Photolysis of Acetaldehyde in the Presence of Deuterium Sulfide. Deuterium Atom Abstraction from Deuterium Sulfide Molecules by Methyl Radicals

By Naomi IMAI, Takaaki DOHMARU and Osamu TOYAMA

(Received September 3, 1964)

Previous studies of the catalytic effect of hydrogen sulfide on the photolysis[1] and pyrolysis[2] of acetaldehyde, as well as on the pyrolysis of dimethyl ether,[3] have shown that hydrogen atom abstraction from hydrogen sulfide molecules by methyl radicals:

$$CH_3+H_2S \rightarrow CH_4+HS \qquad (6')$$

plays an important role in these reactions. The rate constant of this metathetical reaction has been determined by photolyzing acetone[4] and acetaldehyde[1] in the presence of hydrogen sulfide, with the result that the reaction is much faster than ordinary hydrogen abstractions by methyl radicals.

In order to establish further the mechanism of the hydrogen sulfide catalysis, the study of the deuterium sulfide-catalyzed pyrolysis of acetaldehyde is now in progress. Here, in place of reaction 6′, the following reaction:

$$CH_3+D_2S \rightarrow CH_3D+DS \qquad (6)$$

is expected to play a similar role. In this work a mixture of deuterium sulfide and acetaldehyde was photolyzed, and the relative rate of reaction 6 was determined against that of reaction 5:

$$CH_3+CH_3CHO \rightarrow CH_4+CH_3CO \qquad (5)$$

which competes with reaction 6.

Experimental

Materials. — Acetaldehyde was supplied commercially, dried by potassium chloride, and purified by repeated bulb-to-bulb distillations. Deuterium sulfide was prepared by dropping deuterium oxide (99.8 mol.%) on aluminum sulfide in an evacuated vessel, dried by passing it through a trap at −78°C, and purified by bulb-to-bulb distillations.

Apparatus.—The apparatus used was similar to that described previously.[1] The photolysis was carried out in a cylindrical quartz vessel with a capacity of about 110 cc. A medium-pressure mercury arc was used as the light source, and the light of the wavelength region shorter than 2800 Å was cut off in front of the vessel by a thin glass plate in order to avoid absorption by deuterium sulfide. The light intensity was kept constant by the use of a voltage stabilizer.

Procedure. — Required quantities of deuterium sulfide and acetaldehyde were admitted to the reaction vessel. After the gases had been allowed to mix thoroughly for a few minutes, light was admitted into the vessel. After irradiation for a certain time, the reaction mixture was led into a trap at the temperature of liquid air; the non-condensable fraction was then collected and measured by a Toepler gauge. In some runs, this fraction was analyzed by a gas chromatograph and by a mass spectrometer. No peaks at $(m/e)=19$ and 20 corresponding to methane-d_3 and -d_4 were found by mass spectrometry. The methane-d_0: -d_1: -d_2 ratio was determined from the intensities of the peaks at $(m/e)=16$, 17 and 18. Since the three components contribute to these peaks, the quantity of each component was calculated by means of simultaneous equations. The mass spectra of methane-d_1 and -d_2 were constructed from the measured mass spectrum of pure methane by the method of Schissler, Thompson and Turkevich;[5] the validity of the construction was confirmed by the close agreement between measured and calculated values for the peak at $(m/e)=15$.

Results and Discussion

It was found by gas chromatographic analysis of the non-condensable products of the photolysis in the presence of deuterium sulfide that

---

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

[2] N. Imai, Y. Yoshida and O. Toyama, ibid., 35, 752, 758 (1962).

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

[4] N. Imai and O. Toyama, ibid., 33, 652 (1960).

[5] D. O. Shissler, S. O. Thompson and J. Turkevich, *Discussions Faraday Soc.*, **10**, 46 (1951).

the fraction consists merely of methane and carbon monoxide in equal amounts within the range of experimental error. This fact indicates that acetaldehyde decomposes stoichiometrically to methane and carbon monoxide, as was observed in non-catalyzed[6] and hydrogen sulfide-catalyzed[1] photolyses. Consequently, the rate of decomposition was determined by measuring the amount of the non-condensable fraction of the products.

