THE PHOTOLYSIS OF t-BUTYL, ISOPROPYL AND ETHYL NITRITES AT 254 nm
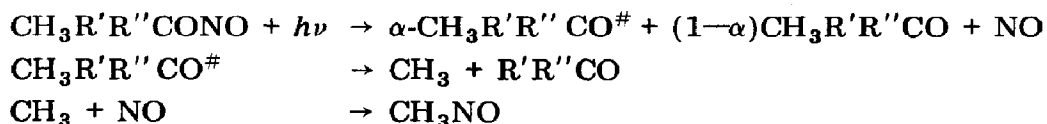
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Summary

The main primary photochemical process for alkyl nitrites is fission to nitric oxide and alkoxy radicals, a proportion of which may be sufficiently excited to decompose spontaneously. The photolysis of t-butyl, of isopropyl and of ethyl nitrite at 254 nm, in the gas phase, each yields nitrosomethane and an aldehyde or ketone. The overall reaction, in presence of nitric oxide, corresponds to:

$$CH_3R'R''CONO + h\nu \rightarrow \alpha\text{-}CH_3R'R'' CO^{\#} + (1-\alpha)CH_3R'R''CO + NO$$
$$CH_3R'R'' CO^{\#} \rightarrow CH_3 + R'R''CO$$
$$CH_3 + NO \rightarrow CH_3NO$$

where R' and R'' are either H or CH_3.

The dependence of the quantum yield of nitrosomethane and of other products on the pressure of alkyl nitrite, of nitric oxide and of other added gases was investigated to seek confirmation of the excited alkoxy mechanism, to determine primary yield and to obtain information about the deactivation of excited radicals.

The results for t-butyl nitrite fully confirm the excited alkoxy mechanism. A value of 0.87 is derived for the quantum yield of t-butoxy radicals sufficiently excited to undergo decomposition, in excellent agreement with a previous estimate. The results for ethyl nitrite also support the excited alkoxy mechanism, with the quantum yield of excited ethoxy radicals estimated to be 0.45. The results for isopropyl nitrite differ in several respects from those for the other two systems. A contribution from a primary process involving an intramolecular rearrangement to nitrosomethane and acetaldehyde cannot be excluded, although an alternative explanation in terms of an excited alkoxy mechanism is suggested.

Introduction

Alkyl nitrites absorb light in a banded region from 320 to 400 nm and more strongly in a continuous region below 300 nm. In both regions the main primary photochemical process [1] can be represented by:

$$PR'R''CONO + h\nu \rightarrow \alpha\text{-}RR'R''CO^{\#} + (1 - \alpha)RR'R''CO + NO \qquad (1)$$
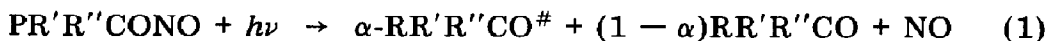
where R,R'R'' are alkyl radicals or H atoms. α represents the fraction of alkoxy radicals which are sufficiently excited to undergo fission according to reaction (2):

$$RR'R''CO^{\#} \rightarrow R'R''CO + R \qquad (2)$$

As in the thermal reaction [2] it is, predominantly, the largest alkyl substituent on the carbon which splits off leaving the corresponding aldehyde or ketone. At 254 nm, Φ_1 and α have been reported to be near unity for isopropyl [3], t-butyl [4] and t-amyl nitrites [5]. At 366 nm Φ_1 is near unity [6] for t-butyl nitrite but is less for other nitrites [7]; at this wavelength the contribution from excited alkoxy decomposition is small. Methyl radicals have been detected [8] in the flash photolysis of t-butyl, isopropyl and ethyl nitrites in accordance with their formation from excited alkoxy radicals:

$$(CH_3)_3CO^{\#} \rightarrow CH_3 + CH_3COCH_3 \qquad (2a)$$

$$(CH_3)_2CHO^{\#} \rightarrow CH_3 + CH_3CHO \qquad (2b)$$

$$CH_3CH_2O^{\#} \rightarrow CH_3 + CH_2O \qquad (2c)$$

The photolysis of t-butyl nitrite at 254 nm has been previously investigated [4] in some detail. Quantum yields of acetone are in accord with its formation as in the above mechanism and provide evidence for the collisional deactivation of excited alkoxy radicals by nitric oxide and other gases (3)

$$RR'R''CO^{\#} + M \rightarrow RR'R''CO + M' \qquad (3)$$

Methyl radicals can either recombine (4) or react with nitric oxide (5) formed in the primary process to form nitrosomethane:

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (4)$$

$$CH_3 + NO \rightarrow CH_3NO \qquad (5)$$

In presence of nitric oxide at a pressure sufficient to suppress reaction (4) the yield of nitrosomethane should equal that of the carbonyl compound. Although nitrosomethane is a well established product [9, 10] of the photolysis of t-butyl nitrite its quantitative estimation has proved difficult [4, 11], and quantum yields for its formation were not reported.

No detailed account of the photolysis, at 254 nm, of isopropyl nitrite has been published but a quantum yield of 0.86 for acetaldehyde formation in this system has been cited [1, 3] as evidence that both Φ_1 and α are near unity. There is little quantitative information about the photolysis

of ethyl nitrite at 254 nm. There is no evidence for the formation of excited ethoxy radicals in the photolysis of peroxides [12] or of esters [13] under conditions where excited t-butoxy and isopropoxy radicals contribute to the reaction.

The reaction of nitrosomethane with nitric oxide to form nitrogen dioxide affords a method for its determination [10], [14]. In this investigation nitrosomethane yields, along with those of some of the other products, in the photolysis of t-butyl, isopropyl and ethyl nitrite at 254 nm have been determined in order to obtain further information about the primary photochemical quantum yields and to compare the behaviour of excited alkoxy radicals formed under similar conditions.

Experimental

Materials

The alkyl nitrites prepared [9, 10] from the corresponding alcohols were stored at low temperature and redistilled *in vacuo* immediately before preparing reaction mixtures. Nitric oxide (Air Products Ltd.) was purified by repeated distillation at low temperature on the vacuum line. Nitrogen dioxide, obtained from the action of oxygen on nitric oxide, was redistilled *in vacuo*. White spot nitrogen was passed repeatedly through a trap cooled in liquid nitrogen. Other chemicals were degassed and, where appropriate, purified by redistillation on the vacuum line.

Apparatus and procedure

Two optical arrangements were used. In apparatus A nitrosomethane was determined from the amount of nitrogen dioxide ultimately formed after the addition of a standard pressure of nitric oxide. The radiation source was a Hanovia low pressure mercury lamp, 90% of whose energy output is at 254 nm. The light filtered by 1 cm of a solution containing 350 g/dm^3 hydrated cobalt sulphate and 105 g/dm^3 hydrated nickel sulphate was focused within the diameter of the reaction vessel, a silica spectrophotometer cell, 10 cm in length and 2 cm in diameter, which received about 1.5×10^{14} quanta/s of light essentially at 254 nm. After irradiation of a reaction mixture, nitric oxide was added to a pressure of 300 Torr. After one hour when the thermal reaction was complete the nitrogen dioxide was determined from its absorption at 450 nm using a Unicam SP500 spectrophotometer. The nitrosomethane yield, which is proportional to the nitrogen dioxide yield, was calculated from the previously determined proportionality constant [10].

In apparatus B the nitrosomethane was determined from the rate [14] of formation of nitrogen dioxide, on the addition of nitric oxide using a balanced photomultiplier system similar to that described previously [15]. The radiation source was a Hanovia medium pressure lamp with Vycor envelope, whose output was restricted to the region of 254 nm by filtering

