Thermal Decomposition of Acetaldehyde in the Presence of Hydrogen Sulfide. I. Kinetics of the Reaction

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Hydrogen sulfide was found by Fromherz¹⁾ to exert a catalytic effect on the thermal decomposition of acetaldehyde. Roth and Rollefson²⁾ studied this catalyzed decomposition and presented an approximate rate equation, but the mechanism of the catalysis was left unexplained. Recently the present authors have investigated the hydrogen-atom abstraction reaction of hydrogen sulfide molecules with methyl radicals³⁾ and the photolysis of acetaldehyde in the presence of hydrogen sulfide⁴⁾.

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1) H. Fromherz, *Z. physik. Chem.*, **B25**, 301 (1934).
2) W. L. Roth and G. K. Rollefson, *J. Am. Chem. Soc.*, **64**, 1707 (1942).
3) N. Imai and O. Toyama, This Bulletin, **33**, 652 (1960).
4) N. Imai and O. Toyama, ibid., **33**, 1120 (1960).

These studies have clarified the nature of various elementary reactions taking place in the systems of acetaldehyde and hydrogen sulfide. In this work, we have therefore undertaken to reinvestigate the pyrolysis of acetaldehyde in the presence of hydrogen sulfide in order to elucidate the catalytic effect of the latter. This paper reports on the kinetics of the reaction, and the following paper, Part II, on the effects of various chain-inhibitors on the reaction.

Experimental

Materials.—Acetaldehyde was prepared by distillation of paraldehyde, containing a small quantity of sulfuric acid, and was purified by bulb-to-bulb distillation. Hydrogen sulfide was prepared by dropping water on aluminum sulfide in an evacuated vessel, dried by passing it through a trap at −78°C, and purified by bulb-to-bulb distillation.

Apparatus.—The apparatus used in the present work was similar to that described previously5). Three cylindrical vessels were used: A, a quartz vessel of 118 cc., with a ratio of its surface area to its volume of $S/V=1.05\,\text{cm}^{-1}$; B, a glass vessel of 137 cc., $S/V=1.20\,\text{cm}^{-1}$; C, a glass vessel of 127 cc. packed with glass tubes, $S/V=15.9\,\text{cm}^{-1}$.

Procedure.—Required quantities of reactant gases were mixed at room temperature for about 30 min. prior to pyrolysis. They were then introduced into the reaction vessel, which had already been brought to the experimental temperature. In most runs, the change in total pressure with time was followed on a manometer. The products of the decomposition in some runs were analyzed quantitatively in the same way as has been described previously3). A Hitachi RMC remodeled mass spectrometer was used to analyze the products in several runs.

Results and Discussion

It has been established by many workers that the products of the thermal decomposition of acetaldehyde are almost exclusively equal quantities of methane and carbon monoxide6). Roth and Rollefson2), analyzing the reaction products in the decomposition of acetaldehyde with added hydrogen sulfide, found that the only appreciable products were about equal amounts of methane and carbon monoxide and that hydrogen sulfide remained unconsumed throughout the course of the reaction. Table I shows the results of the analysis of the reaction products obtained in the present study, together with the pressure changes observed.

TABLE I. PRODUCTS OF DECOMPOSITION

Temp. °C	Vessel	Initial press. mmHg		Time min.	Press. of products mmHg			Press. increase mmHg
		CH_3CHO	H_2S		CH_4	CO	C_2H_6	
370	B	69	53.5	10	5.1	5.0		4.9
		128	53.5	10	9.8	9.9		10.5
		154	53.5	10	10.6	10.3		10.8
		215	53.5	10	14.2	14.5		14.1
		247	53.5	10	16.0	16.4		16.6
400	C	69	30	5	6.7	6.7		6.4
		111	30	5	10.1	10.0		9.5
		154	30	5	12.8	12.3		12.2
		245	30	5	20.1	20.4		
		278	30	5	20.4	20.4		20.3
430	C	30	28.5	2	3.8	3.8		
		59	28.5	2	8.3	8.9		
		127	28.5	2	13.8	14.0		13.5
		208	28.5	2	20.4	21.1		
		285	28.5	2	24.6	25.8		23.0
460	B	105	5.7	1.67	0.86	0.87		
		135	5.7	1.67	0.92	0.92		
		183	5.7	1.67	1.07	1.10		
469[a]	A	135	10	1	22.8	25.2	0.007	
		180	10	1	29.1	31.4	0.017	
		183	40	90	173	182	4.7	
		314	44	4.5	200	247	0.78	