By analogy with the hydrogen sulfide catalysis, the photolysis of acetaldehyde in the presence of a small amount of deuterium sulfide can be explained by the following mechanism:

$$CH_3CHO + h\nu \rightarrow CH_3 + CHO \qquad (1)$$

$$CHO \rightarrow CO + H \qquad (2)$$

$$H + CH_3CHO \rightarrow H_2 + CH_3CO \qquad (3)$$

$$H + D_2S \rightarrow HD + DS \qquad (4)$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \qquad (5)$$

$$CH_3 + D_2S \rightarrow CH_3D + DS \qquad (6)$$

$$DS + CH_3CHO \rightarrow HDS + CH_3CO \qquad (7)$$

$$CH_3CO \rightarrow CH_3 + CO \qquad (8)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \text{[7]} \qquad (9)$$

Figure 1 shows the progress of decomposition with time. In the photolysis of 300 mm. of acetaldehyde with 10 mm. of deuterium sulfide (run B), the decomposition curve shows, though slightly, autocatalytic behavior in the initial stage. Such behavior is probably to be attributed to the replacement of reaction 6 by the faster reactions 6′′ and 6′:

$$CH_3 + HDS \rightarrow CH_4 + DS \qquad (6'')$$

$$CH_3 + H_2S \rightarrow CH_4 + HS \qquad (6')$$

as a result of the conversion of hydrogen sulfide-d_2 to -d_1 or -d_0 by reaction 7 or 7′:

$$HS + CH_3CHO \rightarrow H_2S + CH_3CO \qquad (7')$$

No autocatalytic behavior can be recognized unless the ratio of deuterium sulfide to acetaldehyde is sufficiently low, as in run B. In the experiments with small amounts of deuterium sulfide, consequently, care was taken to determine the initial decomposition rate by short-time irradiation.

In Fig. 2 the initial decomposition rate is

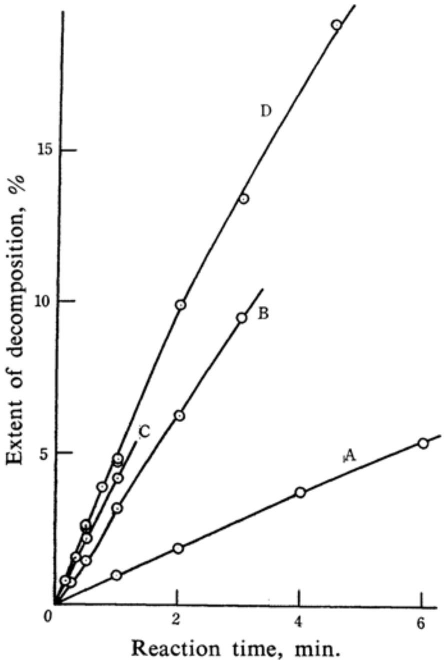

Fig. 1. Photolysis of acetaldehyde in the absence and presence of hydrogen sulfide and deuterium sulfide at 300°C.
A D_2S : 0, CH_3CHO : 100 mmHg
B D_2S : 10 mmHg, CH_3CHO : 300 mmHg
C D_2S : 13.5 mmHg, CH_3CHO : 100 mmHg
D H_2S : 10 mmHg, CH_3CHO : 300 mmHg

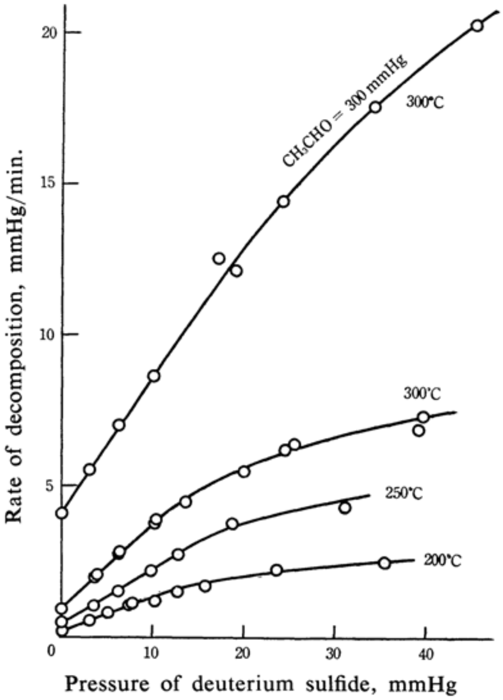

Fig. 2. Dependence of the rate of decomposition in the presence of deuterium sulfide on its pressure.
CH_3CHO : 100 mmHg unless otherwise described.

---

6) F. E. Blacet and D. Volman, *J. Am. Chem. Soc.*, **60**, 1243 (1938); F. E. Blacet and W. J. Blaedel, ibid., **62**, 3374 (1940); R. E. Dodd and J. D. Waldron, *Nature*, **167**, 655 (1951).

