Studies in Vacuum Ultraviolet Photochemistry. Part III.† 2-Methyl-2-nitropropane, 2-Methyl-2-nitrosopropane, and t-Butyl Nitrite

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2-Methyl-2-nitropropane, t-butyl nitrite and 2-methyl-2-nitrosopropane have been photolysed in the gas phase at 147 and 123·6 nm to conversions of <1%. The main primary processes are (i)—(iii). For the nitrite there is

$$Bu^t\text{–}NO_2 + h\nu \longrightarrow Bu^t + NO_2 \qquad (i)$$

$$Bu^t\text{–}ONO + h\nu \longrightarrow Bu^t + NO_2 \qquad (ii)$$

$$Bu^t\text{–}NO + h\nu \longrightarrow Bu^t + NO \qquad (iii)$$

another important process (iv), the nitric oxide being produced in an electronically excited state which fluoresces.

$$Bu^t\text{–}ONO + h\nu \longrightarrow Bu^tO + NO(A^2\Sigma^+) \qquad (iv)$$

The overall photochemistry is interpreted on the basis of these primary processes, and subsequent reaction of the fragments produced in these processes.

THE gas-phase photochemistry of nitro- and nitroso-alkanes and alkyl nitrites is known to be complex. Studies to date have utilised radiation of wavelength longer than 200 nm, when the major photodissociative process in alkyl nitrites is homolytic cleavage of the RO–NO bond[1,2] [reaction (1)]. Molecular processes

$$RO\text{–}NO + h\nu \longrightarrow RO + NO \qquad (1)$$

such as reaction (2) have been shown to be unimportant

$$RCH_2ONO + h\nu \longrightarrow RCHO + HNO \qquad (2)$$

at 366 nm. The dominant primary dissociative process in nitroalkanes[3] is the homolysis (3). Formation of

$$R\text{–}NO_2 + h\nu \longrightarrow R + NO_2 \qquad (3)$$

nitrous acid and an olefin [reaction (4)] may be important in some nitroalkanes.[3] Limited data on aliphatic

$$RCH_2CH_2NO_2 + h\nu \longrightarrow RCH{=}CH_2 + HNO_2 \qquad (4)$$

nitroso-compounds[4,5] indicate that the homolysis (5)

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† Part II, ref. 15.

[1] G. R. McMillan, *J. Phys. Chem.*, 1963, **67**, 931.

[2] G. R. McMillan, *J. Amer. Chem. Soc.*, 1962, **84**, 4007.

[3] H. Feuer, 'The Chemistry of Nitro and Nitroso Groups,' Interscience, London, 1969.

[4] J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, p. 476.

[5] J. R. Dickson and B. G. Gowenlock, *Annalen*, 1971, **745**, 152.

is important even at 700 nm. A molecular process

$$\text{R-NO} + h\nu \longrightarrow \text{R} + \text{NO} \tag{5}$$

[reaction (6)], analogous to reaction (4) for nitro-compounds, may also occur for nitroso-compounds.[5]

$$\text{RCH}_2\text{CH}_2\text{NO} + h\nu \longrightarrow \text{RCHCH}_2 + \text{HNO} \tag{6}$$

We have photolysed the compounds 2-methyl-2-nitropropane, 2-methyl-2-nitrosopropane, and t-butyl nitrite at 147 and 123 nm in the vacuum u.v. region of the spectrum to compare the photochemistry with that occurring in the near u.v.

EXPERIMENTAL

The apparatus and experimental procedure have been described previously.[6] Pressures (0—250 Torr) were measured with an SE Laboratories SE42 pressure transducer. Photolyses were carried out at ambient temperature (*ca.* 23 °C) to conversions of 0·05—1%. Product analysis was by g.l.c. on the following columns: (a) 2 m di-isodecyl phthalate, (b) 2, 4, and 7 m squalane, (c) 1·2 m Linde 5A molecular sieve, (d) 4 m Phasepak P, and (e) 2 m Carbowax 20M. In some photolyses gases non-condensable at 77 or 146 K were analysed on an A.E.I. MS10 mass spectrometer operating at low electron voltages (10, 15, and 20 eV). Some analyses were performed on an A.E.I. MS30 integrated g.l.c.–m.s. instrument.

