Thermal Decomposition of Dimethyl Ether in the Presence of Hydrogen Sulfide and Nitric Oxide

By Naomi Imai and Osamu Toyama

(Received September 28, 1961)

We have recently studied the catalytic effect of hydrogen sulfide on the thermal decomposition of acetaldehyde[1,2] and of dimethyl ether[3]. It has been suggested from the effects of chain inhibitors such as propylene and isobutylene that the hydrogen sulfide-catalyzed decomposition of acetaldehyde involves two mechanisms, i. e., a free radical chain mechanism and a non-chain molecular mechanism, while the hydrogen sulfide-catalyzed decomposition of dimethyl ether has been explained solely by a radical chain mechanism. There is, however, an indication[2] that nitric oxide catalyzes the molecular decompositon of dimethyl ether even though it suppresses the chain decomposition of the ether almost completely. It seems, therefore, possible that the molecular decomposition of dimethyl ether is also catalyzed by hydrogen sulfide. Although the contribution of such a catalysis, if present, must be considered from the results given above to be usually so small that its existence can hardly be recognized, it may be expected that the suppression of the chain decomposition by a suitable inhibitor will enable the hydrogen sulfide-catalyzed molecular decomposition to be measured.

This paper reports such an attempt, carried out with nitric oxide as an inhibitor, which has been found to be the most efficient of the inhibitors investigated.

Experimental

Materials.—Dimethyl ether was prepared by the dehydration of methyl alcohol by concentrated sulfuric acid at 80°C, decarbonated and dried over potassium hydroxide and calcium chloride. Hydrogen sulfide was prepared by dropping water on aluminum sulfide and dried by passing through a trap at −78°C. Nitric oxide was produced by the reaction of a concentrated sodium nitrite solution with a hydrochloric acid solution of ferrous chloride, decarbonated by a potassium hydroxide solution and dried by concentrated sulfuric acid and phosphorus pentoxide. All of these gases were prepared in evacuated vessels and purified by repeated bulb-to-bulb distillation.

Apparatus and Procedure. —The apparatus used was one for ordinary statical experiments similar to that described previously[4]. The rate of decomposition in most cases was followed by measuring the total pressure change, but, in some runs, the major decomposition products uncondensable at −196°C, i. e., methane, carbon monoxide and hydrogen, were analyzed by a Yanagimoto GCG-2 type gas chromatograph.

Results and Discussion

Figure 1 shows the results of a series of experiments in which the time of pyrolysis was varied under otherwise constant conditions. It had previously been found that the rate of formation of carbon monoxide in the uninhibited reaction[3] is approximately equal to that of hydrogen but smaller than that of methane, and that the total pressure-time curve is of a sigmoidal form. These findings have been explained by decomposition in two stages, i. e., by the reaction $CH_3OCH_3 \rightarrow CH_4 + HCHO$, followed by $HCHO \rightarrow H_2 + CO$, though neither of them is a simple reaction; both are radical chain reactions catalyzed by hydrogen sulfide. Figure 1 shows that the rate of the formation of carbon monoxide in the inhibited pyrolysis is lower than that of methane, but it is about ten times as great as that of hydrogen, indicating that formaldehyde does not decom-

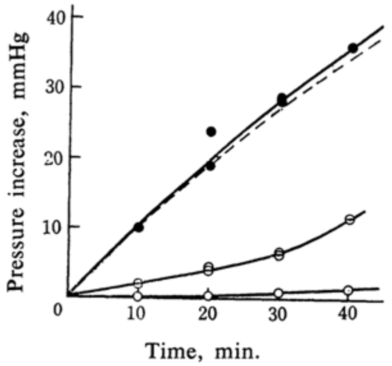

Fig. 1. Dependence of total pressure and pressures of products on reaction time. $CH_3O\cdot CH_3 = 100$ mmHg, $H_2S = 30$ mmHg, NO = 10 mmHg, 500°C. ●, CH_4; ⊖, CO; ○, H_2. Dotted line represents total pressure increase.

---

[1] N. Imai, Y. Yoshida and O. Toyama, This Bulletin, 35, 752 (1962).

[2] N. Imai, Y. Yoshida and O. Toyama, ibid., 35, 758 (1962).

[3] N. Imai and O. Toyama, ibid., 34, 328 (1961).

[4] N. Imai and O. Toyama, ibid., 33, 1408 (1960).

