sium chlorate on silver acetate in 10% dioxane solutions, and of potassium chlorate on silver acetate in 20% dioxane, have also been investigated. The corresponding Debye–Hückel a parameters have been calculated.

The Born equation even when corrected for interionic effects fails to account for the course of the solubilities as the percentage of dioxane increases, predicting in each case lower solubilities than those observed. The differences increase in media of higher dioxane content, pre-

diction and observation disagreeing even as to order of magnitude in solvents containing more than 50% dioxane by weight. The disagreement is not diminished appreciably by substitution of mole fractions for volume concentrations, showing that this question is of minor importance as a factor in the application of the Born equation.

Modifications to be superimposed on the Born equation to bring it into line with the observations are discussed.

Kinetic Studies on Iodine Derivatives. I. The Thermal Decomposition of Acetyl Iodide[1]

BY J. LESLIE JONES

The thermal[2] and photochemical[3] decomposition of acetaldehyde into methane and carbon monoxide has been investigated by numerous authors. Since the deduction of a possible free radical mechanism for the thermal and photochemical decomposition of acetaldehyde by Rice and Herzfeld,[4] a great deal of controversy has arisen concerning its validity. The opposing theory[2c] assumes that the activation process, thermal or photochemical, is followed by a rearrangement of the acetaldehyde directly into the final products, methane and carbon monoxide.

On the basis of previous investigations[5] it seems probable that the thermal decomposition of alkyl iodides occurs by the breaking of the carbon–iodine bond (temperature range of 250–350°) as the primary process. This reaction is followed by the secondary reactions of the free radicals. By the substitution of an iodine atom for the hydrogen atom of the aldehyde group in acetaldehyde

it is possible to study the thermal decomposition of the product, acetyl iodide, in the same temperature range as the alkyl iodides. Such a study casts light upon the mechanism of the thermal decomposition of acetaldehyde, supporting the free radical mechanism. In addition information is gained concerning the secondary reactions of the free radicals involved.

Experimental Section

The rate of decomposition of the acetyl iodide was followed by the pressure change method, employing essentially the apparatus of Jones and Ogg.[5] The quartz spiral manometer prevented the iodine evolved in the reaction from reacting with the mercury in the absolute manometer. A hollow barrel stopcock was employed to close the reaction vessel, employing a plasticizer as lubricant. The compound, di-o-xenzyl-monophenyl phosphate,[6] has a vapor pressure of 5 mm. at 285° and a viscosity of 170 centipoises at 60°. The liquid was warmed in a high vacuum system for several hours in order to remove all solvents. All observations indicated that it was unaffected by the iodine generated in the system, as its structure suggested. It was necessary to heat the stopcock closing the reaction vessel to about 110° in order to prevent condensation of iodine.

The acetyl iodide was prepared by the treatment of Eastman Kodak Co. acetyl chloride with an excess of dry hydrogen iodide gas at 0°. The brown crude product (90% yield) was protected from the air and vacuum distilled in an all-glass fractionating system two times, large amounts of the first and third fractions being discarded. A third fractionation was carried out in high vacuum, the product being distilled directly into the reservoir of the system employed for the study of the reaction rates. In

(1) A preliminary report of this paper was presented at the Symposium on the Kinetics of Homogeneous Gas Reactions, University of Wisconsin, June 20–22, 1939.

(2) (a) Fletcher and Rollefson, THIS JOURNAL, **58**, 2135 (1936); (b) Letort, J. chim. phys., **34**, 265 (1937); (c) Staveley and Hinshelwood, J. Chem. Soc., 1568 (1937); (d) Brenschede and Schumacher, Ber., **70B**, 452 (1937); (e) Rollefson and Faull, THIS JOURNAL, **59**, 625 (1937).

(3) (a) See P. A. Leighton, J. Phys. Chem., **42**, 749 (1937), for a complete review to that date; (b) Blacet and Volman, THIS JOURNAL, **60**, 1234 (1938); (c) Gorin, J. Chem. Phys., **7**, 256 (1939); (d) Rollefson and Grahame, paper presented at the "Symposium on the Kinetics of Homogeneous Gas Reactions," University of Wisconsin, June 20–22, 1939.

(4) Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

(5) See Jones, ibid., **60**, 1877 (1938), for complete references to earlier research.

(6) Furnished through the courtesy of the Dow Chemical Company, Midland, Mich.

general about 30–40 g. of acetyl iodide was utilized as a middle fraction from 150–200 g. of crude acetyl iodide. Three different preparations were employed in the experiments and there was no difference in the behavior of each. The product colored brown in the presence of air. Light was excluded from the reservoir. The boiling point of the product was 60° at 145 mm.