Authentic samples of photolysis products (except nitrosomethane) were used to calibrate the g.l.c. for retention times and for peak enhancement. Nitrosomethane was identified from g.l.c.–m.s. (large *m/e* at 45, 30 and 15), and by u.v. absorption. The products of the photolysis were condensed into a small sample tube, and warmed and cooled a number of times to promote dimerisation of monomeric *C*-nitroso-compounds. All compounds volatile at room temperature were removed by pumping at high vacuum, leaving small quantities of a white, involatile solid. The u.v. spectrum of this solid in ether showed $\lambda_{\text{max.}}$ 280 nm. Extraction of the ether solution with water gave a solution with $\lambda_{\text{max.}}$ 270 and 205 nm. This is characteristic of the *trans*-dimeric nitrosomethane in ether changing to the *cis*-dimer in water, with some formation of the oxime in the hydroxylic solvent.[7]

TABLE 1

Photolysis of 2-methyl-2-nitropropane at an initial pressure of 5 Torr

λ/nm Additive (Torr)	123 Non	123 O_2 (2)	123 H_2S (1)	123 N_2 (700)	147 None	147 O_2 (2)	147 N_2 (700)
Methane	2	2	21	3	0·6	0	0·5
Acetylene	0·4	0·6	0·2	0·2	0·1	*a*	*a*
Ethylene	0·6	0·7	0·4	0·3	0·2	*a*	*a*
Ethane	0·6	0·1	0·2	0·5	*a*	0	*a*
Propene	10	8	8	10	14	16	15
Methylacetylene	0·5	0·4	0·2	0·2			
Methyl nitrite	14	1·6	0·1	17	4	2	3
Allene	0·5	0·3	0·2	0·1	0·1	0·1	0·1
Isobutane	0·4	*a*	63	0·8	*a*	*a*	*a*
Isobutene	100	100	100	100	100	100	100
Nitrosomethane	52	13	1·5	59	18	3	21
Acetaldehyde	0·7	3		2	*a*	5	*a*
2-Methyl-2-nitrosopropane	62	1	0·4	57	22	*a*	16
Acetone	14	120	*a*	2	15	109	14
Isobutene oxide	12	13	*a*	13	2	49	5
t-Butyl nitrite	7	*a*	0·1	27	9	*a*	26
Isobutyraldehyde	6	17	*a*	11	7	27	8
Methyl nitrate	0·5	60		3	1	20	2

[a] Trace amount.

G.l.c. analysis of nitrosomethane was less reproducible than for the other products. This we assume to be due to dimerisation or to reaction with *e.g.* nitric oxide or nitrogen dioxide, as the g.l.c. peak decreased the longer the mixture was allowed to remain in the reaction vessel after photolysis. A similar, but smaller, effect was observed for 2-methyl-2-nitrosopropane.

Commercial 2-methyl-2-nitropropane was distilled *in vacuo* until pure by g.l.c.

t-Butyl nitrite was prepared from t-butyl alcohol,[8] subjected to repeated distillation *in vacuo* until the vapour was pure by g.l.c., and stored over freshly regenerated crushed molecular sieve to prevent hydrolysis.

trans-Dimeric 2-methyl-2-nitrosopropane was prepared by the method of Gowenlock and Trotman,[9] purified by recrystallisation, and distilled *in vacuo*. The *trans*-dimer was converted to the monomer before use, and stored at 77 K in a blackened bulb. When pressures of 5 Torr or less were used only small amounts of impurity could be detected. At higher pressures there was evidence of decomposition, either on the walls of the vacuum system, or in the g.l.c. Consequently pressures no greater than 5 Torr were used.

RESULTS

2-Methyl-2-nitropropane.—Photolysis of 2-methyl-2-nitropropane yielded a complex mixture of products; those identified were methane, ethane, isobutane, acetylene, ethylene, propene, methylacetylene, allene, isobutene, acetaldehyde, acetone, isobutene oxide, isobutyraldehyde, nitrosomethane (monomer), 2-methyl-2-nitrosopropane (monomer), methyl nitrite, t-butyl nitrite, methyl nitrate,

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[6] B. G. Gowenlock and C. A. F. Johnson, *J.C.S. Perkin II*, 1972, 1150.

