Thermal Decomposition of Dimethyl Ether in the Presence of Nitrogen Oxide

Kohji TADASA,* Naomi IMAI, Tetsuo INABA, and Yutaka KUBOKAWA**
Faculty of Liberal Arts and Sciences, University of Osaka Prefecture, Sakai, Osaka 591

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The effect of NO addition on the thermal decomposition of CH_3OCH_3 has been studied at 500 °C. The rate of pyrolysis decreases markedly when the amount of NO is small, but increases linearly with increase in amount. Acceleration of pyrolysis was studied. Major reaction products are CH_4, CH_2O, CO, H_2O, and N_2, the minor ones being H_2, N_2O, and C_2H_6. The quantities of all the products were determined under different conditions except CH_2O and H_2O. It was found that the rate of formation is nearly of first order with respect to both NO and CH_3OCH_3. A reaction scheme is proposed. It is suggested that the rate of decomposition is nearly equal to that of the second order reaction $NO + CH_3OCH_3 \rightarrow HNO + CH_3OCH_2$.

The thermal decompositions of lower hydrocarbons, aldehydes, ketones, ethers *etc.* proceed *via* free radical chain reactions in the gas phase. Nitrogen oxide has been used as an effective inhibitor for these free-radical reactions, since it combines readily with free radicals. Nitrogen oxide, however, reacts easily with the molecules of these organic compounds, forming free radicals. Thus, the two effects of nitrogen oxide, inhibitive and accelerative, make the reaction mechanism very complicated.

When nitrogen oxide is added in a free-radical thermal decomposition of an organic substance, the rate of the reaction first decreases and then increases with the amount of addition, giving rise to a minimum rate. The minimum rate is not sufficiently small as compared with the uninhibited rate to suggest that the free-radical reaction is completely surpressed, even at the minimum rate, owing to the accelerating action of nitrogen oxide. In the case of dimethyl ether, however, the minimum rate is very small as compared with the uninhibited rate, and the inhibitive and the accelerative parts are distinctly separated in the nitrogen oxide pressure-rate curve. Thus, dimethyl ether is thought to be suitable for the study of the effects of nitrogen oxide on pyrolysis.

Investigations[1-3] has been carried out on the nitrogen oxide inhibited pyrolysis of dimethyl ether mainly following the total pressure change. We have measured the quantities of the reaction products under different conditions and derived a reaction scheme.

Experimental

Commercial dimethyl ether and nitrogen oxide were purified by repeated bulb-to-bulb distillation.

The reaction was studied at 500 °C in a conventional static system. The products of the pyrolysis were separated by means of cold traps and a Toepler pump, and analyzed quantitatively by gas chromatography. The apparatus, techniques of separation and analysis are similar to those described previously.[4]

Results

All the runs were carried out at 500 °C. The quantitative analyses were made for CH_4, CO, N_2, N_2O, H_2, and C_2H_6, among the products of pyrolysis. CH_2O and H_2O were formed in large amounts, but these were not determined because of inaccuracy of the measurements.

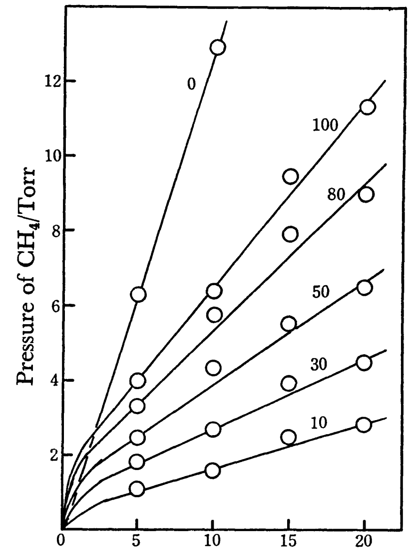

Fig. 1(a).

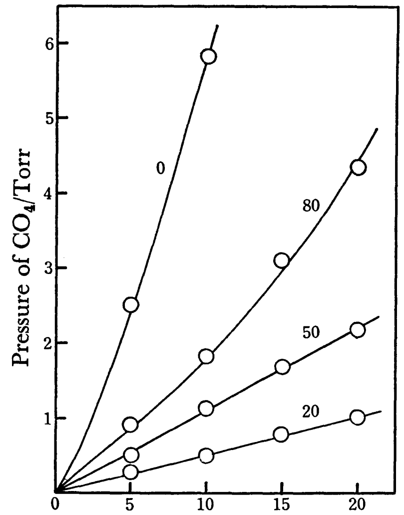

Fig. 1(b).