through 2 cm of the above cobalt–nickel filter and 2 cm of chlorine at atmospheric pressure. The light was deflected through 90 ° by a silica coated aluminized mirror and focused within the reaction vessel, which was 7.5 cm in length and 4 cm in diameter. The incident light intensity was about 6×10^{14} quanta/s. After irradiation of a reaction mixture, nitric oxide was added to a pressure of 300 Torr, the photomultiplier system was balanced and after 10 minutes the off-balance current was measured. From appropriate calibration under identical conditions the pressure of nitrogen dioxide formed in 10 minutes was related to the yield of nitrosomethane. The photolysis of 1:30 methyl iodide to carbon dioxide mixture in presence of 10 Torr nitric oxide was used as a source of nitrosomethane, assumed to be formed under these conditions [16] with a quantum yield of unity, so that errors which might arise from loss of nitrosomethane by dimerization and other reactions were minimized.

Nitrosomethane was also estimated by gas chromatography using a flame-ionization detector as described previously [14]. The system was insensitive to nitric oxide but was calibrated for other possible products such as acetone, acetaldehyde, ethanol, propan-2-ol and methyl iodide.

Quantum yield determination

For both optical systems quantum yields were determined by reference to the potassium ferrioxalate actinometer [17]. The radiation incident on the reaction vessel for each run was measured by simultaneously exposing a cell containing actinometer solution to a fixed proportion of the output of the lamp. The percentage absorption of light by the reaction mixture was estimated from the measured extinction coefficient. System A was checked by measuring the quantum yield of iodine produced in the photolysis of methyl iodide + nitric oxide mixtures. After photolysis, the contents of the reaction vessel were condensed into 2 cm^3 of carbon tetrachloride in a trap cooled to liquid nitrogen temperature and the iodine formed was determined from its optical density at 500 nm at room temperature. Using a 1:30 methyl iodide/carbon dioxide mixture in the presence of 10 Torr nitric oxide the quantum yield was found to be 0.48 ± 0.02 provided the pressure of the mixture ⩾ 100 Torr (% absorption ⩾75%) in agreement with the expected value of 0.5. At lower pressure the quantum yield of iodine, (and of nitrosomethane), apparently decreased presumably because of diffusion effects or inadequate allowance for incomplete light absorption. For the quantum yield determination in the nitrite systems the total pressure of the reaction mixture was 200 Torr or greater and the percentage absorption by the nitrite (4 to 10 Torr) of light at 254 nm exceeded 78%. The usual duration of exposure was 20 minutes in apparatus A and 5 minutes in apparatus B. The percentage conversion of nitrite did not exceed 4%. All runs were carried out at room temperature normally in the range 17 to 20 °C.

Results

Photolysis of t-butyl nitrite

The main results for t-butyl nitrite are given in Table 1. Each quantum yield is the mean of from 2 to 8 determinations. The most precise values for nitrosomethane are those obtained with apparatus B, where quantum yields were reproducible to ±1%. For the nitrosomethane yields obtained by method A the standard error is typically ±0.02. The gas chromatographic analysis was intended to provide qualitative information only, but approximate estimation of the quantum yields of nitrosomethane and of acetone proved possible. The standard error in these yields is about ±0.1. The retention times for ethane and for nitric oxide are similar but the detector is so insensitive to nitric oxide (4 Torr is just observable) that for runs without added nitric oxide ethane can be unambiguously identified. The presence of iodine at its vapour pressure at room temperature is insufficient to suppress completely the reaction of methyl radicals with nitric oxide as is shown by the following comparison:

Mixture	Φ_{CH_3NO}
CH_3I(3.33 Torr) + NO(0.14 Torr) + I_2(0.15 Torr) + CO_2(97 Torr)	0.14
t-BuONO(4 Torr) + I_2(0.15 Torr) + CO_2(196 Torr)	0.14

The two mixtures were each irradiated for 10 minutes in apparatus B. The nitric oxide added to the methyl iodide mixture is half that estimated to be formed in the t-butyl nitrite photolysis.

