

982. *Reactions in the Diethyl Peroxide–Nitric Oxide System. Part II.¹ The Kinetics of Cross Disproportionation and Combination Reactions between the Ethoxyl Radical and Nitric Oxide.*

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A study of competing disproportionation and combination reactions between ethoxyl radicals and nitric oxide, at 95 and 135°, shows that disproportionation to form acetaldehyde and nitroxyl has zero activation energy, and a rate constant, based on that calculated for the recombination reaction, of 1×10^{10} mole⁻¹ cm.³ sec.⁻¹. The disproportionation : combination ratio, Δ , divided by the number of possible abstractable hydrogen atoms in the alkoxy radical, is constant for methoxyl-, ethoxyl-, and isopropoxyl–nitric oxide systems.

PART I of this Series¹ described the products of the reactions between ethoxyl radicals, from the pyrolysis of diethyl peroxide, and nitric oxide, at 95 and 135°. At 135°, the products are ethyl nitrite, acetaldehyde, and ethanol, with small amounts of nitrogen, nitrous oxide, and hydrogen. At 95°, with peroxide : nitric oxide ratios greater than about 1·25, the products were essentially the same, but at lower ratios, chain formation of nitrogen and nitrogen dioxide occurred by way of nitroxyl and nitrosomethane. The mechanism of the latter reactions was discussed in Part I;¹ there is evidence of a direct reaction between nitrogen dioxide formed and the peroxide, which makes kinetic treatment of the results difficult. In this Paper, the kinetics of the main reactions between the ethoxy radical and nitric oxide, under conditions where chain formation of nitrogen and nitrogen dioxide does not occur, are considered with special reference to cross disproportionation : combination ratios.

EXPERIMENTAL

The experimental technique was described in Part I.¹ Tables 1 and 2 give details of the products obtained at 135 and 95°, respectively.

TABLE 1.
Reaction at 135°.

Initial press. (mm.)			Yield (mm.)					% DEP* reacted	S †	Δ
DEP *	NO	DEP : NO	EtO·NO	Me·CHO	EtOH	N ₂	N ₂ O			
132·5	68·3	1·94	10·35	3·73	2·15	0·06	0·54	6·1	0·85	0·36
134·3	135·1	0·99	10·44	3·54	1·91	0·26	0·34	6·0	0·92	0·35
132·6	134·9	0·98	10·67	3·07	1·50	0·24	0·49	5·7	1·00	0·29
134·1	139·2	0·96	17·09	5·43	2·88	0·54	0·65	9·5	1·01	0·33
132·5	181·7	0·73	12·41	4·33	1·92	0·29	0·48	7·0	0·83	0·36
136·1	274·7	0·50	13·18	3·95	1·50	0·46	0·53	6·8	0·92	0·32
103·3	214·4	0·48	9·46	3·04	1·47	0·46	0·31	6·8	1·07	0·35
136·1	416·3	0·33	23·88	6·38	2·49	0·82	1·53	12·0	0·84	0·28
131·6	449·9	0·29	23·53	5·82	2·02	0·70	1·00	11·9	1·00	0·26
76·1	443·3	0·17	14·08	3·12 (?)	1·35	0·48	1·03	12·2	—	0·23
20·6	411·8	0·05	3·58	0·86	‡	0·07	0·95	11·2	—	0·25

* DEP Diethyl peroxide. † For meaning of S, see text. ‡ Not estimated.

Hydrogen is omitted from the products, since it was shown in Part I that it is probably formed from the peroxide itself by a heterogeneous reaction.

¹ Arden and Phillips, Part I, preceding Paper.

TABLE 2.

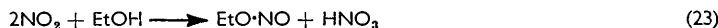
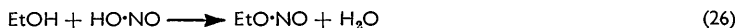
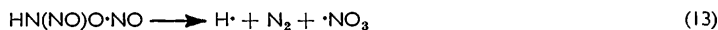
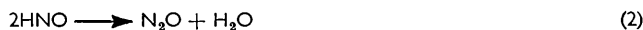
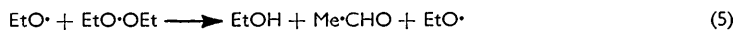
Reaction at 95°.

Initial press. (mm.)			Yields (mm.)					% DEP * reacted	S †	Δ
DEP *	NO	DEP : NO	EtO·NO	Me·CHO	EtOH	N ₂	N ₂ O			
133·6	66·7	2·00	11·91	3·97	2·20	0·43	0·10	6·7	0·88	0·35
132·5	75·6	1·75	13·28	3·69	2·32	0·40	0·30	7·3	1·06	0·29
133·5	89·5	1·49	13·17	3·74	3·16	0·45	0·36	7·5	1·03	0·30
138·6	110·5	1·25	16·84	3·72	‡	1·50	0·12	7·4	1·07	0·26

Refs. as for Table I.

DISCUSSION

The reaction mechanisms involved, which were discussed in Part I, are as follows: *



Since only the early stages of reaction are considered, radical attack on ethyl nitrite and acetaldehyde is neglected; this is supported by the absence of carbon monoxide, which would be a product of such reactions with acetaldehyde. The possible propagation step



is excluded, since it was shown in Part I that removal of hydrogen atoms by means of reaction (20) is probably as fast.

