[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Addition Compounds of Gallium Trichloride with Methyl Halides[1,2]

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RECEIVED MARCH 11, 1953

The phase diagrams for the methyl chloride–gallium chloride system were determined at three temperatures, −78.5, −64 and −50°. A 1:1 addition compound exists in the solution phase as shown by molecular weight determinations. Solid phases corresponding to both 1:1 and 1:2 compounds, $CH_3Cl:GaCl_3$ and $CH_3Cl:Ga_2Cl_6$, were identified. The heat of dissociation, $CH_3Cl:GaCl_3(s) \rightleftarrows CH_3Cl(g) + {}^1/_2Ga_2Cl_6(s)$ is 11.78 kcal./mole and $CH_3Cl:Ga_2Cl_6(s) \rightleftarrows Ga_2Cl_6(s) + CH_3Cl(g)$ is 9.34 kcal./mole. The heat of solution of the 1:1 compound in methyl chloride is 2.15 kcal./mole and the calculated m.p. is 4.8°. Similar 1:1 addition compounds were shown to exist by an examination of the systems of gallium chloride with methyl bromide and methyl iodide. The exchange of the halogen between dissolved gallium chloride and methyl bromide at −80° is slow—approximately 2% in 24 hours. It is concluded that ionization of the addition compound must be a slow reaction, if it occurs at all. It is, therefore, proposed that the initial stage of the Friedel–Crafts reaction, usually considered to be $RX + MX_3 = R^+ + MX_4^-$, should be revised to the reaction, $RX + MX_3 = RX:MX_3$, with the ionization of the addition compound as a possible, but not necessarily essential, second stage in the reaction.

Introduction

The Friedel–Crafts reaction is generally believed to proceed through the mechanism[4,5]

$$RX + MX_3 \rightleftarrows R^+ + MX_4^-$$
$$R^+ + ArH \longrightarrow RAr + H^+$$
$$H^+ + MX_4^- \longrightarrow HX + MX_3$$

As part of our program to study the mechanism of Friedel–Crafts reactions, we undertook an examination of the action of typical Friedel–Crafts catalysts on alkyl halides. Since aluminum chloride turned out to be essentially insoluble in methyl chloride, we concentrated our efforts on gallium chloride, reported in the present paper, and on aluminum bromide, reported in the succeeding paper.[6]

TABLE I

THE METHYL CHLORIDE–GALLIUM CHLORIDE SYSTEM AT −78.5°

Mole ratio $CH_3Cl/GaCl_3$	Press.,[a] mm.	Calcd. mol. wt.		Mole ratio $CH_3Cl/GaCl_3$	Press.,[a] mm.
		Assuming no compd. formed	Assuming 1:1 compd. formed		
	34.00			4.53[b]	26.84
18.56	32.16	166	175	3.86[b]	25.74
17.12	31.96	161	171	3.10[b]	26.64
16.78	31.91	158	170	2.06[b]	26.64
14.97	31.81	170	182	1.68[b]	26.64
14.04	31.56	162	174	1.46[b]	26.59
12.48	31.21	157	171	1.34[b]	26.39
11.66	31.07	162	177	1.02[b]	14.99
10.88	30.82	156	172	0.96[b]	7.99
9.48	30.42	157	176	.91[b]	7.84
8.45	29.92	153	173	.85[b]	7.99
7.73	29.57	134	154	.72[b]	7.89
6.54	28.97	154	182	.37[b]	2.31
5.81	28.03	142	171	.27[b]	2.34
5.23[b]	27.04	131	162	.16[b]	2.39

[a] The pressure decrease was observed directly by a differential method. [b] Solid present.

Results and Discussion

The System: Methyl Chloride–Gallium Chloride.—Gallium chloride is readily soluble in methyl chloride at −78.5° forming a clear, colorless solution which appears to be stable indefinitely. As the mole ratio $CH_3Cl/GaCl_3$ is decreased, the pressure drops smoothly until, at a mole ratio of 5.2, a solid appears and the pressure remains sensibly constant at a value of 26.6–26.7 mm. At a mole ratio of 1:1 there is a sudden drop in the pressure to a new plateau at 7.9 mm. Finally at a mole ratio of 1:2 there appears a new plateau at 2.3 mm. The data are summarized in Table I and Fig. 1.