[7] B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1955, 4190.

[8] W. A. Noyes, *Org. Syntheses*, 1936, **16**, 7.

[9] B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1956, 1670.

and nitromethane. Nitrogen dioxide, nitric oxide, and trace amounts of nitrogen and hydrogen were also present. Typical results are shown in Table 1. There was no significant change in product distribution at pressures of 3—20 Torr, but a number of products became increasingly important as conversion increased (0·05—1%). These were the two nitroso-compounds, methyl nitrite, acetone, isobutene oxide, and isobutyraldehyde. t-Butyl nitrite increased at first and then became essentially constant. At a pressure of 1 Torr increased yields of the smaller hydrocarbons, especially unsaturated ones, were obtained. In the presence of hydrogen sulphide the major products were isobutene, isobutane, propene, and methane. When nitric oxide was used as a radical scavenger isobutene and propene were the major hydrocarbon products, together with nitrosomethane and 2-methyl-2-nitrosopropane as the other important products.

t-Butyl Nitrite.—Photolysis of t-butyl nitrite proved less complex than that of the nitro-compound. Products identified were methane, ethane, isobutane, acetylene, ethylene, propene, methylacetylene, allene, isobutene, acetone, methyl nitrite, nitrosomethane, and 2-methyl-2-nitrosopropane. 2-Methyl-2-nitropropane was not a product, but very small quantities of t-butyl nitrate were formed. Nitrogen dioxide, nitric oxide, and trace amounts of nitrogen, hydrogen, and possibly nitrous oxide were indicated from mass spectrometric analysis. Typical results are shown in Table 2. Little variation in product distribution occurred at pressures of 4—25 Torr and up to 0·6% conversion. In the presence of hydrogen sulphide the major products are methane, isobutene, acetone, isobutane and some nitrosomethane. In the presence of nitric oxide the major products are nitrosomethane, acetone, isobutene, 2-methyl-2-nitrosopropane, and some methyl nitrite.

TABLE 2

Photolysis of t-butyl nitrite at an initial pressure of 5 Torr

λ/nm Additive (Torr)	123 None	123 NO (1)	123 H_2S (1)	123 N_2 (700)	147 None	147 NO (1)	147 H_2S (1)	147 N_2 (700)
Methane	16		360	24	18		230	32
Acetylene	*a*	*a*	*a*	*a*	0·2	0·3	*a*	0·1
Ethylene	3	3	4	3	1	1·5	*a*	1
Ethane	20	0·6	3	16	25	0	3	16
Propene	9	10	11	11	11	13	12	14
Methylacetylene	*a*	0·2	0·2	0·2	0·2	0·2	*a*	0·3
Methyl nitrite	46	15	3	31	22	3	*a*	
Allene	*a*	0·2	0·3	*a*	0·1	0·2	*a*	*a*
Isobutane	*a*	0	38	0·7	1	0	40	2
Nitrosomethane	250	230	24	190	176	210	29	200
Isobutene	100	100	100	100	100	100	100	100
Acetone	180	134	142	178	201	173	187	223
2-Methyl-2-nitrosopropane	53	50	0	31	97	92	0	56

[a] Trace amount.

2-Methyl-2-nitrosopropane.—Photolysis of this compound gave isobutene, propene and nitrosomethane as the most important products. Typical results are shown in Table 3. At pressures of *ca.* 1 Torr a wide range of small hydrocarbons were produced, indicating extensive fragmentation of the parent molecule. Trace amounts of t-butyl nitrite, t-butyl nitrate, and 2-methyl-2-nitropropane were detected in one photolysis taken to *ca.* 10% conversion.

TABLE 3

Photolysis of 2-methyl-2-nitrosopropane

λ/nm	147	147	123	123
Pressure (Torr)	5	5	5	1
Additive	None	H_2S	None	None
Methane	3·7	84	3	103
Acetylene	*a*	*a*	*a*	22
Ethylene	1·4	1·0	1·0	18
Ethane		*a*	0·5	31
Nitrosomethane	68	4	56	150
Propene	24	26	20	29
Methylacetylene	*a*	*a*	*a*	31
Allene	0·6	0·4	0·2	37
Isobutane	1·1	42	1	5·7
Isobutene	100	100	100	100

[a] Trace amount.

