The Thermal Decomposition of Formaldehyde in the Presence of Nitric Oxide

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The pyrolysis of formaldehyde was investigated in the presence of nitric oxide at 500 °C. The kinetics of the reaction suggests that the pyrolysis proceeds by means of a mechanism which is initiated by this reaction:

$$NO + CH_2O \longrightarrow HNO + CHO$$

and which involves this reaction:

$$HNO + HNO \longrightarrow N_2 + 2OH$$

as one of the chain-carrying steps.

Nitric oxide has generally been used as an inhibitor in the free-radical reactions in the gaseous phase. This compound, however, has been found to have an accelerative effect on the free-radical reaction in addition to an inhibitive one. Thus, the mechanisms of reactions containing nitric oxide are so complex that the reaction schemes proposed by various workers do not necessarily coincide with each other.

Both effects of nitric oxide are typically exhibited in the pyrolysis of dimethyl ether;[1-3] that is, the pyrolysis is suppressed almost completely by the addition of a small amount of nitric oxide, and, after maximal inhibition, it is linearly accelerated by an increased amount of nitric oxide. Thus, the inhibitive and accelerative parts in the kinetics are very clearly separated in the case of dimethyl ether, suggesting that this compound is suitable for a study of the effects of nitric oxide.

It is known that the free-radical decomposition of dimethyl ether follows this stoichiometric relation:

$$CH_3OCH_3 \longrightarrow CH_4 + CH_2O$$

and that the formaldehyde thus formed decomposes easily by a chain reaction following this stoichiometric relation:

$$CH_2O \longrightarrow CO + H_2.$$

In the presence of nitric oxide, however, the amount of hydrogen in the product of dimethyl-ether pyrolysis is very small compared with that of carbon monoxide, in contrast to the case of the absence of nitric oxide, suggesting that the reaction mechanism is complex, though the kinetics is very simple.

This work was attempted in order to investigate the effect of nitric oxide on the thermal decomposition of formaldehyde; we expected to obtain valuable information about its effect on that of dimethyl ether.

Experimental

Materials. The formaldehyde was prepared by the distillation of paraformaldehyde at about 120 °C, condensing the methanol and water involved by means of at −78 °C. The nitric oxide was obtained from the Takachiho Kagaku Co. Ltd. in a research-grade purity of 99.6%. It was subjected to several trap-to-trap distillations.

Apparatus. The reaction was studied in a conventional static system, and was carried out in a cylindrical Pyrex glass vessel of 210 cm^3 placed in an electric furnace, which was itself wrapped in asbestos and placed inside a cylindrical aluminium collar (20 cm in length, 9 cm in diameter, and with walls 1.6 cm thick) to hold the temperature constant.

Procedure. Required quantities of formaldehyde and nitric oxide were introduced into the vessel, which had until then been kept at the experimental temperature. In order to avoid the decomposition of the formaldehyde alone, the two substances were introduced in the order of (i) nitric oxide and (ii) formaldehyde. The products of decomposition were analyzed quantitatively by means of a gas chromatograph.

Analysis. After the pyrolysis, using a Toepler gauge, the unreacted reactants and products were passed through a trap at −78 °C, where a part of the unreacted formaldehyde and the high-boiling-point products, methanol and water, were condensed. The uncondensable fraction at −78 °C was passed through a trap at −196 °C, where the remaining parts of the unreacted formaldehyde, the unreacted nitric oxide, the carbon dioxide, and the nitrous oxide were condensed, while the uncondensable fraction at −196 °C was collected and measured by means of the Toepler gauge. That fraction was composed of carbon monoxide, hydrogen, and nitrogen. The quantity of each fraction of the products was measured by means of a gas chromatograph. Carbon monoxide, hydrogen, and nitrogen were analysed on a 2 m Molecular Sieve 5A column at room temperature, the carbon dioxide and nitrous oxide, on a 4 m Porapak Q column at room temperature, and the methanol, on a 2 m PEG-400 column at 80 °C. No quantitative analysis of formaldehyde was carried out; some of it polymerized on a glass tube of the collecting system, so accurate measurement was very difficult. Identification was achieved by using IR, a mass spectrometer, NMR measurements, and an elemental analyzer as well as a gas chromatograph.