Analysis of the gaseous products was done with a modified Bone–Wheeler apparatus handling a maximum of 3 ml. Bromine water was used to measure unsaturates, ammoniacal cuprous chloride for carbon monoxide, cupric oxide combustion for hydrogen and an explosion combustion for saturated hydrocarbons. A 5% sulfuric acid solution was kept in the measuring buret to maintain a constant vapor pressure. The apparatus was not satisfactory, but it was estimated that concentrations could be determined within 5%. Due to the simple products of the reactions, the apparatus was sufficiently accurate to indicate the main reaction involved.

Homogeneity of the Thermal Decomposition.—In order to determine the effect of packing upon the rate of thermal decomposition, a series of experiments were carried out in a 250-ml. spherical Pyrex flask packed with glass tubing to yield a surface–volume ratio of 5.1 cm.$^{-1}$. Experiments were also performed in the same bulb without glass packing, at a surface–volume ratio of 0.72 cm.$^{-1}$. A third series of experiments were carried out in a 1000-ml. flask of surface–volume ratio 0.44 cm.$^{-1}$. The experimental determination of the rate constant directly indicated that the rate of the decomposition was inhibited by packing the reaction vessel.

Further experiments were performed using helium and nitrogen as inert gases. The tank gases were purified by passage over copper screen heated to red heat and then through a liquid-air trap to remove condensable vapors. The gases were purified directly as needed and admitted to the reaction vessel.

Experimental Results

The Stoichiometric Reaction.—The average ratio of the final pressure, P_f, in the reaction to the extrapolated initial gas pressure of pure acetyl iodide, P_i, was 1.45. This value of P_f/P_i was apparently independent of the initial pressure and temperature of the reaction. Such a value indicated that three molecules of gaseous products were formed from two molecules of acetyl iodide. Free iodine was formed quantitatively from the acetyl iodide, as determined by titration of the iodine condensed in a liquid-air trap after an experiment. The residual gas on analysis was shown to consist of equal volumes of carbon monoxide and methane, within an error of ±5%. Observation of the reaction vessel after two or three experiments indicated that a solid product was being deposited on the surface of the vessel. After a half dozen experiments, the surface of the vessel was dark brown in color. The solid prod-

uct was a closely adherent, non-crystalline substance. All of this evidence indicated that the stoichiometric reaction was probably

$$2CH_3COI = CH_4 + CO + I_2 + CH_2CO \text{ (solid polymer)}$$
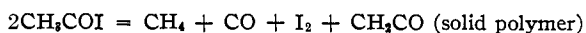
The solid product was considered to be polymerized ketene. Because of its adherence to the glass surface, an amount sufficient for analysis could not be obtained. However, a material balance of the reaction products gave its empirical formula. The research of Rice and Greenburg[7a] indicated that the polymerization of ketene was a heterogeneous reaction at room temperature in a Pyrex vessel. Williamson[7b] found that ketene polymerized rapidly at 400–500°. An initial rapid lowering of the gas pressure was followed by a pressure increase. This phenomenon depended upon the initial gas pressure and thus indicated that the polymerization was not a unimolecular reaction.

Kinetics of the Reaction.—The data measuring the rate of decomposition of acetyl iodide fitted most closely the unimolecular expression

$$-d(CH_3COI)/dt = k(CH_3COI)$$

The pressure of acetyl iodide at any time t was given by

$$(CH_3COI) = (1.45P_0 - P_t)/0.45$$

The value of k, the rate constant, was obtained for each experiment by plotting the values of log (CH_3COI) against time. The graphs was straight lines for the experiments performed in unpacked flasks. The linearity of the graphs was maintained up to 65–76% decomposition at the lower temperatures (292–314°), while at 338° the rate constant was maintained up to 90–95% decomposition. The reaction rate constant was definitely a function of the initial pressure of acetyl iodide and, as Table I indicates, increased with the initial pressure. Other data indicated that the reaction was not a simple unimolecular reaction and therefore it was useless to apply the theory of Kassel–Rice–Ramsperger to the falling off of the value of k. If one considered the disappearance of acetyl iodide during the course of our experiment to occur to the extent of 80% before the value of k began to decrease, then the pressure of acetyl iodide fell to about 5–7 mm. before this effect occurred at 338°. Similar limiting pressures were obtained at lower temperatures. In view of the fact that the rate con-

(7) (a) Rice and Greenburg, THIS JOURNAL, **56**, 2132 (1934); (b) Williamson, *ibid.*, **56**, 2216 (1934).

stant for a particular experiment was maintained over a very large change in the concentration of acetyl iodide and yet is a function of the initial acetyl iodide pressure, one must conclude that the products of the decomposition are very efficient in maintaining the proposed chain mechanism over a wide pressure range.

