The Thermal Decomposition of Acetaldehyde in the Presence of Methanethiol

By Naomi IMAI and Osamu TOYAMA

(Receiced April 16, 1960)

It is well known that reactions between thiols and free redicals, and between organic compounds and thiol radicals occur easily compared to other radical-molecule reactions. But only a few kinetic studies about these reactions are found in the literature[1,2]. The present authors have recently studied the photochemical[3] as well as the thermal[4] decomposition of acetaldehyde in the presence of hydrogen sulfide. These studies have shown that the chain decomposition of acetaldehyde is catalyzed by hydrogen sulfide, and this catalytic effect has been attributed to a chain mechanism involving reactions between methyl radical and hydrogen sulfide and between hydrosulfide radical and acetaldehyde. In a mixture of acetaldehyde and a thiol, a similar catalysis may be expected to take place. In this work a kinetic study of the thermal decomposition of acetaldehyde in the presence of methanethiol has been carried out to obtain information on elementary reactions involving methanethiol or its radical.

Experimental

Materials.—Acetaldehyde was prepared by distillation of paraldehyde containing a small quantity of sulfuric acid and purified by bulb-to-bulb distillation. Methanthiol was obtained[5] by adding a sodium hydroxide solution to *S*-methyl isothiourea sulfate, which was prepared by the reaction between dimethyl sulfate and thiourea. It was then passed through a trap containing concentrated sulfuric acid and through a tower containing dry calcium chloride, and finally purified by bulb-to-bulb distillation.

Apparatus. — The thermal decomposition was carried out in a cylindrical glass vessel of 137 cc. placed in an electric furnace. The reaction vessel was connected to a mercury manometer, to an analytical system, to storage bulbs and to a bulb in which acetaldehyde and methanethiol were mixed before they were admitted to the reaction vessel. The reaction vessel, the manometer, the bulbs for storage and mixing and the analytical system were all attached to a conventional vacuum line.

Procedure.—Required quantities of acetaldehyde and methanethiol were admitted into the mixing bulb at room temperature and left for about 30 minutes to allow them to mix thoroughly. The mixed reactant gases were then introduced into the reaction vessel, which had already been kept at the experimental temperature, and the change in the total pressure with time was followed on a manometer. The products of decomposition in several runs were analyzed quantitatively in the same way as described previously[6].

Results

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 monoxide[7]. Similarly in this work, i. e., in the presence of methanethiol, it has been confirmed by analysis that the rate of formation of methane is identical with that of carbon monoxide, and the pressure of either one of these products corresponds to the total pressure increase within the experimental error. Thus, irrespective of the presence of methanethiol, the total pressure increase is always equal to the decrease in the pressure of acetaldehyde due to decomposition. Accordingly, the initial rate of decomposition was determined from the initial slope of a total pressure-time curve with the results shown in Figs. 1 and 3 and Table I. Fig. 1 shows the dependence of the rate of decomposition on the pressure of acetaldehyde in the experiments with acetaldehyde alone. Table I and Fig. 3 show the dependence of the rate of decomposition in the presence of methanethiol on the pressures of methanethiol and of acetaldehyde, respectively.

Discussion

It is generally agreed that the main feature of thermal decomposition of acetaldehyde can

---

[1] R. N. Birrell, R. F. Smith, A. F. Trotman-Dickenson and H. Wilkie, *J. Chem. Soc.*, **1957**, 2807.

[2] J. A. Kerr and A. F. Trotman-Dickenson, ibid., **1957**, 3322.

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

[4] Unpublished work.

[5] F. Arndt, *Ber.*, **54**, 2236 (1921).

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

[7] C. J. M. Fletcher and C. N. Hinshelwood, *Proc. Roy. Soc.* (London), **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).

