Thermal Decomposition of Acetaldehyde in the Presence of Hydrogen Chloride

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(Received August 1, 1964)

Hydrogen chloride and bromide have been shown to catalyze decompositions of a number of alcohols and other substances in the gas phase.[1,2] The present paper reports, as an additional example of hydrogen halide catalysis, the hydrogen chloride-catalyzed decomposition of acetaldehyde. The study of this reaction was undertaken in connection with our previous work on the hydrogen sulfide-catalyzed decomposition of acetaldehyde and dimethyl ether.[3-7]

The catalytic action of hydrogen sulfide on the pyrolysis of acetaldehyde has been attributed to the replacement of the chain-propagating reactions 8 and 6:

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

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

in the decomposition of acetaldehyde alone, by the faster-propagating cycle of reactions 9, 10 and 6:

$$CH_3 + H_2S \rightarrow CH_4 + HS \quad (9)$$

$$HS + CH_3CHO \rightarrow H_2S + CH_3CO \quad (10)$$

both reactions, 9 and 10, being faster than reaction 8. The methanethiol-catalyzed pyrolysis of acetaldehyde[8] and the hydrogen sulfide-catalyzed pyrolysis of dimethyl ether[6] have been explained by similar mechanisms.

Hydrogen chloride may be expected to exert a similar catalytic effect in the pyrolysis of acetaldehyde if reactions 4 and 5:

$$CH_3 + HCl \rightarrow CH_4 + Cl \quad (4)$$

$$Cl + CH_3CHO \rightarrow HCl + CH_3CO \quad (5)$$

proceed faster than reaction 8, as was the case with reactions 9 and 10. That such a situation is very probable may be seen by a comparison of the following reported expressions for the rate constants (in mol^{-1} cc. sec^{-1}):

$$\begin{aligned} k_4 &: 10^{11.7}\exp(-2100/RT)^{9)} \\ & 10^{12.2}\exp(-4500/RT)^{10)} \\ k_5 &: 10^{13.3}\exp(-5000/RT)^{11)} \\ k_8 &: 10^{11.3}\exp(-6800/RT)^{12)} \end{aligned}$$

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[1] 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; R. L. Failes and V. R. Stimson, ibid., **1962**, 653; R. A. Ross and V. R. Stimson, ibid., **1962**, 1602; M. Flowers, L. Batt and S. W. Benson, *J. Chem. Phys.*, **37**, 2662 (1962).

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

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

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

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

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

[7] N. Imai and O. Toyama, ibid., **35**, 860 (1962).

[8] N. Imai and O. Toyama, ibid., **33**, 1408, (1960).

[9] R. J. Cvetanivic and E. W. R. Steacie, *Can. J. Chem.*, **31**, 158 (1953).

[10] H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **77**, 2629 (1955).

[11] Estimated from W. A. Alexander and H. J. Schumacher, *Z. physik. Chem.*, **B44**, 57 (1939).

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

Experimental

Materials. — Acetaldehyde was supplied commercially, purified by repeated bulb-to-bulb distillations, and stored as a liquid below 20°C. Hydrogen chloride was prepared by vaporizing it from concentrated hydrochloric acid, drying it by passing it through phosphorus pentoxide and a trap at −78°C, and purifying it by bulb-to-bulb distillations. The auramine used to absorb the hydrogen chloride was a commercial sample.

Apparatus and Procedure.—An ordinary static method was used in this work. The pyrolysis was carried out in a cylindrical glass vessel of about 181 cc. placed in an electric furnace, which was controlled to ±0.5°C by means of a thermocouple-activated controller.

