characteristic brown color that results from the reaction of Ga(I) salts with water. Magnetic stirring was limited to short periods of time so as to avoid unnecessary heating. Extractions were carried out three or four times, each for about 24 hours duration. Nearly all of the $Ga_2Br_4$ that can be removed comes off in the first solution, although this solution is far short of saturation. The solubility of $Ga_2Br_4$ in benzene is 5.64 g./100 g. solvent at 28°; the solid phase is a benzene complex of this salt.[11,12] The complex was not detected in powder patterns of the residue remaining after extraction with benzene. The solubility of GaBr in benzene is negligible.

Powder patterns were obtained with Ni-filtered Cu K$\alpha$ radiation and a 114.59 mm. Philips camera. Data for the stronger diffractions for the compounds of interest are as follows, in ångströms, with relative intensities in parentheses: $\alpha$-$Ga_2Br_4$: 3.93(5), 3.86(10), 3.54(8), 3.33(7), 3.18(8), 3.06(5), 3.02(5), 2.92(10), 2.89(10), 2.61(6), 2.44(8), 2.25(6), 2.008(6), 1.679(6). $\beta$-$Ga_2Br_4$: 5.37(7), 3.68(3), 3.17(4), 3.12(10), 3.05(9), 2.98(4), 2.83(7), 2.70(4), 2.65(4), 2.35(5), 1.824(9), 1.735(7), 1.542(4). $\alpha$-$GaAlBr_4$: 3.84(5), 3.54(4), 3.31(4), 3.17(10), 3.05(9), 3.00(9), 2.92(9), 2.88(10), 2.61(6), 2.42(6), 2.37(6), 2.25(6), 2.005(6), 1.676(6), 1.552(5). $\beta$-$GaAlBr_4$: 5.33(2), 3.19(10), 3.13(8), 3.04(9), 3.00(7), 2.87(10), 2.36(3), 2.25(4), 2.005(4), 1.676(4), 1.617(4). GaBr: 7.69(8), 3.84(6), 3.52(4), 3.18(6), 3.13(10), 2.96(10), 2.76(5), 2.70(5), 2.61(5), 2.57(5), 2.53(4), 2.33(5), 1.992(4), 1.925(4), 1.860(5), 1.768(6), 1.686(5). More nearly complete correspondence between the $Ga_2Br_4$ and $Ga(AlBr_4)$ $\alpha$ and $\beta$-forms is found when weaker reflections are also considered.

**Acknowledgment**.—The authors are indebted to Frank Albers for the measurement of the powder patterns and to Dr. Richard McMullan for some of the preliminary observations in this work.

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[11] R. E. Rundle and J. D. Corbett, THIS JOURNAL, **79**, 757 (1957).

[12] This has been identified as $C_6H_6 \cdot Ga_2Br_4$. Jacob Kleinberg, private communication.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

# A New Method for the Preparation of Gallium Dihalides and Some Observations on their Properties

BY RICHARD C. CARLSTON, ERNEST GRISWOLD AND JACOB KLEINBERG

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A simple, rapid method utilizing reaction between metallic gallium and mercury(I) or mercury(II) halides has been developed for the preparation of gallium dihalides. The compounds $Ga_2Cl_4 \cdot C_6H_6$ and $Ga_2Br_4 \cdot C_6H_6$ have been identified. The behavior of gallium dichloride in benzene solution toward hydrogen sulfide is consistent with the $Ga^I[Ga^{III}Cl_4]$ formulation.

There has been a recent revival of interest in the gallium dihalides, particularly with regard to their structure. X-Ray diffraction studies with crystalline gallium dichloride[1] have indicated it to consist of $GaCl_4^-$ tetrahedra and $Ga^{+1}$ ions. The Raman spectrum of the fused compound[2] also points to the formulation $Ga^I[Ga^{III}Cl_4]$. Independent evidence for this interpretation of the structure of the dichloride has been obtained by Corbett and coworkers.[3]

The present communication describes a novel, simple method for the preparation of gallium dihalides in essentially quantitative yield and, in addition, presents some observations which are most reasonably interpreted in terms of the Ga(I)–Ga(III) nature of gallium dichloride.

