[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Iodides of Lower Valent Aluminum

BY WALTER C. SCHUMB AND HOWARD H. ROGERS[1]

By the use of an electrodeless discharge at low pressures produced in the vapor of pure aluminum(III) iodide at a temperature not exceeding 50°, and condensing the iodine formed by means of a Dry Ice trap, a solid was obtained from the walls of the discharge tube. Exhaustive extraction with anhydrous benzene, followed by vacuum drying, yielded a buff-colored solid, the chemical analysis of which and the powder X-ray diffraction data are consistent with a mixture of metallic aluminum and a monoiodide, $(AlI)_n$. Freedom from free iodine or unchanged AlI_3 was assured by the absence of any volatile products when heated *in vacuo* for two hours at 200°. The existence of halides of lower valent aluminum, which had previously been strongly indicated by experiments with aluminum halides in the gas phase or in solution, is therefore corroborated by the isolation of solid products showing empirical compositions such as $Al_{1.22}I$.

Until recently, the existence of halides of lower valent aluminum had been considered doubtful.[2] Within the last few years, however, such compounds have been shown to exist in the vapor state,[3] while aluminum(I) ion has been shown to exist in solution.[4]

Klemm and Voss[5] sublimed a mixture of aluminum(III) fluoride and aluminum metal repeatedly *in vacuo*, obtaining a mixture which approached aluminum(I) fluoride in composition. It was concluded that a volatile monofluoride was produced which disproportionated on condensation into the metal and trifluoride.

Other work by Klemm[6] gave similar results for the chloride, bromide and iodide.

Aluminum(I) chloride was shown to exist in the vapor state in a spectroscopic investigation[3] of the high-temperature reaction between aluminum(III) chloride and aluminum, and Miescher[7] has described the band spectrum of aluminum(I) iodide. Moreover, according to calculations made by Irmann,[8] the lower aluminum halides should be capable of independent existence.

In the present work the method of the electrodeless discharge[9] was chosen because it uses a high-energy gas discharge that is capable of decomposing a volatile trihalide, while the temperature on the walls, upon which a monohalide would be expected to form, remains below 50°.

Preparation.—The apparatus used for the decomposition of aluminum(III) iodide was in the shape of an inverted U, one arm of which was 32 mm. in diameter while the rest of the apparatus was of 20-mm. Pyrex tubing. A glass capsule, filled with 40 g. of aluminum(III) iodide, evacuated and sealed, was placed in the 32-mm. arm, while an iron capsule containing metallic lithium was placed in the 20-mm. arm.

The 32-mm. arm of the apparatus was placed in the solenoid so that the lower end of the solenoid coincided with the upper end of the aluminum(III) iodide capsule, prepared as described below. The generator was turned on and the aluminum(III) iodide warmed until a discharge started, as evidenced by a purple glow in the portion of the tube within the coil. A dewar flask, filled with Dry Ice and trichloroethylene, was placed around the vertical 20-mm. tube in order to condense any iodine that might be formed.

Three runs were made with this apparatus: The first and second with an air stream directed at the coil for cooling, and the third without this cooling aid. The source of heat used to volatilize the aluminum(III) iodide in the first run was an oil-bath kept at 110–120° during the run, which lasted six hours. In runs 2 and 3 the heat generated by the discharge alone was used to volatilize the aluminum(III) iodide, so that all the volatilized material passed through the discharge zone, as it did in run 1. Run 2 required 13 hours, while run 3 needed 30 hours to volatilize all the aluminum(III) iodide. Power inputs varied from 25 to 175 watts, depending on the conditions in the discharge tube and the desired operating temperature.

After the completion of a run the trap contained solid iodine, and the walls of the main discharge tube were coated with a brown and black mottled solid deposit. The reaction tube was removed to a dry-box and broken open in order to remove the tenacious deposit on the walls. In one run the products were held so tightly (probably due to the long running time) that on removal they were found to be contaminated with bits of glass.

