other hand, LuValle and Schomaker's observations[22] of a shortening of 0.07 Å. in the bond between the adjacent carbonyl groups would indicate that this middle bond is somewhat stronger than a single carbon–carbon bond. Although it is difficult to make any decision as to which primary step actually occurs, on the basis of this latter evidence, reaction (1″) would seem to be more probable than reaction (1′).

Summary

1. The kinetics of the decomposition of diacetyl between 383 and 436° have been investigated by analyzing for the diacetyl present after different time intervals. The pressure increases corresponding to the different amounts of decomposition have been determined.

2. With variation of the initial pressure the reaction is first order, but during a run the first order constants fall off.

3. The first order rate constant can be expressed as $k = 8.7 \times 10^{15} e^{-63,200/RT}$ sec.$^{-1}$.

4. Determinations of the amount of ketene present during the decomposition show that the yield of ketene increases as the percentage of decomposition decreases.

5. Addition of propylene retards the decomposition of diacetyl.

(22) LuValle and Schomaker, THIS JOURNAL, 61, 3520 (1939).

The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of Methyl Chloride[1]

BY G. H. MESSERLY AND J. G. ASTON

This paper presents the results of a low temperature calorimetric investigation of methyl chloride. The work was begun several years ago to permit a comparison between the third law entropy and the value calculated from molecular constants for an organic compound containing methyl groups uncomplicated by the question of restricted rotation. The measurements had to be discontinued, however, because of the destruction by fire of a considerable portion of the Cryogenic Laboratory and have only recently been completed. Egan and Kemp have since published low temperature calorimetric data on methyl bromide and found good agreement between the calorimetric and "spectroscopic" entropy.[2] Our data on methyl chloride confirm the results of Egan and Kemp with methyl bromide.

Purification of Methyl Chloride.—A commercial sample was used as the starting material. About 150 cc. of liquid was distilled in the absence of air through an efficient vacuum-jacketed low temperature fractionating column (section 1 × 70 cm. packed with glass helices). An 80-cc. middle portion was redistilled and the middle cut of about 50 cc. after drying over P_2O_5 and removal of the last traces of air, was condensed in a weighed glass sample bulb.

Vapor pressure measurements taken on the first and last portions of the final sample as the distillation proceeded had shown that no further purification of the material could be effected by fractionation. Two samples from different batches of starting material were prepared in this way. The second of these was used for all measurements. Only the melting point of the first sample was determined.

The Apparatus.—When the first sample prepared was being cooled to liquid hydrogen temperatures in the apparatus previously described[3] most of the apparatus was destroyed by a fire in the laboratory. The rebuilt apparatus was similar to the one destroyed except that the calorimeter itself was made entirely of gold and somewhat larger (present capacity 47 cc.) than the original gold-plated copper calorimeter. Heat conduction was provided for by eight radial vanes instead of the horizontal copper disks previously used. The single standard thermocouple at the bottom of the old calorimeter was replaced by two standard thermocouples which were fastened into horizontal platinum wells gold-welded on the top and bottom of the new calorimeter. The hydrogen liquefier that was an integral part of the old apparatus has been eliminated; liquid hydrogen produced in the laboratory liquefier and other refrigerants are added to the dewar surrounding the cryostat can through a vacuum jacketed german silver transfer tube. The present calorimeter is thus practically identical with the one described by Giauque and Egan.[4] It will hereafter be designated calorimeter C. The earlier calorimeter, only the winding of which was destroyed, is designated calorimeter

(2) Egan and Kemp, THIS JOURNAL, 60, 2097 (1938).
(3) Aston and Messerly, ibid., 58, 2354 (1936).
(4) Giauque and Egan, J. Chem. Phys., 5, 45 (1937).

A. Calorimeter C was used in all the thermal measurements reported.

At the time that this apparatus was being rebuilt, data upon the performance of the adiabatic calorimeter[5] had not yet been obtained. It was for this reason that the destroyed isothermal calorimeter was replaced with one of the same type rather than the adiabatic apparatus, which has shown itself capable of greater accuracy than the isothermal calorimeter above 190 °K.

