1285. *Reactions of Methoxyl, Ethoxyl, and t-Butoxyl with Nitric Oxide and with Nitrogen Dioxide*

By G. Baker and R. Shaw

Methoxyl, ethoxyl, and t-butoxyl radicals have been produced by pyrolysing the corresponding dialkyl peroxides. The rates of pyrolysis agreed well with literature values. The reactions of each radical with nitric oxide and nitrogen dioxide were studied, and the relative rate constants measured at 130°. $MeOOMe \longrightarrow 2MeO$ (1), $MeO + NO \longrightarrow MeONO$ (2), $MeO + NO_2 \longrightarrow MeONO_2$ (3), $MeO + NO_2 \longrightarrow HNO_2 + CH_2O$ (5), $k_2/k_3 = 2{\cdot}7$, and $k_5/k_3 = 0{\cdot}10$. For $MeO + NO \longrightarrow HNO + CH_2O$ (4), if $k_4/k_2 = 0{\cdot}5$ (ref. 5), then $k_2 : k_3 : k_4 : k_5 = 1{\cdot}00 : 0{\cdot}37 : 0{\cdot}50 : 0{\cdot}04$. $EtOOEt \longrightarrow 2EtO$ (6), $EtO + NO \longrightarrow EtONO$ (7), $EtO + NO_2 \longrightarrow EtONO_2$ (8), $EtO + NO_2 \longrightarrow HNO_2 + MeCHO$ (10), $k_7/k_8 = 2{\cdot}5$, and $k_{10}/k_8 = 0{\cdot}46$. For $EtO + NO \longrightarrow HNO + MeCHO$ (9), if $k_9/k_7 = 0{\cdot}3$ (ref. 6), then $k_7 : k_8 : k_9 : k_{10} = 1{\cdot}00 : 0{\cdot}40 : 0{\cdot}30 : 0{\cdot}18$. $Bu^tOOBu^t \longrightarrow 2Bu^tO$ (11), $Bu^tO + NO \longrightarrow Bu^tONO$ (12), $Bu^tO + NO_2 \longrightarrow Bu^tONO_2$ (13), $k_{12}/k_{13} = 1{\cdot}7$. The relative rate constants for disproportionation and combination of alkoxyls with nitric oxide and nitrogen dioxide are used quantitatively to explain the effect of additives on the decomposition of alkyl nitrites and nitrates.

Compared with the extensive information [1-3] on the combinations and disproportionations of alkyl radicals not a great deal is known about the corresponding reactions of alkoxyl radicals. No directly measured absolute rate constants have been reported for the combinations of alkoxyl radicals, and only one ratio of rate constants (for the combination of methoxyl with nitric oxide and nitrogen dioxide) has been measured.[4] The ratio, Δ, of rate constants for disproportionation and combination has been measured for nitric oxide with methoxyl,[5] ethoxyl,[6] and isopropoxyl,[7] for methyl with methoxyl,[8,9] and trideuteromethoxyl,[10] for ethyl with ethoxyl,[11] for methoxyl with methoxyl,[12] and for ethoxyl with ethoxyl.[13] In the present work the ratio of rate constants for the combination of alkoxyls with nitric oxide and nitrogen dioxide has been measured for methoxyl, ethoxyl, and t-butoxyl, and the ratio of rate constants for disproportionation and combination has been measured for nitrogen dioxide with methoxyl and ethoxyl.

Results

The experimental results are in Table 1 and the rate constants derived from them are in Table 2. The basic reaction scheme is as follows.

