Thermal Decomposition of Trimethylacetyl Chloride

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Abstract: Trimethylacetyl chloride decomposes in the gas phase at 353–426° into isobutylene, carbon monoxide, and hydrogen chloride in a first-order manner with rate given by $k_1 = 2.52 \times 10^{14} \exp(-55150/RT)$ sec^{-1}. The reaction is a molecular one, and two possible transition states are proposed.

The gas-phase decomposition of acetyl bromide in the presence of large amounts of toluene at 600–800° has been studied by Szwarc and Murawski.[1] The reaction produced mainly methyl bromide and carbon monoxide, but a little hydrogen bromide was also found. Significantly no methane or bibenzyl was found, and the authors conclude that even at these high temperatures the decomposition does not produce radicals. Surface-catalyzed decompositions of several acid chlorides at 400° yield carbon monoxide, olefin, and hydrogen chloride, with only small amounts of carbon dioxide and other products presumably of radical origin.[2] Di- and triaryl-substituted acetyl chlorides lose carbon monoxide at below 200° with exceptional ease to produce the appropriate olefin or substituted methyl chloride;[3] however, there is no evidence that these reactions are genuine gas-phase decompositions. Some decomposition yielding carbon monoxide accompanies Friedel–Craft substitutions by tertiary acyl chlorides in nonhydroxylic solvents; cationic mechanisms are involved.[4]

Apparently then, the gas-phase decomposition of a suitable acyl halide into olefin, hydrogen halide, and carbon monoxide is possible, and it seems that the nature of R of RCOX may have a significant effect on the course of the reaction. We have therefore chosen to investigate the pyrolysis of trimethylacetyl chloride.

Experimental Section

Materials and Procedures. Trimethylacetyl chloride, prepared from trimethylacetic acid (Shell Co.) and thionyl chloride and fractionated through 12 in. of Fenske helices, had bp 100.3 ± 0.1° (674.1 mm), n_D^{19} 1.4132 (lit.[4] bp 106.5°, n_D^{20} 1.4126). Infrared analysis showed no free acid and gas chromatographic analysis gave only one peak. The other materials, apparatus, and general procedures have been described previously.[5] The reaction vessel had a volume of 265.5 cc and $S/V = 1$ cm^{-1}; the packed vessel of similar dimensions had $S/V = 7.7$ cm^{-1}. A surface coating formed originally by decomposing allyl bromide and previously used in another investigation[5] was used. No new coating was necessary. When the decomposition was carried out by itself, the rates in successive runs rose slowly to an increase of *ca.* 10%. Addition of cyclohexene to the reaction gave consistent rates identical with the low values and independent of the amount used. This procedure was mostly used. When the reaction vessel was left for long periods, isobutylene or cyclohexene was left in it.

Gas Chromatography. An acetonylacetone on Celite column described previously[6] was used. Cyclopropane and isobutylene were completely separated with retention times 219 and 243 sec, respectively. Seven standard mixtures were made up and the peak heights compared. A composition-peak height graph was constructed and the analyses lay on a smooth curve with deviations of *ca.* 1% absolute. This curve was used in the estimation of the unknown mixtures.

Final Pressures and Kinetics. Pressures increased smoothly to *ca.* $3P_0$. Four values of P_f/P_0 at 409–426° gave 2.96 ± 0.03. The $t_{0.5}/t_{0.25}$ ratios on the basis of 1 vol. → 3 vol. were 2.41 (17 values at 400–426°). Satisfactory first-order plots of pressure increase to *ca.* 70% reaction were obtained at all temperatures (Figure 1). The equilibrium

$$i\text{-C}_4\text{H}_8 + \text{HCl} \rightleftarrows t\text{-C}_4\text{H}_9\text{Cl}$$

is well known,[7,8] and it is clear that very little combination takes place at the temperatures used. The decomposition of *t*-butyl chloride is quite fast at temperatures above 350° where $t_{0.5}$ = *ca.* 1 min. If it were formed in the decomposition of trimethylacetyl chloride under the present conditions, it would not be detected and the pressure increase would be unimpaired.