Chemical and Physical Tests.—A portion of the product removed from the tube used in run 1 was allowed to react with 5% sodium hydroxide solution and the gas evolved was collected in a eudiometer. Identification of the gas as hydrogen was accomplished by mixing a small amount of oxygen with the gas and igniting the mixture; whereupon an explosion occurred followed by a large decrease in volume. This hydrogen could only have come from the reaction of metallic aluminum, or of a lower valent aluminum compound, with the solution.

Further evidence that the product from the electric discharge contained a compound of lower valent aluminum was offered by the following data. The end of an evacuated Pyrex tube containing the products of the reaction was cautiously heated by means of an electric sleeve. The external temperature of the tube was registered by means of a thermocouple. At about 100° a minute quantity of iodine sublimed and collected on the cooler portions of the tube. Continued heating to about 200° resulted in a clear melt containing a brown solid in suspension, while a white deposit formed outside the hot zone of the tube. Further heating to approximately 300° produced no further visible change. By tilting the tube so that the liquid contents were caused to come into contact with the sublimed iodine, it was noted that the brown suspended material dissolved, but no purple coloration of the melt resulted, indicating that the iodine had reacted with the brown solid, converting it into a soluble, colorless material.

Since aluminum(III) iodide is freely soluble in benzene and a halide of lower valent aluminum would be expected to be less soluble, extraction with benzene seemed to be a logical separation technique. The first extraction with dry benzene formed a pale violet solution with a brown suspension, similar to the one noted above. This suspension was centrifuged and the extraction continued. The second ex-

---

[1] Taken in part from the thesis to be presented by Howard H. Rogers in partial fulfillment of the requirements for the Ph.D. degree in the Department of Chemistry.

[2] *Cf.* for example, J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 5, Longmans, Green and Co., London, 1924, pp. 301, 311, 324; J. N. Friend, "A Text-Book of Inorganic Chemistry," Vol. 4, Charles Griffin and Co., London, 1921, pp. 63–70.

[3] L. M. Foster, A. S. Russell and C. N. Cochran, THIS JOURNAL, **72**, 2580 (1950).

[4] A. W. Davidson and J. Kleinberg, Abstracts of Papers, Division of Physical and Inorganic Chemistry, A. C. S., Detroit, Mich., April, 1950, p. 50; A. W. Davidson and F. Jirik, THIS JOURNAL, **72**, 1700 (1950).

[5] W. Klemm and E. Voss, *Z. anorg. Chem.*, **251**, 233 (1943).

[6] W. Klemm, "FIAT Rev. of Ger. Sci., 1939–1946, Inorganic Chemistry," Part 2, Office of Military Government for Germany, Field Information Agencies, Technical, British, French, United States, 1948, p. 5.

[7] E. Miescher, *Helv. Phys. Acta*, **8**, 279 (1935).

[8] F. Irmann, *Helv. Chim. Acta*, **33**, 1449 (1950).

[9] W. C. Schumb, E. L. Gamble and M. D. Banus, THIS JOURNAL, **71**, 3225 (1949).

traction produced an essentially colorless solution, while the quantity of material remaining decreased markedly. After a number of extractions the volume of brown residue remained constant. It was dried under vacuum, yielding a light yellow-brown product.

The same procedure was employed in separating the product obtained in the second run, which yielded about 100 mg. of a buff-colored solid. Sublimation *in vacuo* at 200° was attempted on this material with no visible result within two hours, from which it may be concluded that the product could not have contained free iodine or aluminum(III) iodide in perceptible quantities, since these substances would have been detected when volatilized on heating. Since the product obtained was not readily volatile, its behavior on gradual, stronger heating was closely observed. For this purpose a simple furnace was constructed from a cylindrical brass block (50 × 60 cm.) wrapped with a nichrome heating element and asbestos insulation, and bearing a 6-mm. well centrally disposed in the cylinder. The sample was sealed in a Vycor tube in a helium atmosphere. Only the end of this Vycor tube was placed in the furnace well, so that the pressure was maintained approximately atmospheric during the heating. By the time the temperature had reached 700° the substance had become dark gray in color, and at 850° it was black. The small amount of a brown substance collected on the cooler portions of the tube was not sufficient to account for the volume shrinkage.[10] Examination of the black substance showed that it was a fine powder, insoluble in water, in 2 N sodium hydroxide, or in aqua regia. These results indicate that the black product was neither aluminum metal, as might have been expected, nor aluminum(III) iodide.

