

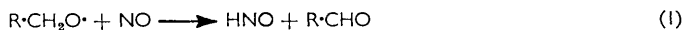
981. *Reactions in the Diethyl Peroxide–Nitric Oxide System. Part I. Oxidation and Reduction of Nitric Oxide: Reactions of Nitrosomethane and Nitroxyl.*

By (the late) E. A. ARDEN and L. PHILLIPS.

The gas-phase reactions of ethoxyl radicals, from the pyrolysis of diethyl peroxide, with nitric oxide have been studied in the range 95–135°. In addition to ethyl nitrite, acetaldehyde, and ethanol, large yields of nitrogen and nitrogen dioxide, which increase with increasing nitric oxide pressure, are formed at 95°, but not at 135°, where yields are small. This is explained in terms of reactions of nitrosomethane and nitroxyl, respectively, with nitric oxide. The former is a chain process, but the latter is not; this is consistent with the kinetics of the propagation and termination reactions involved. Nitrous oxide is formed in small amounts, probably by bimolecular decomposition of nitroxyl.

THE reactions of nitric oxide with alkoxy radicals are of importance in the understanding of the mechanism of pyrolysis of alkyl nitrites and nitrates. The production of

appreciable quantities of nitrous oxide, in the former case, is usually ascribed to the intermediate formation of nitroxyl, HNO ,¹ by reaction between the initial products, nitric oxide and alkoxy radicals,



and its subsequent decomposition



Nitrogen is formed only in very small yields from the simple alkyl nitrites, but in much larger amounts from complex nitrates;² the relevant reaction mechanisms have not been fully elucidated.

The reaction of ethoxy radicals, from the pyrolysis of diethyl peroxide, with nitric oxide was briefly studied by Levy,³ who found that ethyl nitrite (66% yield) and traces of nitrous oxide were the only identifiable products at 180°. The main object of Levy's work was to show that nitrous oxide was formed; no detailed characterisation of the reactions was carried out.

This Paper reports a detailed mechanistic investigation of the reactions of ethoxy radicals, from the pyrolysis of diethyl peroxide, with nitric oxide in the range 95–135°, with special reference to the role of nitroxyl, formed as in reaction (1), in oxidation and reduction of nitric oxide. The reactions of nitroxyl and of nitrosomethane with nitric oxide are compared. The kinetics of disproportionation and combination reactions between ethoxy and nitric oxide are considered in Part II.⁴

EXPERIMENTAL

Materials.—Diethyl peroxide was prepared by the hot ethylation of hydrogen peroxide (100 vol.), according to Wiley.⁵ After five washes with small quantities of ice-cold water, it contained 5–7% of diethyl ether and *ca.* 0.3% of acetaldehyde. Further purification was carried out with a preparative-scale gas-liquid chromatography apparatus, using Apiezon L as the stationary phase. The final product was ether-free, but contained *ca.* 0.3–0.4% each of acetaldehyde and ethanol which could not be removed by further treatment. It was stored at –40° under a vacuum, in the dark.

Nitric oxide was prepared by heating a mixture of potassium nitrite, potassium nitrate, chromic oxide, and ferric oxide, according to Ray and Ogg.⁶ The initial purity was *ca.* 99%; fractionation between liquid-oxygen and -nitrogen traps gave a product with a mass-spectrometric analysis as follows: 99.96% nitric oxide; 0.04% nitrogen.

