The Photolysis of Acetaldehyde in the Presence of Hydrogen Sulfide

By Naomi IMAI and Osamu TOYAMA

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The present authors have recently studied the photolysis of acetone in the presence of hydrogen sulfide in order to obtain information on the hydrogen abstraction from hydrogen sulfide molecules by methyl radicals[1]. The activation energy of the abstraction reaction thus obtained is of such small value that it seems desirable to check it in another way. The present work presents such an attempt on the basis of an investigation on the photolysis of acetaldehyde in the presence of hydrogen sulfide.

We have been interested in this abstraction reaction in conjunction with the mechanism of the thermal decomposition of acetaldehyde in the presence of hydrogen sulfide. The present study is therefore expected to give valuable information also on other elementary reactions involved in common in both kinds of decomposition, photochemical and thermal, in the system consisting of acetaldehyde and hydrogen sulfide.

Experimental

Materials.—Acetaldehyde was prepared by distillation of paraldehyde containing a little quantity of sulfuric acid, and stored in a bulb at 0°C. When the acetaldehyde thus stored was not used at once, it was again purified by distillation befroe use. Hydrogen sulfide was 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.

Apparatus. — Photolysis was carried out in a cylindrical quartz vessel of about 110 cc. placed in an electric furnace with a thin glass window which cuts off the light of a wavelength region shorter than 2800 Å to prevent absorption by hydrogen sulfide. The reaction vessel was connected to a mercury manometer, to an analytical system, to storage bulbs and to a bulb in which acetaldehyde and hydrogen sulfide were mixed before they were admitted to the reaction vessel. The full light from a medium pressure mercury arc was used in the present study, and its intensity was kept constant for a series of runs by using a voltage stabilizer. For experiments with varied intensity, the distance between the light source and the reaction vessel was changed. 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 hydrogen sulfide were admitted into the mixing bulb at room temperature and left for about 30 minutes to allow them to mix thoroughly. The mixed gases were then introduced into the reaction vessel which had already been irradiated, and the change in the total pressure with time was followed on a manometer.

The analytical technique employed was the same as that described previously[1]. In this work the hydrogen sulfide added initially was found by analysis to remain almost unconsumed even after a prolonged photolysis.

Results and Discussion

It has been established by many workers[2] that the products of the photolysis of acetaldehyde above 100°C under normal conditions are almost exclusively methane and carbon monoxide. Similarly in this work, i. e., in the presence of hydrogen sulfide, 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 hydrogen sulfide, the total pressure increase is always equal to the decrease in the pressure of acetaldehyde

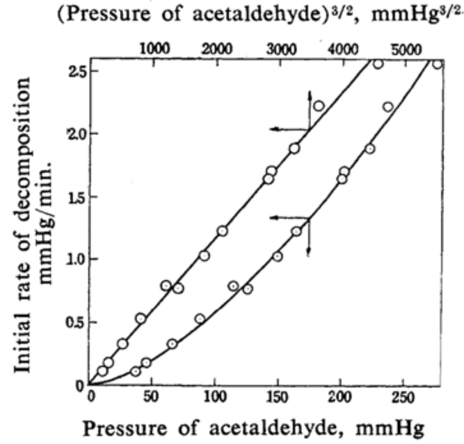

Fig. 1. Rate of decomposition of acetaldehyde alone at 250°C.

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

[2] 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).

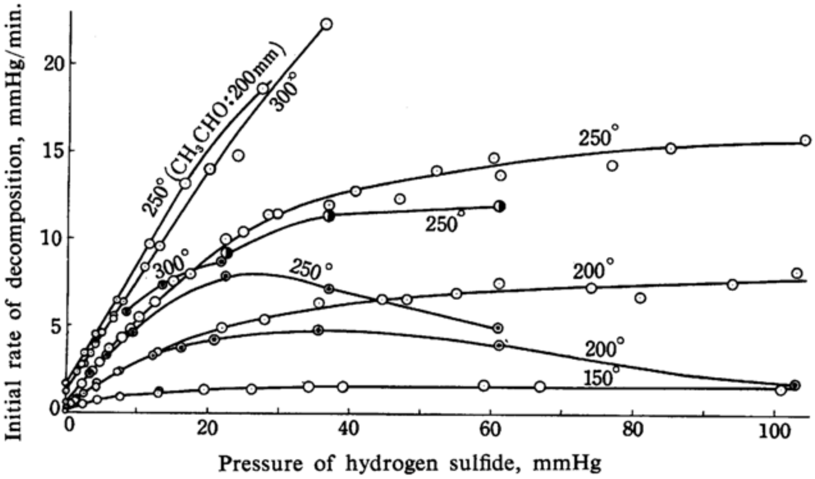

Fig. 2. Dependence of the rate of decomposition in the presence of hydrogen sulfide on its pressure. Relative light intensity : 1. CH_3CHO : 100 mmHg unless otherwise described. ○, without preheating ; ◑, with preheating for 1 min. ; ⊙, with preheating for 5 min.