Analytical Results.—The product separated from run 2 was analyzed chemically and by an examination of the powder X-ray diffraction patterns. The results of chemical analysis showed the presence of 28.7% of inert material insoluble in 2 N sodium hydroxide, which had been filtered off at the beginning of the analysis. This inert material consisted essentially of particles of glass picked up when the product was scraped from the walls of the discharge tube. Since the yield is about 100 mg. as compared with about 40 g. removed from the tube, the inert material represents only 0.6% of the material originally removed from the discharge tube. The mole ratio of aluminum to iodine was found to be 1.22, corresponding to a mixture of some lower iodide and metallic aluminum. The presence of elementary iodine or of aluminum(III) iodide was ruled out by the evidence given above.

The analysis of the products separated from the two runs, and of the aluminum(III) iodide employed in the reaction, was conducted as follows: Approximately 20-mg. samples were loaded into glass-stoppered vials in a dry box and weighed immediately. The contents were dissolved in 0.5 N sodium hydroxide, after which they were neutralized with 5 N nitric acid to a pH of 2, using thymol blue as an indicator. The iodide was precipitated as silver iodide according to a procedure given by Kolthoff and Sandell.[11] To the filtrate 0.1 N hydrochloric acid was added in excess; the solution was boiled and filtered after standing an hour. Aluminum was precipitated as aluminum 8-hydroxyquinolate according to a standard procedure.[12] *Anal.* Found for product from run 2: Al, 14.8; I, 56.6, corresponding to $Al_{1.22}I$. Found for product from run 3: Al, 33.1; I, 65.0, corresponding to $Al_{2.47}I$. Found for AlI_3: Al, 7.20; I, 92.4. Calcd. for AlI_3: Al, 7.09; I, 92.9. The more essential X-ray diffraction data are shown in Table I.

TABLE I

X-RAY DATA. LOWER IODIDE PREPARATIONS

Run 2		Run 2[c]		Aluminum[13]		$Al_2O_3.H_2O$[13]	
d	I/I_1[a]	d[b]	I/I_1[a]	d	I/I_1	d	I/I_1
		6.19	0.5	...	..	6.20	0.72
4.0[d]	>1.0	4.0[d]	>1.0	...	..		
		3.14	0.1	...	..	3.16	1.00
		2.3[e]	.5	2.33	1.0	2.33	0.75
2.0[e]	0.5	2.0[e]	.5	2.025	0.60	1.976	.13
1.4[e]	0.3	1.4[e]	.3	1.43	.50	1.847	.83
		1.65	.5			1.656	.18
1.2[e]	0.3			1.21	.60	1.448	.18

[a] Estimated. [b] See also values for dots given in text. [c] Sample heated to 850°. [d] Diffuse line. [e] Broad band.

A film obtained from the product separated from run 2 showed an intense diffuse band at d 4.0 Å. indicative of an amorphous material. By comparison with a film obtained from metallic aluminum, very weak broad bands, corresponding to the strongest aluminum lines, were also found to be present. A film of the material heated to 850° was similar to that obtained from the unheated material and also showed three very weak lines, probably due to $Al_2O_3 \cdot H_2O$, and a series of dots, due to a small number of crystals.[14] The X-ray data are consistent with the conclusion, previously reached, that a lower iodide of aluminum was present.