The Heat Capacity Measurements.—The method, temperature scale, and accuracy were as already described.[3] Standard thermocouples S-4 and S-7 were used for all temperature measurements. Their calibration was checked at the freezing and boiling points of hydrogen and oxygen, and at the upper transition point of oxygen. There was satisfactory agreement with the original scale.[6] The results of this and other similar comparisons made in this Laboratory from time to time will be discussed in a forthcoming paper. Standard thermocouple S-2 was used for the melting point determination in sample one.

TABLE I

THE MOLAL HEAT CAPACITY OF METHYL CHLORIDE

Mol. wt., 50.495; 0.86666 mole (sample two) in calorimeter; 0 °C. = 273.16 °K.

Temp., °K.	C_p, cal./deg.	Approx. ΔT, °K.	Temp., °K.	C_p, cal./deg.	Approx. ΔT, °K.
			169.60	15.96	5.5
	Series I		182.24	17.83	6.4
96.13	11.251	4.8	189.80	17.77	6.1
101.52	11.800	5.6	197.54	17.75	6.0
109.12	12.401	5.0	204.89	17.68	5.7
114.73	12.839	5.9	211.95	17.78	6.0
120.57	13.215	5.6	214.73	17.79	5.4
163.00	15.600	5.6	228.97	17.83	5.1
168.04	15.879	4.2	239.22	17.94	4.8
171.38	16.040	2.3	245.24	18.06	4.2
173.19	16.011	1.1	249.67	18.07	3.7
174.26	16.543	0.8			
				Series III	
	Series II		11.95	0.393	1.4
56.64	7.716	4.6	14.11	0.640	2.4
61.69	8.299	5.1	17.61	1.187	4.2
67.48	8.989	1.2	21.27	1.865	3.2
74.28	9.645	6.7	26.07	2.751	4.0
81.03	10.215	5.8	30.00	3.503	3.4
86.32	10.760	5.3	33.77	4.127	3.9
92.01	11.101	4.9	38.74	5.509	5.6
97.51	11.454	5.7	44.45	6.037	5.4
118.87	13.093	6.5	50.68	7.014	6.5
125.75	13.427	6.7			
132.86	13.917	7.0		Series IV	
140.23	14.375	7.2	162.89	15.58	5.7
147.86	14.729	6.7	168.20	15.89	4.3
156.81	15.21	7.3	171.62	15.99	2.3
164.11	15.63	5.0	174.01	16.92	2.3

(5) Aston and Eidinoff. This Journal. **61**, 1533 (1939).
(6) Aston, Willihnganz and Messerly, *ibid.*, **57**, 2354 (1935).

One defined calorie was taken as equal to 4.1835 international joules. The density of liquid methyl chloride was obtained from the data of Timmermans.[7a] The heat capacity results are given in Table I and plotted in Fig. 1, where are also plotted some earlier heat capacity data on methyl chloride by Eucken and Hauck.[7b] These latter data may be seen to be unsuitable for third law calculations. The series number in Table I designates to which set of continuous measurements the particular measurement belongs.

The Vapor Pressure Measurements.—The measurements were made as already described,[3] and the results are given in Table II. Except for

TABLE II

THE VAPOR PRESSURE OF METHYL CHLORIDE (SAMPLE TWO)

°C. = 273.16 °K.; b. p., 248.943 °K.; (g for State College = 980.124 I. C. T.)

P obsd. int. mm. Hg	T obsd., °K.	P obsd. − P calcd., mm.	T calcd. − T obsd., °K.
26.32	191.424	−0.02	−0.011
26.24	191.378	− .01	− .006
33.56	194.556	− .01	− .004
47.54	199.272	− .01	− .004
77.41	206.324	+ .01	+ .002
122.58	213.539	− .06	− .008
122.47	213.526	− .08	− .010
212.90	222.999	− .15	− .013
313.07	230.184	.00	.000
442.57	237.125	− .19	− .009
579.23	242.845	+ .11	+ .004
681.09	246.441	+ .33	+ .011
761.47	248.998	+ .33	+ .010
735.42[a]	248.943	+ .39	+ .012
	Triple point pressure		
6.569			
6.566			
6.563			
6.566 (mean)	175.44	+0.09	+0.16