TABLE I

Temp., °K.	P_0,[a] mm.	$k \times 10^3$, sec.[-1]	Temp., °K.	P_0,[a] mm.	$k \times 10^3$ sec.[-1]
565.1	80.8	0.217	599.6	105	2.19
565.3	217	.271	599.3	230	3.24
565.9	275	.341	599.3	280	4.11
566.1	362	.438	597.7	315	3.10
570.3	113	.479	611.5	58.4	2.91
587.7	75	.914	611.3	94.0	3.10
588.7	102	.940	610.6	108	3.96
588.1	186	1.12	611.5	108	3.74
587.9	263	1.61	611.4	111	3.61
588.7	277	1.64	611.2	125	3.89
588.1	282	1.48	611.1	156	4.62
588.3	297	1.66	608.6	167	5.17
602.3	78.0	1.76	611.5	300	6.61
599.5	95.5	1.69	611.3	385	7.78

[a] Initial acetyl iodide pressure.

The study of the effect of packing the vessel cast additional light upon the mechanism of the reaction. The 250-ml. reaction vessel was packed with Pyrex tubing, increasing its surface–volume ratio from 0.72 to 5.1 cm.[-1]. Table II indicates
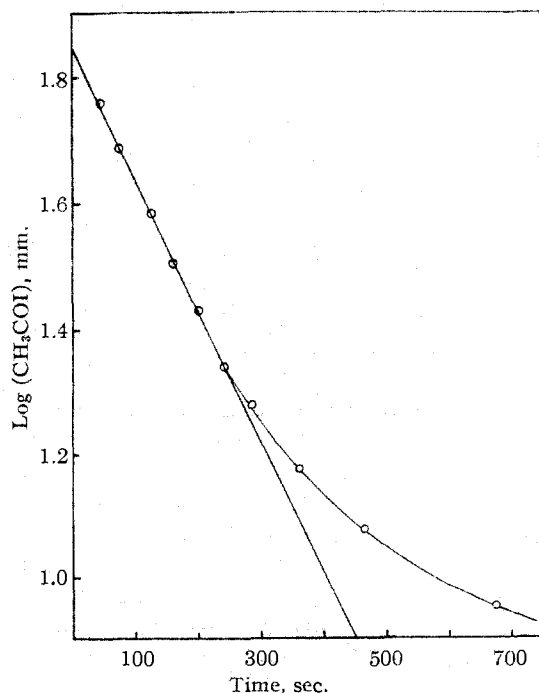

Fig. 1.—Expt. 25, P_1 = 164 mm.

the effect of packing on the rate constants. The values of k are approximately the same in packed and unpacked flasks over the greater portion of the decomposition. At 612°K. in the packed flask, the value of the rate constant began to fall off after about 60% decomposition and in the unpacked flask after about 90% decomposition. This falling off in the value of k is shown graphically in Fig. 1 for experiment number 25. It is evident that the effect of packing is of secondary importance in this reaction for at least 60% of the iodide is decomposed before departure from a first order reaction is noted. Such a departure indicates the existence of secondary chain reactions repressed by the walls of the vessel.

TABLE II

No.	Temp., °K.	P_0, mm.	$k \times 10^3$, sec.[-1]	%[c] decomp.
		PACKED FLASK		
25	612.5	164	4.93	60
26	612.0	208	7.28	70
24	612.5	215	5.52	55
23	611.6	309	6.61	60
27	586.5	145	1.26	75
28	586.3	155	1.22	90
		UNPACKED FLASK		
16[a]	611.2	125	3.89	95
15[a]	611.1	156	4.62	95
22[a]	608.6	167	5.17	85
19[a]	611.5	300	6.61	95
20[a]	611.3	385	7.78	90
33[b]	588.1	186	1.12	80
29[b]	587.9	263	1.61	65
32[b]	588.7	277	1.64	80
30[b]	588.1	282	1.48	80
31[b]	588.3	297	1.66	70

[a] Surface–volume ratio is 0.44 cm.[-1] (1000 ml.). [b] Surface–volume ratio is 0.72 cm.[-1] (250 ml.). [c] % decomposition occurring as unimolecular reaction.