7) In the pyrolysis of acetaldehyde reaction 9 was suggested to be third order (N. Imai, T. Fujii and O. Toyama, This Bulletin, **38**, 410 (1965).) but it is supposed to be second order at lower temperature.

plotted against the deuterium sulfide pressure. At a constant acetaldehyde pressure and light intensity, the rate increases linearly with deuterium sulfide pressure in its low pressure range, but it tends to saturation in its higher pressure range. These phenomena are similar to those found in hydrogen sulfide catalysis and can similarly be explained.

The reaction scheme for the photolysis of acetaldehyde alone[8] (reactions 1, 2, 3, 5, 8 and 9) leads to Rate Eq. I (I_a[9] denotes the rate of the absorption of light quanta):

$$-\mathrm{d}[\mathrm{CH_3CHO}]/\mathrm{d}t = k_5 k_9^{-1/2} I_a^{1/2} [\mathrm{CH_3CHO}] \qquad \text{(I)}$$

while that in the presence of deuterium sulfide (reactions 1—9) leads to Rate Eq. II:

$$-\mathrm{d}[\mathrm{CH_3CHO}]/\mathrm{d}t = k_5 k_9^{-1/2} I_a^{1/2} [\mathrm{CH_3CHO}] + k_6 k_9^{-1/2} I_a^{1/2} [\mathrm{D_2S}] \qquad \text{(II)}$$

Equation II explains the linear relation between the rate and deuterium sulfide pressure, while Eqs. I and II explain the coincidence of the intercepts of the linear curves with the rates in the absence of deuterium sulfide, as may be seen in Fig. 2. At higher deuterium sulfide pressures, the concentration of DS radicals increases in relation to that of methyl radicals, and the contribution of DS radicals to chain termination has now to be taken into account. Thus the rate should be lower than that expected from Eq. II, as may be seen in Fig. 2.

From the slopes and intercepts of the linear portions in Fig. 2, the values for k_6/k_5 were determined; they are listed in Table I. At 300°C the values for 100 and 300 mm. of acetaldehyde approximately agree with each other.

TABLE I. VALUES OF k_6/k_5 AND k_6'/k_5

Temp., °C	k_6/k_5	k_6'/k_5
200	51[a]	121
250	35[a]	80
300	29.2[a] 30.3[b] 28.2[c]	56

a) Obtained from Fig. 2 for 100 mm. acetaldehyde.
b) Obtained from Fig. 2 for 300 mm. acetaldehyde.
c) Obtained from Fig. 3.

The distribution of deuterium in methane was determined mass spectrometrically for the photolysis of 10 mm. deuterium sulfide and 300 mm. acetaldehyde mixtures with varied irradiation times at 300°C. The only methanes detected in appreciable amounts by the mass spectrometer are methane-d_0 and -d_1. The amount of methane-d_2 was negligible. The ratio of methane-d_1 to methane-d_0 is plotted against the time in Fig. 3, in which the ratio falls off with the progress of the reaction. This falling off in the ratio may, again, be attributed to the conversion of hydrogen sulfide-d_2 to -d_1 and -d_0 by reactions 7 and 7',

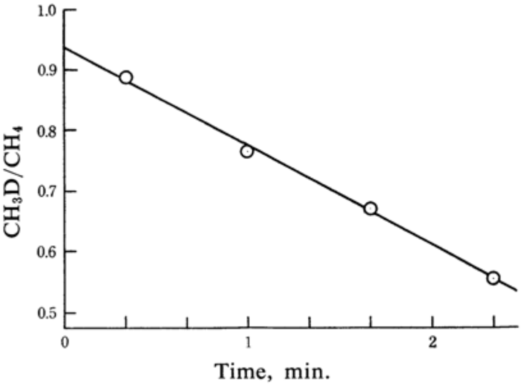

Fig. 3. Dependence of CH_3D/CH_4 ratio on reaction time at 300°C.
CH_3CHO: 300 mmHg; D_2S: 10 mmHg

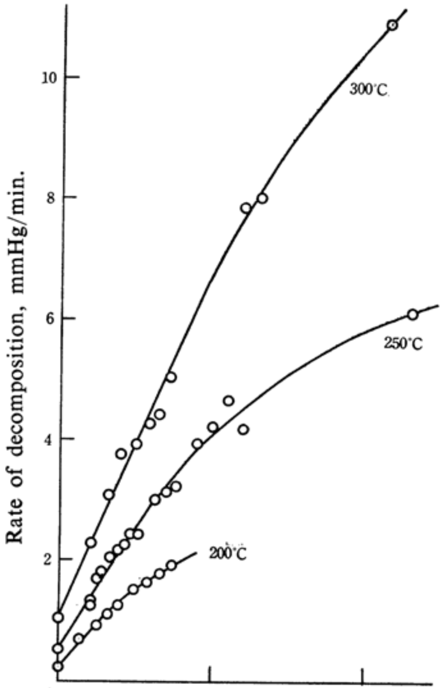

Fig. 4. Dependence of the rate of decomposition in the presence of hydrogen sulfide on its pressure. CH_3CHO: 100 mmHg.