**Preparation of Gallium Dihalides.**—The most common method heretofore employed for the preparation of the dihalidss has essentially involved reaction of the trihalide with gallium metal, followed by removal of the more volatile trihalide by distillation.[4] The diiodide has been obtained also by direct union of stoichiometric quantities of the elements.[5] The dichloride also has been made by heating gallium metal in a stream of dry hydrogen chloride.[6] The preparation of dihalide from metal and trihalide requires rather elaborate equipment and is tedious and time-consuming. On the other hand, the preparative procedure described below, in which gallium metal is heated in a sealed Pyrex tube with the stoichiometric quantity of mercury(I) or mercury(II) halide, is simple and rapid and, moreover, gives practically quantitative yields of dihalide. The same reaction also has been carried out in the presence of benzene. It should be mentioned that gallium dichloride in admixture with the trichloride has been produced by reaction between silver chloride or lead(II) chloride and gallium metal.[7]

## Experimental

The halides employed were the chloride of mercury(I) and the chloride, bromide and iodide of mercury(II), all of C.P. quality. Mercury(I) iodide did not react with gallium metal even at temperatures in the neighborhood of 200°. Gallium of 99.96% purity (Aluminum Company of America) was stored under thiophene-free benzene and samples were pipetted into a weighed Pyrex reaction tube 9 × 70 mm. The tube was heated gently to remove adherent benzene and weighed. Essentially the stoichiometric quantity of mercury halide was added to the gallium, the reaction tube flushed with oxygen-free nitrogen, and sealed. The mixture was then heated to effect reaction; for mercury(I) chloride a temperature range of 100–175° was employed, for mercury(II) bromide 140–160°, and for mercury(II) iodide approximately 200°. The tubes were kept at these temperatures for 2–3 hr. to ensure complete reaction.

After the treatment described above, the tubes were cooled to room temperature, transferred to a dry box and opened. The liquid metal was poured into a weighed 25-ml. beaker, air dried and weighed. The metal was then treated with warm concentrated hydrochloric acid until the gallium had been extracted completely. The residual mercury was dried in a vacuum oven at room temperature and its weight determined.

The solids remaining in the reaction tubes were added to approximately 0.1 $M$ aqueous perchloric acid and the mixtures warmed to effect dissolution and oxidation of the

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[3] S. von Winbush, R. K. McMullan and J. D. Corbett, to be published.

[4] (a) L. S. Foster, *Inorg. Syntheses, IV*, 111 (1953); (b) J. D. Corbett, S. von Winbush and F. C. Albers, THIS JOURNAL, **79**, 3020 (1957).

[5] J. D. Corbett and R. K. McMullan, *ibid.*, **77**, 4217 (1955).

[6] W. C. Johnson, P. Hammond and H. Friedman, Progress Report, "The Chemistry of Gallium," Navy Contract N6-ori-20, Univ. of Chicago, Oct. 1–Dec. 1, 1947.

[7] K. Clusius and F. Hitzig, *Helv. Chim. Acta*, **33**, 506 (1950).

gallium compounds. The solutions were diluted to volume and aliquot portions taken for analysis of gallium and halide. Gallium was determined spectrophotometrically by the method of Moeller and Cohen.[8] Halide was determined by potentiometric titration with silver nitrate using a Beckman Model K Automatic Titrator.

Gallium dichloride and dibromide also were prepared as solutions in benzene, from which under suitable conditions crystalline materials could be obtained (see below). The preparative procedure was similar to that described above, except that about 5 ml. of thiophene-free benzene for each millimole of gallium was added to the reaction tube in a dry box before sealing and the tubes were heated at about 100° to effect complete reaction.

The results of the analyses for mercury produced and gallium and halogen in the products are shown in Table I.

TABLE I

PREPARATION OF GALLIUM DIHALIDES

| Reactants | | Products | |
|---|---|---|---|
| Mercury halide, mmoles | Ga, mmoles | Hg, mmoles | Atomic ratio halogen:Ga in solid |
| $Hg_2Cl_2$, 0.297 | 0.294 | 0.592 | 2.00 |
| 1.89 | 1.90 | 3.79 | 2.02 |
| 2.05 | 2.02 | 4.09 | 2.13 |
| 3.41 | 3.40 | 6.82 | 2.00 |
| 1.34[a] | 1.30 | 2.70 | 2.00 |
| 0.98[a] | 0.97 | 1.96 | 2.02 |
| $HgCl_2$, 1.94[a] | 1.89 | 1.92 | 2.13 |
| $HgBr_2$, 3.07 | 3.08 | 3.05 | 2.26 |
| 1.57 | 1.56 | 1.58 | 2.17 |
| 2.63 | 2.64 | 2.62 | 2.02 |
| 0.669[a] | 0.673 | 0.665 | 2.04 |
| $HgI_2$, 0.606 | 0.582 | 0.582 | 2.02 |

[a] Reaction carried out in benzene.