Procedure.—Sufficient diethyl peroxide to give a pressure of *ca.* 130 mm. in the 150-ml. reaction vessel was vaporised into a 560-ml. flask, and left for 20 min. to ensure uniformity of initial acetaldehyde and ethanol content. A small portion of this was analysed for acetaldehyde and ethanol, using a Perkin-Elmer model 116 Fraktometer at 50°, with a six-foot column of tetraethylene glycol monomethyl ether on Embacel, and hydrogen as carrier gas. The remainder was simultaneously frozen into a 150-ml. pyrex reactor (previously flamed) fitted with a breaker tip and inlet constriction. Sufficient nitric oxide was then let into the 560-ml. flask, and then also frozen into the reactor flask, and the neck of the latter sealed off. The reactor was allowed to warm up to ambient temperature for 30 min., and then refrozen to check whether any air was present. This would have been revealed by the blue colour of N_2O_3 ; check experiments showed that the presence of 1 mm. of air (and probably much less) could easily be detected in this way. After heating for a specified time in a thermostatically controlled Aroclor bath, the reactor flask was quenched in cold water, fitted to a breaker device on a

¹ (a) Levy, *J. Amer. Chem. Soc.*, 1953, **75**, 1801; (b) Gray and Williams, *Nature*, 1960, **183**, 56; Phillips, *J.*, 1961, 3082.

² Gray, Rathbone, and Williams, *J.*, 1960, 3932; 1961, 2620; Gray, Rathbone, and Pearson, *J.*, 1961, 4006.

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

⁴ Arden, Phillips, and Shaw, Part II, following Paper.

⁵ Wiley, U.S.P. 2,357,298 (1944).

⁶ Ray and Ogg, *J. Amer. Chem. Soc.*, 1956, **78**, 5993.

vacuum line, opened, and the products let into a Leroy still at -193° . Fractions were removed at -193 , -170 , and *ca.* -120° into a gas burette, measured, and then analysed on an A.E.I. M.S.3 mass spectrometer. The absence of air-leaks was confirmed by the non-appearance of the argon peak at m/e 40 in the -193° fraction. The Leroy still was then warmed up, and the residual liquids were frozen into a 565-ml. flask and analysed by gas-liquid chromatography, using the apparatus previously described. Where nitrogen dioxide was observed visually to be present at the end of a run, a portion of the vaporised liquid fraction was expanded into a 10-cm. gas infrared cell fitted with Kel-F-coated sodium chloride windows, and the nitrogen dioxide estimated by measuring the optical density at 6.27μ on a Perkin-Elmer model 21 infrared spectrophotometer, after compensating for the absorption of the ethyl nitrite present. This nitrogen dioxide estimation is not very accurate.

Results.—(a) *Reaction at 135° .* Heating times of 10 min. were normally used, since the results of Hanst and Calvert⁷ indicated that *ca.* 6–7% decomposition of the peroxide should occur in this time. In some of the earlier work, heating times of *ca.* 15 min. were used, corresponding to peroxide conversion of *ca.* 12%. The liquid products from a series of runs at various diethyl peroxide (DEP): nitric oxide ratios were ethyl nitrite, acetaldehyde, and ethanol in the approximate ratio 3–4 : 1 : 0.3–0.5. The gaseous products contained nitrogen, nitrous oxide, and hydrogen in the amounts shown in Table 1; detailed results for the liquid products are given in Part II.⁴ The nitrogen balances were very good, so that no major nitrogen-containing compound was left undetected.

TABLE I.

Gaseous products of reaction at 135° .

Initial press. (mm.)			Yields (mm.)			% DEP decomposed
DEP	NO	DEP : NO	N ₂	N ₂ O	H ₂	
144.0	71.7	2.01	0.10	0.55	0.18	5.8
132.5	68.3	1.94	0.06	0.54	0.16	6.1
134.3	135.1	0.99	0.26	0.34	0.17	6.0
132.6	134.9	0.98	0.24	0.49	0.16	5.7
134.1	139.2	0.96	0.54 (?)	0.64	0.27	9.5
132.5	181.7	0.73	0.29	0.48	0.15	7.0
138.1	248.3	0.56	0.43	0.25 (?)	0.18	6.5
136.1	274.7	0.50	0.46	0.53	0.18	6.8
103.3	214.4	0.48	0.46	0.31	0.11 (?)	6.8
136.1	416.3	0.33	0.82	1.53 (?)	0.22	12.0 *
131.6	449.9	0.29	0.70	1.00	0.22	11.9 *
76.1	443.3	0.17	0.48	1.03	0.15	12.2 *
20.6	411.8	0.05	0.07	0.95	0.04	11.2 *

* Heating time, 15 min.