Results

The yields of carbon monoxide, hydrogen, methanol, nitrogen, nitrous oxide, and carbon dioxide were measured at various times during the uninhibited and inhibited pyrolyses of formaldehyde. Some results are shown in Fig. 1. The figure shows that the amount of each product increases linearly with the time after 5 min even though the rate is higher at the beginning of the reaction. In this work the initial rate of the formation of each product was determined from the

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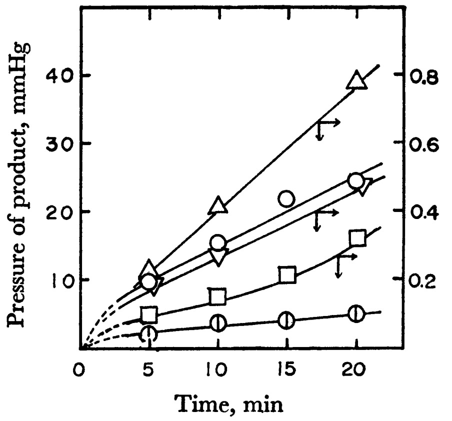

Fig. 1. Yields of products in the pyrolysis of 100 mmHg formaldehyde for 50 mmHg nitric oxide at 500°C.
○: CO, ⦶: N_2, □: N_2O, △: H_2, ▽: CO_2

slope of the line in the yield-time curve, except for the true initial part of the curve.

A series of runs was carried out at 500 °C using a fixed pressure of formaldehyde (100 mmHg) and various pressures of nitric oxide between 10 and 100 mmHg. The results for each product are shown in Figs. 2 and 3. The amount of water, which was measured by means of a gas chromatograph, is not very accurate. The rate of carbon monoxide formation follows a typical inhibition curve. It has a lower limit and then tends to increase with the nitric oxide pressure.

The formation of hydrogen is also inhibited, but after maximal inhibition the rate of its formation is very low compared with that of carbon monoxide, just as in the case of dimethyl ether. The rate of nitrogen formation increases linearly with the pressure of nitric oxide. This means that nitrogen formation is dependent on the first-order kinetics of nitric oxide.

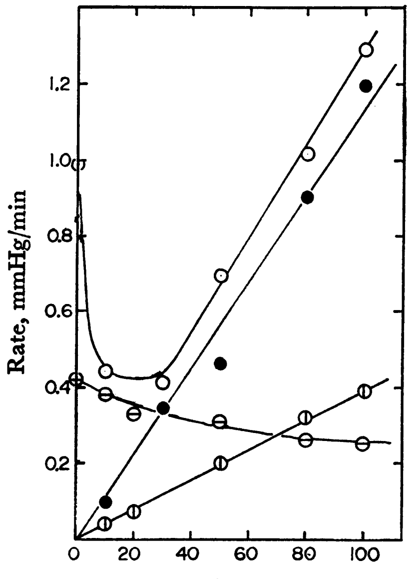

Fig. 2. The rates of product formation as a function of nitric oxide pressure in the pyrolysis of 100 mmHg formaldehyde at 500°C.
○: CO, ●: H_2O, ⦶: N_2, ⊖: CH_3OH.

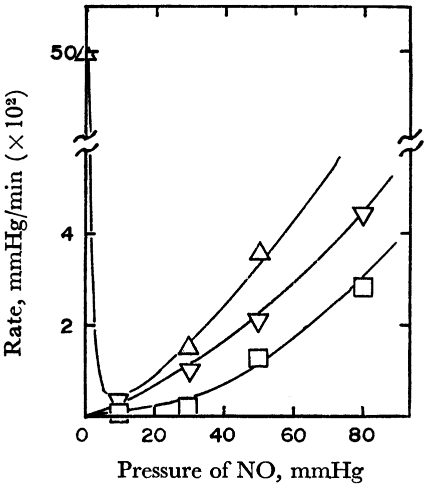

Fig. 3. The rates of product formation as a function of nitric oxide pressure in the pyrolysis of 100 mmHg formaldehyde at 500 °C.
△: H_2, ▽: CO_2, □: N_2O.

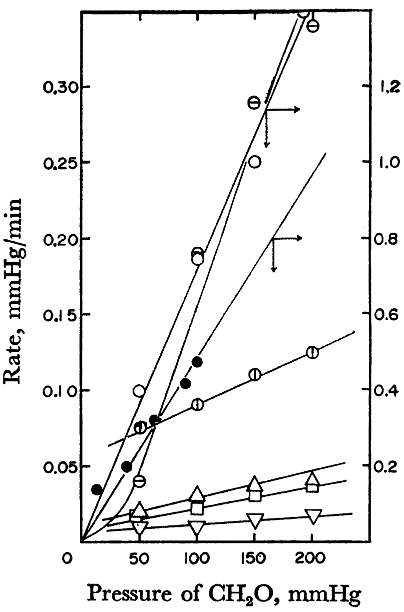

Fig. 4. The rates of product formation as a function of formaldehyde pressure in the pyrolysis of 50 mmHg nitric oxide at 500 °C.
○: CO, ●: H_2O, ⦶: N_2, ⊖: CH_3OH, △: H_2,
▽: N_2O, □: CO_2

The rates of both carbon dioxide and nitrous oxide formation also increase with the nitric oxide pressure, but their dependencies on nitric oxide are not clear because of a poor reproducibility.

