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The Thermal Decomposition of Acetaldehyde in the Presence of Hydrogen Bromide

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The catalytic effect of hydrogen bromide on the thermal decomposition of acetaldehyde has been studied over the temperature range from 326 to 365°C. The experimental results are similar to those previously obtained for the hydrogen chloride catalysis: the reaction is 3/2 order in the aldehyde and is independent of the hydrogen bromide pressure when the $[HBr]/[CH_3CHO]$ ratio is sufficiently high. The most probable reaction scheme to explain this order is: $CH_3CHO + M \rightarrow CH_3 + CHO + M$(1), $CHO \rightarrow CO + H$(2), $H + HBr \rightarrow H_2 + Br$(3), $CH_3 + HBr \rightarrow CH_4 + Br$(4), $Br + CH_3CHO \rightarrow HBr + CH_3CO$(5), $CH_3CO \rightarrow CH_3 + CO$(6), and $Br + Br + M \rightarrow Br_2 + M$(7). The overall rate resulting from this scheme is $k_1^{1/2}k_5k_7^{-1/2}[CH_3CHO]^{3/2}$; the application of this rate equation to the experimental results leads to the Arrhenius expression $k_1^{1/2}k_5k_7^{1/2} = 10^{14.65}$ exp-$(-44000/\boldsymbol{R}T)$mole$^{1/2}$cc$^{1/2}$sec^{-1}, which is consistent with the expression for k_1 reported previously and with those for k_5 and k_7 estimated from the literature. The catalytic efficiency of hydrogen bromide is greater than that of hydrogen chloride by a factor of about forty.

It has been observed by a number of workers that hydrogen sulfide,[1-3] thiols[4,5] and hydrogen halides[6,7] catalyze thermal decompositions of such simple organic compounds as aldehydes, ethers, and alcohols. The hydrogen chloride-catalyzed thermal decomposition of acetaldehyde has recently been studied kinetically with very simple results, and a probable reaction mechanism has been proposed. The present work was undertaken to investigate the similar catalytic effect of hydrogen bromide on the acetaldehyde decomposition, and to compare the results obtained with those for hydrogen chloride.

Experimental

Materials. Acetaldehyde was supplied commercially, purified by repeated bulb-to-bulb distillations, and stored as a liquid below 20°C. Hydrogen bromide was prepared by dropping concentrated hydrobromic acid on calcium bromide, dried by passing it through phosphorus pentoxide and a trap at −78°C, and purified by bulb-to-bulb distillations.

Apparatus and Procedure. An ordinary static method was used in this work. The apparatus and procedure are the same as in a previous work.[8] The rate of decomposition in most cases was followed by measuring the total pressure change, but, in some runs, the major decomposition products uncondensable at the temperature of liquid air were analyzed by a gas chromatograph on a 2-m Molecular Sieve 5 column at room temperature.

Results and Discussion

The experimental results of the present study resemble those of the hydrogen chloride catalysis[8] in that the rate of pyrolysis is abnormally higher in a fresh vessel than in a seasoned one which is activated again by contact with air or by evacuation for a long time at a high temperature. To prevent the effect of a fresh wall, therefore, the reaction mixture after each run was evacuated just before the next one.

In order to investigate whether the presence of hydrogen bromide exerts any effect on the products of the pyrolysis, a mixture of 100 mm of acetaldehyde and 50 mm of hydrogen bromide was pyrolyzed in a seasoned vessel at 355.4°C; the products non-condensable at the temperature of liquid air were analyzed by a gas chromatograph. The detected products were exclusively carbon monoxide and methane in equal amounts. Hydrogen was not detected by a gas chromatograph using a nitrogen carrier. Previous studies of the pyrolyses

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[1] N. Imai and O. Toyama, This Bulletin, **34**, 328 (1961).

[2] N. Imai and O. Toyama, *ibid.*, **33**, 1120 (1960).

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

[4] R. N. Birrel, R. F. Smith, A. F. Trotman-Dickenson and H. Wilkies, *J. Chem. Soc.*, **1957**, 2807.

[5] N. Imai, and O. Toyama, This Bulletin, **33**, 1408 (1960).

[6] V. R. Stimson *et al.*, *J. Chem. Soc.*, **1960**, 2836, 3087, 3090, 3920; **1961**, 1392; **1962**, 653, 1602; M. Flowers, L. Batt and S. W. Benson, *J. Chem. Phys.*, **37**, 2662 (1962); K. H. Anderson and S. W. Benson, *ibid.*, **40**, 3747 (1964).

[7] K. H. Anderson and S. W. Benson, *ibid.*, **39**, 1677 (1963).

