

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

By G. BAKER and R. SHAW

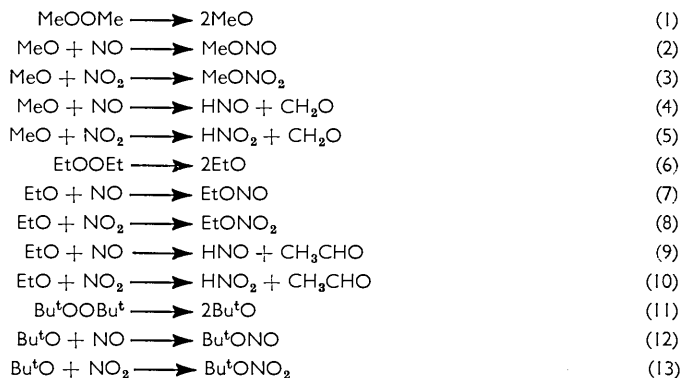
Methoxyl, ethoxyl, and *t*-butoxyl radicals have been produced by pyrolysing the corresponding dialkyl peroxides. The rates of pyrolysis agreed well with literature values. The reactions of each radical with nitric oxide and nitrogen dioxide were studied, and the relative rate constants measured at 130°.  $\text{MeOOME} \longrightarrow 2\text{MeO}$  (1),  $\text{MeO} + \text{NO} \longrightarrow \text{MeONO}$  (2),  $\text{MeO} + \text{NO}_2 \longrightarrow \text{MeONO}_2$  (3),  $\text{MeO} + \text{NO}_2 \longrightarrow \text{HNO}_2 + \text{CH}_2\text{O}$  (5),  $k_2/k_3 = 2.7$ , and  $k_5/k_3 = 0.10$ . For  $\text{MeO} + \text{NO} \longrightarrow \text{HNO} + \text{CH}_2\text{O}$  (4), if  $k_4/k_2 = 0.5$  (ref. 5), then  $k_2 : k_3 : k_4 : k_5 = 1.00 : 0.37 : 0.50 : 0.04$ .  $\text{EtOOEt} \longrightarrow 2\text{EtO}$  (6),  $\text{EtO} + \text{NO} \longrightarrow \text{EtONO}$  (7),  $\text{EtO} + \text{NO}_2 \longrightarrow \text{EtONO}_2$  (8),  $\text{EtO} + \text{NO}_2 \longrightarrow \text{HNO}_2 + \text{MeCHO}$  (10),  $k_7/k_8 = 2.5$ , and  $k_{10}/k_8 = 0.46$ . For  $\text{EtO} + \text{NO} \longrightarrow \text{HNO} + \text{MeCHO}$  (9), if  $k_9/k_7 = 0.3$  (ref. 6), then  $k_7 : k_8 : k_9 : k_{10} = 1.00 : 0.40 : 0.30 : 0.18$ .  $\text{Bu}^t\text{OOBu}^t \longrightarrow 2\text{Bu}^t\text{O}$  (11),  $\text{Bu}^t\text{O} + \text{NO} \longrightarrow \text{Bu}^t\text{ONO}$  (12),  $\text{Bu}^t\text{O} + \text{NO}_2 \longrightarrow \text{Bu}^t\text{ONO}_2$  (13),  $k_{12}/k_{13} = 1.7$ . The relative rate constants for disproportionation and combination of alkoxy radicals 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<sup>1-3</sup> on the combinations and disproportionations of alkyl radicals not a great deal is known about the corresponding reactions of alkoxy radicals. No directly measured absolute rate constants have been reported for the combinations of alkoxy radicals, and only one ratio of rate constants (for the combination of methoxyl with nitric oxide and nitrogen dioxide) has been measured.<sup>4</sup> The ratio,  $\Delta$ , of rate constants for disproportionation and combination has been measured for nitric oxide with methoxyl,<sup>5</sup> ethoxyl,<sup>6</sup> and isopropoxyl,<sup>7</sup> for methyl with methoxyl,<sup>8,9</sup> and trideuteromethoxyl,<sup>10</sup> for ethyl with ethoxyl,<sup>11</sup> for methoxyl with methoxyl,<sup>12</sup> and for ethoxyl with ethoxyl.<sup>13</sup> In the present work the ratio of rate constants for the combination of alkoxy radicals 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.

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



In the dimethyl peroxide system,

$$R(\text{MeONO})/R(\text{MeONO}_2) = k_2[\text{MeO}][\text{NO}]/k_3[\text{MeO}][\text{NO}_2]$$