DISCUSSION

t-Butyl Nitrite.—The major photodissociative process in alkyl nitrites in the near u.v. is homolytic cleavage of the RO–NO bond to form an alkoxyl radical and nitric oxide.[1,2] Photolysis of t-butyl nitrite would occur as in reaction (7). The t-butoxyl radical may be formed

$$\mathrm{Bu^t{-}ONO} + h\nu \longrightarrow \mathrm{Bu^t{-}O} + \mathrm{NO} \qquad (7)$$

in an excited state (vibrational and/or electronic). Subsequent decomposition [reaction (8)] may occur.

$$\mathrm{Bu^t{-}O} \longrightarrow \mathrm{CH_3} + \mathrm{CH_3COCH_3} \qquad (8)$$

Inspection of Table 2 shows that a similar reaction sequence must occur in the far u.v., acetone being a major product.

The RO–NO bond fission (7) is *ca.* 160 kJ mol^{-1} endothermic.[10] Radiation at 123 and 147 nm corresponds to energies of 970 and 815 kJ einstein^{-1} respectively. As reaction (8) is only *ca.* 29 kJ mol^{-1} endothermic,[11] it is not surprising that fragmentation of the t-butoxyl radical occurs. It has been shown in this laboratory[12] that photolysis of both t-butyl and

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[10] P. Gray and A. Williams, *Chem. Rev.*, 1959, **59**, 239.

[11] S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502.

[12] B. G. Gowenlock, C. A. F. Johnson, and I. Kirkhope, unpublished results.

isopropyl nitrites at 123 nm produces an intense emission corresponding to the nitric oxide γ-system ($A^2\Sigma^+ \longrightarrow X^2\pi$). The fluoresence spectrum is centred upon the V', V'' (0,0) transition at 226·6 nm, with bands being observed from *ca.* 300 to 185 nm (the short wavelength limit of the monochromator). Thus an important primary process gives a nitric oxide molecule carrying at least 525 kJ mol^{-1}, possibly as much as 650 kJ mol^{-1}, excess of electronic and vibrational energy. This leaves 155—280 kJ mol^{-1} residing in the t-butoxyl fragment (assuming little excess of translational energy in the NO molecule). Thus reaction (8) may be rapid. Evidence that stable t-butoxyl radicals are produced in this system is lacking. Addition of an atmosphere of nitrogen had no significant effect on the yield of acetone. No t-butyl alcohol could be detected when hydrogen sulphide was added, while reaction with nitric oxide would reform t-butyl nitrite. One product derived from the t-butoxyl radical could be t-butyl nitrate, arising from combination with nitrogen dioxide [reaction (9)]. However, nitrogen dioxide is known

$$\mathrm{Bu^t{-}O + NO_2 \longrightarrow Bu^tONO_2} \qquad (9)$$

to oxidise nitroso-compounds to nitro-compounds[13,14] [reaction (10)]. In principle, an analogous reaction

$$\mathrm{RNO + NO_2 \longrightarrow RNO_2 + NO} \qquad (10)$$

could occur with nitrites to form nitrates [reaction (11)], although there is no report of this reaction in the

$$\mathrm{RO{-}NO + NO_2 \longrightarrow RONO_2 + NO} \qquad (11)$$

literature. Thus reaction (11), rather than reaction (9) could be the source of the very small amounts of t-butyl nitrate detected. The observation that addition of hydrogen sulphide had little effect on the yield of acetone supports the conclusion that rapid decomposition of the t-butoxyl radical occurs.