Figure 4 shows the change in the rates of product formation at 500 °C using a fixed pressure of nitric oxide (50 mmHg) and various pressures of formaldehyde between 20 and 200 mmHg. These results show that each rate of product formation depends linearly on the formaldehyde pressure between 50 and 200 mmHg. However, the amount of water is not so accurate as in the case of Fig. 2.

Discussion

It has been well known that formaldehyde decomposes thermally *via* the reaction resulting from these two simulatneous stoichiometric equations:

$$2CH_2O \longrightarrow CO + CH_3OH \tag{I}$$

$$CH_2O \longrightarrow CO + H_2 \tag{II}$$

The former is a surface reaction,[4] while the latter is the following free-radical chain reaction.[5,6]

$$2CH_2O \longrightarrow CHO + H + CH_2O \tag{1}$$

$$CHO \longrightarrow CO + H \tag{2}$$

$$H + CH_2O \longrightarrow H_2 + CHO \tag{3}$$

$$CHO + CHO \longrightarrow CO + CH_2O \tag{4}$$

Methanol formation decreases slightly upon the addition of nitric oxide; therefore, Reaction (I) may be affected to only a small extent by the addition of nitric oxide. (A slight reduction of the rate of methanol formation by the addition of nitric oxide presumes a mild inactivation of the surface of a reaction cell by nitric oxide.)

On the contrary, the rate of carbon monoxide formation decreases greatly upon the addition of a small amount of nitric oxide; after the rate reaches its minimum, it increases linearly with the amount of nitric oxide added. The minimum rate of carbon monoxide formation, furthermore approximately equals that of methanol, indicating that the free-radical decomposition (II) is inhibited almost completely and that the increased rate after the minimum value is the result of free-radical decomposition accelerated by the addition of nitric oxide. In this paper, hereafter, the effect of nitric oxide on the free-radical decomposition will be described (mainly the accelerated part). The quantity of carbon monoxide produced by the free-radical process may be regarded as the difference between the total amount of carbon monoxide and that of methanol.

In the free-radical chain decomposition of formaldehyde alone (II), equal amounts of carbon monoxide and hydrogen are formed. On the other hand, in the presence of nitric oxide, as is shown in Figs. 2—4, very little hydrogen is produced after maximal inhibition; water, nitrogen, nitrous oxide, *etc.* are formed instead. A very rough ratio of the main products is:

$$CO{:}H_2O{:}N_2 = 1{:}1{:}1/2$$

The rates of their formation are first-order both for formaldehyde and nitric oxide after maximal inhibition.

The addition of nitric oxide to the pyrolysis should cause inhibition by means of the scavenging reaction of the hydrogen atom (3i) and, at the same time, acceleration by means of the inhibition reaction (1i):

$$H + NO \rightleftarrows HNO \tag{3i) (-3i}$$

$$NO + CH_2O \longrightarrow HNO + CHO \tag{1i}$$

The formyl radicals formed by (1i) follow produce a hydrogen atom by means of Reaction (2). The very little formation of hydrogen in the inhibited decomposition shows that hydrogen atoms do not abstract the hydrogen atom as in (3); consequently, the chain decomposition of the formaldehyde propagated by (2) and (3) does not occur. Almost all of the H atom should undergo scavenging (3i), and the nitroxyl thus formed should react further. This reaction of nitroxyl should yield a nearly stoichiometric amount of water, since two atoms of hydrogen are formed for one molecule of carbon monoxide and nearly equal amounts of water and carbon monoxide are produced.