[a] Obtained by mass spectrometric analysis.

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5) N. Imai and O. Toyama, ibid., **33**, 1408 (1960).

6) C. N. Hinshelwood and W. K. Hutchson, *Proc. Roy. Soc.*, **A111**, 380 (1926); C. J. M. Fletcher and C. N. Hinshelwood, ibid., **A141**, 41 (1933); C. A. Winkler and C. N. Hinshelwood, ibid., **A149**, 355 (1935); R. V. Seddon and M. W. Travers, ibid:, **A156**, 234 (1936); E. Leifer and H. C. Urey, *J. Am. Chem. Soc.*, **64**, 994 (1942); Ref. 5.

It is seen that the total pressure increase is equal to the pressure of the methane formed as well as to that of carbon monoxide; this is in agreement with the analytical results obtained above by Roth and Rollefson. Mass spectrometric analysis has shown that hydrogen and ethane are also formed in the decomposition, but their amounts are too small to disturb the above relation significantly. These facts indicate that the total pressure increase corresponds to the decrease in acetaldehyde pressure due to decomposition. Accordingly, the initial rate of decomposition is obtained from the initial slope of a total pressure-time curve.

It is generally agreed that the main features of the thermal decomposition of acetaldehyde can be explained by the following mechanism⁷⁾:

$$CH_3CHO = CH_3 + CHO \tag{1}$$

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

$$H + CH_3CHO = H_2 + CH_3CO \tag{3}$$

$$CH_3CO = CH_3 + CO \tag{4}$$

$$CH_3 + CH_3CHO = CH_4 + CH_3CO \tag{5}$$

$$CH_3 + CH_3 = C_2H_6 \tag{6}$$

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

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_1^{1/2}k_5k_6^{-1/2}[CH_3CHO]^{3/2} \tag{I}$$

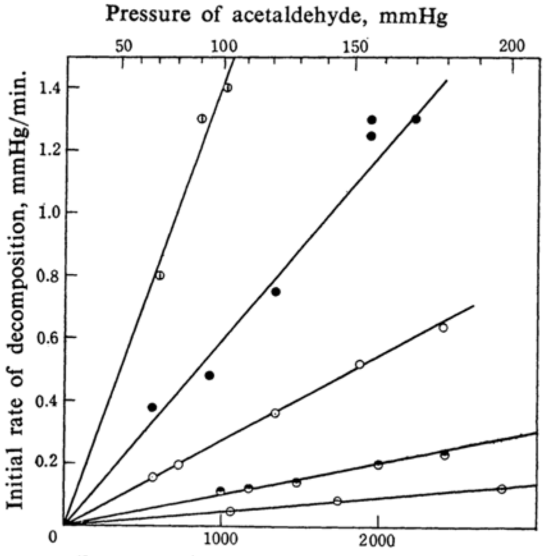

Fig. 1. Rate of decomposition of acetaldehyde alone.
⊖, 380; ◓, 400; ○, 420; ●, 440; ⦶, 460°C

TABLE II. VALUES OF $k_1^{1/2}k_5k_6^{-1/2}$

Temp. °C	$k_1^{1/2}k_5k_6^{-1/2}$ mol$^{-1/2}$ ml$^{-1/2}$ sec^{-1}
380	0.0048
400	0.0105
420	0.030
440	0.067
460	0.18

which is in general agreement with experimental results obtained by various workers. Also in this work, the rate of decomposition was found to be proportional to the 3/2 power of the pressure of acetaldehyde, as is seen in Fig. 1. From the slope of the straight line in the figure, the value of $k_1^{1/2}k_5k_6^{-1/2}$ at each temperature was obtained and listed in Table II.

