

Direct measurements of K at 600–700° give²

$$\log_{10} K = -\frac{31,244}{2.3RT} + 6.31$$

The independent determinations thus confirm one another.

Summary

The combination of ethylene and hydrogen in a Pyrex glass vessel at 475–550° and one atmosphere pressure has been shown to be a homogeneous, second-order reaction. A calculation based on the collision theory indicates that about 10% of the collisions between ethylene and hydrogen molecules possessing the requisite energy (43,150 cal. per mole) eventually result in formation of ethane.

Combination of equations for the rates of ethane formation and of ethane dissociation gives an equation for the equilibrium constant of the reaction



in good agreement with that obtained by direct measurement.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA]

THE PREPARATION AND PROPERTIES OF IODINE MONOCHLORIDE¹

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I. Preparation

Old Method.—Iodine monochloride has usually been prepared by leading chlorine over solid iodine.² The crude product thus obtained was distilled; the portion of the distillate forming between 100 and 102° was retained. The distillate was far from pure. Stortenbecker³ obtained iodine monochloride of good quality by repeatedly recrystallizing the distillate in its own mother liquor.

Improvement of the Old Method.—The present authors found that passing a slow stream of chlorine through the system during distillation and collecting the distillate formed between 100 and 101.5° increased the yield from about 35 to about 85% and also improved the quality of the

¹ From a thesis submitted to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy, by R. A. Karges, August, 1931.

² Gay-Lussac, *Ann. chim.*, **91**, 1 (1814); Serullas, *Ann. chim. phys.*, **22**, 180 (1833); Harmay, *J. Chem. Soc.*, **26**, 815 (1873); *ibid.*, **35**, 269 (1879); Thorpe, *ibid.*, **37**, 174 (1880); **61**, 925 (1892).

³ Stortenbecker, *Rec. trav. chim.*, **7**, 152 (1888).

distillate. They also found that analyzing the distillate and adding the quantity of solid iodine required to cause the compositions to correspond to that implied by the formula of iodine monochloride was a profitable expedient. The iodine monochloride was next liquefied and then slowly cooled, whereupon large, black, prism-shaped crystals formed. When about 80% of the iodine monochloride had crystallized, the remaining liquid was removed by decantation. This process was repeated until the freezing point of the crystals was the same as that of the supernatant liquid. Two or three crystallizations were usually required. At best this older method is a tedious, time-consuming process.

A New Method of Preparation.—The statement of Thomas and Dupuis⁴ that solid iodine added to liquid chlorine leads to the formation of iodine trichloride suggested the method for preparing iodine monochloride about to be described. Approximately 300 ml. of liquid chlorine is led directly from a commercially obtained cylinder of chlorine into a tared 500-ml. flask cooled with a mixture of solid carbon dioxide and ether. A weighed quantity of solid iodine, roughly one-half of a molar equivalent of the chlorine in the flask, is next added. The equivalence may vary rather widely but the weight should be accurate. After the addition of iodine the contents of the flask congeal to a solid. The flask is gradually raised from the cooling mixture and allowed to warm to room temperature. During the warming any uncombined chlorine evaporates. The weight of the flask and contents is next determined. Since the weight of the iodine added and the tare weight of the flask are known, the weight of the chlorine is determined by difference. The weight of both chlorine and iodine being known, the quantity of solid iodine that must be added to cause the composition of the impure product to correspond to that implied by the formula ICl is computed and added. The flask is closed with a glass stopper and allowed to stand in a liquid condition for twenty-four hours or longer. The freezing point of the iodine monochloride is usually within 0.1° of that of the pure article. One or two recrystallizations usually suffice to obtain the pure iodine monochloride. The following manipulative observations are helpful. Iodine monochloride vigorously attacks cork, rubber and the human skin, hence contacts with these substances should be avoided. A dilute (6 *M*) solution of hydrochloric acid is an effective antidote for skin burns. While iodine monochloride in bulk is not notably hygroscopic, yet small quantities of moisture from the air or starting materials will noticeably depress the freezing point. Hence exposure to moisture should be at a minimum. Exposure to atmospheric moisture produces a film of iodine pentoxide on the glass of the containing vessel.

By this new method the authors have been able to prepare pure iodine

⁴ Thomas and Dupuis, *Compt. rend.*, **143**, 282 (1906).

monochloride in one or two kilo lots within two or three hours. Preparation of similar quantities by the older methods required a similar number of days. This procedure serves also for the preparation of iodine trichloride but the authors have investigated this only qualitatively.

