591. *The Pyrolysis of Methyl Nitrite.*

By L. Phillips.

The pyrolysis of methyl nitrite at temperatures between 150° and 240° has been investigated and the products have been analysed. The initial step is O–N bond fission to form methoxyl radicals and nitric oxide, which above ~180° react to form nitroxyl and formaldehyde, the former ultimately giving nitrous oxide and water. The effects of the products and of added hydrogen-donors in relation to the formation of nitrous oxide have been studied. Reaction of ethoxyl radicals with methyl nitrite and [$^2H_3$]methyl nitrite shows that hydrogen-abstraction is slow compared with disproportionation of alkoxyl. A kinetic analysis which accounts for all the major experimental facts has been developed. The effect of added nitric oxide on the pyrolysis of ethyl nitrite has been re-examined and an earlier report that production of nitrous oxide then increased was not confirmed.

As a result of early work by Steacie and Shaw [1] it is usually assumed that alkyl nitrites undergo O–N bond fission on pyrolysis at 200—250°, affording alkoxyl radicals and nitric oxide, the former being converted into alcohols and aldehydes or ketones. Doubt was cast on this simple mechanism by Carter and Travers [2] who found that some nitrous oxide was formed. More recently, Levy [3] showed that, in the pyrolysis of ethyl nitrite, extensive reduction of initially formed nitric oxide to nitrous oxide occurs, and he invoked the reactions:

$$\mathrm{Me{\cdot}CH_2{\cdot}O{\cdot} + NO \longrightarrow HNO + Me{\cdot}CHO}$$

$$\mathrm{2HNO \longrightarrow N_2O + H_2O}$$

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[1] Steacie and Shaw, *Proc. Roy. Soc.*, 1934, *A*, **146**, 388.
[2] Carter and Travers, *Proc. Roy. Soc.*, 1937, *A*, **158**, 495.
[3] Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780.

Arden and Powling [4] studied product-composition profiles in the decomposition flame from methyl nitrite at atmospheric pressure and found almost no reduction to nitrous oxide in the first stage of the flame, suggesting that under these conditions no nitroxyl (HNO) was formed from methoxyl and nitric oxide. Gray and Williams [5] have, however, recently reported that, under flow conditions simulating the decomposition flame, appreciable reduction to nitrous oxide occurs. Shaw and Trotman-Dickenson [6] have also reported that the pyrolysis is more complex than was originally thought.

The following work, carried out in 1957—1959, concerns the various reactions in the pyrolysis of methyl nitrite, which was studied in more detail than hitherto, and enables a fairly complete picture of the mechanism to be drawn.

EXPERIMENTAL

Materials.—Methyl nitrite was initially prepared from methanol and nitrous acid by Gray and Style's method,[7] condensed at −80°, fractionated *in vacuo*, and stored in blackened flasks. In later work the simple exchange between methanol and pentyl nitrite was used. Infrared spectra showed that both products were identical. Ethyl nitrite was prepared by the latter method.

[$^2H_3$]Methyl nitrite was prepared by exchange between [$^2H_4$]methanol (Merck) and pentyl nitrite. Purification was as for methyl nitrite.

Dimethyl peroxide was prepared by Rieche's method.[8] Diethyl peroxide was prepared by hot ethylation of hydrogen peroxide with diethyl sulphate.[9]

Cyclohexene was free from peroxides by shaking it with aqueous ferrous sulphate, then dried and distilled, the fraction boiling at 82—83° being used.

Other substances used were prepared by conventional methods.

Pyrolysis.—Pyrolysis was carried out recently in a conventional static apparatus, including a Pyrex reaction vessel (144 c.c.) fitted with a Pyrex spiral gauge manometer and mirror. The electrically heated furnace was controlled to $\pm 0{\cdot}1°$ with a Sunvic RT 2 resistance-thermometer controller. The original analytical scheme involved freezing reaction products **in** a liquid-nitrogen trap, warming the latter, and sharing the products with an infrared cell at ambient temperature. This method failed because (*a*) polymerisation of formaldehyde occurred, (*b*) formaldehyde hemiacetal, which was formed in the trap, did not completely dissociate into formaldehyde and methanol when warmed and complicated the infrared spectra, and (*c*) results for nitric oxide and unchanged methyl nitrite were inconsistent owing to hydrolysis of the nitrite by the water formed. The method finally adopted, which removed these difficulties, was to expand the hot products into an infrared cell at 120°, as used by Arden and Powling,[4] connecting tubing being electrically heated to about 100° to prevent polymerisation of formaldehyde. The following infrared absorption bands (μ) were used: formaldehyde 3·68, 5·74; methanol 9·68; nitrous oxide 4·5; nitric oxide 5·25; methyl nitrite 12·335; formaldoxime 11·24; hydrogen cyanide 14·05. Allowance was made for the methyl nitrite overlap at 9·68 when estimating methanol. Carbon monoxide and nitric oxide were also estimated mass-spectrometrically after fractionation. Water was estimated by the Fischer method, after removal of volatile material at −50°. The accuracy of the analytical methods was checked against known mixtures.