---

8) E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 890; J. A. Leermakers, *J. Am. Chem. Soc.*, **56**, 1537 (1934); D. C. Grahame and G. K. Rollefson, *J. Chem. Phys.*, **8**, 98 (1940); C. J. Darby, A. S. Buchanan and I. H. S. Henderson, *J. Chem. Soc.*, **1951**, 1426.

9) I_a was found to be proportional to acetaldehyde pressure in the present experimental condition in Ref. 1.

TABLE II. ISOTOPE EFFECT IN ARRHENIUS PARAMETERS OF HYDROGEN ATOM ABSTRACTION REACTIONS BY METHYL RADICALS

Reaction	A_H/A_D	E_D-E_H kcal./mol.	k_H/k_D at 200°C	Ref.
$CD_3+C_2H_6 \rightarrow CD_3H+C_2H_5$ $CD_3+C_2D_6 \rightarrow CD_4+C_2D_5$	1	1.5	5.0	10
$CD_3+C_2H_3D_3 \rightarrow CD_3H+C_2H_2D_3$ $CD_3+C_2H_3D_3 \rightarrow CD_4+C_2H_3D_2$	0.73	1.9	5.5	10
$CH_3+CH_3NH_2 \rightarrow CH_4+CH_3NH$ $CH_3+CH_3ND_2 \rightarrow CH_3D+CH_3ND$	0.78	1.3	3.1	11
$CH_3+CH_3NH_2 \rightarrow CH_4+CH_2NH_2$ $CH_3+CD_3NH_2 \rightarrow CH_3D+CD_2NH_2$	1.3	1.4	5.8	11
$CH_3+CH_3OH \rightarrow CH_4+CH_2OH$ $CH_3+CD_3OH \rightarrow CH_3D+CD_2OH$	1.3	1.3	5.2	11
$CD_3+CH_3COCH_3 \rightarrow CD_3H+CH_3COCH_2$ $CD_3+CD_3COCD_3 \rightarrow CD_4+CD_3COCD_2$	0.80	1.67	4.6	12
	0.83	1.64	4.7	13
$CH_3+CH_3CHO \rightarrow CH_4+CH_3CO$ $CH_3+CH_3CDO \rightarrow CH_3D+CH_3CO$	2.5	1.1	7.8	14
$CH_3+\phi CHDCH_2D \rightarrow CH_4+\phi CDCH_2D$ $CH_3+\phi CHDCH_2D \rightarrow CH_3D+\phi CHCH_2D$	1.7	1.56	8.7	15
$CH_3+HD \rightarrow CH_4+D$ $CH_3+HD \rightarrow CH_3D+H$	0.46	1.3	1.8	16
$CD_3+HD \rightarrow CD_3H+D$ $CD_3+HD \rightarrow CD_4+H$	1.7	0	1.7	16
$CH_3+H_2S \rightarrow CH_4+HS$ $CH_3+D_2S \rightarrow CH_3D+DS$	0.75	1.15	2.4	This work

if the methane-d$_1$ is not subsequently converted to methane-d$_0$.

Provided that methane-d$_0$ is formed only by reaction 5 and methane-d$_1$, by reaction 6 in the initial stage of the photolysis, the extrapolation of the linear plot in Fig. 3 gives the ratio of the rate of reaction 6 against that of reaction 5 and, consequently, the k_6/k_5 ratio shown in Eq. III:

$$\frac{R_{CH_3D}}{R_{CH_4}}=\frac{k_6\,[CH_3]\,[D_2S]}{k_5\,[CH_3]\,[CH_3CHO]}=\frac{k_6\,[D_2S]}{k_5\,[CH_3CHO]} \qquad (III)$$

The value for k_6/k_5 thus obtained shows, as may be seen in Table I, a good agreement with those obtained from Fig. 2.