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* Present address: Department of Agricultural Chemistry, College of Agriculture, Shinshu University, Ina, Nagano 396.

** Present address: Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591.

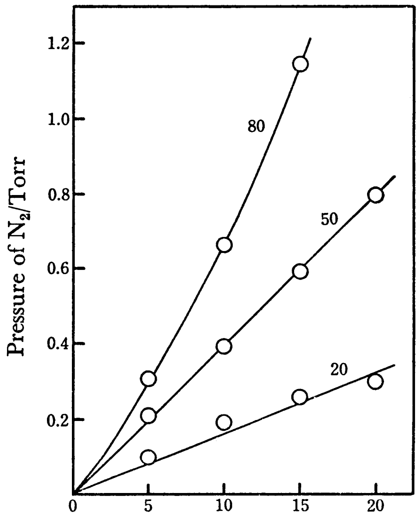

Fig. 1(c).

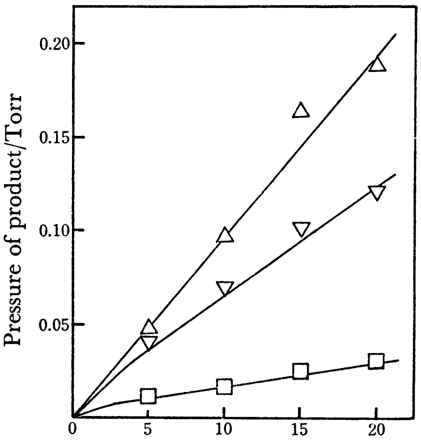

Fig. 1(d).

Fig. 1. Yields of products in the pyrolysis of 100 Torr CH_3OCH_3 and various NO pressures (in Torr) at 500 °C.
(a) CH_4, (b) CO, (c) N_2, (d) △: H_2, ▽: N_2O, □: C_2H_6 (×10).
P_{NO}=50 Torr.

No CH_3OH was observed in detectable amount, although it is an important pyrolysis product of CH_2O.

The yields of the products were determined at different times during the course of uninhibited and inhibited pyrolyses. Some results are shown in Fig. 1. For most products the yields increase linearly with time from the beginning of the reaction. The rate of CH_4 formation, however, is higher in the initial period of the pyrolysis than after 5 min, as is often the case in pyrolysis. The rate of CH_4 formation was obtained from intercept of the slope in the yield-time plot.

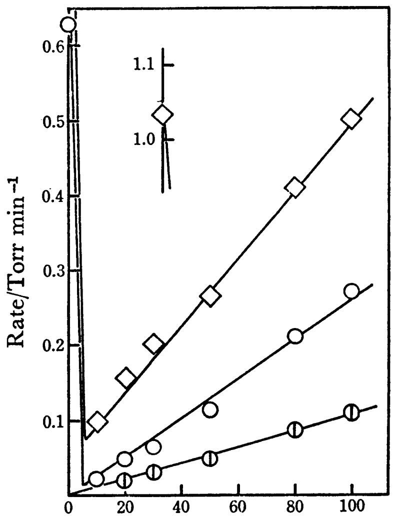

Fig. 2(a).

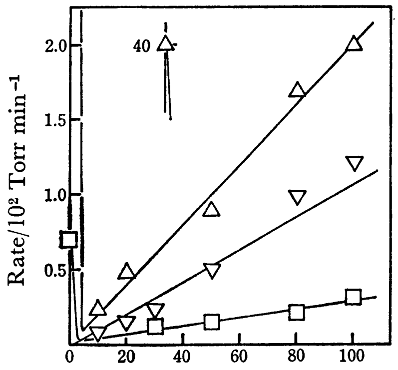

Fig. 2(b).

Fig. 2. Plot of rate of formation *vs.* NO pressure for the pyrolysis of 100 Torr CH_3OCH_3 at 500 °C.
(a) ◇: CH_4, ○: CO, ⦶: N_2,
(b) △: H_2, ▽: N_2O, □: C_2H_6 (×10).