In the presence of hydrogen sulfide, it was found that the rate of decomposition increases linearly with the pressure of hydrogen sulfide, as is seen in Fig. 2. Although the intercepts of the straight lines on the ordinate are located very close to the point of origin, they are in agreement with the corresponding values in Fig. 1, indicating the great catalytic effect of

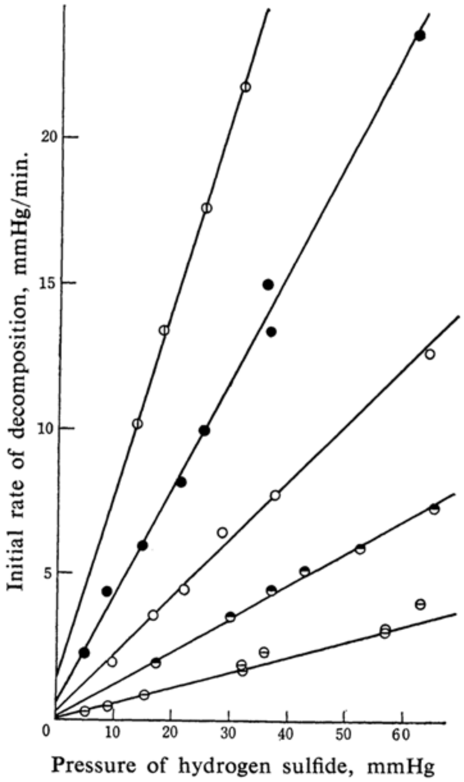

Fig. 2. Dependence of the rate of decomposition of acetaldehyde on the pressure of hydrogen sulfide.
CH_3CHO, 100 mmHg
⊖, 380; ◓, 400; ○, 420; ●, 440; ⦶, 460°C

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7) F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56**, 289 (1934); E. W. R. Steacie, "Atomic and Free Radical Reaction", 2nd Ed., Reinhold Publ. Corp., New York (1954), p. 266.

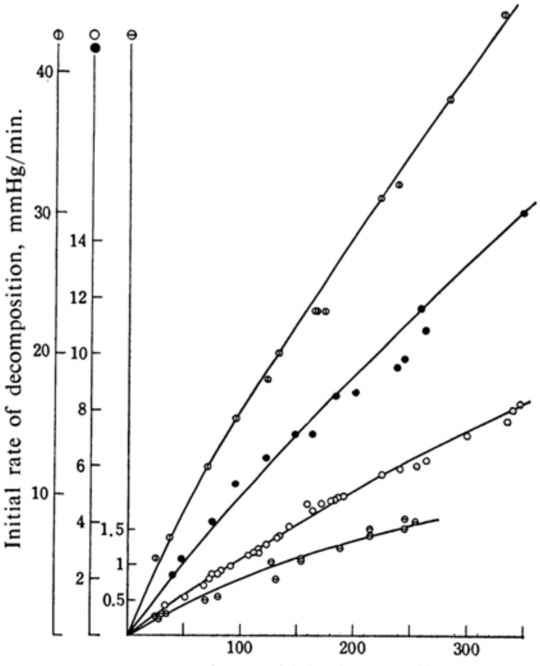

Fig. 3. Dependence of the rate of decomposition of acetaldehyde in the presence of hydrogen sulfide on the pressure of acetaldehyde.
⊖ Series 23, H_2S 28.3 mmHg, 370°C
○ Series 14, H_2S 40 mmHg, 406°C
● Series 7, H_2S 20 mmHg, 431°C
⦶ Series 8, H_2S 20 mmHg, 469°C

hydrogen sulfide. Several series of runs, where the pressure of acetaldehyde was varied while the pressure of hydrogen sulfide was kept constant, are shown in Fig. 3. As shown below, the results represented by Figs. 2 and 3 conform to the rate equation[8]