(b) *Reaction at 95° .* Heating times of 16 hr. were necessary, according to Hanst and Calvert,⁷ to obtain 5–6% decomposition of the peroxide. At peroxide : nitric oxide ratios of 1.25 and above, the products were very similar to those obtained at 135° , in that the liquid products were ethyl nitrite, acetaldehyde, and ethanol in the approximate ratio 4 : 1 : 0.5–0.8, and the gaseous products consisted of small amounts of nitrogen, nitrous oxide, and hydrogen. At lower peroxide : nitric oxide ratios, considerable differences were found; ethyl nitrite in larger amounts was the main product with smaller amounts of acetaldehyde, but large amounts of nitrogen and nitrogen dioxide, together with small amounts of nitrous oxide and hydrogen, were formed. The nitrogen and nitrogen dioxide yields increased almost linearly with initial nitric oxide pressure at constant initial peroxide pressure.

Wherever nitrogen in excess of about 2 mm. and free nitrogen dioxide were found, no free ethanol was present, carbon dioxide was formed in amounts increasing with initial nitric oxide pressure, and smaller amounts of methyl nitrite and ethyl nitrate were found. Water was also formed, but could not be estimated with reasonable accuracy by means of vapour-phase chromatography. Nitromethane in small amount was also probably produced, but was not estimated.

⁷ Hanst and Calvert, *J. Phys. Chem.*, 1959, **63**, 104.

The gaseous products are shown in Table 2; detailed results for the liquid products are given in Part II.⁴

TABLE 2.
Gaseous products of reaction at 95°.

Initial press. (mm.)			Yields (mm.)					% DEP decomposed
DEP	NO	DEP : NO	N ₂	N ₂ O	H ₂	NO ₂	CO ₂	
133.6	66.7	2.00	0.43	0.10	0.20	nil	nil	6.7
132.5	75.6	1.75	0.40	0.30	0.20	nil	nil	7.3
133.5	89.5	1.49	0.45	0.36	0.21	nil	nil	7.5
138.6	110.5	1.25	1.50	0.12	0.17	trace	trace	7.4
139.6	134.0	1.04	3.44	0.14	0.17	†	0.36	7.9
128.4	139.7	0.92	3.16	0.11	0.18	†	0.29	8.3
139.7	280.1	0.50	10.7	0.26	0.17	†	1.72	11.3
126.2	470.8	0.27	17.65	†	0.17	†	3.10	15.7
130.9 *	489.4	0.27	20.28	0.61	0.26	ca. 33	1.96 (?)	15.5
127.9	484.0	0.26	19.13	†	0.13	> 24	2.9	ca. 15
138.2	549.1	0.25	22.30	0.35	0.19	†	3.60	14.5
129.8	487.6	0.27	21.0	0.36	0.14	ca. 33	3.68	ca. 15

* Packed-vessel run. † Present, but not estimated.

DISCUSSION

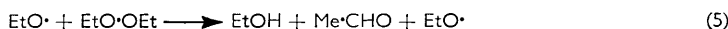
Ethoxyl radicals, produced by pyrolysis of the peroxide, are converted mainly into ethyl nitrite, in agreement with Levy's findings,³ but smaller amounts of acetaldehyde and ethanol are also formed. Ethyl nitrite is clearly formed by addition of nitric oxide to ethoxyl radicals



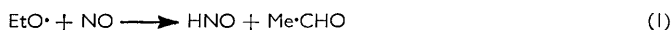
whilst acetaldehyde and ethanol could be formed by disproportionation of ethoxyl radicals



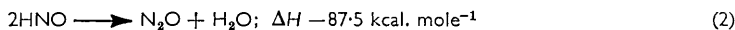
or by hydrogen abstraction from unreacted peroxide by ethoxyl radicals