The flow apparatus used was of the conventional type, inlet and exit reactor pressures being measured with modified oil–mercury magnification manometers (20/1).[10] Products passed through two liquid-oxygen traps which retained all except carbon monoxide, hydrogen, and nitric oxide; these three were pumped into a storage flask and analysed for mass-spectrometrically for nitric oxide; the other products, after warming, were analysed by infrared spectrometry.

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[4] Arden and Powling, *Combustion and Flame*, 1958, **2**, 55.

[5] Gray and Williams, *Nature*, 1960, **188**, 56.

[6] Shaw and Trotman-Dickenson, *J.*, 1960, 3210.

[7] Gray and Style, *Trans. Faraday Soc.*, 1952, **48**, 1137.

[8] Rieche, *Ber.*, 1928, **61**, 951.

[9] Wiley, U.S.P. 2,357,298.

[10] Drucker, Jiméno, and Kangro, *Z. phys. Chem.*, 1915, *A*, **90**, 513.

RESULTS AND DISCUSSION

Pressure–time curves at 190—244° showed a first-order reaction to about 85% completion, in agreement with Steacie and Shaw's results,[1] and rate constants calculated from them and from loss of nitrite were in good agreement. Product analysis and rate constants from runs at starting pressures of 11 cm. are given in Table 1.

TABLE 1. *Product distribution (molar) from pyrolysis of methyl nitrite.*

	244°	220°	200°	190°	180°	147°
CH_2O	0·58	0·63	0·68	0·67	0·56	0·52
Me·OH	0·22	0·19	0·21	0·27	0·30	0·46
NO	0·46	0·45	0·69	0·72	0·78	0·96
N_2O	0·22	0·22	0·14	0·12	0·12	0·02
$CH_2{:}N{\cdot}OH$	0·04	0·04	0·01	0	0	0
HCN	0·01	0·02	0	0	0	0
CO	0·09	0·05	0·03	0·03	—	—
N_2	0·04	0·04	—	—	—	—
H_2O	NE	0·32	NE	NE	NE	
10^5k_1 (sec.$^{-1}$) (*a*)	424	68	13·0	5·0	—	—
(*b*)	1190	130	26·7	11·6	—	—

(*a*) Calc. from rate of loss of nitrate. (*b*) Calc. from Steacie and Shaw's data.[1] NE = not estimated.

Rate constants are approximately half those given by Steacie and Shaw;[1] a similar observation has recently been reported by Shaw and Trotman-Dickenson.[6] Analysis carried out at conversions from 7% upwards showed no marked variation in product distribution throughout the reaction at 180—244°. Atom balances were good for nitrogen but usually slightly low for carbon, presumably owing to polymerisation or slight losses of formaldehyde. At 220°, where water was estimated, hydrogen and oxygen balances are also good. A run carried out at 220° with a starting pressure of 3·5 cm. gave results almost identical with those above, and no fall-off in rate was observed.