A third run was made in an attempt to increase the yield of the desired product. By allowing the discharge tube to run at 100–200°, it was hoped that the aluminum(III) iodide would pass as a vapor through the entire discharge region rather than condense on the walls of the discharge zone due to the forced-air cooling. In other respects the conditions of the experiment were the same as in the other two runs. The product obtained in this case was a grayish-green powder which showed an atomic ratio of aluminum to iodine of 2.47. The X-ray results obtained from the separated product show the same intense diffuse band at d 4.0 Å., along with lines which correspond precisely with those of metallic aluminum. It is probable that the higher temperatures pushed the decomposition reaction too far, so that a higher proportion of metallic aluminum appeared in the product.

Aluminum(III) Iodide.—The aluminum(III) iodide used in these experiments was prepared by heating an excess of 99.9% pure aluminum with iodine, slowly added in a helium atmosphere. The pure white product was analyzed chemically and by X-ray diffraction. That portion of the X-ray data which contained results which differed significantly from the d-values obtained by Hanawalt, Rinn and Frevel,[15] is shown in Table II.

---

[10] This behavior is almost identical with that observed in a similar test on the first run.

[11] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Rev. Ed., The Macmillan Co., New York, N. Y., 1945, pp. 311–313.

[12] Ref. 11, pp. 327–328.

[13] X-Ray Diffraction Data Cards, A.S.T.M.

[14] By making a template and measuring the film, the d-values of these dots were calculated to be 2.59, 2.51, 2.35, 2.10, 1.61, 1.54, 1.42, 1.31, 1.29, 1.11, 1.04, 0.974, 0.943, 0.889, 0.867, 0.863, 0.837, 0.833, 0.80. They were found not to be due to any known compound.

[15] J. E. Hanawalt, H. W. Rinn and L. K. Frevel, *Ind. Eng. Chem.*, **10**, 457 (1938).

Agreement was very satisfactory at *d* values of 1.50 or less.

TABLE II

X-RAY DATA. ALUMINUM(III) IODIDE

Sample I		Sample II		Literature[15]	
d	I/I_1 (est.)	*d*	I/I_1 (est.)	*d*	I/I_1
				3.70	0.05
3.35	1.0	3.43	1.0	3.50	1.00
2.96	0.5	2.98	0.4	3.08	0.50
				2.98	.05
2.10	.7	2.13	.8	2.14	.50
1.80	.9	1.82	.8	1.84	.38
1.77	.2	1.80	.2	1.80	.10
1.73	.2	1.74	.2	1.75	.13

The differences in the highest *d*-values for the two samples may be due to a very slight hydrolysis, which had occurred during the time the capillaries were being loaded. This hydrolysis was evidenced by the development of a very faint yellow tinge, instead of the original pure white powder. The material giving the lower *d*-values had the fainter color, and would be expected to be the purer. Since Hanawalt, Rinn and Frevel do not give their method of preparation of aluminum(III) iodide, nor the purity of the material used in their work, no conclusion from the comparison of results can be drawn.

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 31, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Electrode Potentials in Liquid Ammonia. I. Activities of Potassium and Sodium Chlorides

BY JACOB SEDLET[1] AND THOMAS DE VRIES

The activity coefficients of potassium and sodium chloride in liquid ammonia at −36° were determined from electromotive force measurements of cells of the type: K(Hg), KCl(m), $ZnCl_2\cdot 6NH_3(s)$, Zn(Hg) and Na(Hg), NaCl(m), $ZnCl_2\cdot 6NH_3(s)$, Zn(Hg). The closest distance of approach of the ions and the degree of hydration was estimated according to the method of Stokes and Robinson.

In the development of the chemistry and thermodynamics of liquid ammonia solutions the investigation of galvanic cells should prove as valuable as with aqueous systems. While several cells employing liquid ammonia as the solvent have been measured, liquid junction potentials were present in most cases, and no attempt was made to extrapolate the data to obtain the standard potentials. Several investigators[2] have studied cells of the type: M, MA, M′A′, M′, where M and M′ are metals and MA and M′A′ are soluble salts of the metals. In most cases a salt bridge was interposed between the two half cells.