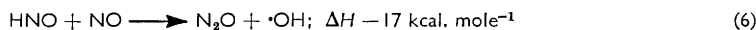
Abstraction from the nitrite or acetaldehyde formed is likely to be insignificant at the low peroxide conversions studied. Both reactions (4) and (5) would give acetaldehyde and ethanol in equal amounts, whereas the results show that the former predominates. The reaction usually postulated in alkyl nitrite pyrolyses, in which nitroxyl and acetaldehyde are formed, must therefore occur:



In alkyl nitrite pyrolyses, nitroxyl is thought to undergo bimolecular decomposition to give nitrous oxide and water, after Harteck.⁸



Another possibility is



but since nitrous oxide yields are always small, and apparently independent of initial nitric oxide concentration, this is unlikely. Since the nitrous oxide yields at 95°

⁸ Harteck, *Ber.*, 1933, **66**, 423.

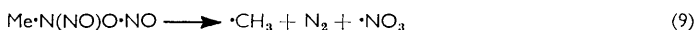
are increased by packing the reactor, reaction (2) appears to have a heterogeneous component. Another possible reaction of nitroxyl is that postulated by Levy for alkyl nitrite pyrolyses.^{1a}



The most surprising features of the results are the large nitrogen and nitrogen dioxide yields obtained at low peroxide : nitric oxide ratios at 95°, but not at 135°. At 95°, these yields increase with increasing initial nitric oxide pressure at constant initial peroxide pressure, and it is difficult to envisage a plausible mechanism not involving nitroxyl and nitric oxide. In a preliminary Note,⁹ it was pointed out that nitroxyl could be regarded as an analogue of nitrosomethane, which is known to react with nitric oxide¹⁰ to form the unstable *N*-methyl-*N*-nitrosohydroxylamine nitrite



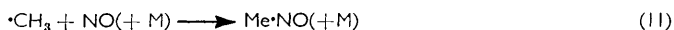
which then decomposes into a methyl radical, nitrogen, and the NO₃ radical



the latter then reacting rapidly with excess of nitric oxide to form nitrogen dioxide.

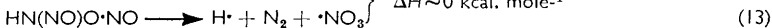
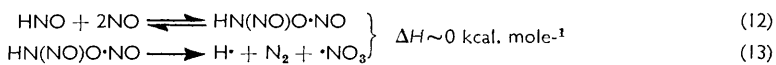


Further reaction of the methyl radical with nitric oxide

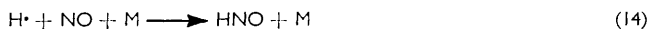


can then lead to a chain mechanism for reduction and oxidation of nitric oxide, to give nitrogen and nitrogen dioxide, respectively.

In the case of nitroxyl, it was suggested that the reactions were



followed by reaction (10), and regeneration of nitroxyl



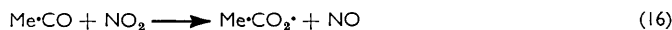
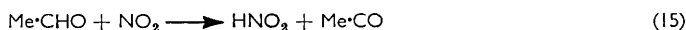
to give a chain reaction for production of nitrogen and nitrogen dioxide. Reaction (12) was thought to be an equilibrium, which might explain why large yields of nitrogen and nitrogen dioxide are obtained at high initial nitric oxide pressures at 95°, but not at 135°.

A re-examination of the results obtained at 95° shows that wherever yields of nitrogen are greater than about 1.5 mm., *i.e.*, at peroxide : nitric oxide ratios less than 1.25, then carbon dioxide, together with very small amounts of methyl nitrite, is formed, and the acetaldehyde yields are less than those obtained at higher initial reactant ratios. No carbon dioxide is detected at 135°, and no similar reductions in the acetaldehyde yields occur. This correlation between low acetaldehyde yields and high nitrogen and carbon dioxide yields at 95° indicates that nitrogen dioxide, produced from nitroxyl in the sequence of reactions (12), (13), and (10), reacts with acetaldehyde, formed in each of the reactions

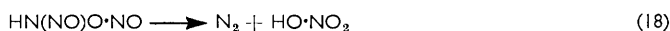
⁹ Arden and Phillips, *Proc. Chem. Soc.*, 1962, 354.