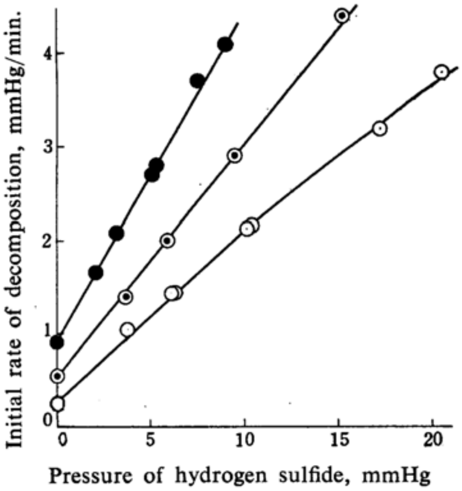

Fig. 3. Dependence of the rate of decomposition in the presence of hydrogen sulfide on its pressure. Relative light intensity : 1/4. CH_3CHO : 100 mmHg, ○, 250° ; ⊙, 300° ; ●, 360°C. All the data were obtained without preheating.

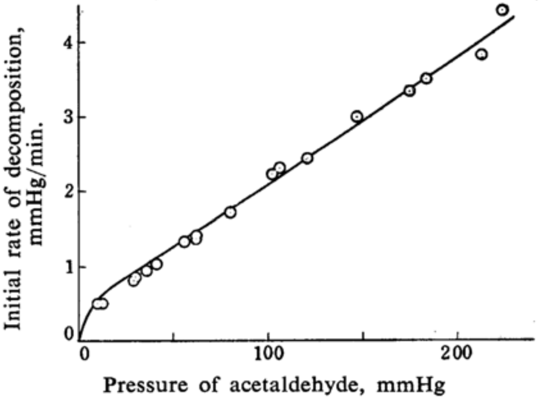

Fig. 4. Dependence of the rate of decomposition in the presence of hydrogen sulfide on acetaldehyde pressure. Temperature : 250°C. H_2S : 3.16 mmHg. Circles and full line represent observed and calculated rates respectively.

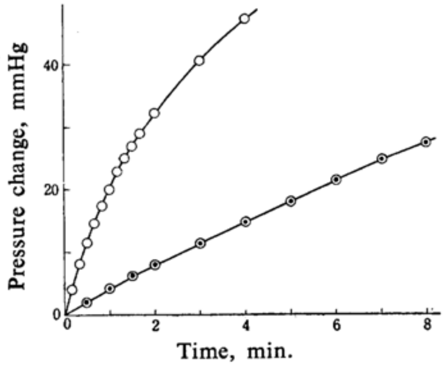

Fig. 5. Pressure-time curves at 300°C. Initial pressure : CH_3CHO, 100 mmHg. H_2S, ⊙, 3.5 ; ○, 36.2 mmHg.

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—4. Fig. 1 shows the dependence of the rate of decomposition on the pressure of acetaldehyde in the experiments with acetaldehyde alone. Figs. 2 and 3 show the dependence of the rate of decomposition in the presence of hydrogen sulfide on its pressure under various experimental conditions. The relative light intensity intensity for the experiments shown in Fig. 2 is four times as great as that in Fig. 3. Fig.

4 shows the dependence of the rate on acetaldehyde pressure in the presence of hydrogen sulfide.

It should be noted that, at a high temperature, in a run with a high concentration of hydrogen sulfide, the rate of decomposition falls off very rapidly, as seen in Fig. 5, compared to the results obtained with low concentrations of hydrogen sulfide. Similar reduction in the rate was observed, as seen in Fig. 2, when the acetaldehyde mixed with a large quantity of hydrogen sulfide was preheated for a few minutes at the experimental temperature prior to irradiation. Although the exact nature of these phenomena has not yet been fully elucidated, it is obvious from these findings that at still higher concentrations of hydrogen sulfide than those given in Fig. 2, determination of the initial rate of decomposition becomes considerably unreliable.