[a] After distilling off half of sample.

the lowest pressures the accuracy depends only upon the temperature. Column 1 gives the temperature as read by standard thermocouple S-7; column 2 the observed pressure and column 3 the difference between the observed pressure and that calculated from equation (1). Column 4 gives the temperature difference corresponding to the pressure difference in column 3.

$$\text{Log}_{10} P_{\text{mm.}} = -1822.60/T - 9.287119 \log_{10} T + 0.00555556\, T + 31.07167 \quad (1)$$

The first thirteen measurements were made with the calorimeter full of material. The measure-

(7) (a) Timmermans, *Bull. soc. chim. Belg.*, **30**, 65 (1921); (b) Eucken and Hauck, *Z. physik. Chem.*, **134**, 161 (1928).

ment marked (*a*) was made after half of the sample had been removed from the calorimeter. The boiling range of the sample is thus negligible.
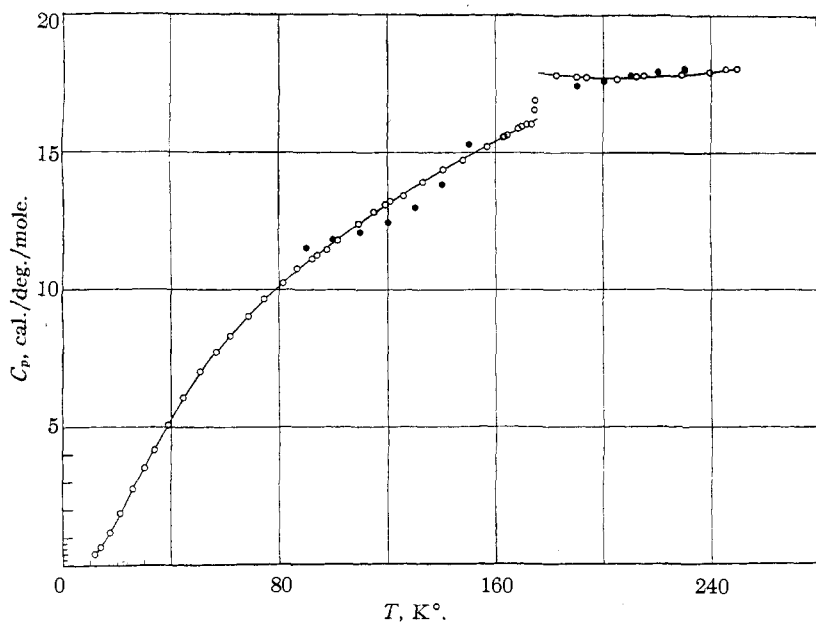

Fig. 1.—The molal heat capacity of methyl chloride: this research, ○; Eucken and Hauck,[7b] ●.

TABLE IIIA

MELTING POINT OF METHYL CHLORIDE (SAMPLE ONE)
0 °C. = 273.16 °K.

% melted	T, °K. resistance thermometer	T, °K. thermocouple S-2
6	175.423	175.421
6[a]	175.423	175.423
13	175.426	175.426
19	175.426	175.427
25	175.428	175.428
45	175.428	175.430
80	175.429	175.430
Melting point	175.43	175.43

[a] This observation taken one-half hour after the previous one.

TABLE IIIB

MELTING POINT OF METHYL CHLORIDE (SAMPLE TWO)
0 °C. = 273.16 °K.

% melted	T, °K. resistance thermometer	T, °K. thermocouple S-4	T, °K. thermocouple S-7
1	175.283	175.329	175.342
10	175.438	175.434	175.447
10[a]	175.436	175.436	175.448
19	175.437	175.438	175.450
41	175.437	175.433	175.447
80	175.438	174.440	175.452
Melting point	175.44	175.44	175.45

[a] This observation taken one hour after the previous one.

Triple Point.—At the bottom of Table II are given the determinations of the triple point pressure.