Nitroxyl is known to react as:[7]

$$HNO + HNO \longrightarrow N_2O + H_2O \tag{5}$$

The very low yield of nitrous oxide, however, indicates that (5) is not the main reaction for nitroxyl under the present conditions. Two reactions have been proposed between nitroxyl and nitric oxide:

$$HNO + 2NO \longrightarrow N_2 + H + NO_3 \tag*{(6)[7]}$$

$$HNO + 2NO \longrightarrow HNO_3 + N_2 \tag*{(7)[8]}$$

Since neither reaction yields water, neither is the main nitroxyl reaction. As another nitrogen formation step, Reaction (8) has been proposed:[9]

$$N_2O + H \longrightarrow N_2 + HO \tag{8}$$

This reaction, combined with Reaction (5) as a nitrous oxide source, should yield nitrogen with a half amount of water. If nitrogen is produced mainly by Reaction (8), however, the nitrogen yield-time curve should have a sigmoidal form and the rate of nitrous oxide formation should fall off. As shown in Fig. 1, this is not the case, indicating that Reaction (8) does not play an important role. (Reaction (8) is known to have a comparatively high activation energy *ca.* 11 kcal/mol.[10])

In the present work, an alternative reaction of nitroxyl (9) is proposed:

$$HNO + HNO \longrightarrow N_2 + 2OH \tag*{(9)*}$$

As far as the energetics of this reaction are concerned, this is likely to occur: $\Delta H = 3.6$ kcal/mol.** The OH radical may produce water *via* Reactions (10)[11] and (11):

$$HO + HNO \longrightarrow H_2O + NO \tag{10}$$

$$HO + CH_2O \longrightarrow H_2O + CHO \tag{11}$$

If most of the hydroxyl radicals react as in Reaction (11), formaldehyde decomposes by means of a chain mechanism propagated by Reactions (3i), (9), (11), and (2). In the chain decomposition, the terminating step should be (5), (7), or (10), since nitroxyl radicals are the most abundant radicals. If formaldehyde does not decompose by means of a chain reaction, nitroxyl radicals are formed by Reactions (1i), (2), and (3), and the radical-consuming step should be Reactions (5), (7), or (10). Table 1 lists the simplified reaction mechanisms using the reactions described above and the rate equations derived from them. In this table, a sufficient long chain is assumed for the chain reactions.

Only Cases (i) and (vi) in the table are consistent

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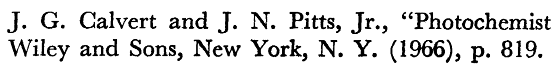
* This may proceed in a manner such as;



$$\begin{matrix} O & & H \\ & N{=}N & \\ H & & O \end{matrix} \longrightarrow \begin{matrix} HO & & \\ & N{=}N & \\ & & OH \end{matrix} \longrightarrow N_2 + 2OH$$

** J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, New York, N. Y. (1966), p. 819.

Table 1. Rate equations from various reaction schemes

Chain reaction[a)]

	Terminating step		
	(5)	(7)	(10)
Reaction scheme	(1i) (2) (3i) (9) (11) (5)	(1i) (2) (3i) (9) (11) (7)	(1i) (2) (3i) (9) (11) (10)
rate equation	$R_{CO}=R_{H_2O}=(2k_{11}k_9/k_5)$-$[CH_2O][NO]$ $R_{N_2}=(1/2)R_{H_2O}$ $R_{N_2O}=k_{11}[CH_2O][NO]$	$R_{CO}=R_{H_2O}$ $=(2k_{11}k_9/k_7^2)[CH_2O]^2$	$R_{CO}=R_{H_2O}=(k_{11}k_9k_5^2/2k_{10}^2)^{1/3}[CH_2O]^{4/3}[NO]^{2/3}$ $R_{N_2}=(1/2)R_{H_2O}$ $R_{N_2O}=(k_5/2k_9)R_{H_2O}$
case	(i)	(ii)	(iii)

Non chain reaction

	Radical consuming step		
	(5)	(7)	(10)
Reaction scheme	(1i) (2) (3i) (5)	(1i) (2) (3i) (7)	(1i) (2) (3i) (9) (10)
rate equation	$R_{H_2O}=R_{N_2O}$	$R_{H_2O}=0$	$R_{CO}=R_{H_2O}=k_{11}$-$[CH_2O][NO]$ $R_{N_2}=(1/2)R_{H_2O}$ $R_{N_2O}=(k_5/2k_9)R_{H_2O}$
case	(iv)	(v)	(vi)

a) sufficient long chain is assumed

with the experimental results (excepting the molecular reaction); that is, both stoichiometric relation:

$$CH_2O + NO \longrightarrow CO + H_2O + (1/2)N_2$$

and the rate equation:

$$R_{CO} = k[CH_2O][NO]$$

hold approximately. We suggest that Reaction (11) progresses fast enough at the present temperature; hence, Case (i) is prefarable to (vi). As there is only a little change in the reaction order in the case of (iii), Reaction (10), besides (5), may be adopted as the termination step.

