo-oxidation of Nitrosamides

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IRRADIATION of nitrosamides causes homolytic cleavage to give nitric oxide and amido-radicals.[1–3] This process is followed by a series of reactions leading to exchange of the nitroso-group and a hydrogen atom to give a 4-nitroso-alkylamide (intramolecular exchange), the parent amide (intermolecular exchange), and other oxidation products.[2,3] The results of photolysis of *N*-hexyl-*N*-nitrosoacetamide (I) in benzene solution under various conditions are summarized in the Table.

No oxidation products, but only hexylacetamide (II) and the *anti*-dimer of *N*-(4-nitrosohexyl)acetamide (III), are formed on irradiation at above 400 nm. under nitrogen or helium (Expt. 1). The formation of *N*-(4-nitratohexyl)-acetamide (IV) and *N*-nitrohexylacetamide (V) in Expt. 2 therefore arises from the secondary photo-process of (III), which has strong absorption at 280—350 nm.[4] Indeed, under the irradiation conditions of Expt. 2,† (III) gives the nitrate (IV) and the parent amide (II).

$CH_3\cdot[CH_2]_5NAcX$
(I) $X = NO$
(II) $X = H$
(V) $X = NO_2$

$(C_2H_5\cdot CHX\cdot[CH_2]_3NHAc)n$
(III) $X = NO, n = 2$
(IV) $X = ONO_2, n = 1$

The dramatic increase of oxidation products (IV) and (V) at the expense of (III) in the presence of oxygen (Expts. 3 and 4) demonstrates the key role played by oxygen in the oxidation processes. Under the same conditions of Expt. 3, *anti*-dimer (III) is quantitatively oxidized to (IV), but not unless irradiated at >280 nm. Simultaneous irradiation of nitrosamide (I) and nitric oxide in benzene solution (Expt. 5) gives only the *anti*-dimer (III) and the parent amide (II), indicating that external nitric oxide does not assist in the oxidation processes. Since nitric oxide-saturated benzene solution absorbs strongly at 280—380 nm.,‡ *anti*-dimer (III) is not directly photoexcited in Expt. 5.

Yields of products (%)[a] *from photolysis of* (I)

Expt. No.	Conditions	(II)	(III)	(IV)	(V)
1	N_2 or He[b] >400 nm.	42	58	0	0
2	N_2 or He[b] >280 nm.	31·4	33·6	19·8	6·2
3	O_2 or air[c] >280 nm.	10	0	62	15·5
4	0_2 or air[c] >400 nm.	25·5	0	46·5	12
5	NO[d] >280 nm.	57·0	35·8	0	0

[a] The % yields are calculated on the basis of one mole of (I) to yield one mole of the products.

[b] Inert gases passed through Fieser's solution.

[c] The % yields fluctuate slightly under various O_2 (or air) pressures. Nitrobenzene and *o*- and *p*-nitrophenols were also detected by g.l.c.

[d] The system was thoroughly flushed with N_2 before NO was introduced.

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† It has been shown that irradiation of a dimer at >280 nm. causes dissociation to *C*-nitroso-monomer (refs. 3 and 5) which is further photolysed to an alkyl radical and nitric oxide (ref. 5).

‡ absorption may be due to some $\cdot NO_2$ present in commercial nitric oxide.

The photo-oxidation (Expt. 3) is a synthetically useful reaction, the scope of which is under investigation. It is assumed that nitric oxide from photodissociation of (I) or the *C*-nitroso-monomer of (III) is quickly oxidized§ to $\cdot NO_3$ which attacks the *C*- or *N*-radicals leading to (IV) or (V). Alternatively, fast combination of *C*- or *N*-radical with oxygen as the initial step of oxidation is also conceivable. The former process is favoured in view of the formation of nitrophenols as by-products in Expts. 3 and 4. Participation of singlet oxygen in the oxidation process is ruled out by the fact that Rose Bengal-sensitized oxygen[9] shows no effect on (III) in methanol solution.

$$\text{(I)} \xrightarrow{h\nu} CH_3\cdot[CH_2]_5\cdot\underset{\bullet}{N}Ac$$

$$CH_3\cdot[CH_2]_5\cdot\underset{\bullet}{N}Ac \rightarrow C_2H_5\cdot\underset{\bullet}{C}H\cdot[CH_2]_3\cdot NHAc$$

$$C_2H_5\cdot\underset{\bullet}{C}H[CH_2]_3\cdot NHAc + NO + O_2 \rightarrow \text{(IV)}$$

$$CH_3\cdot[CH_2]_5\cdot\underset{\bullet}{N}Ac + NO + \tfrac{1}{2}O_2 \rightarrow \text{(V)}$$

Disproportionation to a nitrate during homolytic cleavage of a *C*-nitroso-compound is known, and various mechanisms have been suggested.[10,11] The present results strongly suggest that an excited nitric oxide reacts to give oxygen¶ and that oxygen is the oxidation carrier in Expt. 2. The absence of oxidation products in Expt. 1 may suggest that the nitric oxide generated is not entirely free, but is paired with the amido-radical in a cage during hydrogen transfer. This would also explain the failure to improve the yield of (III) with externally added nitric oxide in Expt. 5.

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§ Gas-phase kinetics show the rates of combination of methyl radical with O_2 and NO are about the same, 10^8 M^{-1} sec.$^{-1}$ (refs. 6 and 7). The reaction of NO with O_2 is complicated (ref. 8) and no reliable rate is available.

¶ Nitrogen and oxygen have been postulated to be the initial products from a reaction of electronically excited nitric oxide (refs. 12 and 13) of either $a^4\Pi_i$ or $A^2\Sigma^2$ states in the gas phase.

[1] O. E. Edwards and R. S. Rosich, *Canad. J. Chem.*, 1965, **45**, 1287.

[2] L. P. Kuhn, G. G. Kleinspehn, and A. C. Duckworth, *J. Amer. Chem. Soc.*, 1967, **89**, 3858.

[3] Y. L. Chow, J. N. S. Tam, and A. C. H. Lee, *Canad. J. Chem.*, in the press.

[4] A. Mackor, Th. A. J. W. Wajer, and Th. J. deBoer, *Tetrahedron Letters*, 1967, 2757.

[5] A. Mackor, Th. A. J. W. Wajer, and Th. J. deBoer, *Tetrahedron Letters*, 1966, 2115.

[6] F. B. Marcotte and W. A. Noyes, jun., *Discuss. Faraday Soc.*, 1951, **10**, 236.

[7] R. W. Durham and E. W. R. Steacie, *J. Chem. Phys.*, 1952, **20**, 582.

[8] J. Heicklen and N. Cohen, *Adv. Photochem.*, 1968, **5**, 157.

[9] D. R. Kearns, R. A. Hollins, A. U. Khan, R. W. Chambers, and P. Radlick, *J. Amer. Chem. Soc.*, 1967, **89**, 5455, 5456; C. S. Fotte, *Accounts Chem. Res.*, 1968, **1**, 104.

[10] J. F. Brown, jun., *J. Amer. Chem. Soc.*, 1957, **79**, 2480.

[11] A. Mackor, Th. A. J. W. Wajer, and Th. J. deBoer, *Tetrahedron*, 1968, **24**, 1623.

[12] O. P. Strausz and H. E. Gunning, *Canad. J. Chem.*, 1961, **39**, 2549.

[13] J. J. McGee and J. Heicklen, *J. Chem. Phys.*, 1964, **41**, 2974.