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_0[CH_3CHO]^{3/2} + k[H_2S][CH_3CHO] + k'[H_2S][CH_3CHO]^{1/2} \qquad \text{(II)}$$

The first term on the right-hand side of the equation, representing the non-catalyzed decomposition, is in most cases much smaller than the other terms and may be neglected. Thus, the rate may be written as

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k[H_2S][CH_3CHO] + k'[H_2S][CH_3CHO]^{1/2} \qquad \text{(III)}$$

Dividing both sides of Eq. III by $[CH_3CHO]^{1/2}$,

$$(-\mathrm{d}[CH_3CHO]/\mathrm{d}t)/[CH_3CHO]^{1/2} = k[H_2S][CH_3CHO]^{1/2} + k'[H_2S] \qquad \text{(IV)}$$

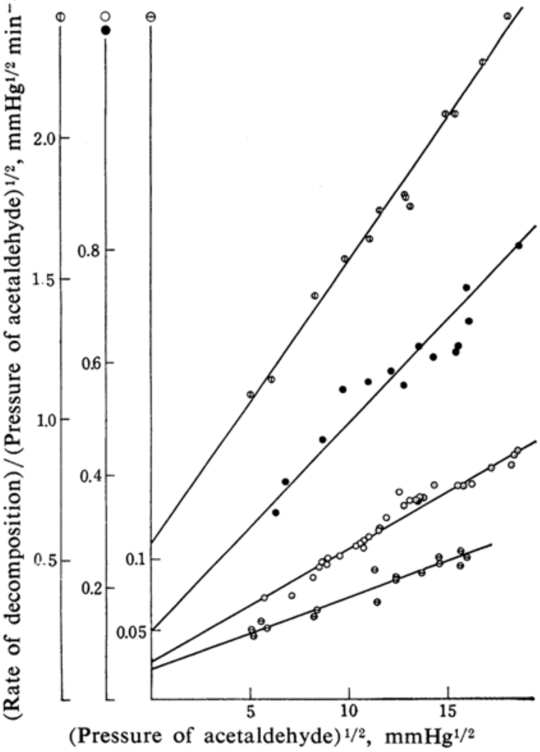

Fig. 4. Plots for Eq. IV.
⊖ Series 23, H_2S 28.3 mmHg, 370°C
○ Series 14, H_2S 40 mmHg, 406°C
● Series 7, H_2S 20 mmHg, 431°C
⦶ Series 8, H_2S 20 mmHg, 469°C

Figure 4 shows that Eq. IV and, accordingly, Eq. III fit the results given in Fig. 3. The slope and intercept of the straight line in the figure give the constants k and k'.

In Table III are listed the values of the constants thus determined by various series of experiments in this work. It is seen that the fluctuation in these values is fairly large, apart from the effect of the reaction vessel. The values of the constants were found to be approximately reproducible when the measurements were carried out successively with the same samples of the gases and with the same vessel, whereas a worse reproducibility was obtained with different samples of the gases even in the same vessel. The results obtained by Roth and Rollefson show an even greater fluctuation in the rate. Presumably, minute quantities of an impurity yet unidentified caused these phenomena[9]. The effect of various reaction vessels, with different ratios of surface area to volume is not clearly seen in Table III,

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[8] Roth and Rollefson proposed the following rate equation

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_a[H_2S][CH_3CHO] + k_b[H_2S][CH_3CHO]/(1+k_c[CH_3CHO])$$

Their experimental data, however, show too great a fluctuation to justify the rate equation.

[9] According to Morris[10], the use of hydroquinone for the purification of acetaldehyde reduces the rate of decomposition of the latter. In this work, however, hydroquinone was not used.

[10] J. C. Morris, *J. Am. Chem. Soc.*, **66**, 584 (1944).