[8] N. Imai, T. Fujii and O. Toyama, This Bulletin, **38**, 410 (1965).

of acetaldehyde alone[9] and in the presence of various catalysts[3,5,8] have shown that the pyrolysis always proceeds according to the stoichiometric equation:

$$CH_3CHO \rightarrow CH_4 + CO\cdot$$

The same stoichiometry, therefore, seems to hold in the present case also.

The amounts of carbon monoxide and methane thus determined are plotted in Fig. 1, together

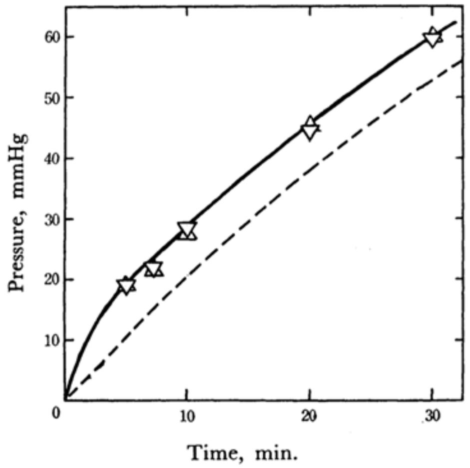

Fig. 1. Products of the pyrolysis of acetaldehyde in the presence of hydrogen bromide.
355.4°C; CH_3CHO : 100 mmHg;
HBr : 50 mmHg.
▽, CH_4; △, CO. Dotted line represents the total pressure rise.

with the total pressure rise, which is represented by a dotted line. The figure shows that the carbon monoxide and methane are formed considerably faster at the initial stage of reaction than in the following period. Such a high initial rate and the enhanced activity of a fresh wall have also been observed in the hydrogen chloride catalysis and attributed to the chain initiation on the wall, which is poisoned by the progress of pyrolysis or inactivated by seasoning. The high initial rate of formation of carbon monoxide and of methane in the present case can probably be attributed to the same causes.

On the other hand, the total pressure-time curve in Fig. 1 shows no initial rapid rise[10] and runs separately from that for the formation of the products. These two separate curves in the figure should, however, coincide with each other if the stoichiometry of decomposition mentioned above is valid and if no other reactions are present. Such a coincidence has really been observed in the hydrogen chloride catalysis. In view of the fact that the temperature range for the pyrolysis is quite low in the present case, a probable reason for the separation of the two curves may be that the polymerization of acetaldehyde to paraldehyde, which takes place as a side reaction but which reaches equilibrium in the initial period,[11] nearly cancels the initial rapid rise in the pressure due to the high initial rate of pyrolysis mentioned above.

Apart from the initial stage of reaction, the two curves in Fig. 1 run parallel to each other. The rate of pyrolysis may, therefore, be determined by the slope of the pressure-time curve except in the very beginning of the reaction. All the rates described below as initial rates are those determined in this way.

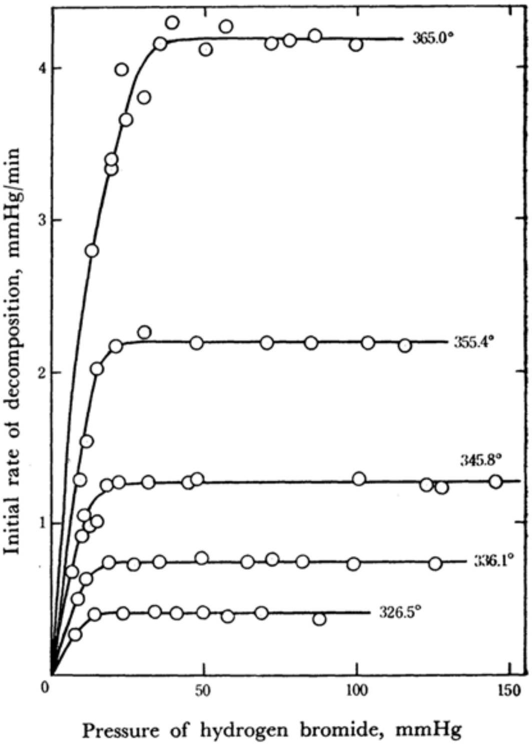

Fig. 2. Dependence of the rate of decomposition on hydrogen bromide pressure. CH_3CHO : 100 mmHg.

Figure 2 shows the dependence of the decomposition rate on the hydrogen bromide pressure in the decomposition of acetaldehyde (100 mmHg)

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[9] C. N. Hinshelwood *et al.*, *Proc. Roy. Soc.*, **A111**, 380 (1929); **A141**, 41(1933); **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).

[10] The initial pressure rise was even slower than in the following period in some runs.

[11] Acetaldehyde does not polymerize to metaldehyde or to higher polymer at room temperature nor at higher temperature, but to paraldehyde at room temperature, and equilibrium yield of paraldehyde decreases with temperature. Hydrogen bromide is an effective catalyst for polymerization of acetaldehyde and depolymerization of paraldehyde.

in the range of temperature from 326.5 to 365.0°C. At all the temperatures cited in the figure, the rate increases with the hydrogen bromide pressure until it attains a constant value. Figure 3 shows the relationship between the pressure of acetaldehyde and the rate of decomposition in the presence of 50 mmHg of hydrogen bromide at 345.8 and 355.4°C.