TABLE I. EFFECT OF METHANETHIOL ON THE PYROLYSIS OF ACETALDEHYDE
Initial pressure of CH_3CHO, 100 mmHg

400°C		420°C		440°C	
Initial press. of CH_3SH (mmHg)	Initial rate of decomp. (mmHg/min.)	Initial press. of CH_3SH (mmHg)	Initial rate of decomp. (mmHg/min.)	Initial press. of CH_3SH (mmHg)	Initial press. of decomp. (mmHg/min.)
0.63	0.40	5.8	2.1	5.8	4.7
1.0	0.50	9.2	2.5	6.9	4.8
3.3	0.64	10.5	2.6	9.5	5.1
3.5	0.77	11.8	2.8	11.1	5.6
5.3	0.88	14.6	2.9	12.3	5.6
8.4	1.04	14.8	3.2	13.6	6.1
13.3	1.32	23.0	3.4	14.8	6.4
15.0	1.4	25.5	3.6	20.0	6.7
20.0	1.6	29	3.9	22.1	7.2
21.3	1.7	33	4.0	24	7.5
21.4	1.7	36	4.4	26	8.0
34	2.0	58	5.4	35	8.2
42	2.3	71	6.0	47	9.8
67	2.7	85	6.7	55	10.4
88	3.1				

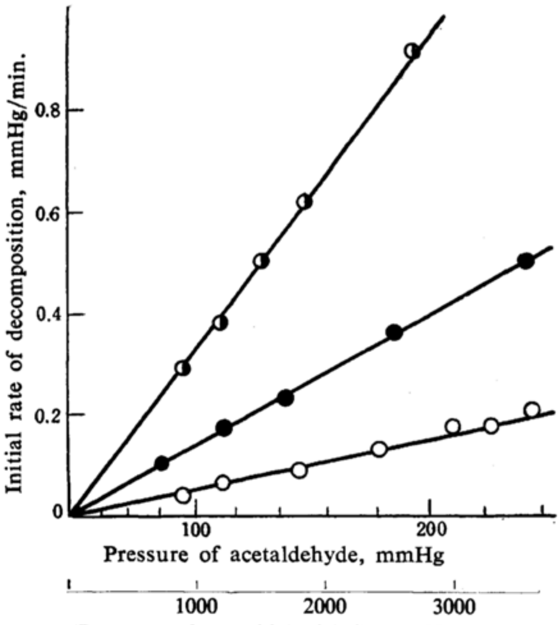

Fig. 1. Rate of decomposition of acetaldehyde alone. ○, 400; ●, 420; ◑, 440°C.

be explained by the following mechanism[8]

$$CH_3CHO = CH_3 + CHO \qquad (1)$$

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

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

$$CH_3CO = CH_3 + CO \qquad (4)$$

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

$$CH_3 + CH_3 = C_2H_6 \qquad (6)$$

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

$$-d\,[CH_3CHO]/dt = k_1^{1/2}k_5\ k_6^{-1/2}\,[CH_3CHO]^{3/2} \qquad (I)$$

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 seen in Fig. 1. From the slopes of the straight lines in the figure, the value of $k_1^{1/2}k_5\ k_6^{-1/2}$ at each temperature was obtained and listed in Table II.

TABLE II. VALUES OF $k_1^{1/2}k_5k_6^{-1/2}$, $k_1k_{11}^2k_{12}^{-1}$ and $k_7k_{11}^2k_{12}^{-1}$

Temp. (°C)	$k_1^{1/2}k_5k_6^{-1/2}$ ($mol^{-1/2}\ cc^{1/2}\ sec^{-1/2}$)	$k_1k_{11}^2k_{12}^{-1}$ (mol^{-1} cc sec^{-1})	$k_7k_{11}^2k_{12}^{-1}$ (mol^{-1} cc sec^{-1})
400	0.045	0.245	7.4
420	0.116	1.40	33
440	0.28	7.4	141

Now in the presence of methanethiol, the additional possibilities may be[9]

$$CH_3SH = CH_3 + SH \qquad (7)$$

$$SH + CH_3SH = H_2S + CH_3S \qquad (8)$$

---

[8] F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934); E. W. R. Steacie, "Atomic and Free Radical Reaction", 2nd Ed., Reinhold Publ. Corp., New York, (1954), p. 206.

