The Thermal Decomposition of Dimethyl Ether in the Presence of Hydrogen Sulfide

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(Received August 23, 1960)

The catalytic action of hydrogen sulfide on the thermal[1] as well as photochemical[2] chain decomposition of acetaldehyde has been studied in this laboratory, and its catalytic effect has been attributed to the reactions between methyl radicals and hydrogen sulfide molecules and between hydrosulfide radicals and acetaldehyde molecules, both taking place faster than the reaction between methyl radicals and acetaldehyde molecules. Methanethiol was also found to have an analogous catalytic action on the thermal decomposition of acetaldehyde[3].

Dimethyl ether has been known to decompose thermally by a chain mechanism involving methyl radicals[4-6] and its decomposition may therefore be expected to be catalyzed by hydrogen sulfide like that of acetaldehyde. In the present work the kinetics of the thermal decomposition of dimethyl ether in the presence of hydrogen sulfide has been studied in the temperature range 360 to 440°C and compared with the results obtained in the absence of hydrogen sulfide.

Experimental

Materials. — Dimethyl ether was prepared by dehydration of methyl alcohol by concentrated sulfuric acid at 80°C, decarbonated and dried by potassium hydroxide and calcium chloride, and purified by bulb-to-bulb distillation. Hydrogen sulfide was

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[1] N. Imai and O. Toyama, unpuhlished work.

[2] N. Imai and O. Toyama, This Bulletin, 33, 1120 (1960).

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

[4] F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, 56, 284 (1934).

[5] S. W. Benson, *J. Chem. Phys.*, 25, 27 (1956).

[6] S. W. Benson and P. V. S. Jain, ibid., 31, 1008 (1959).

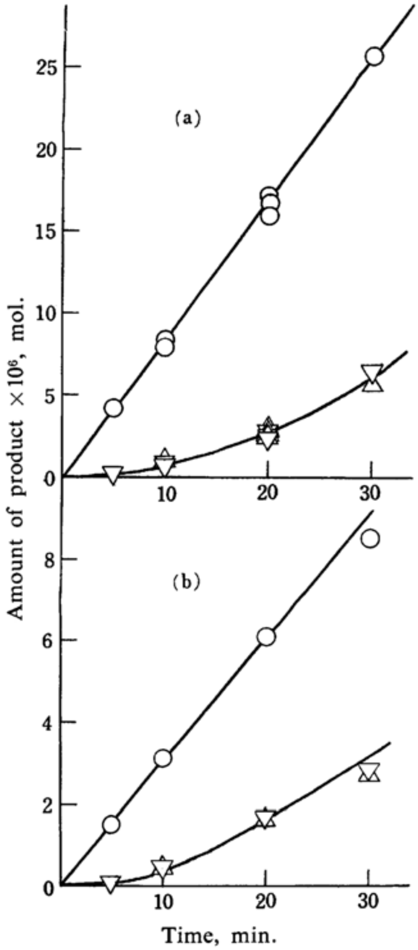

Fig. 1. Dependence of amount of product on reaction time. ○, CH_4; ▽, CO; △, H_2. (a) $[CH_3OCH_3]=2.13\times10^{-6}$ mol. cc^{-1}, $[H_2S]=0$, 440°C; (b) $[CH_3OCH_3]=2.32\times10^{-6}$, $[H_2S]=1.64\times10^{-6}$ mol. cc^{-1}, 380°C.