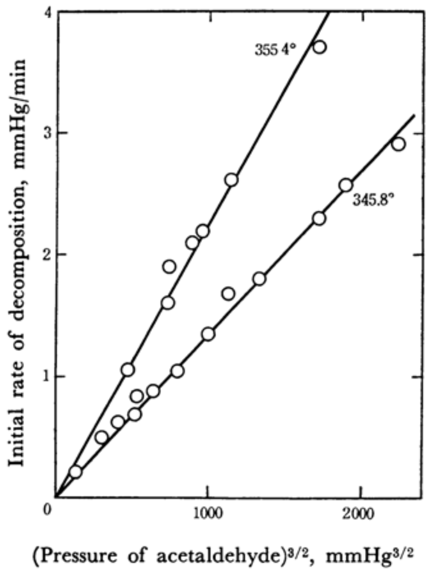

Fig. 3. Dependence of the rate of decomposition on acetaldehyde pressure. HBr : 50 mmHg.

Figures 2 and 3 indicate that the reaction is of the 3/2 order in the aldehyde and is independent of the pressure of hydrogen bromide when the ratio of hydrogen bromide pressure to that of the aldehyde is sufficiently high. The order of 3/2 in the substrate and of zero in the catalyst have been observed in a number of similar pyrolyses, *e. g.*, in the hydrogen chloride-catalyzed decomposition of acetaldehyde[8] and of dimethyl ether[7], and in the hydrogen sulfide-catalyzed decomposition of dimethyl ether.[1]

The catalytic effect of hydrogen bromide on the pyrolysis of acetaldehyde is unexpectedly large. The catalyzed decomposition is estimated[12] to be about four hundred times as fast as the uncatalyzed one, while the rate ratio has been found to be only about ten in the three cases cited above.

The fact that the rate law of the same form applies to the catalytic action of hydrogen bromide as well as to that of hydrogen chloride suggests that the mechanisms for the two reactions are similar to each other:

$$CH_3CHO + M \rightarrow CH_3 + CHO + M \qquad (1)$$

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

$$H + HBr \rightarrow H_2 + Br \qquad (3)$$

$$CH_3 + HBr \rightarrow CH_4 + Br \qquad (4)$$

$$Br + CH_3CHO \rightarrow HBr + CH_3CO \qquad (5)$$

$$CH_3CO \rightarrow CH_3 + CO \qquad (6)$$

$$Br + Br + M \rightarrow Br_2 + M \qquad (7)$$

Applying a steady-state treatment to this scheme, one obtains:

$$-d[CH_3CHO]/dt = k_1{}^{1/2}k_5k_7{}^{-1/2}[CH_3CHO]^{3/2} \qquad (I)$$

which is in agreement with the experimental results.

The chain-terminating process, which is assumed to be reaction (7) in the scheme given above, may be discussed in reference to the following equation, which is required by the steady-state condition:

$$k_4[CH_3][HBr] = k_5[Br][CH_3CHO]$$

or:

$$\frac{[Br]}{[CH_3]} = \frac{k_4[HBr]}{k_5[CH_3CHO]}$$

When the ratio of the amount of hydrogen bromide against that of the aldehyde becomes sufficiently small, the steady-state concentration of methyl radicals will be greater than that of bromine atoms and it will no more be justifiable to neglect the contribution of methyl radicals ot the chain termination. In this case, *i. e.*, when the concentration of bromine atoms is lower than that in the presence of a sufficient amount of hydrogen bromide, the rate will be reduced from the value that would be expected from Eq. (1), though the reaction:

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \qquad (8)$$

contributes to the overall rate of decomposition. Such a prediction is in agreement with Fig. 2, where the rate falls off from a constant value as the concentration of hydrogen bromide is decreased.

It may be seen in Fig. 2 that the higher the temperature, the greater the $[HBr]/[CH_3CHO]$ ratio at which Eq. (I) begins to be applicable. This fact may be explained by the inverse temperature dependence of the k_4/k_5 ratio, that is, by the $E_4 < E_5$ relationship.[13,14]

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12) The rate of decomposition of the aldehyde alone is too low to measure in the present temperature range, but it may be estimated by the Arrhenius expression of the 3/2 order rate constant, $k=10^{12.0}\exp(-43800/\boldsymbol{RT})$ mol$^{-1/2}$ cc$^{1/2}$ sec^{-1}, obtained in the temperature range 400 to 440°C in Ref. 5.

13) $E_4=1.4$ kcal mol^{-1}, G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **1961**, 3037.