[9] Reactions similar to 10, 11 and 12 have been proposed by the following workers: E. F. P. Harris and W. A. Waters, *Nature*, **170**, 212 (1952); K. E. J. Banett and W. A. Waters, *Discussions Faraday Soc.*, **14**, 221 (1953); Ref. 1.

$$SH + CH_3CHO = H_2S + CH_3CO \quad (9)$$

$$CH_3 + CH_3SH = CH_3S + CH_4 \quad (10)$$

$$CH_3S + CH_3CHO = CH_3SH + CH_3CO \quad (11)$$

$$CH_3S + CH_3S = \text{Product} \quad (12)$$

Sehon and Darwent[10] suggest that in the thermal decomposition of methanethiol the split of C–S bond, and not that of S–H, takes place, in view of the fact that major products found by using toluene as a carrier are methane, hydrogen sulfide and dibenzyl. Their suggestion seems reasonable judging from the dissociation energies of C–S and S–H bonds of methanethiol which have been estimated as 74.2 and 88.8 kcal./mol., respectively[11]. Skerrett and Thompson[12] have shown that the product of reaction 12 is mainly methyl disulfide $(CH_3)_2S_2$ by analysis of the products obtained in the photolysis of methanethiol, where the primary reaction is the split of S–H bond of the methanethiol molecule that absorbed light.

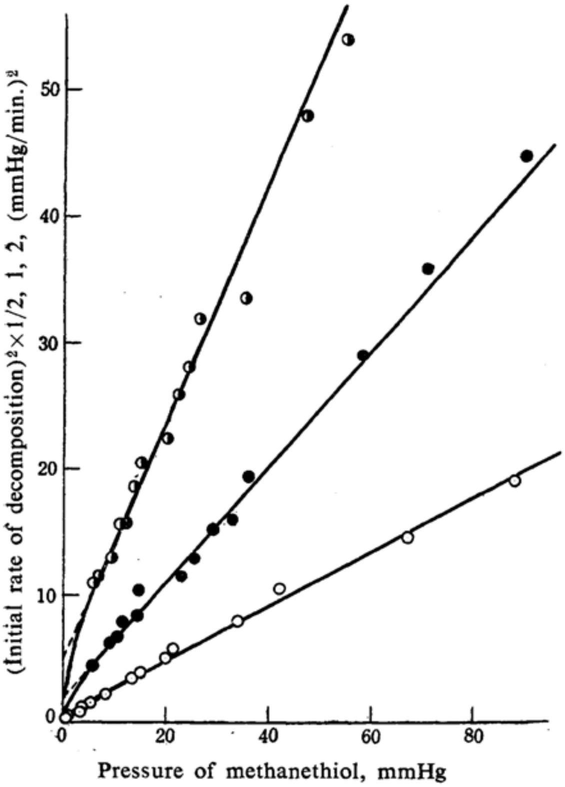

Fig. 2. Dependence of the rate of decomposition in the presence of methanethiol on its pressure. CH_3CHO : 100 mmHg. ○, $(\text{Rate})^2 \times 2$, 400°C; ●, $(\text{Rate})^2 \times 1$, 420°C; ◑, $(\text{Rate})^2 \times 1/2$, 440°C.

When reactions 10 and 11 are much faster than reaction 5, acetaldehyde decomposes mostly by a chain mechanism consisting of reactions 10, 11 and 4. If, in addition, reaction 10 is faster than reaction 11, the concentration of methylthio radicals will be greater than that of methyl radicals and reaction 12. These assumptions lead to the following rate equation.

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_{11}k_{12}^{-1/2}(k_1[CH_3CHO] + k_7[CH_3SH])1/2[CH_3CHO] \quad (II)$$

or

$$(-\mathrm{d}[CH_3CHO]/\mathrm{d}t)^2 = k_{11}^2 k_{12}^{-1}(k_1[CH_3CHO]^3 + k_7[CH_3CHO]^2[CH_3SH]) \quad (III)$$

As seen in Fig. 2, except in a low pressure range of methanethiol, the square of the rate of decomposition increases linearly with the pressure of methanethiol in agreement with equation III. At lower pressures of methanethiol, the relative concentration of methylthio radicals to that of methyl radicals falls off and consequently the importance of the recombination of methyl radicals becomes greater. This explains the deviation from equation III at