Results obtained at 220° were very reproducible over long periods in the same reaction vessel, and could readily be repeated in new vessels cleaned in the same way (nitric acid–water). However, after the same vessel had been used for a very long time, a slight decrease in the yield of nitrous oxide was observed at 220° (0·18—0·19 mol.) and a slight brownish film was produced on the vessel walls. Furthermore, in later work with added formaldehyde, it was found that, if the products of reaction were left in the vessel overnight, a brownish-black tar was deposited on the walls. A straight methyl nitrite run carried out in this vessel gave only 0·08 mol. of nitrous oxide with 0·5 mol. of formaldehyde, 0·35 mol. of methanol and 0·8 mol. of nitric oxide, so that it appears that, under special wall conditions, yields of nitrous oxide can be substantially reduced. This was confirmed by subjecting a clean reaction vessel to repeated allyl bromide pyrolysis (cf. Green *et al.*[11]), thereby leaving a heavy carbonaceous layer on the walls, and then using this vessel for normal runs. Analysis of products showed that gross losses of formaldehyde occurred (presumably owing to polymerisation on the walls), but yields of nitrous oxide were substantially reduced whilst the apparent overall reaction rate increased markedly. After one treatment with allyl bromide, the yield of nitrous oxide was 0·03 mol.; with successive treatments this rose and appeared to become constant at about 0·13 mol.

In clean-wall conditions, however, it appears that heterogeneous reactions are unimportant since packing the reaction vessel with Pyrex tubing (S/V increased 8 times) changed neither the overall rate nor the product distribution. In all further work therefore clean-walled reaction vessels were used, and, in studies on the effect of additives on product distribution, the state of the walls was regularly checked by carrying out straight runs on methyl nitrite to confirm that yields of nitrous oxide were normal (*i.e.*, *ca.* 0·22 mol. at 220°).

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[11] Green and Maccoll, *J.*, 1955, 2450.

The products obtained at 147° appear to substantiate the results of Steacie and Shaw in that the main reactions can be represented:

$$2\mathrm{MeO{\cdot}NO} \longrightarrow \mathrm{CH_2O} + \mathrm{MeOH} + 2\mathrm{NO}$$

but as the temperature is raised, nitrous oxide and, to a smaller extent, formaldehyde increase in amount at the expense of nitric oxide and methanol. Nitrous oxide does not arise from secondary reactions of stable products because it remains virtually constant from about 7% reaction upwards; further, addition of stable reaction products had no effect on this yield.

These observations can be explained on the basis of a mechanism similar to that proposed by Levy[3] for ethyl nitrite, namely:

$$\mathrm{MeO{\cdot}NO} \rightleftharpoons \mathrm{MeO{\cdot}} + \mathrm{NO{\cdot}}$$

$$\mathrm{MeO{\cdot}} + \mathrm{NO} \longrightarrow \mathrm{CH_2O} + \mathrm{HNO}$$

$$2\mathrm{HNO} \longrightarrow \mathrm{H_2O} + \mathrm{N_2O}$$

$$2\mathrm{MeO} \longrightarrow \mathrm{CH_2O} + \mathrm{MeOH}$$

in which the nitrous oxide comes from nitroxyl, which itself arises by hydrogen abstraction from methoxyl by nitric oxide. Gray and Williams[5] proposed a similar mechanism of formation of nitrous oxide from methyl nitrite.

The presence of methoxyl radicals in decomposing methyl nitrite can readily be proved by adding a hydrogen-donor. Thus addition of cyclohexene, which as Rust *et al.*[12] have shown is a good donor in the presence of methoxyl radicals (from methyl t-butyl peroxide) at 195°, increases the yields of methanol and nitric oxide and almost eliminates nitrous oxide, at 220° as shown in Table 3 (the rate of loss of nitrite also increases). These changes are due to preferential reaction of methoxyl with cyclohexene, and support the view that nitrous oxide is formed by reaction of methoxyl with nitric oxide. The failure of added cyclohexene to eliminate formaldehyde suggests that some of the cyclohexenyl radicals may react with methoxyl to regenerate cyclohexene and formaldehyde. Further evidence was obtained from the effects of added formaldehyde and acetaldehyde. Thus added formaldehyde only very slightly decreased the yield of nitrous oxide at 220°, but yields of methanol and carbon monoxide were markedly greater, as was the rate of loss of nitrite (cf. Table 3). When however acetaldehyde was added, then yields of methanol, nitric oxide, formaldoxime, and hydrogen cyanide were markedly greater but no nitrous oxide was formed; the overall rate of reaction was also markedly greater. These observations are understood on the basis of the reactions:

TABLE 2. *Effect of added cyclohexene: molar yields.*[a]

$\mathrm{MeO{\cdot}NO} : \mathrm{C_6H_{10}}$	$\mathrm{CH_2O}$	MeOH	NO	$\mathrm{N_2O}$	CO	$\mathrm{N_2}$	10^5k_1 (sec.$^{-1}$)
1 : 1·1	0·34	0·48	0·90	0·03	0·04	0·02	118
1 : 2·8	0·32	0·51	0·96	0·003	0·05	0·02	130