¹⁰ (a) Brown, *J. Amer. Chem. Soc.*, 1957, **79**, 2480; Donaruma and Carmody, *J. Org. Chem.*, 1957, **22**, 635; Batt and Gowenlock, *Trans. Faraday Soc.*, 1959, **56**, 682; Burrell, *J. Phys. Chem.*, 1962, **66**, 401; Forst and Rice, *Canad. J. Chem.*, 1963, **41**, 562; (b) Strausz and Gunning, *ibid.*, p. 1207.

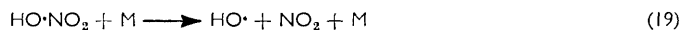
(1), (4), and (5), to produce methyl radicals and carbon dioxide according to the mechanism suggested by Pedler and Pollard¹¹ and recently confirmed here:¹²



The methyl radicals then react with nitric oxide by the sequence of reactions (11), (8), (9), and (10) to give large yields of nitrogen and nitrogen dioxide, and ultimately with nitrogen dioxide to produce nitromethane, methyl nitrite, and methyl nitrate. On this basis, it is necessary to postulate that the reactions between nitrosomethane and nitric oxide involve chains, whilst those between nitroxyl and nitric oxide do not. This is in agreement with the recent work of Strausz and Gunning,^{10b} who postulated, however, that chains are not formed in the nitroxyl–nitric oxide reaction because the intermediate *N*-nitrosohydroxylamine nitrite undergoes proton transfer to form nitric acid and nitrogen directly



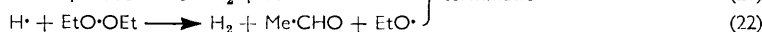
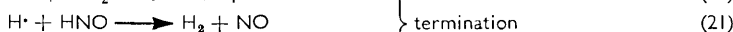
This cannot be reconciled with the present results, which require formation of free nitrogen dioxide from nitroxyl, before the nitrosomethane–nitric oxide chain reaction for production of large nitrogen and nitrogen dioxide yields can occur. Nitric acid, according to the results of Johnston, Foering, and White,¹³ should be very stable at 95° with respect to reaction (19)



and any direct reaction with acetaldehyde in the vapour phase at 95° is likely to be slow. The initial formation of nitrogen dioxide therefore occurs by way of the reaction sequence (12), (13), and (10).

The possibility that methyl radicals are produced by C–C bond fission in the ethoxyl radical can be excluded, because this is not observed in the pyrolysis of ethyl nitrite at *ca.* 200°.¹ Furthermore, this would give rise to large yields of nitrogen at 135°, which is not the case.

The occurrence of chain reactions in the nitrosomethane–nitric oxide system, but not in the nitroxyl–nitric oxide system, can be explained on the basis of the kinetics of the possible propagation and termination steps involved. For the nitroxyl system these are:



Clyne and Thrush¹⁴ give k_{14} as 1.5×10^{16} mole⁻² cm.⁶ sec.⁻¹, where M is hydrogen, but in the present work M will be diethyl peroxide plus nitric oxide. The peroxide should be perfectly efficient as a third body, and, judging from data on the recombination of halogen atoms,¹⁵ is likely to be about ten times as efficient as hydrogen. The efficiency of nitric oxide will not be very different from that of hydrogen; results on the thermal decomposition of nitrogen pentoxide¹⁵ suggest an efficiency ratio (NO/H₂) of about two. Using these relative efficiencies, at pressures of 120 mm. of peroxide and 450 mm. of nitric oxide, k_{14} becomes 5.7×10^{16} mole⁻² cm.⁶ sec.⁻¹, when M is the sum of peroxide plus nitric oxide.

¹¹ Pedler and Pollard, *Trans. Faraday Soc.*, 1957, **53**, 44.

¹² Phillips and Shaw, Tenth Symposium (International) on Combustion, Discussion on Elementary Reactions, Cambridge, 1964, in the press.