Stoichiometry.—On the basis of the above reactions, it can be shown by stoichiometry that the following relationships should hold:

$$[\text{Me}\cdot\text{CHO}(e)] - [\text{Me}\cdot\text{CHO}(5)] = [\text{Me}\cdot\text{CHO}(1)] = [\text{HNO}(1)] = 2[\text{N}_2\text{O}] + [\text{N}_2] + [\text{EtOH}(7)];$$

$$[\text{EtOH}(7)] = [\text{EtOH}(3)] + [\text{EtOH}(23)] + [\text{EtOH}(26)] - [\text{EtOH}(5)];$$

$$[\text{EtOH}(5)] = [\text{Me}\cdot\text{CHO}(5)]; \quad [\text{EtOH}(23)] = \frac{1}{2}[\text{N}_2]; \quad [\text{EtOH}(26)] = [\text{N}_2]$$

where the numbers in parentheses refer to the relevant reactions, and (e) refers to the estimated amount, *i.e.*, that found by analysis of products. It then follows that

$$[\text{Me}\cdot\text{CHO}(e)] = 2[\text{N}_2\text{O}] + 2\frac{1}{2}[\text{N}_2] + [\text{EtOH}(e)]$$

* The numbering used for the reactions mentioned in Part I¹ has been retained in the present Paper.

The ratio S , the right-hand side of this expression divided by the left-hand side, is given in Tables 1 and 2, from which it is seen that the relationships are substantially valid; the scatter is due to inherent experimental difficulties. Errors in the nitrogen determination are unlikely to be large but it was difficult to ensure good accuracy for nitrous oxide because of the variable intensity of the $m/e = 44$ peak obtained in the mass-spectrometric determination of nitric oxide, due to its reaction with carbon on the filament.

Kinetics.—It can readily be shown that

$$R_{\text{EtO}\cdot\text{NO}(3)} = k_3[\text{EtO}\cdot][\text{NO}]$$

where $[\text{EtO}\cdot\text{NO}(3)]$, by stoichiometry, equals $[\text{EtO}\cdot\text{NO}(e)] - \frac{3}{2}[\text{N}_2]$, and that

$$R_{\text{Me}\cdot\text{CHO}(e)} = k_1[\text{EtO}\cdot][\text{NO}] + k_5[\text{EtO}\cdot][\text{DEP}] + k_4[\text{EtO}\cdot]^2$$

$$\text{whence} \quad \Delta = \frac{R_{\text{Me}\cdot\text{CHO}(e)}}{R_{\text{EtO}\cdot\text{NO}(3)}} = \frac{k_1}{k_3} + \frac{k_5[\text{DEP}]}{k_3[\text{NO}]} + \frac{k_4[\text{EtO}\cdot]}{k_3[\text{NO}]} \quad (\text{A})$$

Since radical-recombination reactions have zero activation energy, $E_3 = 0$, so that k_3 can be calculated from the relationship of Trotman-Dickenson,² corrected for the change in the number of reactant and product species:

$$R \ln (A_{-3}/A_3) = \Delta S + R$$

where A_{-3} and A_3 are the frequency factors, and ΔS is the entropy change (in concentration units). Taking Levy's value³ of $6.3 \times 10^{13} \text{ sec}^{-1}$ for A_{-3} , and values of 64.5 and 77.7 e.u., calculated from the additivity rules of Benson and Buss,⁴ for the entropies of the ethoxyl radical and ethyl nitrite, respectively, one obtains $A_3 = 3.2 \times 10^{10} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1} = k_3$. The value of k_4 is not known, but, by comparison with the rate of disproportionation reactions between ethyl radicals,⁵ it is not likely to be greater than about $10^{13} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$. Since $[\text{EtO}\cdot]$ will be negligible in comparison with $[\text{NO}]$, the expression (A) reduces to

$$\Delta = \frac{R_{\text{Me}\cdot\text{CHO}(e)}}{R_{\text{EtO}\cdot\text{NO}(3)}} = \frac{k_1}{k_3} + \frac{k_5[\text{DEP}]}{k_3[\text{NO}]}$$

so that a plot of Δ against $[\text{DEP}]/[\text{NO}]$ should give k_1/k_3 and k_5/k_3 . With the results obtained at 135°, the plot shows a scatter about a straight line with possibly a slight positive slope, giving $k_1/k_3 = 0.28$ and $k_5/k_3 = 0.04$; at 95°, the limited data give $k_1/k_3 = k_5/k_3 = 0.12$. The k_5/k_3 results are clearly incorrect because, judging from available data on hydrogen-abstraction and radical-recombination reactions, $E_5 > E_3$, so that k_5/k_3 at 135° should be greater than at 95°.