The Melting Point.—The equilibrium temperature of both samples was observed over periods of fifteen and eighteen hours with increasing fractions of the sample melted as determined by the heat input. From these results and the heat of fusion, the solid insoluble impurity for both samples was found to be 0.002 ± 0.001 mole per cent. Tables IIIA and IIIB summarize the data.

Values of the melting point were obtained with two different samples and three different standard thermocouples. The value on sample I with thermocouple S-2 was obtained with calorimeter A. The values on sample II were obtained with the rebuilt apparatus.

The final value taken for the melting point was 175.44 ± 0.05°K. (−97.72°C.). Other values given in the literature for the melting point of methyl chloride are: −102.9,[8] −97.6,[9] −91.5,[10] −93[11] (all in °C.).

By solving equation (1) for one atmosphere 248.94 ± 0.02°K. (−24.22°C.) is obtained for the normal boiling point of methyl chloride. Other values given by earlier investigators for the normal boiling point are: −23.73,[12] −24.09,[13] −23.7,[14] −23.7,[7a] −23.8[15] (all in °C.). The values of the physical constants indicate that methyl chloride would be a suitable material for thermometric fixed points. It is curious that the values obtained in this research seem to be the only reliable ones for such a common substance.

The Heats of Fusion and Vaporization.—The heats of fusion were measured as already described, and the results are given in Table IV. The heat of vaporization at the boiling point has

(8) Lndenburg and Krügel, *Ber.*, **33**, 638 (1900).

(9) McIntosh, *J. Chem. Soc.*, **85**, 915 (1904).

(10) Baume, *Compt. rend.*, **148**, 1322 (1909).

(11) Baume and Borowski, *J. chim. phys.*, **12**, 281 (1915).

(12) Regnault, *Jahresber. uber. Fort. Chem.*, 70 (1863).

(13) Gibbs, THIS JOURNAL, **27**, 851 (1905).

(14) Holst, *Commun. Phys. Lab. Univ. Leiden*, No. 144c (1914).

(15) D. N. Shorthose, Food Investigation Board, Dept. of Scientific and Industrial Research (Great Britain), Special Report 19 (1924).

TABLE IV
HEAT OF FUSION OF METHYL CHLORIDE

0°C. = 273.16°K.; mol. wt., 50.495; 0.86666 mole
(sample II); m. p., 175.44 ± 0.05°K.

Temperature interval, °K.	Corrected heat input, cal./mole	$\int C_p \, dt$, cal./mole	ΔH fusion, cal./mole
172.458–179.835	1715.2	178.1	1537.1
171.691–180.681	1754.2	217.7	1536.5
172.679–179.213	1693.1	156.4	1536.7

Mean 1537 ± 1

been calculated from our vapor pressure equation and the equation of state data of Holst,[14] with the liquid density mentioned already. A direct experimental result has been published by Shorthose.[15] These values are compared in Table V. To obtain a final value, the experimental value of Shorthose was averaged with the one derived from the data of Holst. Double weight was given to the latter value. The heat of vaporization also has been calculated assuming a modified Berthelot equation of state for the gas with critical constants cited by Centnerszwer.[16] The agreement obtained justifies the later use of the Berthelot equation in calculating the entropy to the ideal gas state. This comparison could equally well have been made between the gas volumes, but in this case the experimental data of Shorthose would have received no weight.

TABLE V
THE HEAT OF VAPORIZATION OF METHYL CHLORIDE AT THE BOILING POINT

B. p., 248.94°K.; mol. wt., 50.495

		ΔH, cal./mole
(1)	Calculated from eqn. (1) and state data Holst[14] (1914)	5138 ± 10
(2)	Measured (Shorthose,[15] 1924)	5166 ± 20
	Average (2 × (1) + (2))/3	5147 ± 15
(3)	Calculated from eqn. (1) and modified Berthelot eqn. $T_c = 143.2°C.;$[16] $P_c = 65.7$ atm.[16]	5157

The Entropy from Thermal Data.—The calculation is summarized in Table VI. The entropy of the gas at 298.16°K. has been obtained by extrapolation using the spectroscopic data discussed by Stevenson and Beach.[17] The corrections for gas imperfection are based upon a modified Berthelot equation of state for the gas. For completeness the entropy of the superheated liquid has been estimated at 298.16°K.