TABLE I. RATE OF DECOMPOSITION UNDER VARIOUS CONDITIONS

P, initial pressure (mmHg); R, rate of pressure increase (mmHg min^{-1})

440°C

$P_{CH_3OCH_3}=100$
$P_{H_2S}=20$

P_{NO}	R
0	1.44
0.5	0.10
0.7	0.084
1.5	0.060
1.5	0.060
4.5	0.064
7.5	0.073
19	0.078
35	0.106
60	0.142
100	0.205

480°C

$P_{CH_3OCH_3}=100$
$P_{H_2S}=20$

P_{NO}	R
0	8.6
0.5	1.0
1.0	0.33
3.2	0.30
15	0.40
17	0.40
45	0.60
62	0.71
89	0.91

$P_{CH_3OCH_3}=100$
$P_{H_2S}=0$

P_{NO}	R
0	1.80
0	1.86
3	0.026
22	0.14
51	0.31
93	0.58

500°C

$P_{CH_3OCH_3}=100$
$P_{H_2S}=20$

P_{NO}	R
20	0.88
20	0.90
35	1.03
46	1.20

$P_{CH_3OCH_3}=100$
$P_{H_2S}=0$

P_{NO}	R
0	5.0
0	5.4
2.7	0.075
21	0.26
50	0.58
86	1.04

$P_{H_2S}=30$
$P_{NO}=10$

$P_{CH_3OCH_3}$	R
59	0.66
68	0.73
79	0.80
80	0.82
100	1.02
160	1.58
176	1.50
223	2.02
224	2.28
225	2.20

520°C

$P_{CH_3OCH_3}=100$
$P_{H_2S}=20$

P_{NO}	R
20	1.90
39	2.6
55	2.7

$P_{CH_3OCH_3}=100$
$P_{H_2S}=0$

P_{NO}	R
1.4	0.56
3.5	0.40
20	0.80
20	0.82
77	2.07

$P_{CH_3OCH_3}=100$
$P_{NO}=20$

P_{H_2S}	R
0	0.80
0	0.82
28	1.9
48	3.4
68	4.4
88	5.7

pose according to the stoichiometric equation $HCHO \rightarrow H_2 + CO$ in the presence of nitric oxide. Figure 1 also shows that the total pressure increase is almost identical with that of methane in the initial stage of decomposition. In the experiments described below, the initial rate of total pressure increase was determined as a measure of the initial rate of decomposition. These initial rates of pressure increase may be taken as those for the formation of methane, as is shown above.

Table I shows the initial rates of pressure increase obtained with various gaseous compositions in the temperature range 440~520°C. Figure 2 shows the dependence of the rate on the pressure of nitric oxide in the presence and absence of hydrogen sulfide. Table I and Fig. 2 show that for the ether of 100 mmHg pressure, irrespective of the presence of hydrogen sulfide, the maximum inhibition is attained by about 3 mmHg of nitric oxide, and that the rate of maximally inhibited decomposition is only a fraction of that uninhibited in both the presence and the absence of hydrogen sulfide. As has been shown in the decomposition of acetaldehyde in the presence of hydrogen sulfide[2], the residual decomposition remaining after the maximum inhibition is probably of a molecular character. This, however, does not contradict the previous finding that the uninhibited decomposition of dimethyl ether in the presence or absence of hydrogen sulfide is to be explained solely by a radical chain mechanism[3], since the rate of decomposition maximally inhibited by nitric oxide is only a fraction of that uninhibited, as is shown above.

Figure 2 further shows that, in both the presence and the absence of hydrogen sulfide, the rate of inhibited decomposition increases linearly with the pressure of nitric oxide. This probably indicates that the molecular decomposition of dimethyl ether is catalyzed by nitric oxide, as has already been described in a previous paper[3]. The linear parts of the two plots for the rates in the presence and absence of hydrogen sulfide are parallel, suggesting that the inhibited decomposition of dimethyl ether is catalyzed independently by

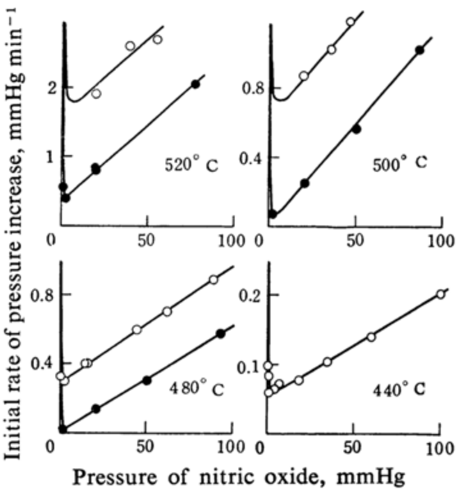

Fig. 2. Dependence of rate of decomposition on pressure of nitric oxide. CH_3OCH_3=100 mmHg ●, H_2S=0 ; ○, H_2=20 mmHg

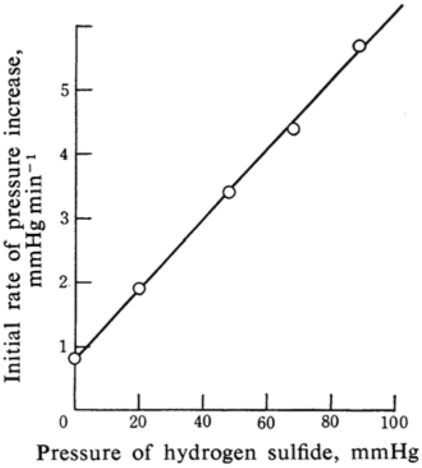

Fig. 3. Dependence of rate of decomposition on pressure of hydrogen sulfide. CH_3OCH_3= 100 mmHg, NO=20 mmHg, 520°C.