The dependence of the rate of product formation on the pressure of NO added to the reaction mixture is shown in Fig. 2 for the pyrolysis of CH_3OCH_3 at 100 Torr pressure and 500 °C. In the uninhibited pyrolysis, the rates of formation are 1.04, 0.63, and 0.40 Torr min^{-1} for CH_4, CO, and H_2 respectively, addition of 10 Torr of NO reducing them to 0.095 (9% of uninhibited rate), 0.015 (2%), and 0.0025 (0.6%), respectively. The addition of an increased amount of NO causes a linear increase in the rates of formation of all products analyzed. The extrapolated straight lines pass through the origin except for CH_4 which has a small intercept on the vertical axis.

Figure 3 shows the relation between the rates of product formation and the CH_3OCH_3 pressure in the pyrolysis with 50 Torr of NO. The plots show linearity except for CH_4, for which the plot gives a curve slightly concave downwards.

Discussion

The thermal decomposition of CH_3OCH_3 has been established by a number of workers to proceed by a free-radical chain process, which is as follows.[5-7]

$$CH_3 + CH_3OCH_3 \longrightarrow CH_4 + CH_3OCH_2$$

$$CH_3OCH_2 \longrightarrow CH_2O + CH_3$$

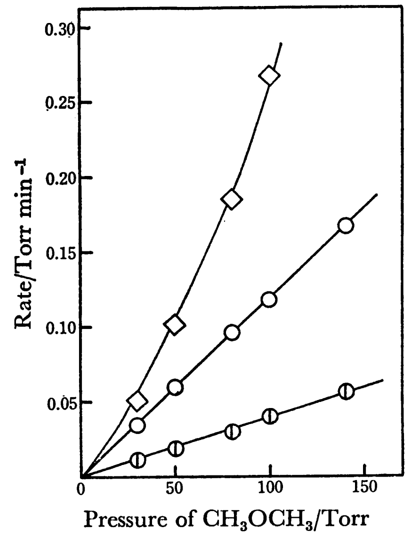

Fig. 3(a).

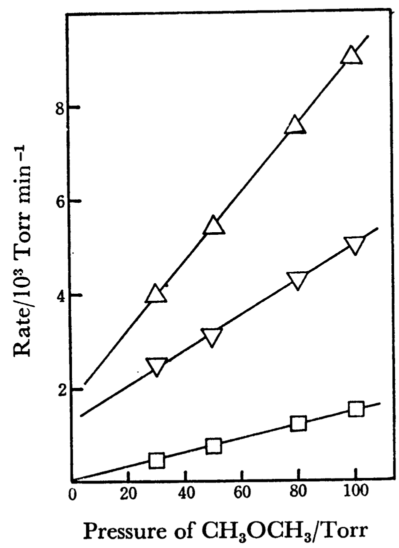

Fig. 3(b).

Fig. 3. Plot of rate of formation *vs.* CH_3OCH_3 pressure for the pyrolysis of 50 Torr NO at 500 °C.
(a) ◇: CH_4, ○: CO, ⦶: N_2,
(b) △: H_2, ▽: N_2O, □: C_2H_6 (×10).

It has been established that CH_2O once produced also undergoes free-radical chain decomposition.[6,8]

$$CH_3 + CH_2O \longrightarrow CH_4 + CHO$$

$$H + CH_2O \longrightarrow H_2 + CHO$$

$$CHO + M \longrightarrow CO + H + M$$

Thus CH_3OCH_3 decomposes by two stoichiometric steps:

$$CH_3OCH_3 \longrightarrow CH_4 + CH_2O \qquad \text{(I)}$$

$$CH_2O \longrightarrow CO + H_2 \qquad \text{(II)}$$

Accordingly the rates of CO and H_2 formation increase with time in the early period. In Fig. 1(b) (NO=0 Torr) a concave curve is shown for the CO yield.

In the pyrolysis with NO, however, the CO yield increases linearly with time, suggesting that CO is not a secondary product. Stoichiometric relation (II) does not hold in the inhibited pyrolysis, since the H_2 yield is much smaller than that of CO.