Additional experiments were performed to determine the effect of the inert gases nitrogen and helium on the rate of decomposition. It was quite evident, on graphing the rate of change of

TABLE III

No.	P_0, mm.	P_1,[b] mm.	$k \times 10^3$, sec.[-1]	% decomp.
		606.9°K. Nitrogen		
45	134.9	108	3.80	>95
43	194.3	140	5.23	>95
44	196.3	205	5.23	>95
		606.9°K. Helium		
47[a]	128	68	5.18	90
46	145	179	5.52	90

[a] Temperature was 608.1°K. [b] P_1 is pressure of inert gas.

acetyl iodide, that the addition of inert gases had little effect on the values of k. Table III gives the values of k in the presence of the inert gases nitrogen and helium, indicating only a slight increase in the value of k on the introduction of an inert gas.

Discussion

All of the above experimental evidence indicates that a chain mechanism is involved in the thermal decomposition of acetyl iodide. The retardation of the decomposition by packing indicates that a chain propagating step is broken by the walls of the vessel. The effect of the products of the reaction in maintaining the rate of pyrolysis during a particular experiment supports the conclusion that the chains are propagated in the gas phase. Addition of the inert gases to acetyl iodide slightly increases the rate constants for the pyrolysis above the value corresponding to the initial pressure of the iodide alone.

In view of the role played by chain reactions, the value of the activation energy obtained by plotting log k vs. t may be of dubious utility unless the activation energies of the elementary chain reactions are known. However, in this particular study the value of the activation energy E has been obtained by plotting the log k against $1/T$ at several initial pressure values for the acetyl iodide (cf. Fig. 2). No claim can be made for high accuracy of the activation energy values but their concordance is satisfactory. The average value of E is 43,100 cal./mole.

Previous investigations[4] indicate that the strength of the carbon–iodine bond is approximately 43,000 cal./mole. Admittedly this is an approximation, disregarding the zero point energies of the atoms. However, the present experimental value of E is essentially the same. In view of this fact one can conclude that the primary rate determining step in the decomposition of acetyl iodide is the scission of the carbon–iodine bond. This primary process is then followed by a series of secondary processes best given by the mechanism shown.

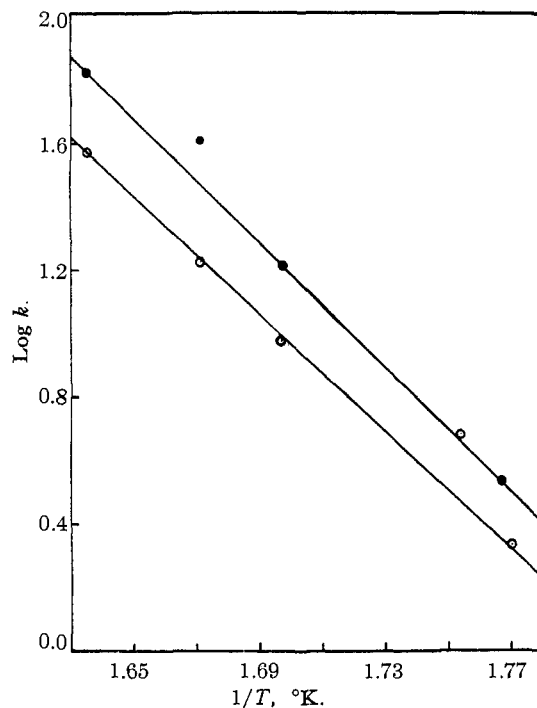|			E, kcal./mole	
CH_3COI	$\longrightarrow$	$CH_3CO + I$	43	k_1
CH_3CO	$\longrightarrow$	$CH_3 + CO$	17	k_2
$CH_3 + I_2$	$\longrightarrow$	$CH_3I + I$	12	k_3
CH_3I	$\longrightarrow$	$CH_3 + I$	43	k_4
$CH_3 + CH_3COI$	$\longrightarrow$	$CH_4 + CH_2COI$	8	k_5
CH_2COI	$\longrightarrow$	$CH_2CO + I$	43	k_6
$CH_2=CO$	$\longrightarrow$	$(CH_2CO)_x(polymer)$		k_7
$2I + M$	$\longrightarrow$	$I_2 + M$	0	k_8

Fig. 2.—●, P_0 approximately 275 mm., $E = 44,400$ cal./mole; ○, P_0 approximately 100 mm., $E = 41,800$ cal./mole.