The Entropy from Molecular Data.—Stevenson and Beach[11] have calculated the entropy of methyl chloride to be 55.99 e. u. for the ideal gas

(16) Centnerszwer. Z. physik. Chem., 49, 199 (1904).
(17) Stevenson and Beach, J. Chem. Phys., 6, 25 (1938).

TABLE VI
THE ENTROPY OF METHYL CHLORIDE FROM THERMAL DATA
Mol. wt., 50.491; 0°C., 273.16°K.

	E. u./mole
0 − 10.00°K., Debye extrapolation	0.075
10.00 − 175.44°K., Graphical	18.402
Fusion 1537/175.44	8.760
175.44 − 248.94°K., Graphical	6.239
Vaporization, 5147/248.94	20.677
Entropy of actual gas	54.153
Correction for gas imperfection[a]	0.119
Entropy of ideal gas, 248.94°K., 1 atm.	54.27 ± 0.15
Entropy of ideal gas, 298.16°K., 1 atm.	55.94
Entropy of liquid, 298.16°K.	36.74

[a] $S_{\text{ideal}} - S_{\text{real}} = 27 \, RT_c \, {}^3P/32T^3 \, P_c$
$T_c = 143.2°C.;$[16] $P_c = 65.7$ atm.[16]

at 298.1°K. The same vibrational frequency assignment was used in the present calculation for the ideal gas at the boiling point. This calculation is summarized in Table VII. The nuclear spin entropy is not included and the effect of isotopic composition has been neglected.

TABLE VII
THE ENTROPY OF METHYL CHLORIDE FROM MOLECULAR DATA AT ONE ATMOSPHERE PRESSURE
Mol. wt., 50.491; 0°C. = 273.16°K.

C–H = 1.10Å. R = 1.9871 cal.(15°)/deg./mole
C–Cl = 1.76Å.
∠H–C–H = 111° hc/k = 1.4325 cm. deg.
I_1 = 5.46 × 10⁻⁴⁰ g. cm.²
I_2 = I_3 = 61.36 × 10⁻⁴⁰ g. cm.²

	E. u./mole	
	248.94°K.	298.16°K.
$S_{\text{trans.}}$ = 3/2 $R \ln M$ + 5/2 $R \ln T - R \ln P - 2.300$	36.785	37.683
$S_{\text{rot.}}$ = $R/2 \ln I_1 I_2 I_3 \times 10^{120}$ + 3/2 $R \ln T - R \ln 3 - 6.851$	17.271	17.809
$S_{\text{vib.}}$ = $\Sigma_n \, S_{\text{Einstein}}$	0.252	0.490
Total	54.31	55.98
Experimental	54.27 ± 0.15	55.94

The agreement between the entropy calculated from calorimetric and from molecular data further confirms the validity of applying the third law to organic compounds.

We gratefully acknowledge the help of the Research Corporation in providing a grant-in-aid which made the work possible. We wish to thank Mr. S. C. Schuman and Mr. R. M. Kennedy for help with the experimental work. We are indebted to Mr. C. W. Brouse for the execution of the fine mechanical work in the apparatus and the supervision of its construction.

Summary

The heat capacity of methyl chloride has been measured from 12°K. to the boiling point.

The melting and boiling points of methyl chloride are 175.44 and 248.94°K. respectively (0°C. = 273.16°K.).

The heat of fusion is 1537 cal./mole and the heat of vaporization is 5147 cal./mole at the boiling point.

The vapor pressure of methyl chloride is represented from the triple point to the boiling point by the equation, $\log_{10} P_{mm.} = -(1822.60/T -$

$9.287119 \log_{10} T + 0.00555556 T + 31.07167.$

The triple point pressure is 6.57 int. mm.