The values of k_6/k_5 in Table I give the Arrhenius expression:

$$k_6/k_5=2.0\exp(3000/\boldsymbol{RT}) \qquad (IV)$$

In this work, the photolysis of acetaldehyde in the presence of hydrogen sulfide was investigated and the results are shown in Fig. 4, which corresponds to Fig. 2. The values of k_6'/k_5 obtained from this figure are also listed in Table I. They yield the expression:

$$k_6'/k_5=1.5\exp(4150/\boldsymbol{RT}) \qquad (V)$$

which is in excellent agreement with $k_6'/k_5=1.7\exp(4000/\boldsymbol{RT})$, a value previously obtained by the method of total pressure measurement.1)

By dividing Eq. V by Eq. IV, we obtain:

$$k_6'/k_6=0.75\exp(1150/\boldsymbol{RT}) \qquad (VI)$$

The ratio here obtained is fully comparable with that for hydrogen and deuterium atom abstraction from HD molecules by methyl radicals, but it is considerably lower than those for other abstraction reactions by methyl radicals as is shown in Table II.

By combining Eqs. IV and V with the $k_5=10^{11.3}\exp(-6800/\boldsymbol{RT})$ mol^{-1} cc. sec^{-1} reported by Ausloos and Steacie,14) we obtain:

$$k_6=10^{11.6}\exp(-3800/\boldsymbol{RT})\ \text{mol}^{-1}\ \text{cc. sec}^{-1} \qquad (VII)$$

and

$$k_6'=10^{11.5}\exp(-2650/\boldsymbol{RT})\ \text{mol}^{-1}\ \text{cc. sec}^{-1} \qquad (VIII)$$

The latter expression is almost identical with

---

10) J. R. McNesby, *J. Phys. Chem.*, **64**, 1671 (1961).

11) P. Gray and J. C. Thynne, *Trans. Faraday Soc.*, **59**, 2275 (1963).

12) J. R. McNesby, T. W. Davis and A. S. Gordon, *J. Am. Chem. Soc.*, **76**, 823 (1954).

13) J. R. McNesby and A. S. Gordon, ibid., **76**, 1416 (1954).

14) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 31 (1955).

15) L. Herk and M. Szwarc, *J. Am. Chem. Soc.*, **82**, 3558 (1960).

16) E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953).

the $k_6'=10^{11.4}\exp(-2600/\boldsymbol{RT})$ mol^{-1} cc. sec^{-1} obtained in the photolysis of acetone in the presence of hydrogen sulfide.[4)]

Summary

The photolysis of acetaldehyde in the presence of deuterium sulfide has been investigated over the temperature range from 200 to 300°C, in order to determine the rate constant for the deuterium atom abstraction from deuterium sulfide molecules by methyl radicals. The effect of deuterium sulfide addition is similar to that of the addition of hydrogen sulfide previously studied. The results obtained with low concentrations of deuterium sulfide can be explained by the following reaction scheme: $CH_3CHO+h\nu \rightarrow CH_3+CHO$ (1), $CHO \rightarrow CO+H$ (2), $H+CH_3\cdot CHO \rightarrow H_2+CH_3CO$ (3), $H+D_2S \rightarrow HD+DS$ (4), $CH_3+CH_3CHO \rightarrow CH_4+CH_3CO$ (5), $CH_3+D_2S \rightarrow CH_3D+DS$ (6), $DS+CH_3CHO \rightarrow HDS+CH_3CO$ (7), $CH_3CO \rightarrow CH_3+CO$ (8), and $CH_3+CH_3 \rightarrow C_2H_6$ (9). The rate equation derived from the scheme, $-d[CH_3CHO]/dt=k_5k_9^{-1/2}I_a^{1/2}[CH_3CHO]+k_6k_9^{-1/2}I_a^{1/2}[D_2S]$, is in agreement with the results. The application of this rate equation leads to $k_6/k_5=2.0\exp(3000/\boldsymbol{RT})$, and to $k_6=10^{11.6}\exp(-3800/\boldsymbol{RT})$ mol^{-1} cc. sec^{-1}, if $k_5=10^{11.3}\exp(-6800/\boldsymbol{RT})$ mol^{-1} cc. sec^{-1}, as has been reported by Ausloos and Steacie. On reinvestigating the effect of hydrogen sulfide addition, it was found that $k_6'/k_5=1.5\exp(4150/\boldsymbol{RT})$, where k_6' refers to the $CH_3+H_2S \rightarrow CH_4+HS$ (6′) reaction. We thus obtain $k'_6/k_6==0.75\exp(1150/\boldsymbol{RT})$.

The authors are grateful to Dr. Setsuo Taniguchi of the Radiation Center of Osaka Prefecture for the mass spectrometric analysis.

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