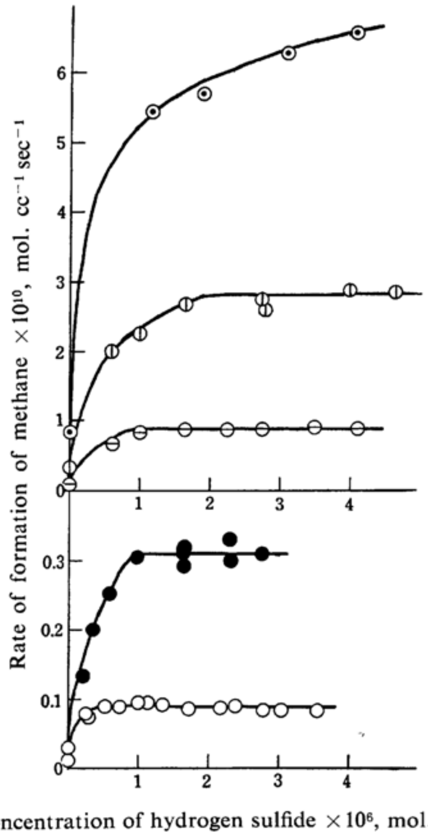

Fig. 3. Dependence of the rate of decomposition in the presence of hydrogen sulfide on its concentration. ○, $[CH_3O\cdot CH_3]=2.39\times10^{-6}$ mol. cc^{-1}, 360°C; ●, $[CH_3OCH_3]=2.32\times10^{-6}$ mol. cc^{-1}, 380°C; ⊖, $[CH_3OCH_3]=2.25\times10^{-6}$ mol. cc^{-1}, 400°C; ⦶, $[CH_3OCH_3]=2.19\times10^{-6}$ mol. cc^{-1}, 420°C; ⊙, $[CH_3OCH_3]=2.13\times10^{-6}$ mol. cc^{-1}, 440°C.

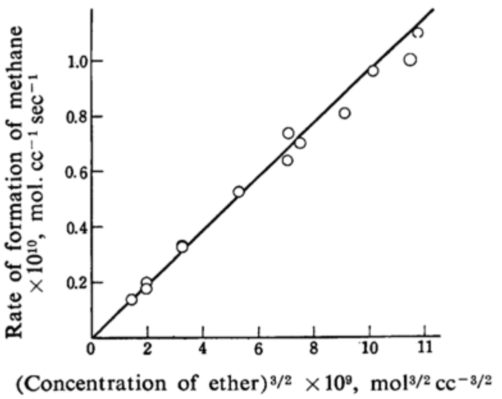

Fig. 2. Dependence of the rate of decomposition of the ether alone on its concentration at 420°C.

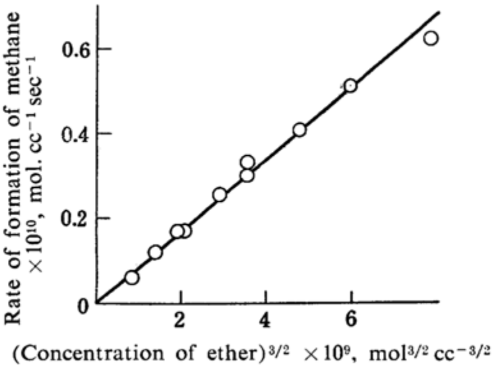

Fig. 4. Dependence of the rate of the decomposition of ether on its concentration in the presence of 2.32×10^{-6} mol. cc^{-1} of hydrogen sulfide at 380°C.