Initial pressure of MeO·NO, 11 cm.

$$\mathrm{MeO{\cdot}} + \mathrm{CH_2O} \longrightarrow \mathrm{MeOH} + {\cdot}\mathrm{CHO}$$

$${\cdot}\mathrm{CHO} \longrightarrow \mathrm{H{\cdot}} + \mathrm{CO}$$

$$\mathrm{H{\cdot}} + \mathrm{NO} \longrightarrow \mathrm{HNO}$$

or

$${\cdot}\mathrm{CHO} + \mathrm{NO} \longrightarrow \mathrm{HNO} + \mathrm{CO}$$

$$2\mathrm{HNO} \longrightarrow \mathrm{N_2O} + \mathrm{H_2O}$$

and

$$\mathrm{MeO{\cdot}} + \mathrm{Me{\cdot}CHO} \longrightarrow \mathrm{MeOH} + \mathrm{CH_3{\cdot}CO{\cdot}}$$

$$\mathrm{CH_3{\cdot}CO{\cdot}} \longrightarrow \mathrm{Me{\cdot}} + \mathrm{CO}$$

$$\mathrm{Me{\cdot}} + \mathrm{NO} \longrightarrow \mathrm{MeNO} \longrightarrow \mathrm{CH_2{:}N{\cdot}OH} \longrightarrow \mathrm{HCN} + \mathrm{H_2O}$$

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[12] Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1950, **72**, 338.

TABLE 3. *Effect of added formaldehyde: molar yields.*[a]

$MeO{\cdot}NO : CH_2O$	CH_2O	MeOH	NO	N_2O	CO	10^5k_1 (sec.$^{-1}$)
1 : 0·9	—	0·40	0·51	0·20	0·21	111
1 : 1·9	—	0·62	0·56	0·19	0·30	117

[a] Initial pressure of MeO·NO, 11cm.

Thus for every methoxyl radical which abstracts hydrogen from formaldehyde, one formyl radical is produced which itself reacts with nitric oxide to form nitroxyl, so that, if the rate of the last reaction is comparable with that between methoxyl and nitric oxide, yields of nitrous oxide should be virtually unchanged. On the other hand, there is no plausible way in which acetyl can react with nitric oxide to form nitroxyl; the reaction $Me{\cdot}CO{\cdot} + NO \longrightarrow CH_2{:}CO + HNO$ can be excluded because yields of carbon monoxide were greatly increased.

One difficulty with the proposed mechanism of nitrous oxide formation is that Levy [3,13] reported that only very small yields of this oxide were obtained from ethoxyl radicals (formed from diethyl peroxide) and nitric oxide at 180°. Similar results have been obtained by treating dimethyl peroxide with nitric oxide at 180°. Thus in 30 minutes at 180° 35 mm. of dimethyl peroxide decomposed completely to give 1½ mol. of methanol and ½ mol. of carbon monoxide according to the mechanism:

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\begin{aligned}
Me_2O_2 &\longrightarrow 2MeO{\cdot} \\
2MeO{\cdot} &\longrightarrow CH_2O + MeOH \\
MeO{\cdot} + CH_2O &\longrightarrow MeOH + {\cdot}CHO \\
MeO{\cdot} + {\cdot}CHO &\longrightarrow MeOH + CO
\end{aligned}
$$

Since this work was completed similar results have been published by Calvert and Hahnst.[14] A mixture of 35 mm. of peroxide and 145 mm. of nitric oxide after 30 minutes at 180° gave only 0·02 mol. of nitrous oxide per methoxyl formed, the main product being methyl nitrite with smaller proportions of formaldehyde, methanol, and carbon monoxide. Pyrolysis of the nitrite under these conditions is negligible. Nitrogen, however, was not estimated, so the possibility remains that nitroxyl could be formed in large yield and then break down in other ways, *e.g.*, $2HNO \longrightarrow N_2 + 2HO{\cdot}$. This was disposed of by repeating Levy's work with diethyl peroxide and nitric oxide; nitrogen and nitrous oxide yields were only 0·03 mol. per ethoxyl radical produced.