*i.e.*,

$$k_2/k_3 = [\text{NO}_2]R(\text{MeONO})/[\text{NO}]R(\text{MeONO}_2)$$

TABLE I

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

Length of run (hr.)	[NO] av. (mm.)	[NO <sub>2</sub> ] av. (mm.)	RONO (mm.)	RONO <sub>2</sub> (mm.)	CO (mm.)	CO <sub>2</sub> (mm.)	Log <i>k</i> (dec.) *	RONO[NO <sub>2</sub> ]/RONO <sub>2</sub> [NO]	1.7(CO)/RONO <sub>2</sub>	CO <sub>2</sub> /RONO <sub>2</sub>
<i>Dimethyl peroxide</i>										
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	
<i>Diethyl peroxide</i>										
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	
<i>Di-<i>t</i>-butyl peroxide</i>										
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		
2	49	62	2.0	1.4			Av. (150°): -3.9	1.9		
2	50	62	2.7	2.7				1.8		
2	48	61	3.3	2.7				1.2		
2	49	60	2.7	1.9				1.6		
2	49	60	2.7	1.9				1.7		
2	48	62	3.2	2.1				1.7		
2	48	62	3.2	2.1				2.0		
2	49	28	4.1	1.8				1.3		
2	49	29	4.1	1.7				1.4		
2	35	60	2.7	2.5				1.8		
2	25	60	2.6	3.2				2.0		
							Av. (130°): -4.7	1.6		
							Combined av.:	1.7		

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

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

TABLE 2

Summary of rate constants (sec.<sup>-1</sup>)

	log $k_1$	log $k_6$	log $k_{11}$	$k_2/k_3$	$k_5/k_8$	$k_7/k_8$	$k_{10}/k_8$	$k_{12}/k_{13}$
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°.

$k_7/k_8$  and  $k_{12}/k_{13}$  are obtained similarly, and all three ratios did not vary when  $[\text{NO}_2]/[\text{NO}]$  was varied from 0.6 to 2.8.

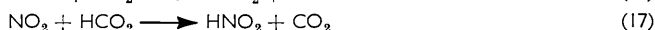
When nitrogen dioxide alone is present with dimethyl peroxide,

$$R(\text{MeONO}_2)/R(\text{CH}_2\text{O}) = k_3[\text{MeO}][\text{NO}_2]/k_5[\text{MeO}][\text{NO}_2]$$

*i.e.*,

$$k_3/k_5 = R(\text{MeONO}_2)/R(\text{CH}_2\text{O})$$

In practice, no formaldehyde was observed, because formaldehyde reacts rapidly with nitrogen dioxide under these conditions<sup>14,15</sup> to produce carbon monoxide and carbon dioxide by reactions (14)–(17).



The ratio  $R(\text{CO})/R(\text{CO}_2)$  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

$$k_3/k_5 = 1.7R(\text{CO})/R(\text{MeONO}_2),$$

independent of  $[\text{NO}_2]$  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.<sup>4,16</sup> When nitrogen dioxide alone is present with diethyl peroxide,

$$R(\text{EtONO}_2)/R(\text{CH}_3\text{CHO}) = R(\text{EtONO}_2)/R(\text{CO}_2) = k_8[\text{EtO}][\text{NO}_2]/k_{10}[\text{EtO}][\text{NO}_2]$$

*i.e.*,

$$k_8/k_{10} = R(\text{EtONO}_2)/R(\text{CO}_2)$$

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  $\alpha$ -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<sup>4</sup> 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

<sup>14</sup> F. H. Pollard and R. M. H. Wyatt, *Trans. Faraday Soc.*, 1949, **45**, 760.

<sup>15</sup> R. Shaw, *J.*, 1964, 1517.

<sup>16</sup> 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.

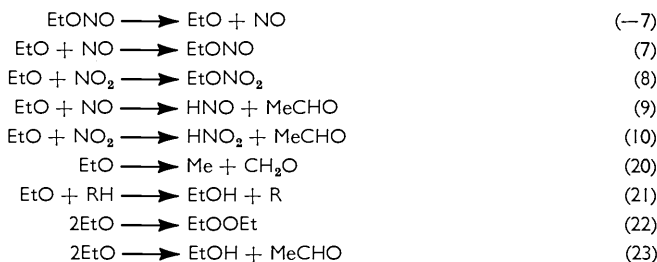
The ratio,  $\Delta$ , of rate constants for disproportionation and combination of ethoxyl and nitrogen dioxide is similar to that found by Arden, Phillips, and Shaw for ethoxyl and nitric oxide. The present  $\Delta$  for methoxyl and nitrogen dioxide is much smaller than that reported for methoxyl 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

$$\begin{aligned} R(\text{CH}_2\text{O})/R(\text{MeONO}) &= (k_4[\text{MeO}][\text{NO}] + k_5[\text{MeO}][\text{NO}_2])/k_2[\text{MeO}][\text{NO}] \\ &> 0.5 \end{aligned}$$

$$\text{i.e., } R(\text{CO}_2) > 0.2R(\text{MeONO})$$

which from the results in Table 1 is not so. The value of  $k_4/k_2 = 0.5$  is also not consistent with the results of Phillips and Shaw<sup>4</sup> 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  $\Delta = 0.5$  was obtained at 175°.