The thermal decomposition was started by introducing the reactant vapor into a reaction vessel already kept at the reaction temperature; the total pressure rise with time due to decomposition was then followed. In some runs, the reaction mixture after the pyrolysis was passed through a trap at the temperature of liquid air and the non-condensable fraction was collected by a Toepler pump. This fraction, consisting exclusively of methane and carbon monoxide, was analyzed by a gas chromatograph on a 2-m Molecular Sieve 5 column at room temperature in use of hydrogen as the carrier. In order to determine the amount of hydrogen chloride remaining unconsumed in the pyrolysis, the condensate in the trap was warmed up to about −120°C and the vaporized fraction was collected by a Toepler pump and measured. This fraction was identified as hydrogen chloride, having been almost completely absorbed by the auramine.

Results

In Fig. 1 are plotted against time the amounts of methane and carbon monoxide formed by the pyrolysis of a mixture of acetaldehyde and hydrogen chloride, and the amount of hydrogen chloride remaining in the mixture during the pyrolysis. The curve in the figure shows the total pressure rise. It may be seen that the total pressure increase is equal to the pressure of the methane formed as well as to that of carbon monoxide, and also that hydrogen chloride is not consumed during the pyrolysis, its amount remaining constant within 1%. No appreciable amount of hydrogen was detected by gas chromatographic analysis using a nitrogen carrier. These facts indicate that the stoichiometry of the pyrolysis of acetaldehyde,[13] i. e.,

$$CH_3CHO \rightarrow CH_4 + CO$$

is not affected by the presence of hydrogen chloride. Similar results had been obtained in previous studies with hydrogen sulfide[4] and methanethiol[8].

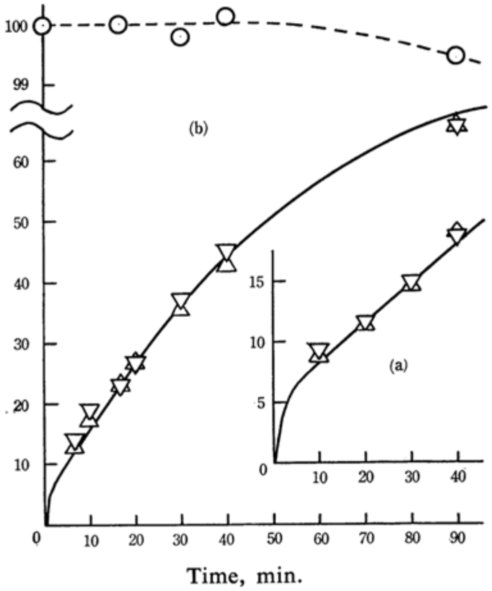

Fig. 1. Pyrolysis of acetaldehyde in the presence of hydrogen chloride.
(a) 401°C; CH_3CHO: 100 mmHg; HCl: 50 mmHg
(b) 423°C; CH_3CHO: 100 mmHg; HCl: 100 mmHg
▽, CH_4; △, CO; ○, HCl. Solid line represents total pressure rise.

Figure 1 also shows that, at the beginning of the pyrolysis, the rate of decomposition is abnormally higher than in the following period. This initial period with a high rate is fairly long with a fresh vessel, but it is shortened with a "seasoned" one. The phenomenon may be attributed to a chain initiation on the wall, which is poisoned by the progress of pyrolysis or inactivated by seasoning.

Figure 2 shows the dependence of the decomposition rate on hydrogen chloride pressure in the decomposition of 100 mmHg acetaldehyde in the range of temperature from 401 to 433°C. The rate increases with the hydrogen chloride pressure until it attains a constant value, which is about seven times the rate in the absence of hydrogen chloride. This ratio of about seven compares with that of about ten previously found for dimethyl ether decomposition catalyzed by hydrogen chloride[2] and by hydrogen sulfide.[6]

Figure 3 shows the relations between the pressure of acetaldehyde and the rate of decomposition in the presence of 100 mmHg of hydrogen chloride at 401 and 423°C.

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[13] C. N. Hinshelwood and W. K. Hutchson, *Proc. Roy. Soc.*, **A111**, 380 (1929); 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).