TABLE III. VALUES OF k AND k'

Temp °C	Series No.	Initial press. of H_2S mmHg	Reaction vessel	k mol^{-1} ml. sec^{-1}	k' mol$^{-1/2}$ ml$^{1/2}$ sec^{-1}
340	18	26.8	C	33	0.043
	22	26.8	B	49	0.046
370	17	28.3	C	120	0.063
	23	28.3	B	130	0.071
380	29	60	B	200	0.12
400	16	30	C	250	0.29
	24	30	B	350	0.27
	27[a]	5.7	B		0.30
406	10	40	A	290	0.38
	14	40	A	360	0.19
430	15	32.5	C	870	0.90
	21	32.5	B	660	0.86
	26[a]	5.7	B		1.00
431	1	20	A	1200	1.8
	4	20	A	1500	1.1
	7	20	A	1300	0.7
	11	40	A	1000	0.7
460	19	35.5	C	2100	3.0
	20	35.5	B	1300	2.8
	25[a]	5.7	B		2.9
469	2	20	A	3100	5.7
	5	20	A	4800	7.5
	8	20	A	3900	3.2
	12	40	A	2300	3.6
494	3	20	A	6600	9.5
	6	20	A	8000	14.6
	9	20	A	5100	11.0
	13	40	A	2600	11.0
	28	20	B	9500	10.2

a Obtained from Fig. 5.

being masked by the fluctuation mentioned above. The effect is, however, not greater than the fluctuation, indicating that the reaction is essentially homogeneous, as has been described by Roth and Rollefson.

In Table III are included the values of the constant k' determined in a somewhat different way: when the pressure of hydrogen sulfide is low, the first term of Eq. III may be negligibly small compared to the second, so that

$$(-\mathrm{d}[CH_3CHO]/\mathrm{d}t)^2/[H_2S]^2 = k'^2[CH_3CHO] \qquad (V)$$

Figure 5 shows that Eq. V is applicable to the results of experiments with a low pressure of hydrogen sulfide. As seen in Table III, the values of the constant k' obtained from the slope of the straight line in Fig. 5[11] are in general agreement with those obtained by the use of Eq. IV.

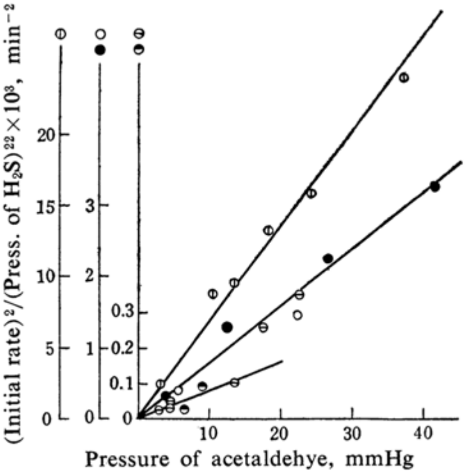

Fig. 5. Plots for Eq. V.
⊖ H_2S 5.7 mmHg, 400°C
◓ H_2S 11.4 mmHg, 400°C
● H_2S 5.7 mmHg, 430°C
○ H_2S 11.4 mmHg, 430°C
⦶ H_2S 5.7 mmHg, 460°C

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[11] In these experiments the rate of decomposition was obtained from an analysis of the products, carbon monoxide and methane, since the pressure could not be followed accurately on a mercury manometer.

As described in Part II, the addition of a sufficient quantity of propylene or isobutylene, both of which are known as chain-inhibitors, completely eliminates the second term of Eq. III, leaving the first term unaffected. This indicates that the decomposition represented by the second term of Eq. III involves a radical-chain mechanism, while the first term probably represents a molecular decomposition catalyzed by hydrogen sulfide.