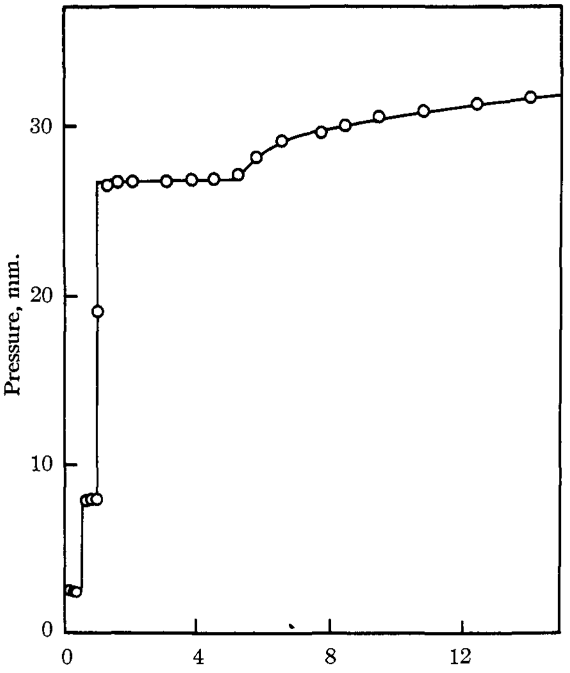

Fig. 1.—The methyl chloride–gallium chloride system at −78.5°.

Evidently the last two plateaus represent the formation of relatively stable 1:1 and 1:2 addition compounds with dissociation pressures of 7.9 and 2.35 mm., respectively.

$$CH_3Cl:GaCl_3(s) \rightleftarrows {}^1/_2CH_3Cl(g) + {}^1/_2CH_3Cl:Ga_2Cl_6(s)$$
$$CH_3Cl:Ga_2Cl_6(s) \rightleftarrows Ga_2Cl_6(s) + CH_3Cl(g)$$

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[1] The Catalytic Halides. VII.

[2] Abstracted in part from a thesis presented by Lowell P. Eddy in partial fulfillment of the requirements for the Ph.D. degree.

[3] In part this study was supported by a grant from the Atomic Energy Commission. This assistance is gratefully acknowledged.

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.

[5] C. C. Price, "Organic Reactions," Vol. III, Chapt. 1, John Wiley and Sons, New York, N. Y., 1946.

[6] H. C. Brown and W. J. Wallace, THIS JOURNAL, **75**, 6279 (1953).

The first plateau then corresponds to a methyl chloride solution which is saturated with respect to the 1:1 addition compound.

It was of interest to establish whether this 1:1 compound exists as such in solution or must be considered to be a crystal lattice compound which exists only in the solid state. Accordingly the molecular weights were calculated from the observed drop in the vapor pressure of the solvent (Table I) assuming that gallium chloride is present in the unsolvated form. The molecular weights obtained evidently correspond to the existence of gallium chloride in the monomeric form in solution ($GaCl_3$ = 176). However, the calculated molecular weights show a continual drop as the solutions become more and more concentrated.

The molecular weight was then calculated assuming that one mole of solvent is effectively removed to form the addition compound which exists as such in solution. In this case the molecular weight showed a satisfactory constancy. If we omit the point at mole ratio 7.73 and the last point where solid had begun to separate, we obtain a value for the molecular weight of 174.5 ± 3.3, in excellent agreement with the 176 value calculated for monomeric gallium chloride. It is, therefore, concluded that the addition compound $CH_3Cl:GaCl_3$ exists as such in solution.

Similar phase studies were made at −64 and −50°. In each case the results are similar. Three plateaus are observed, the first two corresponding to the dissociation of the 1:1 and 1:2 addition compounds, the third to a saturated solution of the 1:1 addition compound in methyl chloride (Fig. 2).