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[1] J. N. Bradley, *J. Chem. Phys.*, 1961, **35**, 748.
[2] A. F. Trotman-Dickenson, Tilden Lecture, *Proc. Chem. Soc.*, 1964, 249.
[3] J. A. Kerr and A. F. Trotman-Dickenson, " Progress in Reaction Kinetics," vol. 1, ch. 4, Pergamon Press, Oxford, 1961.
[4] L. Phillips and R. Shaw, Tenth Symposium (International) on Combustion.
[5] L. Phillips, unpublished results, quoted by ref. 6.
[6] E. A. Arden, L. Phillips, and R. Shaw, *J.*, 1964, 5126.
[7] G. R. McMillan, *J. Amer. Chem. Soc.*, 1961, **83**, 3018.
[8] M. H. J. Wijnen, *J. Chem. Phys.*, 1957, **27**, 710.
[9] J. C. J. Thynne and P. Gray, *Trans. Faraday Soc.*, 1963, **59**, 1149.
[10] M. H. J. Wijnen, *J. Chem. Phys.*, 1958, **28**, 939.
[11] M. H. J. Wijnen, *J. Amer. Chem. Soc.*, 1960, **82**, 3034.
[12] J. Heicklen and H. S. Johnston, *J. Amer. Chem. Soc.*, 1962, **84**, 4030.
[13] J. Heicklen and H. S. Johnston, *J. Amer. Chem. Soc.*, 1962, **84**, 4394.

$$\mathrm{MeOOMe} \longrightarrow 2\mathrm{MeO} \tag{1}$$

$$\mathrm{MeO} + \mathrm{NO} \longrightarrow \mathrm{MeONO} \tag{2}$$

$$\mathrm{MeO} + \mathrm{NO_2} \longrightarrow \mathrm{MeONO_2} \tag{3}$$

$$\mathrm{MeO} + \mathrm{NO} \longrightarrow \mathrm{HNO} + \mathrm{CH_2O} \tag{4}$$

$$\mathrm{MeO} + \mathrm{NO_2} \longrightarrow \mathrm{HNO_2} + \mathrm{CH_2O} \tag{5}$$

$$\mathrm{EtOOEt} \longrightarrow 2\mathrm{EtO} \tag{6}$$

$$\mathrm{EtO} + \mathrm{NO} \longrightarrow \mathrm{EtONO} \tag{7}$$

$$\mathrm{EtO} + \mathrm{NO_2} \longrightarrow \mathrm{EtONO_2} \tag{8}$$

$$\mathrm{EtO} + \mathrm{NO} \longrightarrow \mathrm{HNO} + \mathrm{CH_3CHO} \tag{9}$$

$$\mathrm{EtO} + \mathrm{NO_2} \longrightarrow \mathrm{HNO_2} + \mathrm{CH_3CHO} \tag{10}$$

$$\mathrm{Bu^tOOBu^t} \longrightarrow 2\mathrm{Bu^tO} \tag{11}$$

$$\mathrm{Bu^tO} + \mathrm{NO} \longrightarrow \mathrm{Bu^tONO} \tag{12}$$

$$\mathrm{Bu^tO} + \mathrm{NO_2} \longrightarrow \mathrm{Bu^tONO_2} \tag{13}$$

In the dimethyl peroxide system,

$$R(\mathrm{MeONO})/R(\mathrm{MeONO_2}) = k_2[\mathrm{MeO}][\mathrm{NO}]/k_3[\mathrm{MeO}][\mathrm{NO_2}]$$