This apparent anomaly finds ready explanation in the activation energies for the competing reactions in dialkyl peroxide–nitric oxide systems. Thus that forming methyl nitrite, $MeO{\cdot} + NO \longrightarrow MeO{\cdot}NO$, should have zero activation energy, but that leading to nitroxyl, $MeO{\cdot} + NO \longrightarrow HNO + CH_2O$, will certainly be greater than zero. The latter will therefore be favoured by higher temperatures, as is in fact found in pyrolysis of methyl nitrite, and the formation of any nitrous oxide at 180° by reaction between dialkyl peroxides and nitric oxide can be regarded as evidence for the formation of larger yields in this way at higher temperatures. Direct proof cannot be obtained because if peroxide and nitric oxide were allowed to react at, say, 220° pyrolysis of the methyl nitrite formed would yield nitrous oxide.

A further apparent anomaly is that on the basis of the postulated mechanism addition of nitric oxide would be expected to increase the yield of nitrous oxide, whereas no such effect is observed in 1 : 2 nitrite–nitric oxide mixtures, although the yield of formaldehyde increases and that of methanol decreases whilst the rate of loss of nitrite remains virtually unchanged. Again these observations can be explained on the basis of the various reactions competing for methoxyl and will be dealt with below. The above result is in direct contradiction to that of Levy,[3] who found that addition of nitric oxide markedly increased yields of nitrous oxide in the pyrolysis of ethyl nitrite; repetition of Levy's work

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[13] Levy, *J. Amer. Chem. Soc.*, 1953, **75**, 1801.

[14] Calvert and Hahnst, *J. Phys. Chem.*, 1959, **63**, 104.

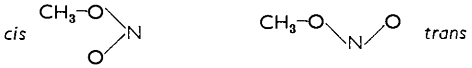
with ethyl nitrite at 200° did not confirm his finding, the yield of nitrous oxide being unchanged by addition of nitric oxide whilst that of acetaldehyde increased and that of ethanol decreased.

The above observations on the effect of nitric oxide refer to the condition where its concentration is relatively large. In the very early stages of pyrolysis without added nitric oxide, it might be expected that yields of nitrous oxide would increase progressively with time because of the build-up of nitric oxide concentration. Some evidence of this has been obtained by studying the reaction at low pressures (2—5 mm.) in a flow system at 295°, as shown in Table 4.

TABLE 4. *Effect of reaction time on yields of nitrous oxide in a flow system.*

Reaction time (sec.)	0·48	0·93	2·0	6·0
Decomposition (%)	3	6	19	45
NO : N_2O	250	220	30	8

An alternative mechanism for formation of nitrous oxide, which may occur conjointly with the nitric oxide–methoxyl reaction, is direct intramolecular elimination of nitroxyl, $MeO{\cdot}NO \longrightarrow CH_2O + HNO$, as postulated for the pyrolysis and photolysis of higher alkyl nitrites.[15] More recently Brown and Pimentel,[16] in matrix isolation studies at 20° K on the photolysis of nitromethane and methyl nitrite, identified nitroxyl by infrared spectroscopy and ascribed it to intramolecular elimination from the *cis*-form of the nitrite, although they do not exclude the possibility of reaction between methoxyl and nitric oxide.



If nitrous oxide is formed by elimination of nitroxyl in this way, it would be expected that the *cis*-form would become more abundant as the temperature was raised because it has been shown above that yields of nitrous oxide increase from 147° to 220°. However, Tarte's infrared data[17] for −80° and +23° suggest that the *trans*-form becomes more abundant as the temperature is raised. This has been confirmed at 25—230°; Table 5 shows the ratios of the optical densities of the 5·95 and 6·15 μ peaks which Tarte has assigned to the *trans*- and *cis*-$\nu_{N=O}$ vibrations respectively. Intramolecular elimination cannot therefore be supported.

TABLE 5. *Variation of* cis/trans *ratio, determined from optical densities, with temperature.*

Temp. (c)	−253°	−80°	+25°	+120°	+180°	+230°
cis/trans	1·7 [a]	1·4 [b]	1·13	0·88	0·81	0·71

[a] Ref. 16. [b] Ref. 17.