The entropy of methyl chloride in the ideal gas state has been found from calorimetric data to be 54.27 e. u. and 55.94 e. u. at 284.94 and 298.16°K., respectively. The corresponding values calculated from spectroscopic and molecular data are 54.31 e. u. and 55.98 e. u.

STATE COLLEGE, PA. RECEIVED JANUARY 12, 1940

# Proof of Structure of 6-Chloro-8-chloromethyl-1,3-benzodioxane by Oxidation[1]

BY C. A. BUEHLER, B. CALVIN BASS, ROBERT B. DARLING AND MILTON E. LUBS

In studying the action of formaldehyde on p-chlorophenol[2] in the presence of hydrochloric acid, a compound (I) thought to be 6-chloro-8-chloromethyl-1,3-benzodioxane was obtained. That the condensation product was a dioxane was shown by oxidation with chromium trioxide in acetic acid by the method of Borsche and Berkhout.[3] The 6-chloro-8-chloromethyl-1,3-benzodioxane-4-one, II, thus obtained gave, on alkaline hydrolysis, 2-hydroxy-3-methylol-5-chlorobenzoic acid, III.
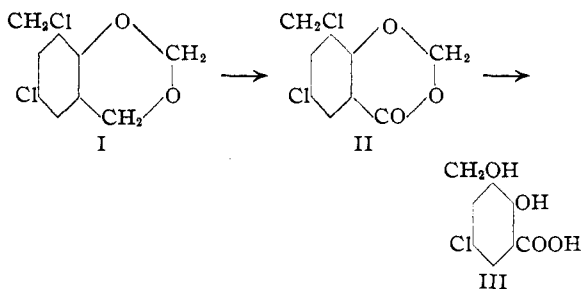
To prove the structure of the original dioxane, I, a new oxidizing mixture, potassium permanganate in acetic acid, was tried and it was found that complete disruption of the dioxane ring was possible in one step. In this oxidation five products, IV, V, VI, VII and VIII, were isolated. Considering the effect of time and concentration of oxidizing agent on the amounts of the products obtained, we are inclined to support the oxidation sequence as indicated below. Of the first-formed products, IV appears in greater amounts than V,

although the former apparently is consumed more rapidly as the oxidation proceeds.
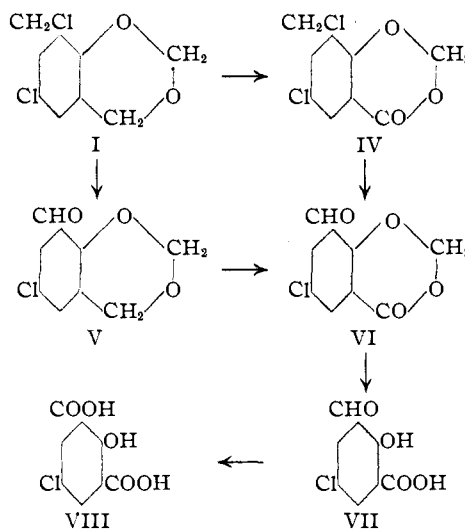
The 6 - chloro - 8 - chloromethyl - 1,3 - benzodioxane-4-one, IV, and 6-chloro-8-aldo-1,3-benzodioxane, V, were isolated only in small quantities. The former, identical with II, gave the corresponding alcohol on alkaline hydrolysis while the latter was identified by conversion into its phenylhydrazone.

Of all the oxidation products, perhaps 6-chloro-8-aldo-1,3-benzodioxane-4-one, VI, is the most interesting because of the ease with which the dioxanone ring is broken. Not only does this opening occur on standing and on titration with standard alkali, since the neutral equivalent is fairly satisfactory and 2-hydroxy-3-aldo-5-chlorobenzoic acid, VII, may be recovered from the titration mixture, but catalytic reduction, in which

(1) Presented at the 99th meeting of the American Chemical Society, Cincinnati, Ohio, April, 1940.

(2) For a similar reaction of phenol, see *Chem. Zentr.*, **103**, I, 2997(1932).

(3) Borsche and Berkhout. *Ann.*, **330**, 92 (1904).