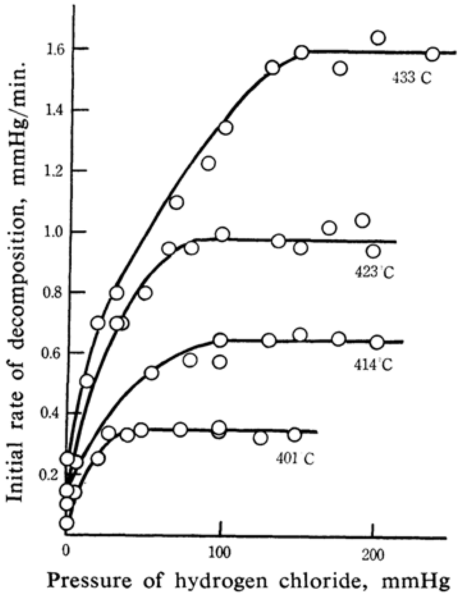

Fig. 2. Dependence of the rate of decomposition on hydrogen chloride pressure. CH_3CHO : 100 mmHg

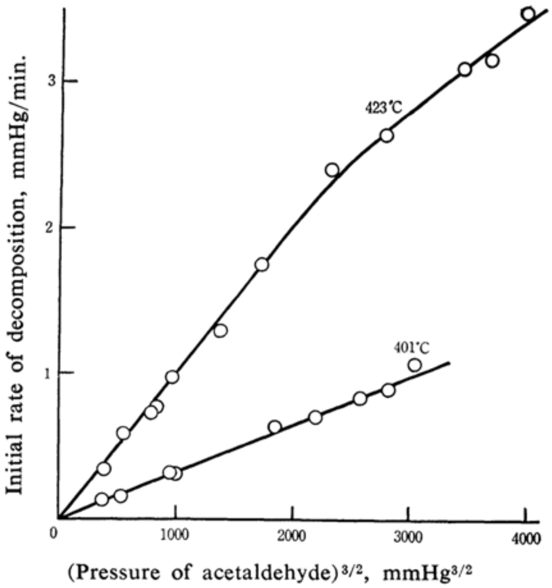

Fig. 3. Dependence of the rate of decomposition on acetaldehyde pressure. HCl : 100 mmHg

Figures 2 and 3 indicate that the reaction is of the 3/2 order in the aldehyde and is independent of hydrogen chloride when the ratio of the hydrogen chloride pressure to that of the aldehyde is sufficiently high.

Discussion

A probable reaction scheme that explains the 3/2 order kinetics given above may be presented as follows:

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

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

$$H + HCl \rightarrow H_2 + Cl \quad (3)$$

$$CH_3 + HCl \rightarrow CH_4 + Cl \quad (4)$$

$$Cl + CH_3CHO \rightarrow HCl + CH_3CO \quad (5)$$

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

$$Cl + Cl + M \rightarrow Cl_2 + M \quad (7)$$

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

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

which is in agreement with the experimental results.

Since the chain-propagating steps are reactions 4, 5 and 6, the steady-state condition requires that:

$$k_4[CH_3][HCl] = k_5[Cl][CH_3CHO] \quad (II)$$

or

$$\frac{[Cl]}{[CH_3]} = \frac{k_4[HCl]}{k_5[CH_3CHO]} \quad (III)$$

If the right hand side of Eq. III is very large, the concentration of chlorine atoms is much higher than that of methyl radicals and the chain terminates solely by reaction 7, as is assumed in the above scheme. On the contrary, when the right hand side of Eq. III is small, or when the concentration of methyl radicals is large, the combination of methyl radicals or that of methyl radicals and chlorine atoms will be important in chain termination. The rate then should be smaller than that which can be expected from Eq. I. Thus it is explained why the plots deviate from the straight lines in Figs. 2 and 3 when the relative amount of hydrogen chloride is low. The difference in activation energies $E_4 - E_5$ is negative, as may be seen in the expressions of rate constants cited above. This explains the fact that the higher the temperature, the greater is the $[HCl]/[CH_3CHO]$ ratio at which Eq. I begins to be applicable, as may be seen in Figs. 2 and 3.