In the near u.v., photolysis of alkyl nitrites occurs almost exclusively by process (7). The data in Table 2 show that in the far u.v., process (7) is not the sole primary process. Formation of 2-methyl-2-nitrosopropane, and of isobutane when H_2S is added, implies production of t-butyl radicals in a primary process [reaction (12)]. If the t-butyl radical carries an excess

$$\mathrm{Bu^t{-}ONO} + h\nu \longrightarrow \mathrm{Bu^t + NO_2} \qquad (12)$$

of energy, then decomposition in processes such as (13) and (14) may occur. Minor products such as

$$\mathrm{Bu^t \longrightarrow H + C_4H_8} \qquad (13)$$

$$\mathrm{Bu^t \longrightarrow CH_3 + C_3H_6} \qquad (14)$$

ethylene, allene, and methylacetylene could result either from further decomposition of the olefins formed in reactions (13) and (14) or from subsequent photolysis of the olefins. The overall C_1—C_4 hydrocarbon product distribution is not unlike that produced in the vacuum u.v. photolysis of 2,2,3,3-tetramethylbutane[6] and of 2,2,4-trimethylpentane,[15] both of which give C_4 radical fragments.

Methyl nitrite, nitrosomethane, and 2-methyl-2-nitrosopropane would be produced in the combination reactions (15)—(17). The decrease in yield of these

$$\mathrm{CH_3 + NO_2 \longrightarrow CH_3ONO} \qquad (15)$$

$$\mathrm{CH_3 + NO \longrightarrow CH_3NO} \qquad (16)$$

$$\mathrm{Bu^t + NO \longrightarrow Bu^tNO} \qquad (17)$$

compounds, together with a corresponding increase in methane and isobutane, when hydrogen sulphide was added is consistent with this scheme.

In our studies we could not determine whether the possible primary process (18) occurred. The HNO_2

$$\mathrm{Bu^tONO} + h\nu \longrightarrow \mathrm{C_4H_8 + HNO_2} \qquad (18)$$

species would not have been detected in our analyses, and the isobutene would be indistinguishable from that produced in reaction (13), unless all the t-butyl radicals could be intercepted by radical scavengers. As appreciable amounts of isobutene are produced in processes unaffected by change in pressure or by addition of radical scavengers, reaction (18) may occur to some extent.

If it is assumed that the amount of acetone is a measure of primary process (7), and the sum of isobutene, propene, and 2-methyl-2-nitrosopropane is a measure of primary processes (12) and (18), then the ratio (1) : (12) + (18) is *ca.* 1 at both wavelengths. The data also indicate that the ratio methyl radical : t-butyl radical is higher at the shorter wavelength, suggesting faster decomposition of the t-butyl radicals with increasing incident energy.

2-*Methyl-2-nitropropane*.—Photolysis of 2-methyl-2-nitropropane is complicated by the occurrence of a number of secondary reactions. Photolysis of mixtures of H_2S and 2-methyl-2-nitropropane yield methane, propene, isobutane, and isobutene as the major hydrocarbon products. By analogy with the near u.v. photolysis, the main primary dissociation is likely to be that producing t-butyl radicals and nitrogen dioxide [reaction (19)]. The product yield in the presence of H_2S

$$\mathrm{Bu^tNO_2} + h\nu \longrightarrow \mathrm{Bu^t + NO_2} \qquad (19)$$

can be explained on the basis of this primary process, if the t-butyl radicals are produced in varying degrees of excitation, and some decompose [reactions (20) and (21)]. These conclusions are reinforced by the

$$\mathrm{Bu^t \longrightarrow H + C_4H_8} \qquad (20)$$

$$\mathrm{Bu^t \longrightarrow CH_3 + C_3H_6} \qquad (21)$$

observation that isobutene, propene, nitrosomethane,

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[13] L. Phillips and R. Shaw, 10th Symposium on Combustion, Combustion Institute, Pittsburgh, 1965, p. 453.

[14] P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *J.C.S. Perkin II*, 1972, 1379.

[15] B. G. Gowenlock, C. A. F. Johnson, and E. Senogles, *J.C.S. Perkin II*, 1972, 1386.

and 2-methyl-2-nitrosopropane are the major products when nitric oxide is added to the photolysis.