## Discussion

It is evident from the data of Table I that when gallium metal and mercury halides are brought together as described above mercury metal is produced in quantitative yield and materials with a halogen:gallium atomic ratio of 2:1 are formed. Proof that the gallium compounds obtained are identical with the dihalides produced by other methods is offered by the following observations. The chloride compound melted to give a colorless liquid at 175–176° (cor.); the value reported for the dichloride prepared by interaction of the trichloride and gallium metal is 170.5°.[9] Moreover, the hydrolytic behavior of the two compounds was identical. In agreement with the observation of Corbett and Hershaft,[10] the bromide was found to exist in two crystalline forms, one melting at 153° and the other at about 165°. Finally, the color of the solid iodide (yellow) and of the melt (deep red), as well as the X-ray powder pattern, were identical with the corresponding properties of the diiodide as described by Corbett and McMullan.[5]

Although there is evidence that gallium dichloride forms an addition compound with benzene, and there has been some speculation regarding its structure,[11] no report of the composition of such a compound has appeared. We have succeeded in isolating definite addition compounds of both the dichloride and dibromide with benzene. The dichloride was prepared in benzene in the manner described above. The benzene solution was then chilled to −5° and the solvent removed by pumping at this temperature. The white solid product which remained was brought to room temperature without apparent change. It was then dissolved in warm 1 *M* $HNO_3$ and analyzed for gallium and chloride. *Anal.* Calcd. for $Ga_2Cl_4.C_6H_6$: Ga, 38.80; Cl, 39.47. Found: Ga, 37.6; Cl, 40.1. The dibromide was made in a similar fashion and cooled to Dry Ice temperature, whereupon a white solid and a clear liquid were obtained. After removal of the liquid phase, the solid was warmed to room temperature. It was then dissolved in warm 1 *M* $HClO_4$ and analyzed. Another sample was prepared and treated in the same manner. Analytical data for both preparations are given below. *Anal.* Calcd. for $Ga_2Br_4 \cdot C_6H_6$: Ga, 25.96; Br, 59.50. Found: Ga, 26.0, 25.6; Br, 59.4, 59.6.

**Reaction of Gallium Dichloride with Hydrogen Sulfide.**—In view of the fact that various lines of evidence[1–3] have indicated gallium dichloride to be $Ga^{I}[Ga^{III}Cl_4]$, it seemed of interest to explore chemical reactions which might differentiate between the gallium(I) and the gallium(III) in the compound. To this end the action of hydrogen sulfide on gallium dichloride dissolved in benzene was studied. The results were qualitatively consistent with the proposed complex structure.

## Experimental

Gallium dichloride was prepared by reaction of mercury(I) chloride with gallium metal in the absence of solvent as described above, or by reduction of the trichloride with gallium.[4a] Solutions in benzene (*ca.* 1–2 millimoles of $GaCl_2$ in 40 ml. of thiophene-free benzene) were prepared in a dry box and transferred to a reaction tube equipped with gas inlet and exit tubes. Purified nitrogen was bubbled through each solution for a short period of time. Then dried hydrogen sulfide was passed into the solution until precipitation appeared to have ceased, whereupon the system was again flushed with nitrogen to sweep out hydrogen sulfide. During the course of precipitation appreciable quantities of hydrogen chloride were evolved from the benzene solution. The white precipitate which had formed was filtered in a dry box and allowed to stand until adherent benzene had evaporated, leaving a free-flowing powder. The benzene filtrate was shaken with warm 1 *M* $HClO_4$, the benzene phase separated, and the aqueous phase, after warming to remove residual benzene, analyzed for gallium and chloride. The white precipitate (or a portion of it) was added to dilute perchloric acid, the solution heated, and a stream of purified nitrogen passed through and into a measured volume of standard silver nitrate solution until precipitation of silver sulfide appeared to have stopped. The excess silver nitrate was titrated potentiometrically and the percentage of sulfur in the white solid determined from the quantity of silver nitrate consumed. The solution remaining after removal of sulfide was analyzed for gallium and chloride by the usual procedures.

In a number of cases a portion of the white precipitate also was tested for reducing character in the following manner. The material was treated with ammoniacal silver nitrate to yield a black solid. This solid was then stirred with deaerated sodium cyanide solution, leaving a black residue. That this residue was metallic silver, and not silver sulfide, was shown by the fact that after oxidation with concentrated nitric acid no test for sulfate was found in the solution which, however, gave a positive test for silver ion. In a control test, silver sulfide freshly precipitated from ammoniacal silver nitrate dissolved completely and rapidly in sodium cyanide solution.

## Results and Discussion

The sulfide precipitation experiments yielded a number of striking facts, all of which could be rea-

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[10] J. D. Corbett and A. Hershaft, *ibid.*, **80**, 1530 (1958).