In this work, the major products analyzed are CH_4, CO, and N_2, the N_2 yield being about half that of CO. The same ratio of CO and N_2 is also observed in the CH_2O–NO pyrolysis, where the following stoichimetry holds approximately.

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

A similar ratio of CO and N_2 found in the CH_3OCH_3–NO pyrolysis seems to suggest that they are formed by processes similar to the CH_2O–NO pyrolysis. By the addition of NO, CH_3OCH_3 seems to decompose according to two stoichiometric relations:

$$CH_3OCH_3 \longrightarrow CH_4 + CH_2O \qquad \text{(I)}$$

$$CH_3OCH_3 + NO \longrightarrow CH_4 + CO + H_2O + (1/2)N_2 \qquad \text{(II)}$$

Thus the following relation is expected to hold between the rates of product formation.

$$R_{\mathrm{CH_2O}} = R_{\mathrm{CH_4}} - R_{\mathrm{CO}}$$

$$R_{\mathrm{H_2O}} = R_{\mathrm{CO}} = 2R_{\mathrm{N_2}}$$

McKenney *et al.*[3] studied the NO inhibited pyrolysis of CH_3OCH_3 over the temperature range 500—600 °C and proposed a reaction mechanism, which indicates that NO inhibits the reaction by

$$CH_3 + NO \rightleftarrows CH_3NO \rightleftarrows CH_2NOH \longrightarrow \text{products}$$

and

$$CH_3 + CH_2NOH \longrightarrow CH_3CH_2\text{-}NOH \longrightarrow C_2H_6 + NO$$

while it accelerates the reaction by

$$NO + CH_3OCH_3 \longrightarrow HNO + CH_3OCH_2$$

According to their scheme, CH_3 and H, the latter being formed by the decomposition of HNO,

$$HNO + M \longrightarrow H + NO + M$$

take part in the chain decomposition of CH_3OCH_3, even when a sufficient amount of NO is added. According to their argument, $R_{\mathrm{CH_4}}$ is expressed by

$$R_{\mathrm{CH_4}} \propto [CH_3OCH_3]^{3/2}$$

being independent of [NO]. $R_{\mathrm{H_2}}$ should be equal to a half of the NO accelerated part of the rate of CH_3OCH_3 decomposition. Their prediction concerning $R_{\mathrm{CH_4}}$ and $R_{\mathrm{H_2}}$ is not consistent with the results we obtained at 500 °C.

The results we obtained show kinetics and stoichiometry which lead to the following scheme.

$$NO + CH_3OCH_3 \longrightarrow HNO + CH_3OCH_2 \qquad (1)$$

$$NO + CH_3OCH_2 \longrightarrow HNO + CH_3 + CHO \qquad (2)$$

$$NO + CH_3OCH_2 \longrightarrow CH_3NO + CH_2O \qquad (3)$$

$$NO + CH_3 \longrightarrow CH_3NO \qquad (4)$$

$$NO + CHO \longrightarrow HNO + CO \qquad (5)$$

$$CH_3NO + HNO \longrightarrow CH_4 + NO + NO \qquad (6)$$

$$HNO + HNO \longrightarrow OH + OH + N_2 \qquad (7)$$

$$OH + HNO \longrightarrow H_2O + NO \qquad (8)$$

$$CH_3OCH_3 + M \longrightarrow CH_3 + CH_3O + M \qquad (9)$$

$$NO + CH_3O \longrightarrow HNO + CH_2O \qquad (10)$$

In contrast to that of McKenny *et al.*, the scheme indicates that HNO and CH_3NO do not decompose, but they react with each other or react with radicals, *i.e.*, Eqs. 6—8.

The above reaction Schemes (1—10) give the following relations with regard to the reaction rates.

$$R_{CH_4} = R_6 = R_1 + R_9 = k_1[NO][CH_3OCH_3] + k_9[CH_3OCH_3][M] \qquad \text{(i)}$$

$$R_2 = \{k_2/(k_2+k_3)\}R_1$$

$$R_3 = \{k_3/(k_2+k_3)\}R_1$$

$$R_5 = R_2 = 2R_7 = R_8$$

$$R_{CO} = R_5,\ R_{N_2} = R_7,\ R_{H_2O} = R_8$$

hence

$$R_{CO} = R_{H_2O} = 2R_{N_2} = \{k_1k_2/(k_2+k_3)\}[NO][CH_3OCH_3] \qquad \text{(ii)}$$

$$R_{CH_2O} = R_3 + R_{10} = R_3 + R_9 = \{k_1k_3/(k_2+k_3)\}[NO][CH_3OCH_3] + k_9[CH_3OCH_3][M] \qquad \text{(iii)}$$