Photolysis of isopropyl nitrite

The results are given in Table 2, each value given being the mean of from 4 to 8 determinations. Quantum yields of nitrosomethane, even those determined using apparatus B, were less reproducible for this system, as the recorded standard errors indicate. The nitrite itself showed less tendency to thermal decomposition than did t-butyl nitrite and gas chromatography of the unphotolyzed mixtures revealed no trace of possible decomposition products such as acetone and propan-2-ol. No ethane was detected in the irradiation of isopropyl nitrite in the absence of added nitric oxide; comparison with the other systems indicates that a quantum yield $\geqslant 0.02$ would have been observed. Methyl iodide, if formed in the runs with added iodine, would not have been detected as the retention time corresponds with that of the nitrite. No acetone or propan-2-ol was detected in any of the irradiated mixtures.

The standard error in the acetaldehyde yields determined by gas chromatography is about ±0.1.

Photolysis of ethyl nitrite

Fewer experiments were carried out with this system. The results, given in Table 3, are generally the mean of two determinations agreeing within 3%. Formaldehyde and acetaldehyde, if formed, would not have

TABLE 1

Photolysis of t-butyl nitrite

Composition of reaction mixture				Products				
				Φ_{CH_3NO}			$\Phi_{CH_3COCH_3}$	Others detected
RONO/Torr	CO_2/Torr	NO/Torr	Added gas (Torr)	Method A	Method B	G.c.		
8	392	0.0				0.44[a]	0.81	C_2H_6
8	392	0.0	I_2(0.15)			0.09[a]	0.73	CH_3I, C_2H_6
8	392	10.0				0.74	0.86	
8	392	300		0.70	0.68			
4	196	10.0		0.58	0.56			
4	196	300		0.76	0.76			
10	190	10.0		0.64	0.62			
					0.73			
4	0.0	300	C_2H_6(196)		0.52			
4	0.0	10.0	N_2(196)		0.78			

[a]For 20 minute run using apparatus A. Φ_{CH_3NO} increases with duration of exposure.

TABLE 2

Photolysis of isopropyl nitrite

Composition of reaction mixture				Products	
RONO/Torr	CO_2/Torr	NO/Torr	Added gas (Torr)	Φ_{CH_3NO}	Φ_{CH_3CHO}
8	392	0.0		0.67	0.63
8	392	0.0	I_2(0.15)	0.31	0.66
8	392	10.0		0.74 $\Big\}$ 0.74 ± 0.03	0.74
8	392	300		0.73	
4	196	10		0.90 $\Big\}$ 0.90 ± 0.05	0.67
4	196	300		0.89	

TABLE 3

Photolysis of ethyl nitrite

Composition of reaction mixture				Products	
RONO/Torr	CO_2/Torr	NO/Torr	Added gas (Torr)	Φ_{CH_3NO}	Others detected
8	392	0.0		0.24	C_2H_6
8	392	0.0	I_2(0.15)	0.09	CH_3I, C_2H_6
8	392	10.0		0.37	
8	622	10		0.31	
8	392	300		0.25	

been detected by gas chromatography as their retention times correspond with that of the nitrite. Ethanol was not observed in any of the irradiated mixtures.

Discussion

t-Butyl nitrite

The results for t-butyl nitrite (Table 1) fully confirm the mechanism based on the fission of excited alkoxy radicals. In presence of nitric oxide at a pressure of 10 Torr or greater all methyl radicals are converted to nitrosomethane and the quantum yield of nitrosomethane equals that of acetone as required by reactions (2a) followed by (5). The agreement within experimental error of the quantum yields of nitrosomethane determined by three methods involving two optical arrangements shows that quantitative determination of this elusive product has been achieved.