TABLE I. PYROLYSIS OF DIMETHYL ETHER IN THE ABSENCE AND PRESENCE OF HYDROGEN SULFIDE

Temp. °C	Initial concentration ×10^6 mol./cc.		Reaction time min.	Amount of product ×10^6 mol.		
	CH_3OCH_3	H_2S		CH_4	CO	H_2
360	2.39	0	100	0.79	0.082	—
		0	100	0.81	0.073	—
		0.263	30	2.32	0.187	—
		0.287	30	2.17	0.17	—
		0.527	30	2.64	0.23	—
		0.742	30	2.60	0.31	—
		1.00	30	2.78	0.38	—
		1.13	30	2.80	0.40	—
		1.36	30	2.96	0.48	—
		1.72	40	3.35	0.65	—
		2.18	30	2.55	0.46	—
		2.39	40	3.51	0.74	—
		2.78	40	3.28	0.72	—
		3.04	30	2.46	0.43	—
		3.57	30	2.43	0.44	—
380	2.32	0	50	1.51	0.067	—
		0	100	2.86	0.186	—
		0	100	2.92	0.21	—
		0.204	20	2.6	0.38	—
		0.344	20	3.9	0.40	—
		0.580	20	4.9	0.66	—
		0.975	5	1.49	0.099	—
		1.64	5	1.51	0.11	—
		1.64	10	3.1	0.49	0.46
		1.64	20	6.1	1.72	1.62
		1.64	30	8.5	2.83	2.7
		2.32	10	3.25	0.50	—
		2.32	20	5.88	1.62	1.3
		2.76	10	3.00	0.54	—
	0.91	2.32	20	1.21	0.237	—
	1.25		20	2.32	0.676	—
	1.53		20	3.28	0.76	0.6
	1.63		20	3.33	0.78	—
	2.03		20	4.94	1.06	0.9
	2.32		10	3.25	0.50	—
	2.32		20	5.88	1.60	1.3
	2.83		20	8.00	1.90	1.7
	3.27		20	10.0	2.46	1.7
	3.94		10	6.13	0.97	—
400	2.25	0	50	4.61	0.34	—
		0	100	8.86	1.03	1.1
		0.61	12	7.9	1.06	1.2
		1.00	10	8.1	1.35	1.4
		1.65	10	8.3	1.64	1.5
		2.25	20	16.9	5.68	5.4
		2.75	10	8.6	1.72	1.5
		3.49	10	8.8	2.08	2.1
		4.12	10	8.6	2.09	1.9

Table I (Continued)

420	1.27	0	30	4.00	0.376	—
	1.55	0	30	5.13	0.48	0.5
	1.56	0	30	5.79	0.68	0.5
	2.19	0	20	6.36	0.504	0.5
	2.19	0	40	12.8	1.72	1.5
	3.02	0	30	15.3	1.86	2.1
	3.67	0	30	18.6	2.31	1.6
	3.69	0	30	21.5	3.0	3.0
	3.83	0	30	20.4	2.14	2.6
	4.35	0	30	26.5	3.49	3.2
	4.68	0	20	18.8	5.02	2.2
	5.05	0	20	20.0	2.30	2.2
	5.16	0	20	21.4	2.24	1.7
	2.19	0.59	5	9.72	1.64	1.8
		1.00	5	11.0	2.02	2.0
		1.65	5	13.0	3.0	2.8
		2.73	5	13.4	3.16	3.2
		2.78	5	12.6	3.02	2.9
		3.99	5	14.0	3.9	3.5
		4.64	5	13.9	3.68	3.8
440	2.13	0	5	4.10	0.28	—
		0	10	7.9	0.70	1.0
		0	10	8.3	0.91	—
		0	20	15.9	2.42	2.4
		0	20	16.7	2.74	2.8
		0	20	17.1	2.5	2.5
		0	30	25.6	6.5	5.6
		1.15	2	10.6	1.69	1.1
		1.88	2	11.1	2.19	2.3
		3.08	2	12.3	2.34	2.5
		4.08	2	12.8	2.69	2.9

prepared by dropping water on aluminum sulfide in an evacuated vessel, dried by passing through a trap at −78°C and purified by bulb-to-bulb distillation. The cupric oxide used in analysis was a commercial sample.

Apparatus. — The apparatus used in the present work is similar to that described previously[3]. The reaction vessel is a glass cylinder of about 162 cc. capacity.