Products. Trimethylacetyl chloride (17.7 cm, 1.108 mmoles) reacted at 404.8° to $P = 20.7$ cm, 8.7%, during 3.4 min with $10^4k_1 = 4.3$ sec^{-1}. The products were trapped at −180° and transferred into excess sodium hydroxide solution. Total acid (2.082 mmoles) and chloride ion (1.09 mmoles) were found titrimetrically, the amounts calculated from pressure change on the basis of the reaction stated below being 2.119 and 1.11 mmoles, respectively (method A). In method B the products were drawn through a −80° trap into a −180° trap, and the contents of the latter, hydrogen chloride but not trimethylacetyl chloride, was titrated with baryta. The results of these experiments to various extents of reaction are listed in Table I and show that the chloride ion found remains constant at 100%, *i.e.*, that hydrogen chloride is a product of the reaction, and that pressure increase is consistent with trimethylacetyl chloride reacted.

Trimethylacetyl chloride (10.22 cm) reacted in the presence of cyclohexene (*ca.* 25.46 cm) at 399.9° for 25.6 min to $P = 43.38$ cm, 37.7% reaction, with $k_1 = 3.02 \times 10^{-4}$ sec^{-1}. The products were drawn through a −180° trap, those caught were returned to the reaction vessel, and the pressure was measured (39.52 cm). The loss of uncondensed gas, identified by mass spectrographic analysis as only carbon monoxide, was 3.86 cm, 100.2%. Six such experiments listed in Table II show that carbon monoxide production is consistent with pressure increase. The products from a similar reaction at 404.6° were expanded into a 5-l. bulb containing sodium hydroxide and magnesium perchlorate, where unchanged reactant, hydrogen chloride, and water were absorbed. The residual gas caught at −180°, identified as only isobutylene by gas chromatographic comparison with an authentic sample, was estimated by comparison with cyclopropane (*ca.* 9 cm) added as a marker. The results are shown in Table II.

Results and Discussion

At temperatures 353–426° trimethylacetyl chloride decomposes in the gas phase into isobutylene, carbon monoxide, and hydrogen chloride.

$$(\text{CH}_3)_3\text{CCOCl} \longrightarrow (\text{CH}_3)_2\text{C}{=}\text{CH}_2 + \text{CO} + \text{HCl}$$

No trace products were found and satisfactory analyses

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Table I. Extent of Reaction by Pressure Change and by Analysis at 404.8°

P_0,[a] cm	10^4k_1, sec^{-1}	% reaction by pressure	Chloride, mmoles Found	Chloride, mmoles Theory	Acid, mmoles Found	Acid, mmoles Theory	Method
17.7	4.3	8.7	1.09	1.11	2.08	2.12	A
17.1	3.8	12.5			0.134	0.134	B
32.6[b]	4.1	16.8			0.345	0.344	B
10.3	4.2	22.4			1.00	1.15	A
10.8	4.3	22.9	0.64	0.68	1.13	1.20	A
21.2[b]	4.3	35.3			2.03	2.19	A
18.3	4.2	46.9	1.04	1.15	1.63	1.76	A

[a] Initial pressure of trimethylacetyl chloride. [b] With *ca.* 15 cm of cyclohexene.

Table II. Extent of Reaction by Pressure Change and Product Formation

Temp, °C	P_0,[a] cm	10^4k_1, sec^{-1}	% decomposition By pressure	% decomposition By CO loss	% decomposition By isobutylene
399.9	38.6	3.4	13.3	13.2	
	29.8	3.1	22.0	22.3	
	25.6	3.1	23.3	24.0	
	28.5	3.1	28.1	28.6	
	10.2	3.0	37.7	37.8	
	16.1	3.1	55.9	58.0	
404.6	33.0	3.8	13.3		16.2
	24.9	4.2	15.4		17.3
	21.5	4.0	28.5		29.0
	14.8	4.2	48.1		51.6

[a] With 8–28 cm of cyclohexene.

Table III. Rates with Various Initial Pressures of Trimethylacetyl Chloride at 389.2°

P_0,[a,b] cm	10^4k_1, sec^{-1}	P_0,[a,b] cm	10^4k_1, sec^{-1}
5.3	1.56	15.4	1.60
10.5	1.50	17.2	1.55
10.7	1.63	19.7	1.57
11.7	1.57	21.1	1.61
11.8	1.56	21.8	1.57
11.8	1.54	22.4	1.66
12.2	1.57	29.4	1.58
14.5	1.47		
		Mean:	1.57 ± 0.02

[a] Variation: six times. [b] In the presence of 10–45 cm of cyclohexene.