The experimental results satisfy the reaction orders in Eqs. i, ii, and iii. In Eq. i the first term represents the rate of the reaction between NO and CH_3OCH_3 (1), and the second one represents that of the initiating step in the thermal chain decomposition of CH_3OCH_3 alone (9). This might be due to the fact that the second term is very small compared with the first term in Eq. i, the CH_4 line intersects the Y axis just above the origin in Fig. 2(a), and the CH_4-curve is slightly concave in Fig. 3(a). The reaction orders of the CO and N_2 formation in Eq. ii are satisfied by the results in Figs. 2(a) and 3(a). Eqs. i, ii, and iii give the relation

$$R_{CH_2O} = R_{CH_4} - R_{CO}$$

which is also supported by the results.

The following reactions are proposed for the formation of minor products H_2, N_2O, and C_2H_6.

$$HNO + HNO \longrightarrow H_2 + NO + NO \qquad (11)$$

$$HNO + HNO \longrightarrow H_2O + N_2O \qquad (12)$$

$$CH_3NO + CH_3NO \longrightarrow C_2H_6 + NO + NO \qquad (13)$$

When the rates of Eqs. 11, 12, and 13 are much smaller than those of Eqs. 6, 7, and 8, the following rate equations result from Schemes 1—13.

$$R_{H_2} = R_{11} = (k_{11}/k_7)R_7 = (k_{11}/2k_7)R_2 = \{k_1k_2k_{11}/2k_7(k_2+k_3)\}[NO][CH_3OCH_3]$$

$$R_{N_2O} = R_{12} = (k_{12}/k_7)R_7 = (k_{12}/2k_7)R_2 = \{k_1k_2k_{12}/2k_7(k_2+k_3)\}[NO][CH_3OCH_3]$$

$$R_{C_2H_6} = \{2k_1(k_2+k_3)k_7k_{13}/k_2k_6^2\}[NO][CH_3OCH_3]$$

These rate equations coincide with the reaction orders found experimentally (Fig. 2(b) and Fig. 3(b)). Since Eqs. 11, 12, and 13 are much slower than Eqs. 1—8, the addition of Eqs. 11, 12, and 13 to Schemes 1—10 does not cause any serious change in the rate equations (Eqs. i, ii, and iii).

The following ratios of the rate constants are obtained from the results.

$$k_2/k_3 = 1.5$$

$$k_{11}/k_7 = 0.017$$

and

$$k_{12}/k_7 = 0.011$$

It is well-known that HNO reacts with itself by Eq. 12,[9] but Eq. 7 has been suggested to take place more quickly at about 500 °C.[4,10] Both reactions (Eqs. 7 and 11) involve the internal rearrangement of $(HNO)_2$, while, in Reactions 6, 8, 11, and 13, HNO or CH_3NO release H or CH_3 when they react with each other or react with radicals. Reactions of the latter type have been proposed by Szabó.[11]

In the reaction schemes proposed above, radicals, CH_3OCH_2, CHO, and CH_3O are attached by NO before they decompose. Even if these radicals decompose first and then the fragment radicals or atoms combine with NO, the above rate equation does not change. As an example, replacement of Eq. 5 by the following two steps

$$CHO + M \longrightarrow CO + H + M$$

and

$$H + NO + M \longrightarrow HNO + M$$

does not alter the rate of the CO formation (Eq. iii).

NO undergoes disproportionation to N_2 and NO_2 in the presence of free radicals, according to the following mechanism.[12]

$$NO + R \longrightarrow RNO$$

$$RNO + 2NO \longrightarrow RNO(NO)_2 \longrightarrow RN_2ONO_2$$

$$\longrightarrow R + N_2 + NO_3$$

$$NO_3 + NO \longrightarrow NO_2 + NO_2$$

The reactions do not seem to be important since they cannot explain the reaction order of N_2 formation. No NO_2 was observed amongst the pyrolysis products.

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