Procedure.—Required quantities of dimethyl ether and hydrogen sulfide were mixed and left at room temperature for about 30 min. before pyrolysis, and then introduced into the reaction vessel which had already been kept at the experimental temperature. After an appropriate time of reaction, usually corresponding to less than five per cent decomposition, the reaction mixture was expanded into an analytical system. Methane and carbon monoxide in products were analyzed quantitatively in the same way as described previously[7]. Hydrogen was oxidized by cupric oxide at 260°C to water vapor and the amount of the latter was determined from its pressure by an oil manometer. As it was found that the adsorption of the water on the glass wall led to incorrect estimates of hydrogen, calibration was made with known amounts of hydrogen. The amounts of hydrogen thus corrected seem to be still not very accurate. When the amount of hydrogen formed by the decomposition was very small, it was not determined.

Results and Discussion

In Table I are listed the amounts of methane, carbon monoxide and hydrogen formed by the decomposition of dimethyl ether both in the absence and in the presence of hydrogen sulfide at various conditions. It has been well known that dimethyl ether decomposes thermally according to the following stoichiometric equations[6,8,9].

$$CH_3OCH_3 \rightarrow CH_4 + CH_2O$$

$$CH_2O \rightarrow CO + H_2$$

It is shown in Table I that, even in the presence of hydrogen sulfide, the amount of

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[7] N. Imai and O. Toyama, This Bulletin, 33, 652 (1960).

[8] P. J. Askey and C. N. Hinshelwood, *Proc. Roy. Soc.*, **A115**, 251 (1927).

[9] E. Leifer and H. C. Urey, *J. Am. Chem. Soc.*, **64**, 994 (1942).

carbon monoxide formed is always equal to that of hydrogen within the experimental error and is always less than 30% of that of methane. Fig. 1 shows plots of the amounts of methane, carbon monoxide and hydrogen against the time obtained from series of runs (a) in the absence and (b) in the presence of hydrogen sulfide under otherwise constant conditions. It is seen in the figure that the rate of formation of methane remains constant for 30 min. during which 7.4 (a) and 2.3 (b) % of the ether have decomposed, while those of carbon monoxide and hydrogen increase with time. These observations indicate that carbon monoxide and hydrogen are produced by the decomposition of formaldehyde as represented by the above equation in the presence of hydrogen sulfide as well as in its absence.

It is generally agreed that the main feature of the thermal decomposition of dimethyl ether can be explained by the following chain mechanism[4)].

$$CH_3OCH_3 \rightarrow CH_3+OCH_3 \tag{1}$$

$$OCH_3+CH_3OCH_3 \rightarrow CH_3OH+CH_3OCH_2 \tag{2}$$

$$CH_3+CH_3OCH_3 \rightarrow CH_4+CH_3OCH_2 \tag{3}$$

$$CH_3OCH_2 \rightarrow CH_2O+CH_3 \tag{4}$$

$$CH_3+CH_3 \rightarrow C_2H_6 \tag{5}$$

The steady state equations derived from this scheme yield the rate equation

$$-\mathrm{d}[CH_3OCH_3]/\mathrm{d}t=R_{CH_4}=k_1^{1/2}k_3k_5^{-1/2}\ [CH_3OCH_3]^{3/2} \tag{I}$$

in general agreement with experimental results obtained by various workers[6,8,9)]. Also in this work, the rate of decomposition of the ether alone was found to be proportional to the 3/2 power of the concentration of dimethyl ether at 420°C as seen in Fig. 2. From the slope of the straight line in the figure, the value of $k_1^{1/2}k_3k_5^{-1/2}$ was obtained. At other temperatures, values of $k_1^{1/2}k_3k_5^{-1/2}$ were calculated from the concentration of ether and the rate of formation of methane, making use of Eq. I. They are listed in Table II.

TABLE II. VALUES OF $k_1^{1/2}k_3k_5^{-1/2}$ AND $k_1^{1/2}k_7k_8^{-1/2}$

Temp. °C	$k_1^{1/2}k_3k_5^{-1/2}\times10^3$ ($\mathrm{mol}^{1/2}\,\mathrm{cc}^{1/2}\,\mathrm{sec}^{-1/2}$)	$k_1^{1/2}k_7k_8^{-1/2}\times10^2$ ($\mathrm{mol}^{1/2}\,\mathrm{cc}^{1/2}\,\mathrm{sec}^{-1/2}$)
360	0.223	0.240
380	0.855	0.847 0.864[a)]
400	2.73	2.60
420	9.68	8.75
440	28.8	

a) Obtained from a series of runs with varied ether concentrations and a constant hydrogen sulfide concentration (Fig. 4).