The radical-chain decomposition represented by the second term of Eq. III is explained on the basis of the previously studied photolysis of acetaldehyde in the presence of hydrogen sulfide[4]. The kinetics of the photolysis showed that, in the presence of not too much hydrogen sulfide, the decomposition takes place through a chain mechanism which involves, in addition to reactions 1—6, the following reactions[12]:

$$\mathrm{CH_3+H_2S=CH_4+HS} \qquad (7)$$

$$\mathrm{HS+CH_3CHO=H_2S+CH_3CO} \qquad (8)$$

The reaction sequence 1—8, when applied to the thermal decomposition in the presence of hydrogen sulfide, leads to the rate equation

$$(-\mathrm{d}[\mathrm{CH_3CHO}]/\mathrm{d}t)_{\mathrm{chain}} = k_1^{1/2}k_5k_6^{-1/2}[\mathrm{CH_3CHO}]^{3/2} + k_1^{1/2}k_7k_6^{-1/2}[\mathrm{H_2S}][\mathrm{CH_3CHO}]^{1/2} \qquad (\mathrm{VI})$$

The first term of the right-hand side of the equation corresponds to the first term of Eq. II, which was neglected in Eq. III, and the second term of Eq. VI explains the second term of Eq. III. It follows, therefore, that

$$k' = k_1^{1/2}k_7k_6^{-1/2}$$

The Arrhenius plots of $k_1^{1/2}k_5k_6^{-1/2}$ and $k_1^{1/2}k_7k_6^{-1/2}$ obtained from the results given in Tables II and III are shown in Fig. 6. These yield

$$k_1^{1/2}k_5k_6^{-1/2} = 10^{12.1\pm0.24}\exp(-43300\pm1100/\boldsymbol{RT})\ \mathrm{mol^{-1/2}\,ml^{1/2}\,sec^{-1}} \qquad (\mathrm{VII})$$

$$k_1^{1/2}k_7k_6^{-1/2} = 10^{12.8\pm0.27}\exp(-41100\pm1200/\boldsymbol{RT})\ \mathrm{mol^{-1/2}\,ml^{1/2}\,sec^{-1}} \qquad (\mathrm{VIII})$$

If E_1 (the activation energy of reaction 1) $=75.0$[13], $E_5=6.8$[14] and $E_6=0$ kcal. mol^{-1}, $E_{\mathrm{VII}}=1/2(E_1-E_6)+E_5=44.3$ kcal. mol^{-1}. The value of E_{VII} compares satisfactorily with the 43.3 kcal. mol^{-1} found above. Similarly, when E_7 is taken as 2.6 kcal. mol^{-1} [15], $E_{\mathrm{VIII}}=1/2(E_1-E_6)+E_7=40.1$ kcal. mol^{-1}, which is again in agreement with the above experimental value of 41.1 kcal. mol^{-1}.

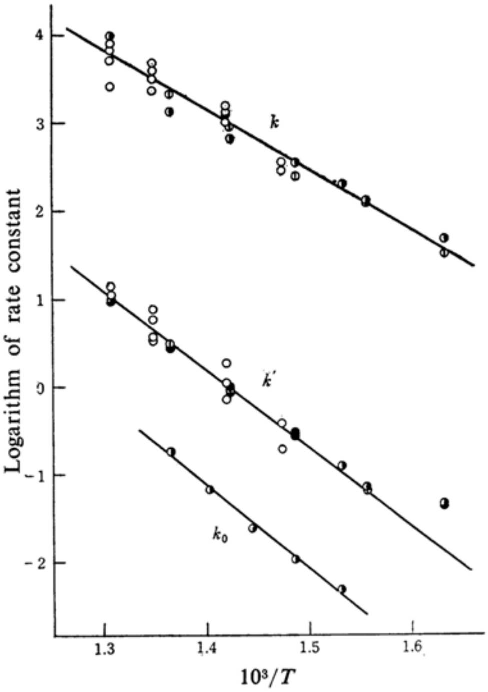

Fig. 6. Arrhenius plots of k_0, k' and k.
○ Vessel A; ◑ Vessel B; ⦶ Vessel C;
● Obtained from Fig. 5.