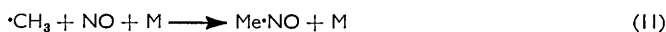
¹³ Johnston, Foering, and White, *J. Amer. Chem. Soc.*, 1955, **77**, 4208.

¹⁴ Clyne and Thrush, *Trans. Faraday Soc.*, 1961, **57**, 1305; 1962, **58**, 2283.

¹⁵ Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, pp. 84, 87.

For the possible termination reactions, Clyne and Thrush¹⁴ find $k_{21} > k_{14}$ ($M = H_2$), and from the results of Berlie and Leroy¹⁶ on the reaction of hydrogen atoms with ethane, k_{22} would appear to be about 3×10^8 mole⁻¹ cm.³ sec.⁻¹ at 95°. The presence of hydrogen in the products in the present work suggested that reactions (21) and (22) might be important termination reactions, but control experiments have shown that it is formed in similar amounts from the peroxide alone at 95°. Furthermore, if reactions (21) and (22) were important, hydrogen yields could never exceed nitrogen yields, assuming that hydrogen atoms are formed by way of reaction (13), whereas the results at 135° show that, at low nitric oxide pressures, this does happen. The virtual independence of hydrogen yields on nitric oxide pressure, and the dependence on peroxide pressure, strongly suggests that hydrogen is being formed directly from the peroxide by a mechanism not involving hydrogen atoms. The marked increase in hydrogen produced at 95° by packing the reaction vessel suggests a heterogeneous reaction. It is concluded, therefore, that the terminating reaction is (20), for which the results of Ashmore and Tyler,¹⁷ Rosser and Wise,¹⁸ and Phillips and Schiff¹⁹ give an average value for k_{20} of about 4×10^{13} mole⁻¹ cm.³ sec.⁻¹. It can then be shown that, at pressures of 120 mm. of peroxide, 450 mm. of nitric oxide, and 1 mm. of nitrogen dioxide, hydrogen atoms will be removed by the propagation reaction (14) about ten times more rapidly than by the termination reaction (20).

With the nitrosomethane–nitric oxide system, the propagation step is



and the only possible termination steps are



Reactions involving hydrogen abstraction by methyl radicals can be excluded, because methane is not a product. Hoare²⁰ gives k_{11} equal to 3.2×10^{17} mole⁻² cm.⁶ sec.⁻¹ with acetone as M , whilst Phillips and Shaw,¹² by comparing reactions (23) and (24) with (10) find k_{23} equal to 4.6×10^{12} mole⁻¹ cm.³ sec.⁻¹, and k_{24} to 1.4×10^{12} mole⁻¹ cm.³ sec.⁻¹ at 90°. Taking (23) as the main termination reaction, with pressures of reactants and nitrogen dioxide and the third-body efficiencies as before, it is found that methyl radicals are removed by the propagation reaction (11) about two hundred times faster than they are removed by termination.

The nitrosomethane–nitric oxide system is, therefore, far more favourable for chain formation of nitrogen and nitrogen dioxide than is the nitroxyl–nitric oxide system. Taking into account uncertainties in rate constants and third-body efficiencies, it is probable that termination will remove hydrogen atoms almost as rapidly as propagation at nitrogen dioxide pressures not much more than 1 mm. For the nitrosomethane–nitric oxide system, the present results indicate an average chain length of 6 to 12, based on the ratio of nitrogen to carbon dioxide; this should be compared with a minimal value of 4 to 12 reported by Strausz and Gunning.^{10b}

The stoichiometry of the reactions of nitroxyl and nitric oxide shows that twice as much nitrogen dioxide is formed as can react with hydrogen atoms produced, and therefore some will theoretically be available for reaction with acetaldehyde at 135°. However, the results show that, even at high initial nitric oxide pressures, nitrogen yields are low and no carbon dioxide is formed, so that reaction of the excess of nitrogen dioxide with acetaldehyde does not occur at 135°. This is in direct contrast to the results obtained at

¹⁶ Berlie and Leroy, *J. Chem. Phys.*, 1952, **20**, 200; *Discuss. Faraday Soc.*, 1953, **14**, 50.