*Decomposition of Nitrites and Nitrates.*<sup>17</sup>—The present results for the reactions of methoxyl and ethoxyl with nitrogen and nitric oxide, together with previous work on methoxyl<sup>5</sup> and ethoxyl<sup>6</sup> 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<sup>18</sup> is:



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  $k_7/k_9 = 3.3$  (ref. 6),  $k_0 = k_{-7}/4.3$ . If the temperature is raised, or if nitrogen dioxide or RH is added, then  $k_0$  will increase from  $k_{-7}/4.3$  to a maximum value of  $k_{-7}$ . Thus, Levy<sup>18</sup> 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<sup>19</sup> 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  $k_8/k_{10} = 0.46$  from the present work, the rate

<sup>17</sup> S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, 1960, p. 419.

<sup>18</sup> J. B. Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780.

<sup>19</sup> F. H. Pollard, A. E. Pedler, and C. J. Hardy, *Nature*, 1954, **174**, 979.

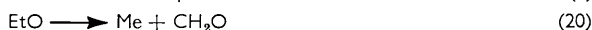
constant for the decomposition of ethyl nitrite in nitrogen dioxide is calculated to be  $6 \times 10^{-4} \text{ sec.}^{-1}$  at  $190^\circ$ . The rate constant of the decomposition in the absence of nitrogen dioxide is calculated from Levy's Arrhenius parameters<sup>18</sup> to be  $1.3 \times 10^{-4}$  at  $190^\circ$ . Thus, the rate constant in the presence of nitrogen dioxide is  $4.6 k_0$ , in excellent agreement with the present work.

Similarly, in the decomposition of methyl nitrite,



In the absence of added nitrogen dioxide or RH,  $-\text{d} \ln[\text{MeONO}]/\text{d}t = k_0 = k_2 k_2 / (k_2 + k_4)$ . As  $k_2/k_4 = 0.5$  (ref. 5),  $k_0 = 0.33 k_2$ . Phillips<sup>20</sup> found that added cyclohexane doubled  $k_0$  for methyl nitrite, but, as in Levy's experiments,<sup>18</sup> 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 alkoxy-nitric oxide chemistry is superimposed on alkoxy-nitrogen dioxide chemistry. Taking ethyl nitrate as an example,



$$-\frac{\text{d} \ln[\text{EtONO}_2]}{\text{d}t} = k_0 = \frac{k_{-8}(k_{10}[\text{NO}_2] + k_7[\text{NO}] + k_9[\text{NO}] + k_{20} + k_{21}[\text{RH}])}{k_8[\text{NO}_2] + k_{10}[\text{NO}_2] + k_7[\text{NO}] + k_9[\text{NO}] + k_{20} + k_{21}[\text{RH}]}$$

Levy<sup>21</sup> 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  $k_8/k_{10} = 0.46$ ,  $k_0 = 0.3 k_{-8}$ . If nitric oxide or RH is added, then  $k_0 = k_{-8}$ . From Levy's results with added nitric oxide or RH,  $k_8 = 10^{-3} \text{ sec.}^{-1}$  at  $181^\circ$ , and when a large excess of nitrogen dioxide was added,  $k_0$  fell to  $10^{-4} \text{ sec.}^{-1}$  at  $181^\circ$ , in reasonable agreement with the value of  $3 \times 10^{-4} \text{ sec.}^{-1}$  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.<sup>22</sup> This, then, is why added nitrogen dioxide retards the rate of decomposition of ethyl nitrate<sup>23</sup> 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  $k_{-8} k_{10} / (k_8 + k_{10})$ , whereas, 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,<sup>24</sup> nitric oxide, nitrogen dioxide, and acetaldehyde<sup>4</sup> 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.<sup>25</sup> *t*-Butyl nitrate was prepared by the action of silver nitrate on *t*-butyl chloride in ether.<sup>26</sup> After distillation, the peroxides, nitrites, and nitrates were stored at  $-40^\circ$ .

<sup>20</sup> L. Phillips, *J.*, 1961, 3082.

<sup>21</sup> J. B. Levy, *J. Amer. Chem. Soc.*, 1954, **76**, 3790.

<sup>22</sup> J. B. Levy, *J. Amer. Chem. Soc.*, 1954, **76**, 3254.

<sup>23</sup> L. Phillips, *Nature*, 1950, **165**, 564.

<sup>24</sup> G. Baker, J. H. Littlefair, R. Shaw, and J. C. J. Thynne, following Paper.

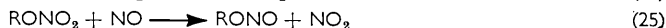
<sup>25</sup> *Org. Synth.*, Coll. Vol. II, 108.

<sup>26</sup> 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  $\text{NO}_2$ - $\text{N}_2\text{O}_4$  mixture, the pressure of  $\text{NO}_2$ , assuming complete dissociation of the  $\text{N}_2\text{O}_4$ , was calculated. After immersion in a silicone oil bath at  $130^\circ$ , 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  $-196^\circ$ , 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  $12.2 \mu$ , ethyl nitrite  $12.4 \mu$ , t-butyl nitrite  $12.35 \mu$ , methyl nitrate  $11.7 \mu$ , ethyl nitrate  $11.7 \mu$ , t-butyl nitrate  $7.7 \mu$ , and carbon dioxide  $4.3 \mu$ . 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  $40^\circ$  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).



MINISTRY OF AVIATION, E.R.D.E., WALTHAM ABBEY, ESSEX.

[Received, June 28th, 1965.]

---