A further possibility for nitroxyl formation involves splitting of the initially formed methoxyl radical:

$$MeO{\cdot} \longrightarrow CH_2O + H{\cdot};\quad \Delta H\ 25\ \text{kcal. mole}^{-1}$$

$$H{\cdot} + NO \longrightarrow HNO$$

as proposed by Gray and Style[7] in their photolytic work. In their work, however, this reaction was made possible by the excess of energy remaining after irradiation; in the present instance it is unlikely on energetic grounds. Its non-occurrence has been demonstrated by decomposing methyl nitrite in the presence of acetaldehyde, when the reaction $H{\cdot} + Me{\cdot}CHO \longrightarrow H_2 + Me{\cdot}CO{\cdot}$ would be expected: no hydrogen was detected in the products.

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[15] Purkis and Thompson, *Trans. Faraday Soc.*, 1936, **32**, 1466; Gowenlock, *Chem. Soc. Special Publ.*, *No.* 10, 1957, p. 82.

[16] Brown and Pimentel, *J. Chem. Phys.*, 1958, **29**, 884.

[17] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570.

Methoxyl radicals not reacting with nitric oxide might react in several ways to give methanol and formaldehyde. The reactions proposed by Steacie and Shaw, namely:

$$\mathrm{MeO\cdot} \longrightarrow \mathrm{H\cdot} + \mathrm{CH_2O}$$

$$\mathrm{H\cdot} + \mathrm{MeO\cdot} \longrightarrow \mathrm{MeOH}$$

can be discounted for reasons given above. Disproportionation has been suggested by several workers, *e.g.*, Powling and Arden,[4] in the sense:

$$2\mathrm{MeO\cdot} \longrightarrow \mathrm{CH_2O} + \mathrm{MeOH};\ \Delta H\ -75\ \text{kcal. mole}^{-1}$$

and it is energetically very favourable. The abstraction reaction,

$$\mathrm{MeO\cdot} + \mathrm{MeO{\cdot}NO} \longrightarrow \mathrm{MeOH} + \mathrm{CH_2O} + \mathrm{NO};\ \Delta H\ -39\ \text{kcal. mole}^{-1}$$

analogous to that proposed by Phillips[18] for the alkyl nitrates, has been discounted by Levy[13] who showed that ethoxyl did not abstract hydrogen atoms from ethyl nitrite at 180°. This conclusion was based on the fact that no change in ethyl nitrite concentration occurred when mixtures of nitrite and diethyl peroxide were heated for sufficient time completely to decompose the latter. It is, however, not unequivocal because, as Levy showed, nitric oxide produced in the abstraction could react rapidly with the ethoxyl radicals from the peroxide to regenerate ethyl nitrite. In an attempt to resolve this point, diethyl peroxide was heated in the presence of methyl nitrite for sufficient time at 180° to decompose all of the former (under these conditions pyrolysis of the nitrite is negligible). If hydrogen abstraction occurred, then *ethyl* nitrite should be found in the products:

$$\mathrm{EtO\cdot} + \mathrm{MeO{\cdot}NO} \longrightarrow \mathrm{EtOH} + \mathrm{CH_2O} + \mathrm{NO}$$

$$\mathrm{NO} + \mathrm{EtO\cdot} \longrightarrow \mathrm{EtO{\cdot}NO}$$

An initial mixture of 41·4 mm. of methyl nitrite and 21·1 mm. of diethyl peroxide gave 38·0 mm. of methyl nitrite and 2·7 mm. of ethyl nitrite. Control experiments showed that no ethyl nitrite was formed by exchange between ethanol (from the peroxide) and methyl nitrite. It appears, therefore, that only about 6·5% of the ethoxyl radicals produced abstract hydrogen from methyl nitrite. Since even this evidence might be confused by exchange between ethoxyl and the methyl nitrite, ethoxyl (from the peroxide) was allowed to react with [$^2H_3$]methyl nitrite. [$^2H_1$]Ethanol, estimated mass spectrometrically, amounted to about 8% of the available ethoxyl radicals; this is in good agreement with the above result. Therefore, on the assumption that the reactivities of methoxyl and ethoxyl are similar, it is considered that hydrogen abstraction from methyl nitrite at 180° is very slow.

Another reaction possibly leading to methanol is that proposed by Levy:[3]

$$\mathrm{MeO\cdot} + \mathrm{HNO} \longrightarrow \mathrm{MeOH} + \mathrm{NO};\ \Delta H\ -14\ \text{kcal. mole}^{-1}$$

This appears feasible, especially as Dalby[19] has shown that nitroxyl has a comparatively long life, but, on balance, it is considered that the energetically more favourable disproportionation of methoxyl is more likely.