If one sets up in the usual manner equations expressing the stationary state concentrations of methyl and acetyl radicals and methyl iodide, then the rate of disappearance of acetyl iodide is given by the equation

$$-d(CH_3COI)/dt = 2k_1(CH_3COI)$$

The introduction of another possible elementary reaction

$$CH_3CO + I_2 \longrightarrow CH_3COI + I$$
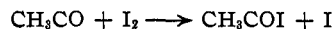
results in a first power term with respect to iodine concentration as a denominator of the above equation. There is no evidence that iodine acts as an inhibitor, except possibly the results obtained in the packed flask and these are of secondary importance.

The evidence is insufficient to justify a statement as to the exact value of the carbon–iodine bond strength, but the value is not markedly affected by the presence of the carbonyl group. The stability of the acetyl radical is in dispute,[8] but the acetyl radical undoubtedly decomposes very rapidly in the temperature region employed in these experiments. Gorin,[8] on the basis of the photolysis of acetone in the presence of iodine,

(8) Gorin, J. Chem. Phys., 7, 256 (1939); Barak and Style, Nature 135, 307 (1935); Spence and Wild, J. Chem. Soc., 352 (1937).

ascribes a minimum activation energy of 17 kcal. to reaction (2).

The formation and dissociation of methyl iodide, as postulated by reactions (3) and (4), has been established by the work of Ogg[9] on the reduction of methyl iodide by hydrogen iodide. Similar reactions of other lower alkyl iodides have been demonstrated by Jones and Ogg.[10] Rollefson and Faull,[11] in order to account for the iodine-catalyzed decomposition of acetaldehyde, proposed a mechanism involving the above equilibrium. In addition, Etzler and Rollefson[12] in a recent note indicated that a liquid product thought to be methyl iodide had been isolated from the products of the photolysis of acetyl iodide at room temperature.

Rice and Herzfeld in their original paper[3] on the free radical mechanism of acetaldehyde pyrolysis postulated the reaction

$$CH_3CHO + CH_3 \longrightarrow CH_3CO + CH_4$$

ascribing to it an activation energy of 15 kcal. Akeroyd and Norrish[13] have deduced a value of 9.8 kcal. for the above apparent reaction by photochemical methods. However, Burton[14] has calculated a value of 115 kcal. for the strength of the carbon–hydrogen bond in the aldehyde group and thus renders improbable this proposed elementary reaction of Rice and Herzfeld. Taylor and Burton[15] have modified the Rice–Herzfeld mechanism, introducing the radical CH_2CHO as an intermediate instead of the radical CH_3CO. The present research is in agreement with their proposal for here the radical CH_2COI is involved. This radical is able to decompose in this tem-

perature range to yield a stable molecule, ketene, and atomic iodine, in contrast to the inability of the CH_2CHO radical to lose a hydrogen atom. There is existing evidence[6,7] on the polymerization of ketene. Free radicals undoubtedly accelerate this process.

Smith and Taylor,[16] utilizing methyl radicals produced by the photolysis of mercury dimethyl, studied the reactions of hydrocarbons with the methyl radicals. They found a value of 8.3 kcal. for the activation energy of the reaction between ethane and methyl radical to form methane. This evidence supports the probability that the methane is formed essentially in this decomposition by the interaction of methyl radicals and acetyl iodide. Hence, it is also the methyl group of the acetaldehyde which is the principal donor of the hydrogen to form methane, not the aldehyde group.

Further research is in progress on the mechanism of the decomposition of other iodine substituted derivatives with particular reference to iodomethyl ether.

Summary

The thermal decomposition of gaseous acetyl iodide was studied in the temperature range 290–340°. The main products of the reaction were identified as carbon monoxide, methane, iodine and polymerized ketene. The decomposition was unimolecular with respect to the acetyl iodide and the rate constants were dependent upon the initial pressure of iodide. The effects of packing the reaction vessel and introducing inert gases were studied. A chain mechanism has been proposed for the decomposition and justified in terms of independent research. The mechanism involves as a primary step the scission of the carbon–iodine bond.

(9) Ogg, THIS JOURNAL, 56, 526 (1934).

(10) Jones and Ogg, ibid., 59, 1931 (1937).

(11) Rollefson and Faull, ibid., 59, 625 (1937).

(12) Etzler and Rollefson, J. Chem. Phys., 6, 653 (1938).

(13) Akeroyd and Norrish, J. Chem. Soc., 890 (1936).

(14) Burton, J. Chem. Phys., 6, 818 (1938).

(15) Taylor and Burton, paper presented at the "Symposium on the Kinetics of Homogeneous Gas Reactions," University of Wisconsin, June 20–22, 1939.

(16) Smith and Taylor, J. Chem. Phys., 7, 390 (1939).