The iodine monochloride prepared as described had a freezing point of 27.19° as compared with the Stortenbecker value of 27.20° . The thermometer used was marked in 0.1° divisions and had been compared with a similar thermometer calibrated by the United States Bureau of Standards. A second criterion of purity was that afforded by gravimetric analysis. The method was a modification of the one described by Stortenbecker.⁵ Duplicate analyses of the same sample would not vary by more than 0.2%, generally by not more than 0.1%, from each other and from the theoretical composition of iodine monochloride. A third criterion of purity was the similarity of values obtained for the electrical conductivity of iodine monochloride obtained in different runs.

The conjunction of the criteria led to the belief that the iodine monochloride used in these experiments was approximately pure.

II. Vapor Pressure

The vapor pressure was measured by the method of Smith and Menzies.⁶ Iodine monochloride was the confining liquid. When heated above 70° the rate of decomposition of iodine monochloride becomes so rapid that consistent measurements were not obtained. The average of four experimentally determined vapor pressure values at each temperature is recorded in the third column of Table I. The individual measurements did not vary more than 0.25 mm.

TABLE I
VAPOR PRESSURE AND OTHER DATA CONCERNING IODINE MONOCHLORIDE

Temp., °C.	Absolute temp., °K.	Vapor pressure of ICl, mm.	ΔH , molar heat of vaporization, cal.	$\Delta H/T$, boiling entropy of vaporization, cal.
35	308.1	48.0	10,140	27.18
40	313.1	62.5	10,290	27.59
45	318.1	81.0	10,080	27.02
50	323.1	103.6	10,200	27.34
55	328.1	131.9	10,100	27.08
60	333.1	166.0	10,302	27.66
65	338.1	209.0	10,460	28
70	343.1	261.7		

The values for molar heat of vaporization given in column four were computed by the use of the integrated form of the Clausius-Clapeyron equation.

$$2.302 \log \frac{P_2}{P_1} = \frac{\Delta H}{R} \frac{T_2 - T_1}{T_2 T_1}$$

⁵ Stortenbecker, *Z. physik. Chem.*, **10**, 192 (1892).

⁶ Smith and Menzies, *THIS JOURNAL*, **32**, 1427 (1910).

P_2 and P_1 are vapor pressures at temperatures T_2 and T_1 , respectively. ΔH is the molar heat of vaporization.

According to Trouton's rule, the entropy of vaporization for non-associated liquids is 21 calories.

Since iodine monochloride dissociates on boiling at atmospheric pressure, its boiling point is not definite. The literature gives values as low as 94.7 and as high as 102. The value used in the computation of column 4 is 100° or 373.1°K . The values given in column 5 indicate that iodine monochloride is an associated or polar liquid. J. H. Hildebrand⁷ makes the point that, for the application of Trouton's rule, the entropy of vaporization should be taken, not when liquids are boiled under atmospheric pressure, but rather when temperature and pressure are so chosen as to give the same volume of vapor per mole of material in each case.

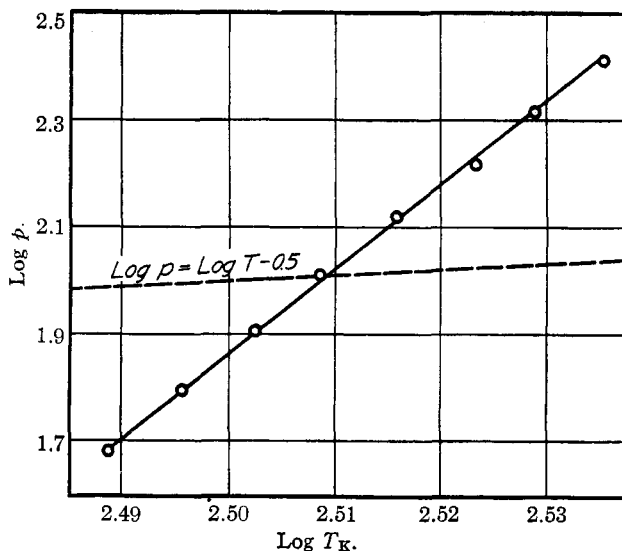


Fig. 1.

By applying a modification of the Clausius-Clapeyron equation to the data given graphically in Fig. 1, the value of the entropy of vaporization of iodine monochloride is computed as 33.4 cal. at the concentration of 0.00507 mole per liter. Hildebrand gives the values of this constant at this concentration as 32.4 cal. for liquid ammonia, 32 cal. for water and 33.4 cal. for ethyl alcohol. For ten known non-associated liquids he gives the average value of 27.4 cal. at this concentration.