Now in the presence of a sufficient amount of hydrogen sulfide, the reactions of methyl and methoxyl radicals with hydrogen sulfide may be so much faster than those with dimethyl ether, that the latter reactions may be neglected compared to the former. Hence reaction 2 may be replaced by reaction 2′ and reaction 3 by reactions 6 and 7.

$$OCH_3+H_2S \rightarrow CH_3OH+HS \tag{2′}$$

$$CH_3+H_2S \rightarrow CH_4+HS \tag{6}$$

$$HS+CH_3OCH_3 \rightarrow H_2S+CH_3OCH_2 \tag{7}$$

If, in addition, the concentration of hydrosulfide radicals is much higher than that of methyl radicals, the chain will terminate by reaction 8, reaction 5 being negligible compared to reaction 8.

$$HS+HS \rightarrow \text{products} \tag{8}$$

The above chain mechanism consisting of reactions 1, 2′, 6, 7, 4 and 8 leads to the following rate equation.

$$-\mathrm{d}[CH_3OCH_3]/\mathrm{d}t=R_{CH_4}=k_1^{1/2}k_7k_8^{-1/2}[CH_3OCH_3]^{3/2} \tag{II}$$

If the chain is sufficiently long, it is readily shown that in the steady state

$$k_6[CH_3][H_2S]=k_7[HS][CH_3OCH_3]$$

or

$$[HS]/[CH_3]=(k_6/k_7)([H_2S]/[CH_3OCH_3]) \tag{III}$$

Therefore, when the quantity in the right-hand side of Eq. III is very large, the rate of decomposition will be represented by Eq. II.

Fig. 3 shows the dependence of the rate of formation of methane on the concentration of hydrogen sulfide at varied temperatures. The rate increases with the increase in the concentration of hydrogen sulfide, until it attains a constant value. Fig. 4 shows that the rate of formation of methane in the presence of 2.32×10^{-6} mol. cc^{-1} of hydrogen sulfide at 380°C is proportional to the 3/2 power of the concentration of the ether. Both Figs. 3 and 4 thus indicate that Eq. II holds when the ratio $[H_2S]/[CH_3OCH_3]$ is large. Values of $k_1^{1/2}k_7k_8^{-1/2}$ determined from the constant values of the rate in Fig. 3 and from the slope of the straight line in Fig. 4 are listed in Table II together with those of $k_1^{1/2}k_3k_5^{-1/2}$. The fairly good agreement of the two values of $k_1^{1/2}k_7k_8^{-1/2}$ at 380°C obtained by different methods shows again the validity of Eq. II.

The values given in Table II lead to the following Arrhenius expressions:

$$k_1^{1/2}k_3k_5^{-1/2}=10^{15.16\pm0.13}\times\exp\{-(54{,}500\pm400)/\boldsymbol{RT}\}\ \mathrm{mol}^{-1/2}\,\mathrm{cc}^{1/2}\,\mathrm{sec}^{-1/2}$$

$$k_1{}^{1/2}k_7k_8{}^{-1/2}=10^{15.26\pm0.24}\times\exp\{-(51{,}800\pm700)/\boldsymbol{RT}\}\ \mathrm{mol^{-1/2}\,cc^{1/2}\,sec^{-1/2}}$$

The expression for $k_1{}^{1/2}k_3k_5{}^{-1/2}$ shows a good agreement with that of $10^{15.11}\exp(-55{,}600/\boldsymbol{RT})$ $\mathrm{mol^{-1/2}\,cc^{1/2}\,sec^{-1/2}}$ obtained by Benson and Jain⁶⁾ who studied the thermal decomposition of dimethyl ether in the temperature range from 490 to 550°C.