A further primary process [reaction (22)], analogous to reaction (18) for the nitrite, may also participate in the photolysis.

$$\mathrm{Bu^tNO_2} + h\nu \longrightarrow \mathrm{C_4H_8} + \mathrm{HNO_2} \qquad \text{(22)}$$

When the nitro-compound is photolysed in the absence of radical scavenger, a number of secondary reactions occur. We propose reactions (23)—(31) to account for the observed product distribution. Formation of t-butyl nitrite is not a direct isomerisation, but recombination of a t-butyl radical with nitrogen dioxide [reaction (23)], because the nitrite yield approaches zero when radical scavenger is added. It is known[16] that formation of alkyl nitrites in the gas phase by reaction (23) is energetically unfavourable. To prevent subsequent RO–NO fission, energy of *ca.* 85 kJ $\mathrm{mol^{-1}}$ has to be dissipated by collision; if either of the combining species carries an excess of energy, then this too must be dissipated. Thus at low pressures reaction (24), followed by reaction (25), occurs. Greater yields of nitrite are produced when an atmosphere of nitrogen is added to the system.

$$\mathrm{Bu^t} + \mathrm{NO_2} \longrightarrow \mathrm{Bu^t{-}ONO} \qquad \text{(23)}$$

$$\mathrm{Bu^t{-}ONO} \longrightarrow \mathrm{Bu^tO} + \mathrm{NO} \qquad \text{(24)}$$

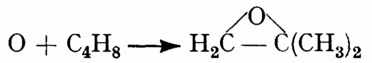
$$\mathrm{Bu^tO} \longrightarrow \mathrm{CH_3} + \mathrm{CH_3COCH_3} \qquad \text{(25)}$$

$$\mathrm{NO_2} \longrightarrow \mathrm{NO} + \mathrm{O} \qquad \text{(26}$$

$$\mathrm{Bu^t} + \mathrm{NO} \longrightarrow \mathrm{Bu^tNO} \qquad \text{(27)}$$

$$\mathrm{CH_3} + \mathrm{NO} \longrightarrow \mathrm{CH_3NO} \qquad \text{(28)}$$

$$\mathrm{CH_3} + \mathrm{NO_2} \longrightarrow \mathrm{CH_3ONO} \qquad \text{(29)}$$



$$\mathrm{O} + \mathrm{C_4H_8} \longrightarrow \mathrm{H_2C}\overset{\mathrm{O}}{\text{—}}\mathrm{C(CH_3)_2} \qquad \text{(30)}$$

$$\mathrm{O} + \mathrm{C_4H_8} \longrightarrow \mathrm{(CH_3)_2CHCO} \qquad \text{(31)}$$

Reaction (26) must be important as the amount of nitric oxide produced is too great to be accounted for by reaction (24) alone, and production of some of the oxygen-containing compounds requires the participation of oxygen atoms. Combination of methyl and t-butyl radicals with nitric oxide results in the nitroso-compounds [reactions (27) and (28)], while combination of methyl radicals and nitrogen dioxide results in the preferential formation of the nitrite [reaction (29)], only trace amounts of nitromethane being detected. It should be noted that formation of 2-methyl-2-nitrosopropane is by combination [reaction (27)], and not by direct dissociation of the nitro-compound [reaction (32)], the parallel to which is believed to occur in some aromatic nitro-compounds, because the formation of nitroso-compound is inhibited by addition of $\mathrm{H_2S}$.

$$\mathrm{Bu^tNO_2} + h\nu \longrightarrow \mathrm{Bu^tNO} + \mathrm{O} \qquad \text{(32)}$$

Production of isobutene oxide and isobutyraldehyde implies reaction of oxygen atoms with isobutene, by addition to the double bond followed either by ring closure or isomerisation [reactions (30) and (31)]. Both are important products of the reaction between oxygen atoms and isobutene.[17] The increase in the oxygen-containing compounds, especially of acetone, when oxygen is added to the photolysis suggests that additional reactions are occurring in which radicals and/or olefins are being oxidised. Cvetanovic[17] noted a very significant increase in yield of acetone when molecular oxygen was added to photolysing mixtures of isobutene–nitrogen dioxide.

The source of the minor hydrocarbon products is presumably from breakdown of other hydrocarbon products such as isobutene or propene due to either an excess of energy carried over from the primary step, or by direct photolysis.