14) k_5 is estimated as $10^{13.6}\exp(-8000/\boldsymbol{RT})$ mol^{-1}·cc sec^{-1}. *Cf.*, J. Stauff and H. J. Schumacher, *Z. phisik. Chem.*, **B48**, 145 (1941); G. C. Fettis, J. H. Knox and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **1960,** 4177.

TABLE 1. VALUES OF $k_1{}^{1/2}k_5k_7{}^{-1/2}$

Temp. °C	$k_1{}^{1/2}k_5k_7{}^{-1/2}$ (mol$^{-1/2}$ cc$^{1/2}$ sec^{-1})	
	from Fig. 2	from Fig. 3
326.5	0.042	
336.1	0.077	
345.8	0.132	0.140
355.4	0.228	0.229
326.0	0.45	

As was discussed in detail in a previous paper on hydrogen chloride catalysis (*cf.* Table 1 in Ref. 8), only the chain termination by a combination of bromine atoms yields a rate equation which is of the 3/2 order in the reactant but which is independent of the catalyst concentration. The termination by the third-order combination of bromine atoms, combined with the 3/2 order kinetics, leads to a second-order initiation reaction, *i. e.*, reaction (1). The mechanism assuming a chain initiation by the decomposition of hydrogen bromide does not yield the rate law obtained experimentally.[15]

Table 1 shows the values of $k_1{}^{1/2}k_5k_7{}^{-1/2}$ in Eq. (I) as determined from the constant values of the rates in Fig. 2 and from the slopes of the straight lines in Fig. 3. The values obtained by the two different methods agree within the range of experimental error. The Arrhenius expression obtained from Table 1 is:

$$k_1{}^{1/2}k_5k_7{}^{-1/2} = 10^{14.65}\exp(-44000/\boldsymbol{R}T)$$
$$\mathrm{mol}^{-1/2}\,\mathrm{cc}^{1/2}\,\mathrm{sec}^{-1}$$

By combining $k_1 = 10^{20}\exp(-73800/\boldsymbol{R}T)$ mol^{-1}·cc sec^{-1}, as reported by Trenwith,[16] with $k_5 = 10^{13.6}\exp(-8000/\boldsymbol{R}T)$ mol^{-1} cc sec^{-1} [14] and $k_7 = 10^{17.4}$ mol^{-2} cc^2 sec^{-1},[17] one obtains:

$$k_1{}^{1/2}k_5k_7{}^{-1/2} = 10^{14.9}\exp(-45000/\boldsymbol{R}T)$$
$$\mathrm{mol}^{-1/2}\,\mathrm{cc}^{1/2}\,\mathrm{sec}^{-1}$$

which is in good agreement with the experimental expression given above.

For the hydrogen chloride catalysis, the overall rate constant has been found to be:

$$k_1{}^{1/2}k_{5'}k_{7'}{}^{-1/2} = 10^{13.0}\exp(-44000/\boldsymbol{R}T)$$
$$\mathrm{mol}^{-1/2}\,\mathrm{cc}^{1/2}\,\mathrm{sec}^{-1}$$

where $k_{5'}$, and $k_{7'}$, refer, respectively, to the following reactions:

$$\mathrm{Cl + CH_3CHO \rightarrow HCl + CH_3CO} \qquad (5')$$
$$\mathrm{Cl + Cl + M \rightarrow Cl_2 + M} \qquad (7')$$

By combining this rate constant expression with that obtained in this work, we obtain:

$$k_5k_7{}^{-1/2}/k_{5'}k_{7'}{}^{-1/2} \approx 40$$

The ratio on the left hand side may be close to $k_5/k_{5'}$, since k_7 is approximately equal to $k_{7'}$, as Table 2 indicates. Accordingly the hydrogen atom transfer reaction between bromine atom and acetaldehyde may be considerably faster than that for chlorine atoms, though an opposite relation has been suggested for the halogen-hydrocarbon transfer reaction.[25]

TABLE 2. VALUES OF k_7 AND $k_{7'}$

M	$k_7 \times 10^{-15}$ (mol^{-2} cc^2 sec^{-1})	$k_{7'} \times 10^{-15}$ (mol^{-2} cc^2 sec^{-1})
Br_2	49[18] 260[19] 48[20] <50[21]	
Cl_2		29[22] 20[23]
Ar	2.7[18] 2.0[19]	4[22] 4.25[24]

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15) R. L. Failes and V. R. Stimson, *Australian J. Chem.*, **17**, 851 (1964).

16) A. B. Trenwith, *J. Chem. Soc.*, **1963**, 4426.

17) Estimated from Table 2.

18) M. R. Basila and R. L. Strong, *J. Phys. Chem.*, **67**, 521 (1963).

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24) E. Hutton and M. Wright, *Trans. Faraday Soc.*, **61**, 78 (1965).

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