As has already been described, small quantities of hydrogen and ethane are found among the products of decomposition. Their formation in early stages of the decomposition may be explained by reactions 3 and 6. Their small quantities indicate that the chain length is fairly large.

As has also already been described, the first term of Eq. III probably represents the rate of homogeneous molecular decomposition catalyzed by hydrogen sulfide. Stoichiometrically, the reaction is written as

$$\mathrm{CH_3CHO+H_2S=CH_4+CO+H_2S} \qquad (9)$$

since the products obtained in the decomposition are almost exclusively equal amounts of methane and carbon monoxide. The Arrhenius plot of constant k, given in Fig. 6, yields

$$k=10^{12.7\pm1.0}\exp(-31400\pm3100/\boldsymbol{RT}) \qquad (\mathrm{IX})$$

Although this appears to be a reasonable expression for a simple bimolecular process in the gas phase, a detailed mechanism for the catalysis cannot be determined at present from the kinetics alone. It has been known that

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[12] In the photolysis, the primary step is $\mathrm{CH_3CHO}+h\nu=\mathrm{CH_3+CHO}$

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

[14] P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*. **33**, 31 (1655).

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

the decomposition of acetaldehyde to methane and carbon monoxide is catalyzed by hydrogen chloride and hydrogen bromide in the gas phase[16]. The mechanism of the decomposition is, however, not yet clear in these cases. Recently, Stimson et al.[17] have shown that the hydrogen halides-catalyzed decomposition of alcohols into water and olefins in the gas phase is largely homogeneous and molecular in character in the temperature range 300 to 500°C. Although they present various possible mechanisms for the catalysis, no definite conclusion has yet been obtained. Information from other sources seems necessary to elucidate the mechanism of these reactions.

Summary

The hydrogen sulfide-catalyzed thermal decomposition of acetaldehyde has been investigated over the temperature range 340 to 494°C. The initial rates of decomposition approximately fit the rate equation

$$-\mathrm{d}[\mathrm{CH_3CHO}]/\mathrm{d}t = k[\mathrm{H_2S}][\mathrm{CH_3CHO}] + k'[\mathrm{H_2S}][\mathrm{CH_3CHO}]^{1/2}$$

where

$$k = 10^{12.7\pm1.0}\exp(-31400\pm3100/\boldsymbol{RT}) \quad \mathrm{mol^{-1}\,ml.\,sec^{-1}}$$

and

$$k' = 10^{12.8\pm0.27}\exp(-41100\pm1200/\boldsymbol{RT}) \quad \mathrm{mol^{-1/2}\,ml^{1/2}\,sec^{-1}}$$

A comparison of the above results with those of the decomposition inhibited by propylene and isobutylene, which will be reported on in the following paper, suggests that the first term of the rate equation probably represents a molecular decomposition catalyzed by hydrogen sulfide, while the second represents a radical-chain decomposition. Combining the chain mechanism generally accepted for the pyrolysis of acetaldehyde alone with the reactions $\mathrm{CH_3 + H_2S = CH_4 + HS}$ and $\mathrm{HS + CH_3CHO = H_2S + CH_3CO}$, both of which have been shown to be important in the photolysis of acetaldehyde with added hydrogen sulfide, a rate equation is derived by which the second term of the experimental rate equation and the temperature depedennce of its rate constant k' can be explained.

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[16] R. P. Bell and R. Le G. Burnett, *Trans. Faraday Soc.*, **35**, 474 (1939); K. E. Howlett and D. H. R. Barton, ibid., **45**, 735 (1949).

[17] A. Maccoll and V. R. Stimson, *J. Chem. Soc.*, **1960**, 2836; K. G. Lewis and V. R. Stimson, ibid., **1960**, 3087; R. A. Ross and V. R. Stimson, ibid., **1960**, 3090; V. R. Stimson and E. J. Watson, ibid., **1960**, 3920; V. R. Stimson and E. J. Watson, ibid., **1961**, 1392.