i.e.,

$$k_2/k_3 = [\mathrm{NO_2}]R(\mathrm{MeONO})/[\mathrm{NO}]R(\mathrm{MeONO_2})$$

TABLE 1

Reaction of dialkyl peroxides with nitric oxide and nitrogen dioxide at 130°

Length of run (hr.)	[NO] av. (mm.)	$[\mathrm{NO_2}]$ av. (mm.)	RONO (mm.)	$\mathrm{RONO_2}$ (mm.)	CO (mm.)	$\mathrm{CO_2}$ (mm.)	Log k (dec.) *	$\frac{\mathrm{RONO[NO_2]}}{\mathrm{RONO_2[NO]}}$	$\frac{1·7(\mathrm{CO})}{\mathrm{RONO_2}}$	$\frac{\mathrm{CO_2}}{\mathrm{RONO_2}}$
					Dimethyl peroxide					
0·5	49	62	2·4	1·2		<1	−4·3	2·5		
1·5	48	62	6·5	3·0		<1	−4·4	2·8		
2	46	59	7·3	4·1		<1	−4·3	2·3		
1	49	27	5·3	1·0		<1	−4·3	2·9		
1·5	46	28	7·7	1·8		<1	−4·3	2·6		
1·5	22	61	4·7	4·3		<1	−4·3	3·0		
1·5	24	59	4·9	3·9		<1	−4·4	3·1		
2		64		8·4	0·5	<1	−4·5		0·10	
3		64		13·6	0·8	<1	−4·4		0·10	
3		140		15·6	1·0	<1	−4·3		0·11	
						Average:	−4·3	2·7	0·10	
					Diethyl peroxide					
2	44	61	8·9	5·5		4·2	−4·1	2·2		
2	45	62	8·9	4·7		4·4	−4·1	2·6		
2	49	28	10·1	2·4		3·6	−4·2	2·4		
2	51	28	9·5	2·3		3·2	−4·2	2·3		
1·5	22	60	5·3	5·3				2·7		
1·5	23	59	5·1	4·7				2·8		
2		64		9·2		4·4	−4·3			0·48
2		64		8·6		3·8	−4·3			0·44
						Average:	−4·2	2·5		0·46
					Di-t-butyl peroxide					
0·5 (150°)	48	63	5·4	4·4			−3·8	1·6		
0·5 (150°)	48	61	5·1	3·1			−3·9	2·1		
						Av. (150°):	−3·9	1·9		
2	49	62	2·0	1·4			−4·9	1·8		
2	50	62	2·7	2·7			−4·7	1·2		
2	48	61	3·3	2·7			−4·7	1·6		
2	49	60	2·7	1·9			−4·8	1·7		
2	48	62	3·2	2·1			−4·7	2·0		
2	49	28	4·1	1·8			−4·7	1·3		
2	49	29	4·1	1·7			−4·7	1·4		
2	35	60	2·7	2·5			−4·7	1·8		
2	25	60	2·6	3·2			−4·7	2·0		
						Av. (130°):	−4·7	1·6		
							Combined av.:	1·7		

* Where k (dec.) is $-\mathrm{d}\ln[\mathrm{ROOR}]/\mathrm{d}t$.

The nitrogen oxides are in large excess, so their concentrations are essentially constant. Measurement of the yields of methyl nitrite and methyl nitrate then gives k_2/k_3. The ratios k_7/k_8 and k_{12}/k_{13} are obtained similarly, and all three ratios did not vary when $[NO_2]/[NO]$ was varied from 0·6 to 2·8.

TABLE 2

Summary of rate constants (sec.$^{-1}$)

	$\log k_1$	$\log k_6$	$\log k_{11}$	k_2/k_3	k_5/k_3	k_7/k_8	k_{10}/k_8	k_{12}/k_{13}
Exptl. ...	−4·3	−4·2	−4·7, −3·9 †	2·7	0·1	2·5	0·46	1·7 ‡
Calc.* ...	−4·2	−4·3	−4·8, −3·8 †					

* Calculated from Arrhenius parameters quoted by P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, 1959, **63**, 104. † At 150°. ‡ Combined results at 130° and 150°.