Nitrous oxide, since its formation is dependent on more than the first-order kinetics of nitric oxide, may be formed by (12) besides (5), which, as described in (i), leads to a linear relation to nitric oxide upon the nitrousoxide formation:

$$HNO + NO \longrightarrow N_2O + OH \qquad (12)$$

Thus we obtain: $R_{N_2O(12)}=k_{12}[HNO][NO]=(k_{12}k_{11}^{1/2}/k_5^{1/2})[CH_2O]^{1/2}[NO]^{3/2}$. The occurrence of this reaction (12) has little effect on the values of R_{H_2O} and R_{N_2}.

It has been established that nitric oxide is disproportionated by the chain reaction propagated by (3i) and (6) in the presence of the H atom at low temperatures. (This reaction, however, does not affect the rate of CH_2O decomposition reaction.) Judging from the results, the N_2 formation by (6) is negligible in comparison with that by (9):

$$R_{N_2(6)} = k_6[HNO][NO]^2 = (k_6k_{11}^{1/2}/k_5^{1/2})[CH_2O]^{1/2}[NO]^{5/2}$$

Even if, instead of (2), Reaction (13) occurs, it may produce no variation in the kinetics:

$$CHO + NO \longrightarrow CO + HNO \qquad (13)$$

Several workers have proposed different reaction schemes for the accelerating effect of nitric oxide on the gas-phase decomposition of simple organic compounds. Laidler *et al.* studied the pyrolysis of various organic compounds and proposed a chain mechanism.[12)] Applying their scheme to formaldehyde pyrolysis, the chain is initiated by (1i) and propagated by (2) and (3); consequently, hydrogen should be produced in the same amount of carbon monoxide.

Sabo *et al.* studied the pyrolysis of nitric oxide and acetaldehyde or higher aldehydes and proposed a different chain mechanism, where the propagating steps are:[13)]

$$R + NO \rightleftarrows RNO$$
$$RNO + RNO \longrightarrow RCO + RH + NO$$
$$RCO \longrightarrow R + CO$$

Applying this scheme, formaldehyde should yield equal amounts of CO and RH, that is H_2. Clearly, neither of these two schemes can be accepted for formaldehyde pyrolysis because of the low yield of hydrogen.

Pratt's scheme,[14)] which involves the isomerization of a nitroso compound to an oxime, also can not be applied to our system, because the nitroso compound in this system is nitroxyl.

Bibliography

1) N. Imai and O. Toyama, This Bulletin, **35**, 860 (1962).

2) D. J. McKenney, B. W. Wojciechowski, and K. J. Laidler, *Can. J. Chem.*, **41**, 1993 (1963).

3) K. Tadasa, N. Imai, and T. Inaba, unpublished work.

4) J. G. Calvert and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 176 (1951).

5) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, Reinhold Publishing Corporation, New York, N. Y. (1954), p. 205.

6) R. Klein, M. D. Sheer, and L. J. Schoen, *J. Amer. Chem. Soc.*, **78**, 50 (1956).

7) E. A. Arden and L. Phillips, *J. Chem. Soc. A*, **1964**, 5118.

8) O. P. Strausz and H. E. Gunning, *Trans. Faraday Soc.*, **60**, 347 (1964).

9) K. Schofield, *Planet. Space Sci.*, **15**, 643 (1967).

10) F. Kaufman, *Can. J. Chem.*, **47**, 1917 (1969).

11) E. M. Bulewicz and T. M. Sudgen, *Proc. Roy. Soc. Ser. A*, **277**, 143 (1964).

12) M. Eusuf and K. J. Laidler, *Can. J. Chem.*, **42**, 1861 (1964); K. J. Laidler and M. Eusuf, *ibid.*, **43**, 268, 278 (1965); B. W. Wojciechowski and K. J. Laidler, *Trans. Faraday Soc.*, **59**, 369 (1963); K. J. Laidler and D. J. McKenney, *Proc. Roy. Soc. Ser. A*, **278**, 517 (1964).

13) Z. G. Sabo, *Nature*, **170**, 246 (1952); Z. G. Sabo, P. Huhn, and A. Bergh, *Adv. Catal.*, **9**, 343 (1957); Z. G. Sabo and F. Marta, *J. Amer. Chem. Soc.*, **83**, 768 (1961); F. Marta, *Acta Chim. Acad. Sci. Hung.*, **31**, 415 (1962).

14) G. L. Pratt and J. H. Purnell, *Proc. Roy. Soc. Ser. A*, **260**, 317 (1961); R. G. W. Norrish and G. L. Pratt, *Nature*, **199**, 143 (1963); G. L. Pratt, *Proc. Roy. Soc. Ser. A*, **293**, 235 (1966).