The expression of $k_1{}^{1/2}k_3k_5{}^{-1/2}$ divided by that of $k_1{}^{1/2}k_7k_8{}^{-1/2}$ yields

$$(k_3/k_7)(k_8/k_5)^{1/2}=0.8\exp(-2{,}700/\boldsymbol{RT})$$

Assuming k_8/k_5 to be unity, $k_3/k_7=0.8\exp(-2{,}700/\boldsymbol{RT})$ and hence $E_7=E_3-2.7$ kcal./mol., E's denoting activation energies. The result seems reasonable since hydrosulfide radicals have been shown to be more reactive towards organic molecules than methyl radicals. Reported values of E_3 are 8.4¹⁰⁾, 9.5¹¹⁾ and 10.0¹²⁾ kcal./mol. and that of A_3 is of the order of 10^{11} mol⁻¹ cc. sec⁻¹. If we accept the intermediate value of 9.5 kcal./mol. for E_3, it follows that

$$k_7=10^{11}\exp(-6{,}800/\boldsymbol{RT})\ \mathrm{mol^{-1}\,cc.\,sec^{-1}}$$

The present authors found previously that $k_6=10^{11}\exp(-2{,}600/\boldsymbol{RT})$⁷⁾. The combination of these yields

$$k_6/k_7=\exp(4{,}200/\boldsymbol{RT})$$

It follows therefore that k_6/k_7 is much greater than unity at experimental temperatures although it decreases with the rise of temperature. This accounts for the fact that Eq. II holds even when the ratio $[H_2S]/[CH_3OCH_3]$ in Eq. III is not very large and that, the higher the temperature, the greater is the ratio $[H_2S]/[CH_3OCH_3]$ where Eq. II begins to be applicable, as seen in Fig. 3.

Benson and Jain have argued that the activation energy of the initial step, E_1, of 92 kcal./mol., obtained from their value of $E_{\mathrm{overall}}=(1/2)E_1+E_3-(1/2)E_5=55.6$ kcal./mol. combined with $E_3=9.5$ kcal./mol., is too large compared with $E_1=81$ kcal./mol. obtained by Rice and Johnston¹³⁾, who decomposed dimethyl ether in the temperature range from 1010 to 1150°K and determined E_1 by an antimony mirror removal method. In order to explain this discrepancy, they suggest that the chain terminates not only by reaction 5 but also by reactions 9 and 10

$$CH_3+CH_2OCH_3\rightarrow C_2H_5OCH_3 \tag{9}$$

$$2CH_2OCH_3\rightarrow (CH_3OCH_2)_2 \tag{10}$$

and that reaction 4 is not unimolecular but bimolecular

$$CH_2OCH_3+\mathbf{M}\rightarrow CH_2O+CH_3+\mathbf{M} \tag{4$'$}$$

The rate of decomposition is then expressed as

$$-\mathrm{d}[CH_3OCH_3]/\mathrm{d}t=\frac{k_1{}^{1/2}k_3k_5{}^{-1/2}}{1+(k_{10}/k_5)^{1/2}(k_3/k_{4'})}[CH_3OCH_3]^{3/2}$$

Since $E_{10}=E_5=0$, $E_3=9.5$ and $E_4=19$ kcal./mol.¹²⁾, the denominator of the overall rate constant decreases with temperature. This situation, they believe, explains the overall activation energy greater than $(1/2)E_1+E_3-(1/2)E_5$.