It is generally agreed that the main features of the photochemical decomposition of acetaldehyde can be explained by the following mechanism³⁾:

$$CH_3CHO + h\nu = CH_3 + CHO \qquad (0)$$

$$CHO = CO + H \qquad (1)$$

$$H + CH_3CHO = H_2 + CH_3CO \qquad (2)$$

$$CH_3CO = CH_3 + CO \qquad (3)$$

$$CH_3 + CH_3CHO = CH_4 + CH_3CO \qquad (4)$$

$$CH_3 + CH_3 = C_2H_6 \qquad (5)$$

Solution of the steady state equations derived from this scheme yields the rate equation (I_a = the rate of absorption of light quanta)

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_4 k_5^{-1/2} I_a^{1/2} [CH_3CHO] \qquad (I)$$

in general agreement with experimental results obtained by various workers. The existence of a primary reaction other than reaction (0) is well known⁴⁾. This, however, gives no substantial alteration in Eq. I. From the plot given in Fig. 1 it is seen that the rate of decomposition of acetaldehyde alone is proportional to the 3/2 power of its pressure. This simply means that under the present experimental conditions the rate of absorption of light quanta is proportional to the acetaldehyde pressure.

Now in the presence of hydrogen sulfide, the possible additional reactions may be⁵⁾

$$CH_3 + H_2S = CH_4 + HS \qquad (6)$$

$$HS + CH_3CHO = H_2S + CH_3CO \qquad (7)$$

$$HS + HS = \text{products} \qquad (8)$$

If reaction (8) can be neglected and consequently the chain terminates still by reaction (5),

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_4 k_5^{-1/2} I_a^{1/2} [CH_3CHO] + k_6 k_5^{-1/2} I_a^{1/2} [H_2S] \qquad (II)$$

while, if the chain terminates now by reaction (8), the result is

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_7 k_8^{-1/2} I_a^{1/2} [CH_3CHO] \qquad (III)$$

It is readily shown that in the steady state,

$$k_6 [CH_3][H_2S] = k_7 [HS][CH_3CHO]$$

or

$$[HS]/[CH_3] = (k_6/k_7)([H_2S]/[CH_3CHO])$$

Therefore, when the value of $(k_6/k_7)([H_2S]/[CH_3CHO])$ is very small, i. e., the concentration of methyl radical is much higher than that of hydrosulfide radical, the rate of decomposition will be represented by Eq. II. On the contrary, when the value of $(k_6/k_7)([H_2S]/[CH_3CHO])$ is very large, Eq. III will hold.

In Figs. 2 and 3 where the rates of decomposition are plotted against pressures of hydrogen sulfide, it is seen that, in the low pressure range of hydrogen sulfide, except for the experiments with preheating, the rate of decomposition increases linearly with the pressure of hydrogen sulfide in agreement with Eq. II. The fact that the intercept on the ordinate is always equal to the rate of decomposition in the absence of hydrogen sulfide also conforms to Eq. II. According to the equation the slope of the linear part divided by the intercept gives the ratio k_6/k_4. The values of k_6/k_4 thus

TABLE I. VALUES OF k_6/k_4

Initial pressure of CH_3CHO: 100 mmHg

Temp. °C	Relative light intensity=1	Relative light intensity=1/4
200	115	
250	78.7 82.0ᵃ⁾	75.5
300	55.2	54.1
360		38.6

a) Initial pressure of CH_3CHO: 200 mmHg.

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3) E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 890; J. A. Leemakers, *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.

4) (a) F. E. Blacet and D. E. Loeffler, *J. Am. Chem. Soc.*, **64**, 893 (1942). (b) M. A. Khan, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.* (*London*), **A219**, 312 (1953). (c) P. P. Manning, *J. Am. Chem. Soc.*, **79**, 5151 (1957). (d) R. E. Dodd, *Can. J. Chem.*, **33**, 699 (1955).

5) Similar reactions have been proposed by the following workers: (a) E. F. P. Harris and W. A. Waters, *Nature*, **170**, 212 (1952); (b) K. E. J. Banett and W. A. Waters, *Disc. Faraday Soc.*, **14**, 221 (1953); (c) R. N. Birrell, R. F. Smith, A. F. Trotman-Dickenson and H. Wilkie, *J. Chem. Soc.*, **1957**, 2087.

determined are listed in Table I[6]. The fact that neither a two-fold increase in the pressure of acetaldehyde, nor the variation in light intensity by a factor of four, yields any significant change in the values of k_6/k_4 may be taken as additional evidence for the validity of Eq. II.

A further check in favor of Eq. II is provided by Fig. 4, where the plot of the rates of decomposition observed at a constant pressure of hydrogen sulfide against acetaldehyde pressures is shown together with the curve predicted from Eq. II as follows: Since the rate of absorption of radiation in the present investigation is proportional to the concentration of acetaldehyde as mentioned above, the values of $k_4k_5^{-1/2}I_a^{1/2}$ and $k_6k_5^{-1/2}I_a^{1/2}$ required for the calculation of the rate of decomposition by means of Eq. II can be obtained from the data given in Figs. 1 and 2. As seen in Fig. 4, the curve representing the rate thus calculated as a function of acetaldehyde pressure is in satisfactory agreement with the experimental plot over a wide range of acetaldehyde pressure.