$$(CH_3)_3CONO + h\nu \rightarrow \alpha(CH_3)_3CO^{\#} + (1-\alpha)(CH_3)_3CO + NO \quad (1a)$$

$$(CH_3)_3CO^{\#} \rightarrow CH_3COCH_3 + CH_3 \quad (2a)$$

$$(CH_3)_3CO^{\#} + M \rightarrow (CH_3)_3CO + M' \quad (3a)$$

$$(CH_3)_3CO + NO \rightarrow (CH_3)_3CONO \quad (6a)$$
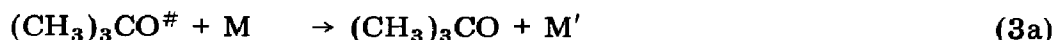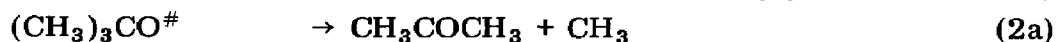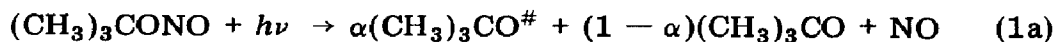
The decrease in Φ_{CH_3NO} with increasing nitric oxide pressure and with increasing total pressure shows that the collisional deactivation of the excited butoxy radical (3a) is competitive with (2a). The deactivated radicals must react with nitric oxide to reform the nitrite (6). Quantitatively the above mechanism predicts that:

$$\frac{1}{\Phi_{CH_3NO}} = \frac{1}{\Phi_{1a}\alpha}\left[1 + \frac{\Sigma k_{3a,M}[M]}{k_{2a}}\right]$$

The results for the 1:50 nitrite to carbon dioxide mixtures using the more precise data obtained by method B are plotted in Fig. 1, where the slope is $k_{3a,\,mix}/\alpha\Phi_{1a}k_{2a}$ independent of the nitric oxide pressure and the intercept is $[k_{2a} + k_{3a,NO}]/\alpha\Phi_{1a}k_{2a}$; $k_{3a,\,mix}$ refers to the 1:50 nitrite to carbon mixture. From the data $\alpha\Phi_{1a} = 0.87 \pm 0.01$ at 20 °C in excellent agreement
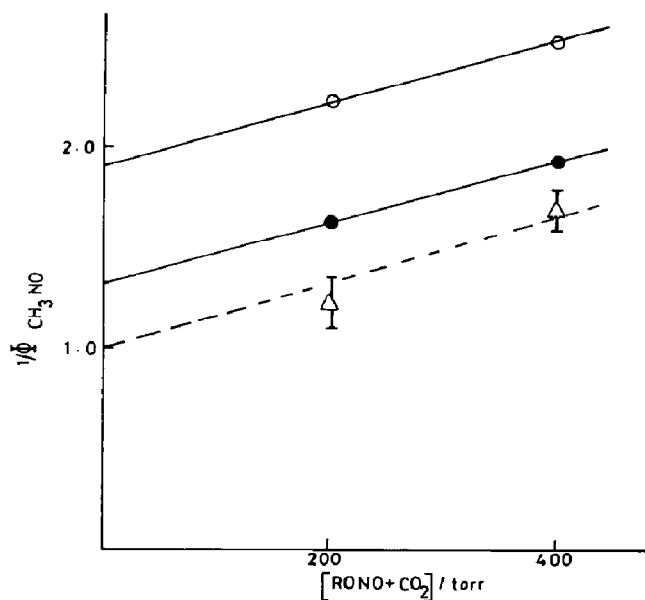
Fig. 1. Variation of $1/\Phi_{CH_3NO}$ with pressure of RONO/CO$_2$ mixture. •, t-Butyl nitrite, [NO]/Torr = 10; ○, t-butyl nitrite, [NO]/Torr = 300; △, isopropyl nitrite, bars showing standard error. The ratio of RONO: CO$_2$ is 1:50.

with the value of 0.87 at 26 °C derived by McMillan [4] from the acetone yields. Values of k_{3a}/k_2 derived for the various gases are compared in Table 4 with previous estimates. There is considerable uncertainty about our nitrite value because of the low proportion of nitrite in the mixtures. The pressure of nitrite was kept low (<10 Torr) to avoid an inhomogeneous concentration of radicals in the reaction vessel. In the previous work the pressure range was 15 to 150 Torr, so that at the higher pressures there must have been a high concentration of radicals formed near the surface of the cell, which might have affected the deactivation. In general, however, the agreement is quite reasonable.