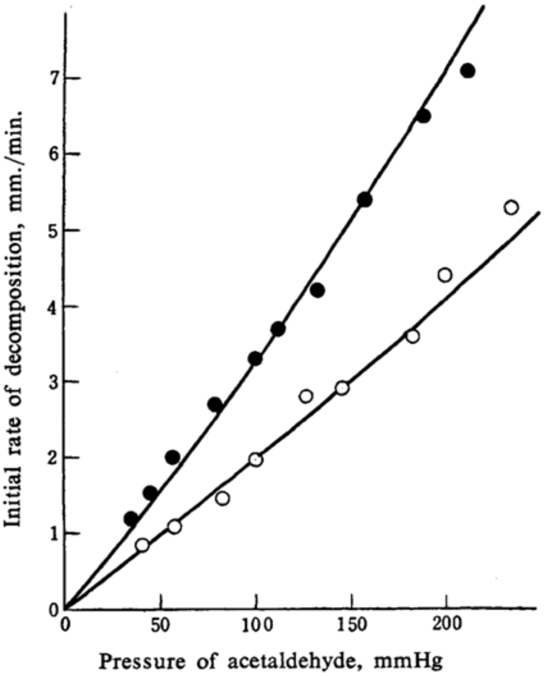

Fig. 3. Dependence of the rate of decomposition in the presence of methanethiol on acetaldehyde pressure. ○, CH_3SH: 33 mmHg, 400°C; ●, CH_3SH : 19 mmHg, 420°C. Circles and full lines represent observed and calculated rates, respectively.

---

[10] A. H. Sehon and B. Darwent, *J. Am. Chem. Soc.*, **76**, 4806 (1954).

[11] J. L. Franklin and H. E. Lumpkin, ibid., **74**, 1023 (1952).

[12] N. D. Skerrett and N. W. Thompson. *Trans. Faraday Soc.*, **37**, 81 (1941).

low pressures of methanethiol. From the intercepts and slopes of the straight lines in Fig. 2 values of $k_1k_{11}{}^2k_{12}{}^{-1}$ and $k_7k_{11}{}^2k_{12}{}^{-1}$ are obtained, which are listed in Table II together with values of $k_1{}^{1/2}k_5k_6{}^{-1/2}$ already mentioned above.

Fig. 3 shows the plots of the rate of decomposition observed at a constant pressure of methanethiol against the pressure of acetaldehyde, together with the curves representing the rate calculated as a function of acetaldehyde pressure by equation II using the values of $k_1k_{11}{}^2k_{12}{}^{-1}$ and $k_7k_{11}{}^2k_{12}{}^{-1}$ given in Table II. The fact that the calculated curves are in satisfactory agreement with the experimental plots over a wide range of acetaldehyde pressure may be taken as an additional evidence for the validity of equation II.

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

$$k_1{}^{1/2}k_5k_6{}^{-1/2}=10^{12.8}\exp(-43{,}500/\boldsymbol{RT})\quad(\mathrm{mol}^{-1/2}\ \mathrm{cc}^{1/2}\ \mathrm{sec}^{-1/2})$$

$$k_1k_{11}{}^2k_{12}{}^{-1}=10^{25.8}\exp(-81{,}300/\boldsymbol{RT})\quad(\mathrm{mol}^{-1}\ \mathrm{cc.\ sec}^{-1})$$

$$k_7k_{11}{}^2k_{12}{}^{-1}=10^{23.7}\exp(-70{,}200/\boldsymbol{RT})\quad(\mathrm{mol}^{-1}\ \mathrm{cc.\ sec}^{-1})$$

The expression for $k_1{}^{1/2}k_5k_6{}^{-1/2}$ agrees with those reported previously by various workers. Combining the expression for $k_1{}^{1/2}k_5k_6{}^{-1/2}$ with that for $k_1k_{11}{}^2k_{12}{}^{-1}$, we obtain

$$(k_5/k_{11})(k_{12}/k_6)^{1/2}=0.8\exp(-2{,}800/\boldsymbol{RT})$$

If we assume that k_{12} has zero activation energy and a pre-exponential factor of the same value as that of k_6, the left-hand side of the equation becomes equal to k_5/k_{11}. The difference in activation energies $E_5-E_{11}=2.8$ kcal./mol. thus obtained compares with 1.6 kcal./mol. obtained by Birrel et al.[1] in the photolysis of mixtures of acetaldehyde and methanethiol. The value of the ratio $A_5/A_{11}=0.8$ also seems reasonable, as pre-exponential factors of these two reactions are expected to be of the same order of magnitude.