Table IV. Variation of Rate with Temperature

Temp, °C	No. of runs	P_0, cm	10^4k_1, sec^{-1}
353.8[a]	3	16–22	0.211
358.7	4	27–50	0.256
359.1[a]	6	14–26	0.264
364.5[a]	2	27–36	0.344
371.0[a]	6	13–21	0.478
377.6[a]	7	9–30	0.746
377.4	2	34–44	0.753
378.8[a,b]	6	9–31	0.863
387.6[a,b]	5	13–30	1.70
389.2[a]	15	5–29	1.57
391.2[a]	6	7–21	1.75
394.9[b,c]	2	15–22	2.19
395.2[a,b]	3	15–30	2.12
396.4[a,b]	4	12–27	2.99
399.9[a,d]	8	10–39	3.12
404.6[a,d]	17	6–33	4.14
404.8[d]	9	10–27	4.22
409.7[a]	6	3–17	5.37
418.2[a]	7	6–24	9.20
426.3[a]	4	8–18	14.3

[a] With cyclohexene. [b] In packed reaction vessel. [c] With isobutylene. [d] Analyses carried out.

for each product and for the loss of the reactant were obtained (Tables I and II). Individual runs followed by pressure increase were of the first-order form, and the first-order rate constants found were consistent for a change of pressure of the reactant of up to six times (Table III). The variation of rate with temperature is shown in Table II, and the Arrhenius equation

$$k_1 = 2.52 \pm 0.5 \times 10^{14} \exp(-55{,}150 \pm 400/RT)\ \text{sec}^{-1}$$

found by the method of least squares, was followed satisfactorily for temperatures above 371°; the points fit the expression with a root-mean square deviation of 1.8%. Below this temperature the graph swings away as though a surface reaction were contributing (Figure 2). Addition of isobutylene (a product) or cyclohexene, established inhibitors of radical chains, to the reaction caused no significant change in rate (Table IV and Figure 2). The reaction was also carried out at several temperatures in a packed vessel and the rates found were unchanged (Table IV and Figure 2). The reaction is therefore believed to be homogeneous and unimolecular.

The *A* factor found is "normal" and the activation energy seems reasonable. Unfortunately there are no kinetic results for other acyl halides with which these rates may be compared in order to decide between possible transition states. A five-membered ring (I)

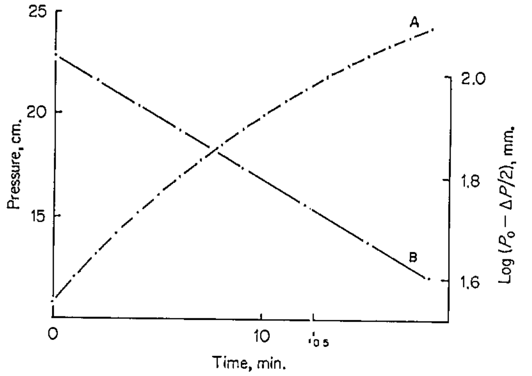


Figure 1. Decomposition of 10.78 cm of trimethylacetyl chloride to 70% reaction at 418.2° in the presence of 26.10 cm of cyclohexene with $10^4k_1 = 9.2$ sec^{-1}.

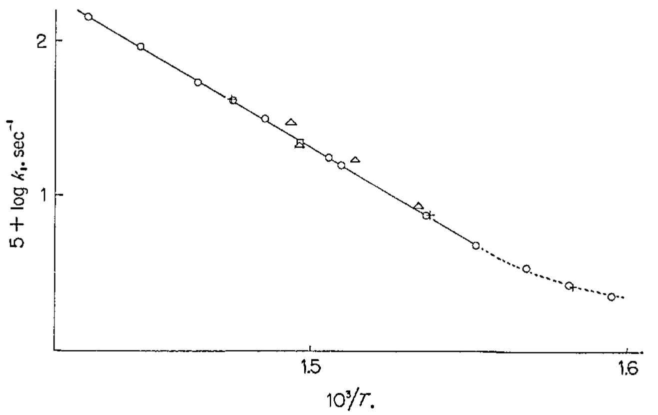
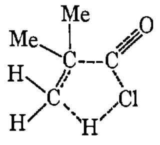