When t-butyl nitrite is photolyzed in absence of added nitric oxide the recombination of methyl radicals (4) is competitive with reaction (5) as is shown by the formation of ethane and the reduction in Φ_{CH_3NO}. The latter yield increases with the duration of exposure as the nitric oxide accumulates. The addition of a small pressure of iodine dramatically reduces the nitro-

TABLE 4

Deactivation of t-butoxy radicals by various gases

	Gas				
	t-BuONO	NO	CO$_2$	C$_2$H$_6$	N$_2$
k_{3a}/k_{2a}(mol^{-1} dm^3)	150 ± 50	18	9	33	7
Previous estimate [4]	34	30	—	72	7

somethane yield because of the rapidity of reaction (7). The quantum yield

$$CH_3 + I_2 \rightarrow CH_3I + I \tag{7}$$

of acetone is not affected. All the evidence supports the excited alkoxy mechanism and is inconsistent with any significant contribution from a molecular split:

$$(CH_3)_3CONO \rightarrow CH_3NO + CH_3COCH_3 \tag{8a}$$

It appears that primary process (1a) occurs with a quantum yield of unity over the entire wavelength region from 366 nm to 123 nm [18] where the energy in excess of that required to break the O–NO bond ranges from 160 kJ to 800 kJ and is very much greater than the endothermicity of process (2a) which is estimated [19] to be 16 kJ/mol. The proportion, α, of excited radicals formed increases from near zero at 366 nm to 0.87 at 254 nm, and is, presumably, unity at 147 nm and 123 nm. At the latter wavelength some 600 kJ of the excess energy appears as electronic excitation of nitric oxide as fluorescence from the $A^2\Sigma^+$ state has been detected [18]. Collisional deactivation of the excited alkoxy radical was not observed at 147 nm or 123 nm, in accord with the expectation that more highly excited alkoxy radicals are formed at these wavelengths.

Isopropyl nitrite

The results for the photolysis of isopropyl nitrite in presence of nitric oxide (Table 2) are similar to those for t-butyl nitrite in that the quantum yields of nitrosomethane approach unity and are equal, within experimental error, to those of acetaldehyde. They differ in that no collisional deactivation by nitric oxide is observed. A pressure effect, however, is manifest in that the average quantum yield is significantly less for the higher pressure of reaction mixture. These yields are plotted in Fig. 1, from which it appears that the deactivation effect of the RONO/CO$_2$ mixture is similar to that observed for t-butyl nitrite, with extrapolation to zero pressure corresponding to a quantum yield of unity for the overall reaction:

$$(CH_3)_2CHONO + h\nu \rightarrow CH_3NO + CH_3CHO \tag{9}$$
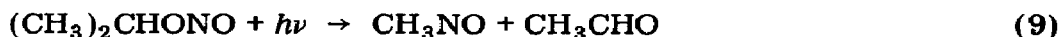
The photolysis, in absence of added nitric oxide, reveals marked differences from the t-butyl nitrite system in that: (i) ethane was not detected (indicating $\Phi_{C_2H_6} \leqslant 0.02$); (ii) Φ_{CH_3NO} is not very greatly reduced from its value in presence of 10 Torr nitric oxide; (iii) iodine reduces Φ_{CH_3NO} but not to the same extent as it did in the case of t-butyl nitrite. Methyl iodide, if formed, would not have been detected as its retention time corresponds with that of the nitrite.

On the basis of the present results a major contribution for a molecular rearrangement according to (9) cannot be excluded. Nor is it inconsistent with the report [3] that Φ_{CH_3CHO} is 0.86 at 254 nm for the photolysis of isopropyl nitrite in the presence of nitric oxide, which has been adduced as evidence for the excited alkoxy contribution. However, the formation of methyl radicals has been observed [8] in the flash photolysis of isopropyl

nitrite. An alternative explanation of our results may be that methyl radicals undergo some other rapid reaction to form nitrosomethane which, in the isopropyl nitrite system is competitive with reactions (4) and (7). The reaction of methyl radicals with alkyl nitrites (10):