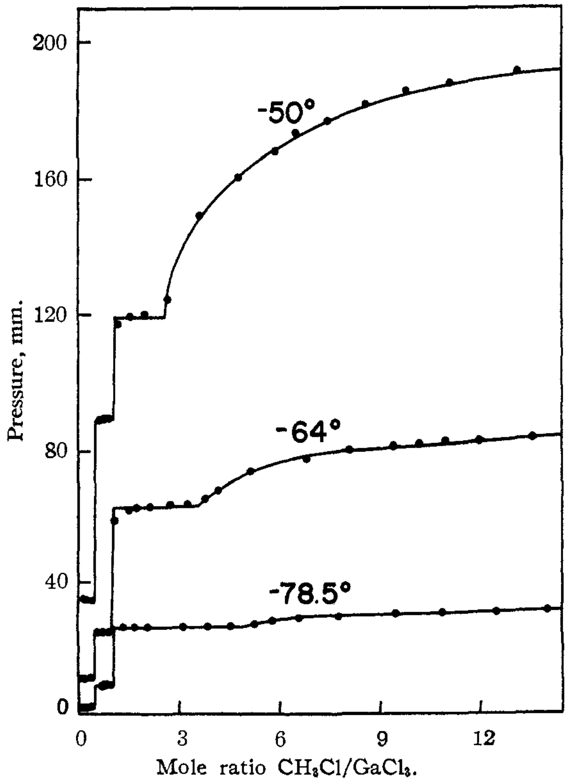


Fig. 2.—The methyl chloride–gallium chloride system at several temperatures.

At −64° the average of 18 observations at methyl chloride/$GaCl_3$ mole ratios of 18.37 to 4.18 results in a molecular weight value of 173.7 ± 2.7 assuming one mole of methyl chloride removed from solution to form the complex. On the basis of the alternative assumption, the calculated molecular weight decreases from 166 in the dilute solution to 119 in the more concentrated solution. Similarly at −50° the first assumption gives a satisfactory constancy of the calculated molecular weight, 173.8 ± 3.8, for 15 observations in the concentration range of methyl chloride/$GaCl_3$ mole ratios from 21.62 to 2.67, whereas the assumption of no complex results in molecular weight values decreasing from 161 in the dilute to 98 in the concentrated solution. From these data it appears certain that the 1:1 addition compound exists as such in the methyl chloride solutions.

From the dissociation pressures of the 1:1 complexes at the three temperatures (7.89 mm. at −78.5°, 25.72 mm. at −64° and 84.45 mm. at −50°), a heat of dissociation of 7.11 kcal./mole may be calculated for the reaction

$$CH_3Cl:GaCl_3(s) \rightleftharpoons {}^1/_2CH_3Cl:Ga_2Cl_6(s) + {}^1/_2CH_3Cl(g)$$

From the dissociation pressures of the 1:2 complexes at the three temperatures (2.34 mm. at −78.5°, 10.02 mm. at −64°, and 34.66 mm. at −50°), a heat of dissociation of 9.34 kcal./mole may be calculated for the reaction

$$CH_3Cl:Ga_2Cl_6(s) \rightleftharpoons Ga_2Cl_6(s) + CH_3Cl(g)$$

From these two heats of reaction the calculated value of 11.78 kcal./mole is obtained for the reaction

$$CH_3Cl:GaCl_3(s) \rightleftharpoons Ga_2Cl_6(s) + CH_3Cl(g)$$

The positions of the saturated solution plateaus fix the solubility at 0.189 mole fraction at −78.5°,