Iodine monochloride is an associated or polar liquid.

⁷ J. H. Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, p. 93.

III. The Conductivity of Iodine Monochloride

An ordinary conductivity cell was used to measure the conductivity of iodine monochloride and of solutions of potassium chloride and ammonium chloride in it. The cell constant was obtained in the usual way by measuring the conductivity of a 0.02 *M* solution of potassium chloride in water. The measurements were made in a thermostat at $35 \pm 0.1^\circ$. The specific conductivity of four different samples of iodine monochloride varied from 0.004572 to 0.004589 reciprocal ohms.

Prolonged exposure of iodine monochloride in a wide weighing bottle to the humid air of a June day caused the sides and bottom of the bottle to become heavily coated with iodine pentoxide. This exposure also influenced the conductivity of iodine monochloride. Removing the stopper of the conductivity cell for two minutes produced no measurable change in conductivity; exposure for twenty minutes in the weighing bottle caused the specific conductivity to increase from 0.004589 to 0.00521 and exposure for one hundred minutes increased the conductivity to 0.01327 reciprocal ohms.

The results of vapor pressure measurements indicate that iodine monochloride is an associated liquid; hence it may be expected to act as an ionizing solvent. The validity of this assumption may be put to experimental proof by preparing solutions of potassium chloride and of ammonium chloride and measuring the conductivity at different dilutions. The results are given in Table II.

TABLE II

CONDUCTIVITY OF SOLUTIONS IN IODINE MONOCHLORIDE AT 35°			
Molal concn. of solute	Specific conductivity of cell	<i>K</i> , specific conductivity of solute	Equivalent conductivity
Potassium chloride as solute			
0	4583×10^{-6}
0.5	18,975	$14,387 \times 10^{-6}$	28.76
.25	12,140	7,522	30.21
.125	8,494	3,996	31.20
.0625	6,491	1,903	30.43
.02083	3,230	642	30.81
.00993	4,797	84	31.19
Ammonium chloride as solute			
0	4588
1	24,175	19,650	19.65
0.5	15,770	10,982	21.96
.33 $\frac{1}{3}$	12,100	7,852	22.64
.16 $\frac{2}{3}$	8,558	3,970	23.82
.08 $\frac{1}{3}$	6,642	2,034	24.64

Columns one and four in Table II are graphically represented in Fig. 2. These data indicate that: (1) Potassium chloride dissolved in iodine mono-

chloride increases the conductivity very decidedly. However, after the first dilution the equivalent conductivity shows no regular increase with dilution. (2) Ammonium chloride also shows evidence of dissociation in the solution. While the equivalent conductivity is less than in water, its increase with dilution is entirely analogous to the behavior of a solution of an electrolyte in water.

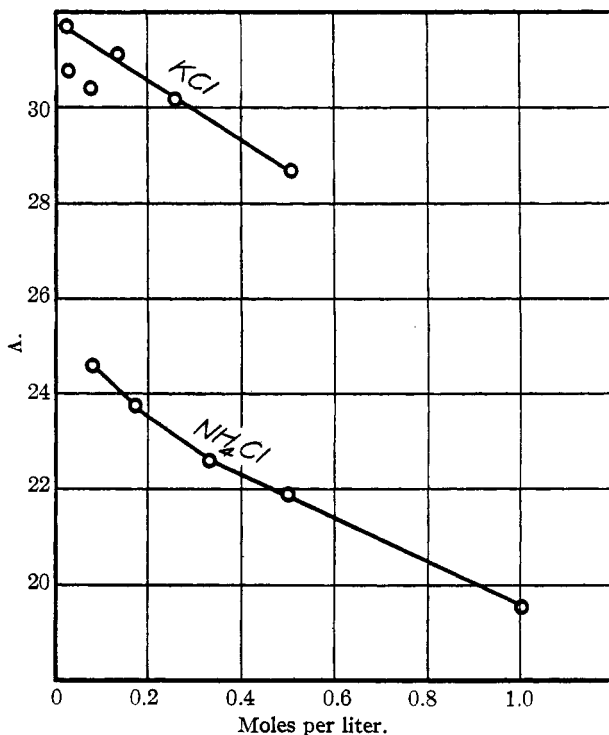


Fig. 2.

Summary

1. Two methods of preparing relatively pure iodine monochloride are described. One is an improvement on traditional methods; the other is a new method.

2. Results of vapor pressure measurements indicate that iodine monochloride is a polar liquid.

3. Conductivity measurements show that iodine monochloride acts as a dissociating solvent on potassium and ammonium chloride.

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