When nitrogen dioxide alone is present with dimethyl peroxide,

$$R(\mathrm{MeONO_2})/R(\mathrm{CH_2O}) = k_3[\mathrm{MeO}][\mathrm{NO_2}]/k_5[\mathrm{MeO}][\mathrm{NO_2}]$$

i.e.,

$$k_3/k_5 = R(\mathrm{MeONO_2})/R(\mathrm{CH_2O})$$

In practice, no formaldehyde was observed, because formaldehyde reacts rapidly with nitrogen ioxide under these conditions [14,15] to produce carbon monoxide and carbon dioxide by reactions (14)—(17).

$$\mathrm{NO_2 + CH_2O \longrightarrow HNO_2 + HCO} \tag{14}$$

$$\mathrm{NO_2 + HCO \longrightarrow HNO_2 + CO} \tag{15}$$

$$\mathrm{HCO + NO_2 \longrightarrow HCO_2 + NO} \tag{16}$$

$$\mathrm{NO_2 + HCO_2 \longrightarrow HNO_2 + CO_2} \tag{17}$$

The ratio $R(\mathrm{CO})/R(\mathrm{CO_2})$ has a constant value of 1·45 at 130°. Estimation of the carbon monoxide (or carbon dioxide) gives the yield of formaldehyde, and the rate expression becomes

$$k_3/k_5 = 1{\cdot}7R(\mathrm{CO})/R(\mathrm{MeONO_2}),$$

independent of $[NO_2]$ as shown by the results.

Similarly, in the diethyl peroxide system, the acetaldehyde produced by reactions (9) and (10) is oxidised quantitatively by nitrogen dioxide to carbon dioxide.[4,16] When nitrogen dioxide alone is present with diethyl peroxide,

$$R(\mathrm{EtONO_2})/R(\mathrm{CH_3CHO}) = R(\mathrm{EtONO_2})/R(\mathrm{CO_2}) = k_8[\mathrm{EtO}][\mathrm{NO_2}]/k_{10}[\mathrm{EtO}][\mathrm{NO_2}]$$

i.e.,

$$k_8/k_{10} = R(\mathrm{EtONO_2})/R(\mathrm{CO_2})$$

There is no evidence that nitric oxide or nitrogen dioxide abstract hydrogen to a significant extent from t-butoxyl. This is reasonable because t-butoxyl has no α-hydrogen atom.

Assuming the reaction mechanism to be correct, the rates of decomposition of the dialkyl peroxides were calculated. The results in Table 2 show that there is good agreement with the literature values.

DISCUSSION

Comparison with Previous Work.—The present value of 2·7 for k_2/k_3 at 130° is considerably higher than the value of 1·8 at 90° found by Phillips and Shaw [4] in the methyl–nitrogen dioxide system. It is unlikely that the discrepancy is due to an activation-energy difference, as combinations are thought to have no activation energy. It is suggested that the difference is due to the approximation, used in calculating k_2/k_3, that the nitrogen oxide concentration may be taken as the average of the initial and final concentrations. In a typical experiment in the previous work, the nitric oxide concentration increased from 32 to 46 mm., giving an average of 39 mm., and the nitrogen dioxide concentration fell from 40 to 16 mm., giving an average of 28 mm. In the present

[14] F. H. Pollard and R. M. H. Wyatt, *Trans. Faraday Soc.*, 1949, **45**, 760.

[15] R. Shaw, *J.*, 1964, 1517.

[16] A. E. Pedler and F. H. Pollard, *Trans. Faraday Soc.*, 1957, **53**, 44.

work, the nitric oxide concentration fell from 51 to 45 mm., giving an average of 48 mm., and the nitrogen dioxide concentration fell from 64 to 60 mm. Clearly, the approximation is more valid in the present case, and it is therefore concluded that the present result of 2·7 for k_2/k_3 is more accurate.