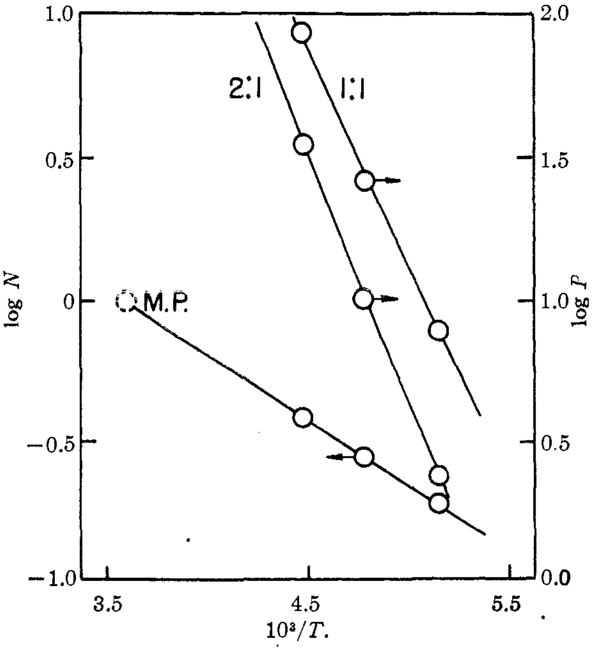


Fig. 3.—The change of dissociation pressures and solubilities of methyl chloride–gallium chloride compounds with temperature.

0.278 at −64° and 0.385 at −50°. Assuming ideal behavior the heat of fusion or solution is 2.15 kcal./mole and the calculated melting point is 4.8°. These data are shown in Fig. 3.

The Systems of Gallium Chloride with Methyl Bromide and Iodide.—It was of interest to examine the $CH_3Br–GaCl_3$ and $CH_3I–GaCl_3$ systems to ascertain whether similar 1:1 addition compounds exist there. However, before a study of these systems could be undertaken it was necessary to determine how rapidly the halogens in the two components undergo exchange.

$$\begin{tikzcd} CH_3Br:GaCl_3 \arrow[r, phantom, "="] & CH_3Cl:GaBrCl_2 \arrow[d, shift left] \\ & CH_3Cl + GaBrCl_2 \arrow[u, shift left] \end{tikzcd}$$

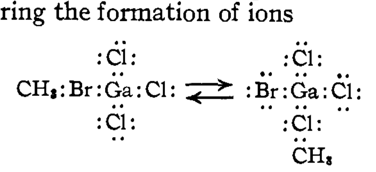
In a typical experiment 1 mole of gallium chloride was dissolved in 5 moles of methyl bromide at −80° and the solution maintained at that temperature for 10 days. The volatile components were removed. From the decrease in weight of gas, the exchange involved only 21% of the available chlorine in the gallium chloride. The increase in weight of the salt corresponded to 16% exchange. In a similar experiment carried on for 24 hours, the observed exchange was too small to detect by these methods. It therefore appears that under these conditions the exchange of methyl bromide with gallium chloride is a relatively slow reaction that proceeds to an extent of approximately 2% in 24 hours.

Similar experiments established that the exchange of methyl iodide with gallium chloride is also sufficiently slow to permit a phase study. However, the phase studies were made as rapidly as possible to minimize the complications resulting from exchange. Accordingly, the data (Figs. 4 and 5) are less precise than those obtained in the methyl chloride system. However, they do establish the existence of stable 1:1 addition compounds: $CH_3Br:GaCl_3$ and $CH_3I:GaCl_3$.

The Role of Friedel–Crafts Catalysts.—The exchange between methyl bromide and gallium chloride presumably occurs either through an ionization

$$\begin{tikzcd} CH_3Br:GaCl_3 \arrow[r, shift left] & CH_3{}^+ \, GaCl_3Br^- \arrow[l, shift left] \arrow[d, shift left] \\ & CH_3Cl:GaCl_2Br \arrow[u, shift left] \end{tikzcd}$$

mechanism or possibly through a rearrangement not requiring the formation of ions



$$CH_3:\underset{..}{\overset{..}{Br}}:\overset{:\overset{..}{Cl}:}{\underset{:\underset{..}{Cl}:}{Ga}}:\overset{..}{\underset{..}{Cl}}: \rightleftarrows :\overset{..}{\underset{..}{Br}}:\overset{:\overset{..}{Cl}:}{\underset{:\underset{..}{Cl}:}{Ga}}:\overset{..}{\underset{..}{Cl}}: \;\; CH_3$$

The slow exchange observed in this study represents, therefore, an upper limit for the rate of ionization.