2-Methyl-2-nitrosopropane.—The limited data obtained for this compound showed the major products to be isobutene, nitrosomethane, and propene. These products can be explained on the basis of the primary process [reaction (33)] producing t-butyl radicals and nitric oxide. Subsequent decomposition of some t-butyl radicals, followed by reaction of nitric oxide and methyl radicals, would account for the observed products [reactions (34)—(36)]. The appearance of methane and isobutane, together with isobutene and propene as major products when $\mathrm{H_2S}$ was added is consistent with this scheme. The minor hydrocarbon products arise from fragmentation of the olefinic products as observed with the nitrite and the nitro-compound.

$$\mathrm{Bu^tNO} + h\nu \longrightarrow \mathrm{Bu^t} + \mathrm{NO} \qquad \text{(33)}$$

$$\mathrm{Bu^t} \longrightarrow \mathrm{H} + \mathrm{C_4H_8} \qquad \text{(34)}$$

$$\mathrm{Bu^t} \longrightarrow \mathrm{CH_3} + \mathrm{C_3H_6} \qquad \text{(35)}$$

$$\mathrm{CH_3} + \mathrm{NO} \longrightarrow \mathrm{CH_3NO} \qquad \text{(36)}$$

There is an excess of methyl radicals over propene, suggesting that a primary process (37) producing methyl radicals occurs. Primary processes of this form may also participate to a much lesser degree in the photolysis of the nitrite and nitro-compounds.

$$\mathrm{Bu^tNO} + h\nu \longrightarrow \mathrm{CH_3} + \mathrm{(CH_3)_2CNO} \qquad \text{(37)}$$

It is to be expected that a number of other products would be produced,[5] derived from addition of radicals to the nitroso-compound, producing initially nitroxides. These products would not be observed in our analyses. This would apply also in the photolysis of the nitrite and nitro-compounds, which both yield nitroso-compounds as products. Nitroso-compounds are known[5] to react with nitric oxide, the final products including nitrogen, nitrous oxide, the nitro-compound, the nitrite, and the nitrate. This would account for the small amounts of these products observed when the photolysis is taken to high conversion.

[16] P. Gray, *Trans. Faraday Soc.*, 1955, **51**, 1367.

[17] R. J. Cvetanovic, *Canad. J. Chem.*, 1958, **36**, 623, 970.

The first ionisation potential of 2-methyl-2-nitrosopropane is 8·6 eV, measured by photoelectron spectroscopy.[18] The 147 nm line corresponds to an energy of 8·4 eV, while the 123 nm line corresponds to 10 eV. It is therefore possible that ionisation occurs at 123 nm. From our data, we are unable to detect any significant change in products at the shorter wavelength, and so the influence of ionisation processes, if they occur, cannot be judged.

The ionisation potentials of nitroethane, 1-nitropropane, and 2-nitropropane are 10·9, 10·8, and 10·7 eV respectively,[19] therefore ionisation of 2-methyl-2-nitropropane would not occur at either of the wavelengths used in this study. Data for simple nitrites are lacking. However, comparison with the nitro-compounds and nitrates (I.P. >11·0 eV) suggests that ionisation processes should be unimportant at both wavelengths.

Conclusions.—When the compounds Bu^t–X, where X = NO_2, ONO, or NO, are photolysed at wavelengths of 123·6 and 147 nm, an important primary process is that involving fission of the Bu^t–X bond. In the case when X = ONO a further process is possible, leading to fission of the Bu^tO–NO bond. The observed overall photochemistry of these systems can then be interpreted in terms of subsequent reactions of the t-butyl and X fragments. In contrast to many hydrocarbon photolyses at these wavelengths there is extensive free radical participation in the overall mechanism, while molecular processes are relatively unimportant.

It is of interest to note that while both the nitrite and nitro-compound undergo R–X fission, producing NO_2, only in the case of the nitro-compound is the NO_2 carrying a sufficient excess of energy to decompose further to nitric oxide and an oxygen atom.

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[18] P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *J.C.S. Perkin II*, 1973, 1853.

[19] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Heron, K. Draxl, and F. H. Field, Nat. Bur. Stand., NSRDS-NBS 26.