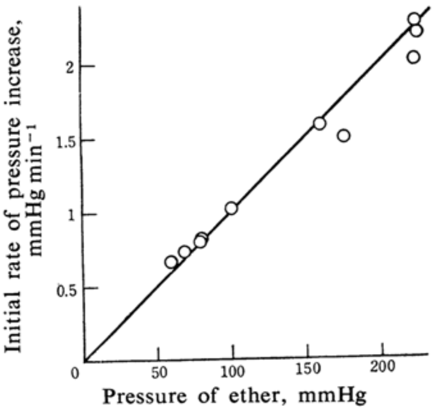

Fig. 4. Dependence of rate of decomposition on pressure of ether. H_2S=30 mmHg, NO=10 mmHg, 500°C.

hydrogen sulfide and by nitric oxide. Figures 3 and 4 show that the rate of inhibited decomposition increases linearly with the pressure of hydrogen sulfide and with that of the ether. The results shown in Figs. 2, 3 and 4 may, therefore, be combined to give a general expression for the inhibited rate:

$$-\mathrm{d}[CH_3OCH_3]/\mathrm{d}t=k[H_2S][CH_3OCH_3] + k'[NO][CH_3OCH_3]$$

The constant k can be determined from the intercept given by extrapolating the linear part of the plot obtained with hydrogen sulfide in Fig. 2 or from the slope of the straight line in Fig. 3, and k' from the slope of linear parts of the plots given in Fig. 2. The results are listed in Table II, where the values of these constants obtained by different methods are in satisfactory agreement with each other. The slope of the straight line in Fig. 4 is 0.0100 min⁻¹, in good agreement with the value of 0.0105 calculated from these values of k and k'. The least square treatments of the values given in Table II yield the following Arrhenius expressions:

TABLE II. VALUES OF RATE CONSTANTS

Temp. °C	k, mol⁻¹ cc. sec⁻¹ (a)	(b)	k', mol⁻¹ cc. sec⁻¹ (c)	(d)
440	22.1		10.6	
480	106		54	49
500	249		97	95
520	486	449	202	186

(a) From intercept of upper line in Fig. 2
(b) From slope of line in Fig. 3
(c) From slope of upper line in Fig. 2
(d) From slope of lower line in Fig. 2

$$k=10^{(14.7\pm0.35)}\exp\{-(43600\pm1200)/\boldsymbol{RT}\}\ \mathrm{mol^{-1}\,cc.\,sec^{-1}}$$

$$k'=10^{(13.4\pm0.10)}\exp\{-(40500\pm600)/\boldsymbol{RT}\}\ \mathrm{mol^{-1}\,cc.\,sec^{-1}}$$

As has already been described, these reactions are probably molecular decomposition of the ether catalyzed by hydrogen sulfide and by nitric oxide respectively. Both expressions appear to be reasonable for a simple bimolecular process. However, as has been described previously for acetaldehyde²⁾, information from other sources than kinetics seems necessary to clarify further the detailed mechanisms of these reactions.

The effect of nitric oxide on the thermal decomposition of dimethyl ether has also been studied by Smith and Hinshelwood⁵⁾. Their

---

5) J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.*, **A180**, 237 (1942).

results, however, differ considerably from those obtained in the present work. According to them, the rate of decomposition was reduced by the addition of an increasing amount of nitric oxide, but after a limiting rate was reached the rate remained constant and did not show any increase with the pressure of nitric oxide. The reason for this discrepancy is not yet clear. On the other hand, Freeman[6] studied the effect of nitric oxide on the thermal decomposition of diethyl ether and found a linear increase of the rate with the pressure of nitric oxide similar to the results shown in Fig. 2.

Summary

Dimethyl ether has been decomposed in the presence of hydrogen sulfide and nitric oxide over the temperature range 440~520°C. On increasing the amount of nitric oxide, the rate of decomposition decreases rapidly but after passing through a minimum value it increases linearly with the pressure of nitric oxide. The minimum value of the rate, which is reached in the presence of a small percentage of nitric oxide, is only a fraction of the uninhibited rate, irrespective of the presence of hydrogen sulfide. The rate of decomposition after being maximally inhibited, which is probably molecular in character, is represented by the equation $-d[CH_3OCH_3]/dt=k[H_2S][CH_3OCH_3]+k'[NO]\cdot[CH_3OCH_3]$, indicating that the inhibited decomposition is catalyzed by hydrogen sulfide and by nitric oxide independently. Arrhenius expressions $k=10^{14.7}\exp(-43600/\boldsymbol{RT})$ and $k'=10^{13.4}\exp(-40500/\boldsymbol{RT})$ mol^{-1}cc. sec^{-1} have been obtained.

Department of Applied Chemistry
College of Engineering
University of Osaka Prefecture
Sakai, Osaka

---

[6] G. R. Freeman, ibid., **A245**, 49 (1958).