The chain-initiation step given above (reaction 1) is represented as a second-order process. The order of such a chain-initiation step, together with those for the chain termination and decomposition of intermediate radicals, has been discussed by a number of workers. The overall order of the present catalyzed decomposition depends upon the orders of these elementary steps; various possibilities,

TABLE I. RATE EXPRESSIONS FOR VARIOUS MECHANISMS

Order	Initiation	1			
	Termination	2		3	
	Decomposition of μ	1	2	1	2
Termination	$\mu\beta$	$[A]^{1/2}[B]^{1/2}$	$[A]^{1/2}[B]^{1/2}[M]^{1/2}$	$[A]^{1/2}[B]^{1/2}[M]^{-1/2}$	$[A]^{1/2}[B]^{1/2}$
	$\mu\beta'$	$[A]$	$[A][M]^{1/2}$	$[A][M]^{-1/2}$	$[A]$
	$\beta\beta$	$[A]^{1/2}[B]$		$[A]^{1/2}[B][M]^{-1/2}$	
	$\beta\beta'$	$[A][B]^{1/2}$		$[A][B]^{1/2}[M]^{-1/2}$	
	$\beta'\beta'$	$[A]^{3/2}$		$[A]^{3/2}[M]^{-1/2}$	
Order	Initiation	2			
	Termination	2		3	
	Decomposition of μ	1	2	1	2
Termination	$\mu\beta$	$[A]^{1/2}[B]^{1/2}[M]^{1/2}$	$[A]^{1/2}[B]^{1/2}[M]$	$[A]^{1/2}[B]^{1/2}$	$[A]^{1/2}[B]^{1/2}[M]^{1/2}$
	$\mu\beta'$	$[A][M]^{1/2}$	$[A][M]$	$[A]$	$[A][M]^{1/2}$
	$\beta\beta$	$[A]^{1/2}[B][M]^{1/2}$		$[A]^{1/2}[B]$	
	$\beta\beta'$	$[A][B]^{1/2}[M]^{1/2}$		$[A][B]^{1/2}$	
	$\beta'\beta'$	$[A]^{3/2}[M]^{1/2}$		$[A]^{3/2}$	

as worked out by Goldfinger, Letort and Niclause,[14] are listed in Table I. Here, following the original terminology of Goldfinger et al., μ denotes a chain-propagating radical that decomposes (CH_3CO in the present case) ; β, a chain-propagating atom or radical in the uncatalyzed decomposition that does not decompose further (CH_3) ; and β', such an atom or radical formed by hydrogen abstraction from a catalyst molecule by a β-radical (Cl). A refers to the reactant to be decomposed (CH_3CHO) ; B to the catalyst (HCl), and M to a third body (CH_3CHO and HCl). Since in the case of $\mu\mu$ termination the rate is not enhanced by the presence of a catalyst except by its effect as a third body, this case is omitted in Table I.

The rate expression that best conforms to the experimental results is obviously $[A]^{3/2}$, derived from the $\beta'\beta'$ termination, but $[A][M]^{1/2}$, resulting from the $\mu\beta'$ termination, might as well explain the result when $[M]\approx[A]$. However, the results obtained show that the $[A]^{3/2}$ kinetics does not hold when the ratio $[B]/[A]$ is low, and, moreover, that the μ-radical, i. e., the acetyl radical, is so unstable[15] above 400°C that its participation in the termination may be ruled out.

Table I shows that the overall rate proportional to $[A]^{3/2}$ is given by either of two different combinations of initiation and termination processes. However, the one involving a second-order termination is improbable, since the β'-radicals are here chlorine atoms. The reaction sequence 1 to 7 thus seems to be the most probable one to explain the 3/2 order kinetics.