Whilst, therefore, it appears that, in the temperature range studied, methoxyl radicals preferentially disproportionate rather than abstract hydrogen from the nitrite, at higher temperatures the position may be reversed since Wijnen[20] has shown that hydrogen abstraction from methyl acetate by methoxyl requires an activation energy of 4·5 kcal. mole^{-1}, to be compared with the expected zero for disproportionation.

[18] Phillips, *Nature*, 1947, **160**, 753; Ph.D. Thesis, London, 1949.
[19] Dalby, *Canadian J. Phys.*, 1958, **10**, 1336.
[20] Wijnen, *J. Chem. Phys.*, 1948, **16**, 353.

The origin of the small amounts of formaldoxime produced at 220° is obscure, but a possibility is:

$$\mathrm{MeOH + HNO \longrightarrow Me{\cdot}NO + H_2O}$$

$$\mathrm{Me{\cdot}NO \longrightarrow CH_2{:}N{\cdot}OH}$$

Gowenlock and Lüttke [21] have pointed out that *C*-nitroso-compounds can react in this way; nitroxyl might react similarly. Some evidence for this is found in the fact that added cyclohexene, which eliminates formation of nitrous oxide, also eliminates that of formaldoxime. The small amounts of carbon monoxide formed clearly come from methoxyl attack on formaldehyde, since they are greatly increased by addition of the latter. Ethylene glycol, stated [22] to be formed by methoxyl attack on methanol at 160°, was not detected.

The reaction mechanism for pyrolysis of methyl nitrite at 180—240° can therefore be represented as follows:

$$\mathrm{MeO{\cdot}NO \longrightarrow MeO{\cdot} + NO} \qquad (1)$$

$$\mathrm{MeO{\cdot} + NO \longrightarrow MeO{\cdot}NO} \qquad (2)$$

$$\mathrm{MeO{\cdot} + NO \longrightarrow CH_2O + HNO} \qquad (3)$$

$$\mathrm{2MeO{\cdot} \longrightarrow MeOH + CH_2O} \qquad (4)$$

$$\mathrm{2HNO \longrightarrow (HNO)_2} \qquad (5)$$

$$\mathrm{(HNO)_2 \longrightarrow N_2O + H_2O} \qquad (6)$$

$$\mathrm{MeO{\cdot} + MeO{\cdot}NO \longrightarrow MeOH + CH_2O + NO} \qquad (7)$$

$$\mathrm{MeO{\cdot} + CH_2O \longrightarrow MeOH + {\cdot}CHO} \qquad (8)$$

$$\mathrm{MeO{\cdot} + {\cdot}CHO \longrightarrow MeOH + CO} \qquad (9)$$

(Reactions leading to small amounts of nitrogen and formaldoxime have been ignored for simplicity of kinetic treatment. The decomposition of nitroxyl into nitrous oxide and water is written as an association followed by a first-order process.[23])

Kinetic analysis of this scheme has to account for the following facts observed at 220°: (*a*) the rate of disappearance of nitrite is of first-order and is substantially unaffected by addition of nitric oxide, (*b*) the rate of formation of nitrous oxide is independent of nitric oxide concentration (except possibly in the early stages of reaction), (*c*) methanol formation is suppressed by addition of nitric oxide, (*d*) formaldehyde yields are, at the most, only slightly increased by addition of nitric oxide, and (*e*) the rate of disappearance of nitrite is increased by addition of hydrogen-donors.

A stationary-state treatment leads to a quadratic expression for methoxyl concentration which would be too cumbersome for simple use. The partial solution

$$[\mathrm{MeO{\cdot}}] = \frac{k_1[\mathrm{MeO{\cdot}NO}]}{(k_2 + k_3)\,[\mathrm{NO}] + k_4[\mathrm{MeO{\cdot}}] + 2k_8[\mathrm{CH_2O}] + k_7[\mathrm{MeO{\cdot}NO}]}$$

is however sufficient, and leads to:

$$-R_{\mathrm{MeO{\cdot}NO}} = k_1[\mathrm{MeO{\cdot}NO}] + \frac{k_1k_7[\mathrm{MeO{\cdot}NO}]^2 - k_1k_2[\mathrm{MeO{\cdot}NO}][\mathrm{NO}]}{(k_2 + k_3)[\mathrm{NO}] + k_4[\mathrm{MeO{\cdot}}] + 2k_8[\mathrm{CH_2O}] + k_7[\mathrm{MeO{\cdot}NO}]}$$