The value of k_5 can be estimated from known frequency factors and activation energies of similar reactions. Thus, Berces and Trotman-Dickenson⁶ find that the frequency factors for hydrogen-abstraction reactions by methoxyl radicals from n-butane and isobutane are about $10^{11} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$; they should be similar for similar ethoxy-radical reactions. Wijnen⁷ finds the activation energy for hydrogen abstraction from ethyl propionate by ethoxyl radicals is 5.5 kcal. mole⁻¹; E_5 should be similar. Using a value for k_5 of $1 \times 10^8 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ at 135°, found by this way, and that calculated above for k_3 , one finds $k_5[\text{DEP}]/k_3[\text{NO}] \cong 3 \times 10^{-3}$, so that the slope of the graph of Δ against $[\text{DEP}]/[\text{NO}]$ should, within experimental error, be negligible. The slopes obtained are clearly incorrect,

² Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, p. 16.

³ Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780.

⁴ Benson and Buss, *J. Chem. Phys.*, 1958, **29**, 546.

⁵ Kerr and Trotman-Dickenson, "Progress in Reaction Kinetics," Vol. I, Pergamon, 1961, p. 111.

⁶ Berces and Trotman-Dickenson, *J.*, 1961, 348.

⁷ Wijnen, *J. Amer. Chem. Soc.*, 1960, **82**, 3034.

owing to the inherent difficulties in product analysis. It is more realistic to reduce expression (A) still further to

$$\Delta = \frac{R_{\text{Me}\cdot\text{CHO}(e)}}{R_{\text{EtO}\cdot\text{NO}(3)}} = \frac{k_1}{k_3}$$

Values of Δ , the disproportionation : combination ratio for reaction between ethoxyl radicals and nitric oxide, obtained in this way are given in Tables 1 and 2. The average value at both 135 and 95° is 0.30, indicating that $E_1 \cong E_3 \cong 0$ kcal. mole⁻¹, which is in accordance with an enthalpy change of -28 kcal. mole⁻¹ for reaction (1). On the basis of the previously calculated value for k_3 , k_1 is therefore *ca.* 1×10^{10} mole⁻¹ cm.³ sec.⁻¹.

Only two other disproportionation : combination ratios for alkoxy radical-nitric oxide reactions are known. McMillan⁸ found that Δ for isopropoxyl radicals and nitric oxide is about 0.15 at 26° and 0.175 at 79°; the difference between the values for the two temperatures is probably due to experimental error, rather than representing an activation energy for the disproportionation reaction, and an average value of 0.16 will be used. Phillips⁹ found that reaction of dimethyl peroxide with nitric oxide at 174° gave a value for Δ of 0.5 for the methoxyl radical-nitric oxide reactions; the activation energy for disproportionation will probably be zero, as in the present work. All three results can be put on a comparative basis by dividing Δ by the number of possible hydrogen atoms, n , which can be abstracted by nitric oxide to give formaldehyde, acetaldehyde, or acetone from the respective alkoxy radicals (see Table 3). Δ/n is constant, within experimental error, in contrast to results obtained in the cross disproportionation of alkyl radicals.¹⁰

TABLE 3.

Radical	n	Δ	Δ/n
MeO·	3	0.5	0.17
EtO·	2	0.3	0.15
PrO·	1	0.16	0.16

The rates of the disproportionation reactions between methoxyl and nitric oxide, and between isopropoxyl and nitric oxide, can be determined by using the above values of Δ , if the rates of the combination reactions are calculated from the entropy relationship used above. Taking 10^{13} sec.⁻¹ for A_3 for methyl nitrite (which is the mean of the results of Steacie and Shaw¹¹ and Phillips¹²), Gray and Pratt's¹³ value of 71.5 e.u. for the entropy of methyl nitrite, and a value of 55.1 e.u. calculated for the entropy of the methoxyl radical from Benson and Buss,⁴ we obtain $A_3 = 4.6 \times 10^{10}$ mole⁻¹ cm.³ sec.⁻¹ for the combination of methoxyl radicals and nitric oxide. Since E_3 will be zero, the rate constant for disproportionation of methoxyl radicals and nitric oxide is *ca.* 2.3×10^{10} mole⁻¹ cm.³ sec.⁻¹. According to Steacie and Shaw,¹⁴ A_{-3} for isopropyl nitrite is 1.3×10^{14} sec.⁻¹, and the entropies of isopropyl nitrite and the isopropoxyl radical, calculated according to Benson and Buss,⁴ are 85.0 and 71.7 e.u., respectively. This gives $A_3 = 6.3 \times 10^{10}$ mole⁻¹ cm.³ sec.⁻¹ for recombination of isopropoxyl and nitric oxide; hence the rate constant for disproportionation is *ca.* 1×10^{10} mole⁻¹ cm.³ sec.⁻¹.

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⁸ McMillan, *J. Amer. Chem. Soc.*, 1961, **83**, 3018.

⁹ Phillips, unpublished work.

¹⁰ Ref. 4, p. 112.

¹¹ Steacie and Shaw, *Proc. Roy. Soc.*, 1934, *A*, **146**, 388.

¹² Phillips, *J.*, 1961, 3082.

¹³ Gray and Pratt, *J.*, 1958, 3403.

¹⁴ Steacie and Shaw, *Proc. Roy. Soc.*, 1935, *A*, **151**, 685.