¹⁷ Ashmore and Tyler, *Trans. Faraday Soc.*, 1962, **58**, 1108.

¹⁸ Rosser and Wise, *J. Phys. Chem.*, 1961, **65**, 532.

¹⁹ Phillips and Schiff, *J. Chem. Phys.*, 1962, **37**, 1233.

²⁰ Hoare, *Canad. J. Chem.*, 1962, **40**, 2012.

95°, and suggests that, at 135°, the excess of nitrogen dioxide is reacting preferentially with a substance other than acetaldehyde. The most likely reaction is that with ethanol which, according to the results of Gray and Yoffe on methanol,²¹ should be fast:



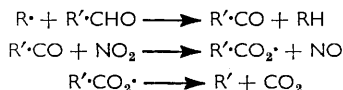
Check experiments showed that reaction (25) is much faster than reaction of nitrogen dioxide with acetaldehyde, (15), at ambient temperature. It is significant that at 95°, where large yields of nitrogen and nitrogen dioxide are found, no free ethanol is detected, whereas at 135°, where only small yields of nitrogen and no free nitrogen dioxide are found, ethanol is always present. It appears, therefore, that at 95°, at nitric oxide pressures greater than *ca.* 100 mm., nitrogen dioxide is being produced at a rate too high for its complete removal by hydrogen atoms (reaction 20) and ethanol. It will be shown in Part II⁴ that reactions (4) and (5) are insignificant under our conditions, so that (7) must be the only ethanol-producing reaction; however, whilst it may have a small activation energy ($\Delta H = -50$ kcal. mole⁻¹), this may not be large enough to explain the build-up of nitrogen dioxide at 95°. Another possibility is that reaction (12) is an equilibrium, which, because the forward reaction is exothermic, will lie more to the right at 95 than at 135°, so that more nitrogen dioxide and nitrogen should be produced from the nitroxyl-nitric oxide system at the lower temperature.

There is evidence from the results obtained at 95°, at high initial nitric oxide pressures, that direct reaction between nitrogen dioxide and diethyl peroxide occurs, probably by hydrogen abstraction,



because the rate of peroxide decomposition is appreciably greater than that (5–6%) predicted from the work of Hanst and Calvert.⁷ This reaction, however, is unlikely to compete with the nitrogen dioxide-acetaldehyde reaction, because of the relative strengths of the C–H bonds to be broken, and it is probably only of importance in the later stages of reaction when high nitrogen dioxide pressures have already been built up.

The chain mechanism for the production of nitrogen and nitrogen dioxide by way of nitrosomethane is of significance in the pyrolysis of the higher organic nitrites. Gray and his co-workers² found extensive reduction of nitric oxide to nitrogen in the pyrolysis of cyclohexyl, 1-methylcyclohexyl, 1-phenylethyl, and benzyl nitrites; carbon dioxide was also a product, but the mechanism of nitrogen production was not clear. It is probable that the mechanism suggested here is applicable, *i.e.*, nitroxyl, produced by reaction of nitric oxide with the alkoxy radical, gives, by way of the reaction sequence (12), (13), and (10), small amounts of nitrogen and nitrogen dioxide, and the latter then reacts with the acetyl-type radicals formed by radical attack on the aldehyde, to give carbon dioxide



and an alkyl or an aryl radical where R· is an alkoxy radical or nitrogen dioxide. The alkyl or aryl radical then reacts with nitric oxide by way of the reaction sequence (11), (8), (9), and (10), to give large amounts of nitrogen and nitrogen dioxide by a chain mechanism. The peroxy-radicals formed are more stable than the acyloxy-radicals, because large yields of the corresponding acids were formed by hydrogen-abstraction reactions.

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²¹ Gray and Yoffe, *J.*, 1951, 1412.