Since reaction (7) is relatively slow, and carbon monoxide yields are relatively small (except when formaldehyde is added),

$$(k_2 + k_3)[\mathrm{NO}] + k_4[\mathrm{MeO{\cdot}}] \gg 2k_8[\mathrm{CH_2O}] + k_7[\mathrm{MeO{\cdot}NO}];$$

hence $$-R_{\mathrm{MeO{\cdot}NO}} \approx k_1[\mathrm{MeO{\cdot}NO}] + \frac{k_1k_7[\mathrm{MeO{\cdot}NO}]^2 - k_1k_2[\mathrm{MeO{\cdot}NO}][\mathrm{NO}]}{[\mathrm{NO}]\{(k_2 + k_3) + k_4[\mathrm{MeO{\cdot}}]/[\mathrm{NO}]\}}$$

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[21] Gowenlock and Lüttke, *Quart. Rev.*, 1958, **12**, 321.

[22] Takezaki and Takeuchi, *J. Chem. Phys.*, 1954, **22**, 1527.

[23] Cf. Harteck, *Ber.*, 1933, **66**, 423.

Now [NO] will be much larger than [MeO•] except in the early stages of reaction, so

$$-R_{\text{MeO·NO}} \approx k_1k_3[\text{MeO·NO}]/(k_2 + k_3),$$

which satisfies point (*a*).

Similarly, the rate of formation of nitrous oxide can be shown to be:

$$R_{\text{N}_2\text{O}} \approx \frac{\frac{1}{2}k_1k_3[\text{MeO·NO}]}{(k_2 + k_3) + k_4[\text{MeO·}]/[\text{NO}]}$$

which, except in the very early stages of reaction, reduces to:

$$R_{\text{N}_2\text{O}} \approx k_1k_3[\text{MeO·NO}]/2(k_2 + k_3),$$

which satisfies point (*b*). In the very early stages of reaction, k_4[MeO•]/[NO] would become appreciable with respect to $(k_2 + k_3)$, and nitrous oxide formation would then show dependence on nitric oxide concentration. This might explain the results obtained under flow conditions.

In a similar manner it can be shown that methanol formation is inversely proportional to, and that of formaldehyde is substantially independent of, nitric oxide concentration. In the presence of an added hydrogen, the reaction

$$\text{MeO·} + \text{RH} \longrightarrow \text{MeOH} + \text{R} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10$$

must be introduced; the rate of loss of nitrite becomes

$$-R_{\text{MeO·NO}} = k_1[\text{MeO·NO}] - \frac{k_1k_2[\text{MeO·NO}][\text{NO}]}{(k_2 + k_3)[\text{NO}] + k_4[\text{MeO·}] + k_{10}[\text{RH}]}$$

With good donors (*e.g.*, cyclohexene, aldehydes), k_{10}[RH] becomes relatively very large, so that the above expression tends to

$$-R_{\text{MeO·NO}} = k_1[\text{MeO·NO}],$$

i.e., the rate of loss of nitrite increases.

The reaction mechanism given above thus accounts for all the major experimental findings.

The temperature-dependence of the rate of loss of nitrite gives the relation:

$$k = 10^{12 \cdot 2} \exp(-34{,}300/\boldsymbol{R}T) \text{ (sec.}^{-1})$$

as compared with

$$k = 1{\cdot}84 \times 10^{13} \exp(-36{,}400/\boldsymbol{R}T) \text{ (sec.}^{-1})$$

found by Steacie and Shaw.[1] Activation energies for the pyrolysis of alkyl nitrites are usually equated with the O–N bond energy.[24] The kinetic analysis developed herein shows that the first-order rate constant approximates to $k_1k_3/(k_2 + k_3)$ which can only equal k_1 if $k_2 \ll k_3$ which is certainly not true since the rate of recombination of methoxyl and nitric oxide is high. The apparent activation energy can at the best be only a rough approximation of the O–N bond energy.

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[24] Gray and Williams, *Chem. Rev.*, 1959, **59**, 250.