From the expressions for $k_1k_{11}{}^2k_{12}{}^{-1}$ and $k_7k_{11}{}^2k_{12}{}^{-1}$ given above, it follows that

$$k_1/k_7=130\exp(-11{,}100/\boldsymbol{RT})$$

The difference in activation energies $E_1-E_7=$ 11 kcal./mol., when combined with $E_1=75$ kcal./mol., yields a value of 64 kcal./mol. for E_7. Franklin and Lumpkin[11] estimated the dissociation energy of C-S bond in methanethiol to be 74.2 kcal./mol. by an electron impact method. Sehon and Darwent[10] obtained a lower dissociation energy of 67 kcal./mol. from the rates of decomposition of methanethiol in the presence of toluene as a carrier, assuming a pre-exponential factor of 3×10^{13} sec^{-1}. The value of 64 kcal./mol. obtained above in the present work is still lower than that of Sehon and Darwent. As can be seen in Fig. 2, the straight lines representing the square of the rate of decomposition as a function of acetaldehyde pressure cut the ordinate axis very close to the origin. Hence the values of the intercept and consequently the expression for k_1/k_7 given above must be accepted with some reserve. In fact, a value of the ratio A_1/A_7 amounting to 1.3×10^2 may be too large. If this ratio has really a smaller value, E_7 is greater than the value estimated above; if A_1/A_7 is put equal to unity, E_7 becomes as large as 70 kcal./mol.

As has been shown above, the results obtained in the present work comform to equation II based upon a mechanism in which the reaction chain terminates by the combination of methylthio radicals, while, in the photochemical[3] and thermal[3] decomposition of acetaldehyde in the presence of hydrogen sulfide, the experimental results indicate that the chain terminates by the combination of methyl radicals and not of hydrosulfide radicals. In these decomposition reactions, factors determining the chain-ending step may be the concentration ratio [RS]/[CH_3], where R represents CH_3 or H, and the relative abilities of radicals to recombine. The former quantity in the steady state is given by k_A[RSH]/k_B[CH_3CHO] where k_A and k_B are respectively the specific rates of the following reactions:

$$CH_3 + RSH = CH_4 + RS \qquad (A)$$

$$RS + CH_3CHO = RSH + CH_3CO \qquad (B)$$

Although our experimental results indicate that the activation energy of reaction A, E_A, is lower than E_B for hydrogen sulfide, and that $k_A=10^{11.4}\exp(-2{,}600/\boldsymbol{RT})$ mol^{-1} [6] cc. sec^{-1} for hydrogen sulfide and E_B is around 4 kcal./mol. methanethiol, we are yet given no complete expressions for all the k_A's and k_B's at present and accordingly cannot compare the value of the ratio [RS]/[CH_3] for methanethiol with that for hydrogen sulfide. If, however, these values were of comparable magnitudes in these experiments, the difference between the chain-ending steps in the experiments with methanethiol and with hydrogen sulfide would mean the lower ability of hydrosulfide radicals to recombine, compared to that of methylthio radicals.

It has been found in the present work that the rate of decomposition falls off during a run faster than can be expected from the rate equation. The higher are the pressure of methanethiol and the temperature, the greater is the extent of this reduction in the rate. Similar phenomena have been observed in the photolysis of acetaldehyde in the presence of hydrogen sulfide[3]. The exact nature of these phenomena are not clear at present.

Summary

Acetaldehyde has been decomposed thermally in the presence of methanethiol over the temperature range from 400° to 440°C. The presence of methanethiol markedly enhances the rate of decomposition. Analysis of the initial rates of decomposition obtained under various experimental conditions suggests: a) one of the chain-carrying steps $CH_3+CH_3CHO=CH_4+CH_3CO$ (5) in the decomposition of acetaldehyde alone is replaced by $CH_3+CH_3SH=CH_4+CH_3S$ (10) and $CH_3S+CH_3CHO=CH_3SH+CH_3CO$ (11) in the presence of methanethiol; b) the reaction $CH_3SH=CH_3+SH$ (7), in addition to $CH_3CHO=CH_3+CHO$ (1), contributes to the chain initiation; c) the chain terminates by the combination of methylthio radicals in contrast to the decomposition in the presence of hydrogen sulfide where the chain-ending step is the combination of methyl radicals under similar experimental conditions; d) $k_5/k_{11}=0.8\exp(-2{,}800/\boldsymbol{RT})$ and $k_1/k_7=130\exp(-11{,}000/\boldsymbol{RT})$, the latter expression being less certain.

The present study was partly supported by the finantial aid of the Ministry of Education, to which the authors' thanks are due.

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