The ratio, Δ, of rate constants for disproportionation and combination of ethoxyl and nitrogen dioxide is similar to that found by Arden, Phillips, and Shaw for ethoxyl and nitric oxide. The present Δ for methoxyl and nitrogen dioxide is much smaller than that reported for methoxyl and nitric oxide. This latter value of 0·5 is not consistent with the present work because, if k_4/k_2 was 0·5, then

$$R(\text{CH}_2\text{O})/R(\text{MeONO}) = (k_4[\text{MeO}][\text{NO}] + k_5[\text{MeO}][\text{NO}_2])/k_2[\text{MeO}][\text{NO}]$$
$$> 0{\cdot}5$$

i.e.,
$$R(\text{CO}_2) > 0{\cdot}2R(\text{MeONO})$$

which from the results in Table 1 is not so. The value of $k_4/k_2 = 0{\cdot}5$ is also not consistent with the results of Phillips and Shaw [4] in the methyl–nitrogen dioxide–nitric oxide system where the methyl radical and hence methoxyl radical balances were good without invoking reaction (4). A possible explanation is that there is an activation energy for reaction (4), because the value $\Delta = 0{\cdot}5$ was obtained at 175°.

Decomposition of Nitrites and Nitrates.[17]—The present results for the reactions of methoxyl and ethoxyl with nitrogen and nitric oxide, together with previous work on methoxyl [5] and ethoxyl [6] with nitric oxide, explain quantitatively some features of the decompositions of alkyl nitrites and nitrates. Taking ethyl nitrite as an example of an alkyl nitrite decomposition, Levy's mechanism [18] is:

$\text{EtONO} \longrightarrow \text{EtO} + \text{NO}$ (−7)
$\text{EtO} + \text{NO} \longrightarrow \text{EtONO}$ (7)
$\text{EtO} + \text{NO}_2 \longrightarrow \text{EtONO}_2$ (8)
$\text{EtO} + \text{NO} \longrightarrow \text{HNO} + \text{MeCHO}$ (9)
$\text{EtO} + \text{NO}_2 \longrightarrow \text{HNO}_2 + \text{MeCHO}$ (10)
$\text{EtO} \longrightarrow \text{Me} + \text{CH}_2\text{O}$ (20)
$\text{EtO} + \text{RH} \longrightarrow \text{EtOH} + \text{R}$ (21)
$2\text{EtO} \longrightarrow \text{EtOOEt}$ (22)
$2\text{EtO} \longrightarrow \text{EtOH} + \text{MeCHO}$ (23)

Reactions (22) and (23) can be neglected because $[\text{EtO}] \ll [\text{NO}]$. It follows that

$$-\frac{d\ln[\text{EtONO}]}{dt} = k_0 = \frac{k_{-7}(k_9[\text{NO}] + k_8[\text{NO}_2] + k_{10}[\text{NO}_2] + k_{20} + k_{21}[\text{RH}])}{k_7[\text{NO}] + k_9[\text{NO}] + k_8[\text{NO}_2] + k_{10}[\text{NO}_2] + k_{20} + k_{21}[\text{RH}]}$$

When ethyl nitrite is pyrolysed, the nitric oxide concentration soon builds up, so that, with or without added nitric oxide, if the temperature, nitrogen dioxide, and RH concentrations are low, then $k_0 = k_{-7}k_9/(k_7 + k_9)$. As $k_7/k_9 = 3{\cdot}3$ (ref. 6), $k_0 = k_{-7}/4{\cdot}3$. If the temperature is raised, or if nitrogen dioxide or RH is added, then k_0 will increase from $k_{-7}/4{\cdot}3$ to a maximum value of k_{-7}. Thus, Levy [18] found that k_0 doubled when acetaldehyde was added initially in the decomposition of ethyl nitrite at 181°. It is clear from Levy's results that the maximum value of k_0 had not been reached. However, in earlier work, Pollard, Pedler, and Hardy [19] added nitrogen dioxide in the decomposition of ethyl nitrite at 190°. At these temperatures, $(k_8 + k_{10}) \sim 100\ k_{21}$, so it would be expected that nitrogen dioxide would be more efficient than acetaldehyde at "scavenging" ethoxyl radicals. This is borne out by Pollard, Pedler, and Hardy's results. From their rate of production of ethyl nitrate, and the value $k_8/k_{10} = 0{\cdot}46$ from the present work, the rate