The Arrhenius plots of the values of k_6/k_4 given in the two series in Table I yielded two parallel straight lines lying close to each other from which the values $E_4-E_6=4.0\pm0.3$ kcal./mol. and $A_6/A_4=1.7\pm0.5$ were obtained, where E denotes the activation energy and A the pre-exponential factor. The ratio $A_6/A_4=1.7$ seems to be reasonable since A factors for most hydrogen abstraction reactions by methyl radicals are of the same order of magnitude. The activation energy difference $E_4-E_6=4.0$ kcal./mol., when combined with $E_4=6.8$ kcal./mol. given by Ausloos and Steacie[7], yields 2.8 kcal./mol. for E_6 which compares satisfactorily with our previous value of 2.6 kcal./mol. obtained in the photolysis of acetone in the presence of hydrogen sulfide[1]. If, instead, $E_4=7.5\sim8.0$ kcal./mol. reported by Brinton and Volman[8] and Dodd[4d] is accepted, the result is $E_6=3.5\sim4.0$ kcal./mol. which is now clearly higher than the previous value but still lower than 5.6 kcal./mol.[9] estimated for the activation energy of hydrogen abstraction from methane thiol by methyl radical, in agreement with our previous conclusion[1].

It is evident from Figs. 2 and 3 that, for the experiments without preheating, the lower the temperature, the lower is the pressure of hydrogen sulfide at which a plot of the rate of the decomposition against the pressure of hydrogen sulfide shows a departure from a straight line. At a temperature as low as 150°C, the plot (Fig. 2) shows a curvature from the very beginning and, in the range of pressure of hydrogen sulfide higher than about 30 mmHg the rate of decomposition attains an almost constant value in agreement with Eq. III.

Presumably, these fact indicate that the ratio k_6/k_7 increases with lowering of temperature, for, with the increase in the ratio k_6/k_7, $[CH_3]/[HS]$ and hence the ratio of the rate of reaction (8) to that of reaction (5) increases, provided the ratio $[H_2S]/[CH_3CHO]$ is constant. Such dependence of the ratio k_6/k_7 on temperature seems to be reasonable since the activation energy for reaction (6) is very low as estimated above so that it is probably lower than that of reaction (7).

The afore-mentioned observation that, in the presence of a large concentration of hydrogen sulfide, the rate of photolysis suffered considerable reduction not only by preheating the reaction mixture, but also during the photolysis at a high temperature, cannot fully be explained at present. It may, however, be possible that a small quantity of a yet unidentified compound produced in the thermal reaction between acetaldehyde and hydrogen sulfide gives rise to the observed phenomena. Birrell et al.[5c] found that the rate of decomposition of acetaldehyde is reduced appreciably by large quantities of isopropanethiol and tertiary-butanethiol below 300°C, and to almost negligible values by small quantities of tertiary-butanethiol and isopropanethiol above 300°C and 340°C respectively. We have also found[10] that the presence of a little quantity of methanethiol lowers remarkably the rates of photolyses of acetone, acetaldehyde and a mixture of acetaldehyde and hydrogen sulfide. In view of the similarity of the phenomena cited, it seems probable that all of these resulted from similar causes which, however, are to be clarified by further studies of these phenomena in future.

Summary

Acetaldehyde has been photolyzed in the presence of hydrogen sulfide over the temperature range from 150 to 360°C. The initial rates of decomposition obtained under various experimental conditions are consistent with a mechanism which involves the reactions $CH_3+H_2S=CH_4+HS$ (6) and $HS+CH_3CHO=H_2S+CH_3CO$ (7) in addition to those established already for the photolysis of acetaldehyde alone. Analysis of the data on this basis gives

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[6] The value of the intercept was actually determined from several repeated runs of the photolysis of 100 mmHg acetaldehyde in the absence of hydrogen sulfide at the same temperature.

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

[8] D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, **20**, 1764 (1952).

[9] T. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **1957**, 3322.

[10] N. Imai and O. Toyama, unpublished work.

a value of 4.0 kcal./mol. for the difference in activation energy E_4-E_6, where E_4 refers to the reaction $CH_3+CH_3CHO=CH_4+CH_3CO$ (4). This result, when combined with $E_4=6.8$ kcal./mol. found by Ausloos and Steacie, gives $E_6=2.8$ kcal./mol. in excellent agreement with our previous value of 2.6 kcal./mol. obtained in the photolysis of acetone in the presence of hydrogen sulfide. As the temperature is lowered and the ratio $[H_2S]/[CH_3CHO]$ increased, the importance of the combination of methyl radicals to ethane as the chain terminating step decreases, until it is replaced by the combination of hydrosulfide radicals. This is explained in terms of the relationship $E_7>E_6$.

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