Figure 2. Arrhenius plot for temperatures 354–426°; +, without additives; ○, with cyclohexene; □, with isobutylene; △, in packed vessel.

appears quite apt in terms of electron movements, but in this case a slightly smaller A factor would seem more appropriate. If the decomposition is akin to those of the alkyl halides,[9] reaction would involve polarization of the molecule in the manner of II. Kinetic investigations with other acyl halides are required to obtain information on the effects of substitutions at significant molecular sites.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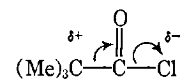
II

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Kinetic Study of the Reaction $CHI_3 + HI \rightleftarrows CH_2I_2 + I_2$. A Summary of Thermochemical Properties of Halomethanes and Halomethyl Radicals[1a]

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Abstract: The rate of the reaction $CHI_3 + HI \rightleftarrows CH_2I_2 + I_2$ has been followed spectrophotometrically from 158.1 to 206.1°. The rate constant for the reaction $I + CHI_3 \rightleftarrows CHI_2 + I_2$ fits the equation, $\log k_1 (M^{-1}\,\text{sec}^{-1}) = (11.75 \pm 0.17) - (9.63 \pm 0.36)/\theta$. This value, combined with the assumption that $E_2 = 0 \pm 1$ kcal/mole, leads to $\Delta H_f{}^\circ{}_{298}(CHI_2\cdot) = 79.9 \pm 2.3$, $DH^\circ{}_{298}(CHI_2\text{–}I) = 45.7 \pm 1.2$, and $DH^\circ{}_{298}(CHI_2\text{–}H) = 102.7 \pm 2.5$ kcal/mole, respectively. The heats of formation of (unmixed) halomethanes and halomethyl radicals are summarized and discussed in terms of Bernstein's interaction scheme and Pauling's bond-energy equations.

In previous papers, we have reported on studies of the equilibrium $2CH_3I \rightleftarrows CH_4 + CH_2I_2$,[2a] the kinetics of $CH_2I_2 + HI \rightleftarrows CH_3I + I_2$, and the iodine-catalyzed process $2CH_3I \rightleftarrows CH_4 + CH_2I_2$,[2b] in which the heats of formation, $\Delta H_f{}^\circ(CH_2I_2)$ and $\Delta H_f{}^\circ(CH_2I)$, and bond dissociation energies, $DH^\circ(CH_2I\text{–}I)$ and $DH^\circ(CH_2I\text{–}H)$, were determined.

The kinetics and thermochemistry of the reaction $CH_3I + HI \rightleftarrows CH_4 + I_2$ have already been reported.[3,4]

In this paper, the kinetics of $CHI_3 + HI \rightleftarrows CH_2I_2 + I_2$ is discussed. This terminates our studies of iodomethanes (CI_4 is not adaptable to study with these methods). A summary of the thermochemical properties of halomethanes and halomethyl radicals is presented, as well.

Experimental Section

Materials. Mallinckrodt reagent grade, resublimed, iodine was used. Matheson anhydrous hydrogen iodide was used after purification by distillation under vacuum. Eastman iodoform was purified by recrystallization in methanol and resublimation under vacuum. The purity of CHI_3 was determined to be greater than 99.5% by nmr measurements.

Apparatus. The slightly modified Cary 15 spectrophotometer, adapted for use with a quartz reaction vessel situated in an Al block oven, has been described in detail previously.[4]

Procedure. The mechanism of the reaction $RI + HI \rightleftarrows RH + I_2$ has been well explained by the scheme proposed by Benson and O'Neal[5]

$$I_2 \rightleftarrows 2I \qquad K_{I_2}\text{(equilibrium)}$$

$$RI + I \underset{2}{\overset{1}{\rightleftarrows}} R\cdot + I_2 \qquad (1, 2)$$

$$R\cdot + HI \underset{4}{\overset{3}{\rightleftarrows}} RH + I \qquad (3, 4)$$

where R is an alkyl or aryl radical. The rate of deiodination of RI

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(1) (a) This work was supported in part by Grant AP0053-04, Public Health Service, Division of Air Pollution; (b) Postdoctoral Research Associate.

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