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[17] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, 1960, p. 419.
[18] J. B. Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780.
[19] F. H. Pollard, A. E. Pedler, and C. J. Hardy, *Nature*, 1954, **174**, 979.

constant for the decomposition of ethyl nitrite in nitrogen dioxide is calculated to be 6×10^{-4} sec.$^{-1}$ at 190°. The rate constant of the decomposition in the absence of nitrogen dioxide is calculated from Levy's Arrhenius parameters [18] to be $1{\cdot}3 \times 10^{-4}$ at 190°. Thus, the rate constant in the presence of nitrogen dioxide is $4{\cdot}6\ k_0$, in excellent agreement with the present work.

Similarly, in the decomposition of methyl nitrite,

$$\mathrm{MeONO} \longrightarrow \mathrm{MeO + NO} \tag{-2}$$
$$\mathrm{MeO + NO} \longrightarrow \mathrm{MeONO} \tag{2}$$
$$\mathrm{MeO + NO} \longrightarrow \mathrm{HNO + CH_2O} \tag{4}$$

In the absence of added nitrogen dioxide or RH, $-\mathrm{d}\ln[\mathrm{MeONO}]/\mathrm{d}t = k_0 = k_{-2}k_2/(k_2 + k_4)$. As $k_2/k_4 = 0{\cdot}5$ (ref. 5), $k_0 = 0{\cdot}33k_{-2}$. Phillips [20] found that added cyclohexane doubled k_0 for methyl nitrite, but, as in Levy's experiments,[18] insufficient RH was added to reach a maximum value of k_0 equal to k_{-2}.

The decomposition of alkyl nitrates is interesting because the nitrogen dioxide produced in the initial step does not build up but is reduced to nitric oxide, with the result that alkoxyl–nitric oxide chemistry is superimposed on alkoxyl–nitrogen dioxide chemistry. Taking ethyl nitrate as an example,

$$\mathrm{EtONO_2} \longrightarrow \mathrm{EtO + NO_2} \tag{-8}$$
$$\mathrm{EtO + NO_2} \longrightarrow \mathrm{EtONO_2} \tag{8}$$
$$\mathrm{EtO + NO_2} \longrightarrow \mathrm{HNO_2 + MeCHO} \tag{10}$$
$$\mathrm{EtO + NO} \longrightarrow \mathrm{EtONO} \tag{7}$$
$$\mathrm{EtO + NO} \longrightarrow \mathrm{HNO + MeCHO} \tag{9}$$
$$\mathrm{EtO} \longrightarrow \mathrm{Me + CH_2O} \tag{20}$$
$$\mathrm{EtO + RH} \longrightarrow \mathrm{EtOH + R} \tag{21}$$

$$-\frac{\mathrm{d}\ln[\mathrm{EtONO_2}]}{\mathrm{d}t} = k_0 = \frac{k_{-8}(k_{10}[\mathrm{NO_2}] + k_7[\mathrm{NO}] + k_9[\mathrm{NO}] + k_{20} + k_{21}[\mathrm{RH}])}{k_8[\mathrm{NO_2}] + k_{10}[\mathrm{NO_2}] + k_7[\mathrm{NO}] + k_9[\mathrm{NO}] + k_{20} + k_{21}[\mathrm{RH}]}$$