That alkyl halides do not instantly undergo ionization under the influence of Friedel–Crafts catalysts is indicated by a study of Fairbrother.[7] He observed that in benzene solution a reaction mixture of triphenylmethyl bromide and stannic bromide shows an increase in absorption which corresponds to less than 0.1% ionization. The triphenylcarbonium ion is unusually stable. The tendency for ionization must be far greater in triphenylcarbonium halides than in simpler alkyl halides. The low upper limit observed by Fairbrother supports the conclusion that the conversion of the simple alkyl halides into ions under the influence of metal halides is not the simple, rapid process that has frequently been postulated in the generally accepted mechanism for the Friedel–Crafts reaction.[4,5]

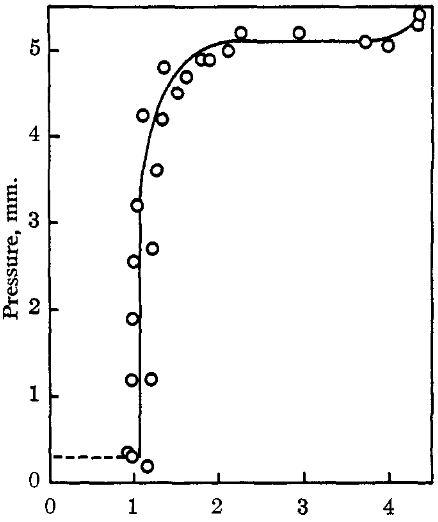


Fig. 4.—The methyl bromide–gallium chloride system at −80°.

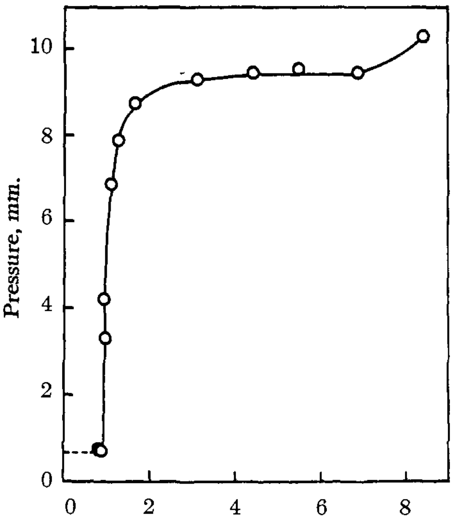


Fig. 5.—The methyl iodide–gallium chloride system at −46°.

It follows that the initial stage in the Friedel–Crafts reaction must be the formation of an addition compound between the alkyl halide and the Friedel–Crafts catalyst

$$RX + MX_3 \rightleftarrows RX:MX_3$$

This addition compound may or may not undergo ionization, depending upon a number of factors,

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[7] F. Fairbrother, *J. Chem. Soc.*, 503 (1945).

such as the nature of the alkyl group R and the experimental conditions. The possibility that the addition compound $RX:MX_3$ itself may be involved in the alkylation step of the Friedel–Crafts reaction should not be ignored.

Experimental Part

Apparatus.—All experiments were carried out in high vacuum system in which the materials came in contact only with glass and mercury. The general techniques are similar to those described by Sanderson[8] and in previous papers of this series.

The apparatus used for the precise study is shown in Fig. 6. The gallium chloride sample was sublimed into the reaction chamber A and methyl chloride from the reservoir C was condensed in the tube to form the solution. The amount of methyl chloride introduced was followed by the pressure change in the reservoir as read on the manometer N. Reaction vessel A contained a stirrer with a glass enclosed iron core which was activated by a solenoid and timer. Several glass beads in the vessel greatly improved the efficiency of the agitation. A sample of the pure solvent was placed in B. The tubes A and B were maintained at the desired temperature in a single bath until equilibrium had been reached and the decrease in the vapor pressure of the solution was measured directly on the manometer M with a cathetometer to the nearest 0.05 mm. The storage bulb C was immersed in a water-bath to minimize the effects of minor variations in the room temperature.