However, if $E_1=81$ kcal./mol. and consequently $(1/2)E_1+E_3-(1/2)E_5=50$ kcal./mol. as they assume, $E_3-E_7=-1.8$ kcal./mol., i. e., $E_3<E_7$ and the catalysis such as shown by Eq. II cannot be expected to take place¹⁴⁾. The interpretation given by Benson and Jain must therefore be regarded as incompatible with the results obtained in the present work. On the other hand, the agreement between the two overall A factors in the absence and presence of hydrogen sulfide seems to support the idea that $k_{\mathrm{overall}}=k_1{}^{1/2}k_3k_5{}^{-1/2}$, since it is probable that $A_3=A_7$ and $A_5=A_8$. The discrepancy between the overall activation energy in the pyrolysis of the ether alone and those of elementary reactions may therefore be attributed to the error in the estimation of E_1. Baughan et al.¹⁵⁾ estimated E_1 as 87 kcal./mol.

As seen in Table I, the time required to produce a definite amount of methane in the absence of hydrogen sulfide is about ten times as great as that in its presence, but the ratio of the amount of carbon monoxide to that of methane, compared with the same amount of the latter, is far less sensitive to the presence of hydrogen sulfide. This indicates that the decomposition of formaldehyde is also catalyzed by hydrogen sulfide. Kodama, Takezaki and Fujie¹⁶⁾ suggested that in the pyrolysis of dimethyl ether, formaldehyde decomposes by the following chain processes:

$$CH_3+CH_2O\rightarrow CH_4+CHO$$

$$CHO\rightarrow CO+H$$

$$H+CH_3OCH_3\rightarrow H_2+CH_3OCH_2$$

$$CH_3OCH_2\rightarrow CH_2O+CH_3$$

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10) M. K. Phibbs and B. B. Darwent, *Can. J. Research*, **B28**, 395 (1950).

11) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

12) R. A. Marcus, B. B. Darwent and E. W. R. Steacie, ibid., **16**, 983 (1948), recalculated in Ref. 11.

13) F. O. Rice and W. R. Johnston, *J. Am. Chem. Soc.*, **56**, 214 (1934).

14) Whether reaction 4 may be unimolecular or bimolecular, Eq. II holds when reactions 5, 9 and 10 are neglected compared with reaction 8.

15) E. C. Baughan, M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

16) S. Kodama, Y. Takezaki and R. Fujie, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 892 (1951).

In the presence of hydrogen sulfide, this scheme may be modified as follows:

$$HS+CH_2O \rightarrow H_2S+CHO$$

$$CHO \rightarrow CO+H$$

$$H+H_2S \rightarrow H_2+HS$$

Summary

Dimethyl ether has been decomposed thermally in the presence and absence of hydrogen sulfide over the temperature range 360∼440°C. The rate of decomposition is enhanced by the presence of hydrogen sulfide, but the rate law is unchanged, i. e., the rate is proportional to the 3/2 power of the ether concentration, irrespective of the presence of hydrogen sulfide.

The catalytic action of hydrogen sulfide is satisfactorily explained by the steps, $CH_3+H_2S \rightarrow CH_4+HS$ (6), $HS+CH_3OCH_3 \rightarrow H_2S+CH_3OCH_2$ (7) and $CH_3OCH_2 \rightarrow CH_2O+CH_3$ (4). Overall rate constants in the absence and presence of hydrogen sulfide are represented by $10^{15.16}\exp(-54{,}500/\boldsymbol{RT})$ and $10^{15.26}\exp(-51{,}800/\boldsymbol{RT})$ $\mathrm{mol.}^{-1/2}\,\mathrm{cc}^{1/2}\,\mathrm{sec}^{-1/2}$ respectively. The combination of these gives $k_3/k_7=0.8\exp(-2{,}700/\boldsymbol{RT})$, where k_3 refers to the reaction $CH_3+CH_3OCH_3 \rightarrow CH_4+CH_3OCH_2$ (3). If, therefore, the activation energy of reaction 3 is 9.5 kcal./mol. as reported by Trotman-Dickenson and Steacie, that for reaction 7 is 6.8 kcal./mol. The results obtained indicate that the decomposition of the formaldehyde formed intremediately is also catalyzed by hydrogen sulfide.

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