Two cells free from liquid junction potentials have been measured at 25°. Elliott and Yost[3] measured the cell: Zn(Hg), $ZnCl_2\cdot 6NH_3(s)$, NH_4Cl(m), Tl(s), Tl(Hg), and Garner, Green and Yost[4] the cell: Zn(Hg), $ZnCl_2\cdot 6NH_3(s)$, NH_4Cl(m), $CdCl_2\cdot 6NH_3(s)$, Cd(Hg). These cells were found to behave reversibly.

In this work the zinc amalgam, zinc chloride electrode was combined with alkali metal amalgam electrodes to form the cells: K(0.2756% amalgam), KCl(m), $ZnCl_2\cdot 6NH_3(s)$, Zn (2 phase amalgam), and Na(0.2000% amalgam), NaCl(m), $ZnCl_2\cdot 6NH_3(s)$, Zn (2 phase amalgam). The composition of solid zinc chloride under the experimental conditions was determined by Biltz and Messerknecht.[5] In the present investigation a stationary pool of amalgam was used, and no reaction between the amalgam and the ammonia could be observed. The cells were measured at −36°, using amalgams of constant composition and varying the salt concentration from approximately 0.002 molal to saturation.

Since no data on the solubility of zinc chloride could be found in the literature, this quantity was determined at −36°. The dielectric constant of liquid ammonia at −36° was also measured since it was needed in the calculations.

Experimental

Materials.—Commercial anhydrous ammonia was dried over sodium and passed through a sintered glass plug to remove solid particles before being condensed in the apparatus.

Zinc amalgam was prepared by electrolyzing a zinc sulfate solution between a mercury cathode and platinum anode until a two-phase amalgam, containing about 2% zinc, was obtained. Potassium and sodium amalgams were prepared by similarly electrolyzing a solution of their carbonates until the desired concentration was obtained. The amalgams were stored over nitrogen.

All salts, except zinc chloride, were reagent grade and were further purified by recrystallization. Zinc chloride was prepared by electrolyzing a zinc sulfate solution with platinum electrodes and dissolving the metal in hydrochloric acid. The solution was evaporated to dryness and the salt dehydrated by heating in a vacuum prior to use.

Apparatus and Procedure.—The thermostat consisted of a one gallon dewar vessel filled with acetone and cooled by alcohol circulated by a centrifugal pump through Dry Ice and then through the bath. A bimetallic regulator controlled the operation of the pump as the bath temperature varied. Temperatures were measured with a five junction copper–constantan thermel calibrated at the sublimation point of carbon dioxide. All measurements were made at −36 ± 0.05°.

The electromotive force cell was of the conventional type with platinum wires sealed into the bottom of the H-cell which was closed at the top with ball and socket joints. A sintered glass plug in the cross arm prevented solid zinc chloride from coming over into the sodium amalgam compartment. The amalgams and zinc chloride were put into the cell with a stream of dry and oxygen-free nitrogen passing through the apparatus. Solutions of salts in liquid

---

[1] Abstracted from the Ph.D. thesis of J. Sedlet, whose present address is Argonne National Laboratory, Chicago, Ill.

[2] F. M. G. Johnson and N. T. M. Wilsmore, *Trans. Faraday Soc.*, **3**, 77 (1907); G. I. Costeanu, *Compt. rend.*, **195**, 778 (1932); **197**, 1113 (1933); V. A. Pleskov and A. M. Monossohn, *Acta Physiochim.* (*U. R. S. S.*), **1**, 871 (1935); **2**, 615 (1935); **6**, 1 (1937); **13**, 659 (1940); **21**, 235 (1946).

[3] N. Elliott and D. M. Yost, THIS JOURNAL, **56**, 1057 (1934).

[4] C. S. Garner, E. W. Green and D. M. Yost, *ibid.*, **57**, 2055 (1935).

[5] W. Biltz and C. Messerknecht, *Z. anorg. Chem.*, **129**, 161 (1923).