$$CH_3 + RONO \rightarrow CH_3NO + RO \qquad (10)$$
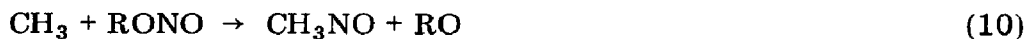
is known to be rapid [20] and may contribute, particularly if the methyl radicals retain some of the energy of the excited radicals. In view of the widespread occurrence of process (1) in the photochemistry of nitrites the explanation in terms of the excited alkoxy mechanism with $\Phi_{1b} = 1$ and $\alpha = 1$ at 254 nm is probably the more plausible. The different behaviour of excited isopropoxy and t-butoxy radicals is unexpected. The endothermicity of the fission of isopropoxy radicals may be estimated to be 29 kJ/mol rather greater than the value of 16 kJ/mol for t-butoxy radicals [19]. The RO—NO bond dissociation energies are very similar [21], so that the isopropoxy radicals might be expected to be less excited with respect to fission and therefore more easily deactivated than the t-butoxy radicals. For light of 254 nm the energy in excess of that required for bond dissociation is about 300 kJ/mol. In the absence of detailed knowledge [22] of how this energy is distributed between vibrational and kinetic energy of the products one cannot be certain about the effective degree of excitement of the alkoxy radicals. If the excited alkoxy mechanism is accepted for isopropyl nitrite our results suggest that the isopropoxy radicals are *more* excited with respect fo fission than are the t-butoxy radicals.

At 366 nm there is no evidence of any contribution from excited propoxy radicals in the photolysis of isopropyl nitrite. The primary quantum yield Φ_{1b} is estimated [3] to be 0.36, as compared with unity for t-butyl nitrite. The unexcited radicals react with nitric acid to reform the nitrite (6b), or to form acetone (11) with a quantum yield of 0.06:

$$(CH_3)_2CHO + NO \rightarrow CH_3COCH_3 + HNO \qquad (11)$$
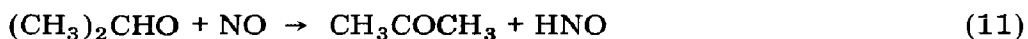
Ethyl nitrite

The results for ethyl nitrite (Table 3) provide evidence for the excited alkoxy mechanism. In the presence of nitric oxide a quantum yield of 0.37 was measured for nitrosomethane. This was reduced by the addition of nitric oxide or of carbon dioxide showing that the excited alkoxy radicals are collisionally deactivated. The photolysis in the absence of added nitric oxide provides evidence for the formation of methyl radicals. Ethane is formed, and methyl iodide in presence of a small pressure of iodine. Although formaldehyde was not detectable in the present investigation other work in this laboratory has shown that it is formed in equivalent yield to that of nitrosomethane [23]. By analogy with t-butyl nitrite the extrapolated value of $\Phi_{1c}\alpha$ is estimated to be about 0.45 and the deactivation ratios $k_{3c,M}/k_{2c}$ are approximately 37 and 18 mol^{-1} dm^3 respectively for nitric oxide and carbon dioxide. The estimated endothermicity for fission (2c) is 43 kJ/mol appreciably greater than that of (2a) (or of 2b). In accord with this excited

ethoxy radicals are formed in smaller yield and are more easily deactivated than are t-butoxy radicals. There is no evidence [23] for a contribution from excited ethoxy decomposition in the photolysis of ethyl nitrite at 366 nm, where Φ_{1c} has been estimated [7] to be 0.59 and the quantum yield of acetaldehyde formed in reaction (12) is 0.18.

$$CH_3CH_2O + NO \rightarrow CH_3CHO + HNO \qquad (12)$$

At 254 nm, where the light absorption is continuous and there is no evidence for any primary process other than the formation of alkoxy radicals, Φ_{1c} is presumably unity and α is about 0.45; the unexcited radicals are expected to react with nitric oxide according to (6c) and (12). Acetaldehyde was not detectable in the present investigation. There was no evidence for the formation of ethanol, a product of the disproportionation of two ethoxy radicals.

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