[11] R. E. Rundle and J. D. Corbett, *ibid.*, **79**, 757 (1957).

sonably explained in terms of a $Ga^{I}[Ga^{III}Cl_4]$ formulation.

TABLE II

THE ACTION OF $H_2S$ ON $GaCl_2$ IN BENZENE

| Formula of starting material | $\frac{\text{Ga in soln.}}{\text{Ga in solid}}$ Predicted | Found | Atomic ratio Cl:Ga remaining in soln. |
|---|---|---|---|
| $GaCl_{2.00}$ | 1.00 | 0.97 | 3.03 |
| $GaCl_{2.02}$ | 1.04 | 1.05 | 3.03 |
| $GaCl_{2.10}$ | 1.22 | 1.24 | 2.95 |
| $GaCl_{2.14}$ | 1.33 | 1.25 | 3.00 |
| $GaCl_{2.11}$ | 1.25 | 1.05 | 2.99 |
| $GaCl^{a}_{2.05}$ | 1.11 | 1.01 | .. |

[a] This material was prepared by the method described in reference 4a.

In a majority of the precipitations the ratio of gallium in the solid to that remaining in the benzene solution was close to the ratio expected from the formula of the starting material, on the assumption that the compound contained both $Ga^{+1}$ and $[GaCl_4]^-$ and that the +1 gallium was precipitated. This point is brought out in Table II. In a number of cases the quantity of gallium in the solid exceeded appreciably that predicted from the formula of starting material. No explanation, beyond the possibility of coprecipitation, is offered for this.

Two additional significant facts came to light. First, as is seen from Table II, the chlorine: gallium atomic ratio in the benzene solution after precipitation was three, within experimental error, indicating that the gallium remaining was in the form of the trichloride. (It was noted in the Experimental section that appreciable chlorine was evolved as hydrogen chloride during precipitation. Moreover, as will be seen below, the precipitate contained chloride.) Second, only the precipitate possessed reducing power toward ammoniacal silver nitrate. Both these observations held even in situations where the precipitate contained more gallium than that expected from the formula of the starting compound.

The sulfide precipitate could not be characterized as a definite compound. The gallium content ranged from 33.4 to 51.3%; sulfide from 13.1 to 18.6%; and chloride from 13.2 to 20.0%. That the chloride was held quite firmly in the precipitate was demonstrated by the fact that neither extraction with benzene nor heating *in vacuo* to about 200° altered its content significantly.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BAYLOR UNIVERSITY]

# Anion Exchange of Titanium(IV) in Hydrofluoric Acid

BY PATRICK H. WOODS[1] AND LEONE D. COCKERELL

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The method of Fronaeus is used to show the existence of anionic fluoride complexes of titanium when the metal is dissolved in hydrofluoric acid. The color and oxidation state of the product has also been studied.

## Introduction

Investigators reporting on the dissolution of titanium in hydrofluoric acid disagree as to the nature and color of the product formed. Glatzel[2] suggests the formation of $TiF_4$, whereas Straumanis[3] indicates that the dissolution proceeds according to the equation

$$2Ti + 6HF \longrightarrow 2TiF_3 + 3H_2$$

The color of the resulting solution is said to be purple[4] by some investigators and green[3] by others. In strongly acid solutions ($pH < 2$) the existence of the $TiO^{++}$ ion usually is assumed.[5,6] As far back as 1908[7] the existence of $TiF_6^{=}$ ion has been suggested. More recently,[8] the failure to extract titanium salt with ether strongly suggests the possibility of an ionic product. If anionic complexes are formed, their existence can be shown by the method outlined by Fronaeus.[9] The purpose of the present investigation was to determine the color, oxidation state and nature of the product formed by the dissolution of titanium in hydrofluoric acid.

## Experimental

**Materials.**—Reagent grade chemicals were used throughout the investigation. Titanium metal (purified by iodide method) was obtained from the Fisher Scientific Co. Purity is better than 99.9%.[10]

Amberlite IRA-400, a strongly basic quaternary ammonium type resin, was converted to the fluoride form with concentrated solutions of potassium fluoride. It was washed until the effluent would no longer give the zirconium-alizarin lake test for fluoride,[11] backwashed, column dried and finally air-dried before use. Its moisture content (18.54%) and ion capacity (1.472 meq./g.) were determined by accepted techniques.[12]

**Preparation of Solutions.**—The stock solution was made in a polyethylene bottle by dissolving titanium metal in hydrofluoric acid. When titanium metal was dissolved in

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(1) Taken from a thesis presented by Patrick H. Woods in partial fulfillment of requirements for the Doctor of Philosophy degree.

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