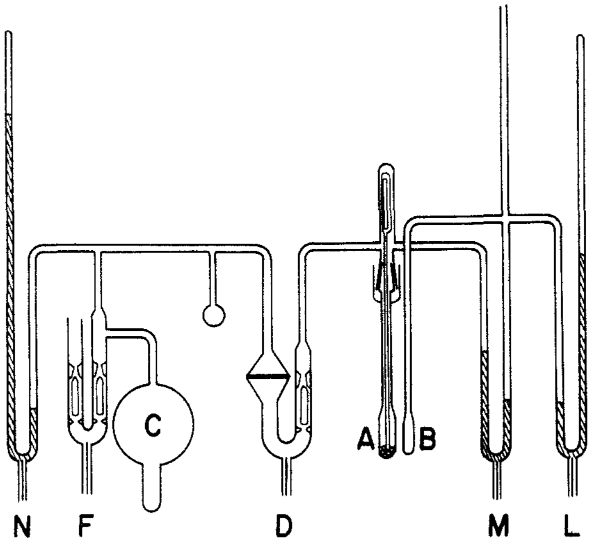

Fig. 6.—Apparatus used in the study of the methyl chloride–gallium chloride system.

To obtain the vapor pressure of a new composition, the valve D was carefully opened and a small quantity of the methyl chloride in the solution was allowed to volatilize from the reaction vessel A into the reservoir C. The float valve F leads to the main manifold of the high vacuum system.

The temperatures were maintained at −78.5° by the use of solid carbon dioxide at 760 mm., and at −64 and −50° by the use of solid–liquid slushes of chloroform and ethyl malonate, respectively. The constancy of the baths was checked by the constancy of the vapor pressure of pure methyl chloride on manometer L.

Materials.—Methyl chloride from a cylinder (Mathieson) was introduced into the vacuum apparatus and there fractionated. An entirely tensiometrically homogeneous product could not be obtained. Phase studies using this material gave erratic results. It was concluded that dimethyl ether was probably present as a contaminant. A sample of liquid methyl chloride was then maintained at −80° in contact with freshly sublimed aluminum chloride for 24 hours with frequent agitation. The product, distilled from a −80° bath, was tensiometrically homogeneous and was used for the phase studies.

Methyl bromide and methyl iodide were commercial products which were purified by fractional distillation in the high vacuum apparatus until they were tensiometrically homogeneous.

Preparation of Gallium Chloride.—The following procedure was developed for the preparation and transfer of small, accurately known samples of pure gallium chloride. A 500-ml. flask fitted with two side arms and a breaker tip was thoroughly degassed through one of the side arms. Dry air was admitted and the second side arm was opened. A small weighed ampule of 99.99% pure gallium metal (Alcoa) was then introduced into the bulb *via* this opening, which was then sealed off and the bulb again evacuated thoroughly. A measured quantity of hydrogen chloride (generally twice the quantity required) was introduced into the bulb and the flask sealed. The flask was then placed in a furnace at 300° and maintained at that temperature for 6 hours.

The flask was then connected to the reaction bulb A (Fig. 6) through a U-tube and the breaker tip in series. The excess hydrogen chloride was condensed in the flask with liquid nitrogen, the break-tip opened, the hydrogen present was removed, and the excess hydrogen chloride passed through the U-tube (−80°) into a calibrated measuring flask. This established that the reaction had proceeded quantitatively. The remaining gallium chloride in the flask was transferred to the attached U-tube (−80°) and the flask was then sealed off.

The tube A was now immersed in an ice-bath and a cone containing Dry Ice was placed around the constricted portion of the tube. The gallium chloride was next distilled from the U-tube into tube A. The U-tube was now removed by sealing, the Dry Ice cone removed, and the gallium chloride permitted to sublime down into the tip of the tube A maintained at 0°. In this way an accurately known sample of pure gallium chloride was obtained in the form of large colorless crystals in the tip of the reaction tube.

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(8) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y.