The second-order initiation step as given in reaction 1 is further supported by the work of Trenwith,[16] who, in the pyrolysis of acetaldehyde alone, has found a rate of the formation of hydrogen proportional to the square of acetaldehyde pressure.[17]

Table II 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 II is:

TABLE II. 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
401	0.0376	0.0363
414	0.071	
423	0.099	0.101
433	0.172	

$$k_1^{1/2}k_5k_7^{-1/2}=10^{13.0}\exp(-44000/\boldsymbol{RT})$$
$$mol^{-1/2}\ cc^{1/2}\ sec^{-1}$$

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[14] P. Goldfinger, M. Letort and M. Niclause, Volume Commémoratif Victor Henri : "Contribution à l'Etude de la Structure Moléculaire," Liège : Desoer (1948), p. 283.

[15] C. A. McDowell and J. H. Thomas, *J. Chem. Soc.*, **1949**, 2217.

[16] A. B. Trenwith, ibid., **1963**, 4426.

[17] The hydrogen sulfide-catalyzed pyrolysis of acetaldehyde was previously explained with a reaction scheme involving a first order initiation step, $CH_3CHO \rightarrow CH_3 + CHO$. In view of the present work and that of Trenwith, it seems preferable to replace this first order initiation by the second order process given in reaction 1. This replacement causes no changes in the other arguments, if the chain termination $CH_3+CH_3 \rightarrow C_2H_6$, at the same time, is replaced by a third order process.

Combining $k_1=10^{20}\exp(-73800/\boldsymbol{R}T)$ mol^{-1} cc. sec^{-1} as reported by Trenwith[16] with $k_5=10^{13.3}\exp(-5000/\boldsymbol{R}T)$ mol^{-1} cc. sec^{-1} [11] and $k_7=10^{17.4}$ mol^{-2} cc^2 sec^{-1},[18] one obtains:

$$k_1{}^{1/2}k_5k_7{}^{-1/2}=10^{14.4}\exp(-41900/\boldsymbol{R}T)$$
$$\text{mol}^{-1/2}\,\text{cc}^{1/2}\,\text{sec}^{-1}$$

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

Summary

The thermal decomposition of acetaldehyde in the presence of hydrogen chloride has been investigated over the temperature range from 401 to 433°C. Hydrogen chloride, though it is not consumed, enhances the rate of decomposition to carbon monoxide and methane, thus acting as a catalyst. The rate law which holds when the [HCl]/[CH_3CHO] ratio is sufficiently high is the same as that which holds in the absence of hydrogen chloride, being represented as $k[CH_3CHO]^{3/2}$ independent of the hydrogen chloride pressure. The most probable reaction scheme for explaining this rate law is $CH_3CHO+M \rightarrow CH_3+CHO+M$ (1), $CHO \rightarrow CO+H$ (2), $H+HCl \rightarrow H_2+Cl$ (3), $CH_3+HCl \rightarrow CH_4+Cl$ (4), $Cl+CH_3CHO \rightarrow HCl+CH_3CO$ (5), $CH_3CO \rightarrow CH_3+CO$ (6), and $Cl+Cl+M \rightarrow Cl_2+M$ (7), yielding the overall rate $k_1{}^{1/2}k_5k_7{}^{-1/2}[CH_3CHO]^{3/2}$. The Arrhenius expression obtained from the experimental results, $k_1{}^{1/2}k_5k_7{}^{-1/2}=10^{13.0}\exp(-44000/\boldsymbol{R}T)$ mol$^{-1/2}$ cc$^{1/2}$ sec^{-1}, is in harmony with those for k_1, k_5, and k_7 available in the literature.

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[18] Estimated from $K_7=10^{16.4}$ mol^{-2} cc^2 sec^{-1} for the reaction $Cl+Cl+Cl_2 \rightarrow Cl_2+Cl_2$ (L. W. Bader and E. A. Ogryzlo, *Nature*, **201**, 491 (1964)).