Levy [21] investigated the effect of additives on the pyrolysis of ethyl nitrate, and his results are in line with the above reaction mechanism. If nitrogen dioxide is added to the system, $k_0 = k_{-8}k_{10}/(k_8 + k_{10})$, and as $k_8/k_{10} = 0{\cdot}46$, $k_0 = 0{\cdot}3\ k_{-8}$. If nitric oxide or RH is added, then $k_0 = k_{-8}$. From Levy's results with added nitric oxide or RH, $k_8 = 10^{-3}$ sec.$^{-1}$ at 181°, and when a large excess of nitrogen dioxide was added, k_0 fell to 10^{-4} sec.$^{-1}$ at 181°, in reasonable agreement with the value of 3×10^{-4} sec.$^{-1}$ derived from the present work. When ethyl nitrate was pyrolysed alone the value of k_0 lay between the two extremes because neither nitric oxide nor nitrogen dioxide built up during the reaction.[22] This, then, is why added nitrogen dioxide retards the rate of decomposition of ethyl nitrate [23] whereas added nitric oxide does not appear to retard the rate of decomposition of ethyl nitrite. When ethyl nitrate is pyrolysed alone, k_0 lies between k_{-8} and $k_{-8}k_{10}/(k_8 + k_{10})$, wheras, when ethyl nitrite is pyrolysed alone, k_0 lies close to $k_{-2}k_2/(k_2 + k_4)$.

EXPERIMENTAL

The preparation of and purification of the dialkyl peroxides,[24] nitric oxide, nitrogen dioxide, and acetaldehyde [4] have been described elsewhere. Samples of methyl nitrite, methyl nitrate, ethyl nitrite, and ethyl nitrate, and calibration charts of their infrared spectra were kindly provided by Dr. L. Phillips. t-Butyl nitrite was prepared by the reaction of nitrous acid with t-butyl alcohol.[25] t-Butyl nitrate was prepared by the action of silver nitrate on t- butyl chloride in ether.[26] After distillation, the peroxides, nitrites, and nitrates were stored at −40°.

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[20] L. Phillips, *J.*, 1961, 3082.

[21] J. B. Levy, *J. Amer. Chem. Soc.*, 1954, **76**, 3790.

[22] J. B. Levy, *J. Amer. Chem. Soc.*, 1954, **76**, 3254.

[23] L. Phillips, *Nature*, 1950, **165**, 564.

[24] G. Baker, J. H. Littlefair, R. Shaw, and J. C. J. Thynne, following Paper.

[25] *Org. Synth.*, Coll. Vol. II, 108.

[26] J. W. Baker and D. M. Easty, *J.*, 1952, 1193.

The reactants were added successively to a 150-c.c. Pyrex reaction flask. From the temperature and pressure of the NO_2–N_2O_4 mixture, the pressure of NO_2, assuming complete dissociation of the N_2O_4, was calculated. After immersion in a silicone oil bath at 130°, the flask was quenched with cold water. The contents were shared into a Pyrex infrared cell, 10-cm. long, volume 150 c.c., with sodium chloride windows protected by a thin layer of KEL-F wax. When mass-spectrometric analysis was required, the sample remaining in the reaction flask was frozen to −196°, and the non-condensable gases expanded into the mass spectrometer (A.E.I., model M.S.2). Apart from the mass-spectrometric analysis, at no time were the reactants or products frozen out. The wavelengths used for infrared analysis were methyl nitrite 12·2 μ, ethyl nitrite 12·4 μ, t-butyl nitrite 12·35 μ, methyl nitrate 11·7 μ, ethyl nitrate 11·7 μ, t-butyl nitrate 7·7 μ, and carbon dioxide 4·3 μ. Small corrections were made when slight overlapping of peaks occurred. The instrument used was a Perkin-Elmer model 21. Mass spectra were kindly provided by Mr. R. A. Livermore.

Gas-chromatographic analysis was first tried, but with a 2-m. column of tetraethylene glycol monomethyl ether on Embacel at 40° with hydrogen carrier gas at 80 c.c./min., using a Perkin-Elmer Fraktometer, t-butyl nitrite decomposed before elution.

Separate experiments showed no evidence of decomposition of the nitrites or nitrates, or of exchange reactions (24) and (25).

$$\mathrm{RONO} + \mathrm{NO_2} \longrightarrow \mathrm{RONO_2} + \mathrm{NO} \qquad (24)$$

$$\mathrm{RONO_2} + \mathrm{NO} \longrightarrow \mathrm{RONO} + \mathrm{NO_2} \qquad (25)$$

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