silanes in the pressure experiments should have resulted in much lower percentages or even none of the chlorofluorosilanes, as was the case with carbon tetrafluoride. Therefore, it may be concluded that the chlorofluorosilanes apparently undergo extensive thermal disproportionation at 500°, whereas at lower temperatures, in the presence of aluminum chloride, no disproportionation was evident.[29] The disproportionation of the chlorofluorogermanes has been reported to take place even at −78°[5] and under the conditions of the reactions employed in this work, the existence of these compounds, if formed, would be transitory. Hence, no chlorofluorogermanes were formed in these reactions.

The order of increasing ability to undergo halogen exchange with metal halides may be stated as follows: reactivity increases → $CF_4 < SiF_4 < GeF_4$.

The lack of reactivity of carbon tetrafluoride is undoubtedly due to its closely-packed structure even though the heat and free energy for such reactions are favorable. High activation energies would be expected for these reactions, whereas, in the loosely-packed silicon and germanium tetrafluorides, the central atom is easily approached and normal activation energies are apparent.

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[29] The possibility of some catalytic activity on the part of aluminum chloride in furthering the disproportionation of the chlorofluorosilanes cannot be entirely excluded, however. For example, the fact that silicon tetrachloride represented a much higher per cent. (76%) of the total products formed in Run 2, Table IV, than in Run 5 Table III (23%), may conceivably be attributed to the fact that in the former case the products were held under pressure in contact with aluminum chloride.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

X-Ray Studies of Fused Salt Systems.[1] II. Indium(III) Iodide

BY R. E. WOOD AND H. L. RITTER

An analysis of the X-ray diffraction pattern of fused InI_3 by the method of Warren, Krutter and Morningstar is reported. The results indicate tetrahedral coördination of I atoms around In atoms rather than trigonal or octahedral coördination. The length of the In–I bond is 2.70 A. It is not possible to establish definitely from the radial distribution curve whether liquid indium iodide is predominantly monomeric or dimeric. It seems probable that both species are present. A geometrical configuration for the dimer which is consistent with the radial distribution curve is proposed.

Introduction

An earlier communication from this Laboratory[1] reported on the structure of aluminum chloride in the molten state. The stoichiometric similarity of $AlCl_3$ to InI_3 and the similarity of the ratio of covalent radii, Al/Cl and In/I, raise the question of whether there may not also be a structural similarity. The structure of InI_3 in the gaseous state has been studied by Brode[2] by means of electron diffraction. Studies of the structures of the liquid and solid states of this substance have not been reported. Brode proposed for the gas a structure consisting of a shared-edge double tetrahedron similar to that found by Palmer and Elliott[3] for gaseous aluminum chloride and to that reported from this Laboratory for liquid aluminum chloride. Stevenson and Schomaker[4] have re-examined Brode's data. They confirmed the existence of dimeric In_2I_6 under Brode's experimental conditions but were unable either to confirm or modify the conformation of the dimer proposed by Brode. We have now examined the X-ray diffraction pattern of liquid InI_3 in order to determine its structure and to compare it with the structure of liquid aluminum chloride.

Experimental

The indium iodide was prepared by gentle heating of a mixture of indium metal shavings and iodine crystals. After the exothermic reaction had subsided, the product was extracted with anhydrous ether and recrystallized twice from the same solvent. The resulting yellow crystalline powder was analyzed for indium using 8-hydroxyquinoline. Found: In, 23.10; calcd: In, 23.16. The anhydrous salt is extremely hygroscopic and the sample tube had to be filled in a dry atmosphere. The crystals in the sample tube were melted alternately under vacuum and atmospheric pressure in order to force all the liquid into one continuous body in the bottom of the capillary tube.

The camera and experimental arrangement have been described before.[1] Crystal-monochromated Mo-Kα radiation at 40 kv. and 20 ma. was allowed to irradiate the sample for 128 hours. The sample, held at 210° during the exposure, was contained in a Pyrex tube 0.31 mm. i.d. and 0.031 mm. wall thickness. The diffraction photograph was microphotometered on a Leeds and Northrup recording microphotometer and film densities used as a measure of relative intensity. The raw intensity curve was corrected for absorption, diffraction effects due to the container, polarization and incoherent scattering in the usual way. The fully corrected diffraction pattern, intensity *vs.* the diffraction angle, θ, is shown in Fig. 1. The intensity scale is absolute, the curve having been fitted at large diffraction angles to the calculated curve for the independent scattering of one In and three I atoms.

The procedure for reducing the data of Fig. 1 to a radial distribution curve has been described by its originators, Warren, Krutter and Morningstar[5] and by the present authors.[1] The density of liquid indium iodide was measured by pycnometer and taken as 4.35 g./cc. The "effective" atomic numbers, K_{In} and K_I, were taken as equal to the true atomic numbers. This is an excellent approximation for elements of high atomic number. The necessary numerical integrations were carried out using the trapezoidal rule and the International Business Machines CPC electronic computer.

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[1] Paper I of this series deals with aluminum chloride: R. L. Harris, R. E. Wood and H. L. Ritter, THIS JOURNAL, **73**, 3151 (1951).

[2] H. Brode, *Ann. Physik*, **37**, 344 (1940).

[3] K. J. Palmer and N. Elliott, THIS JOURNAL, **60**, 1852 (1938).

[4] D. P. Stevenson and V. Schomaker, *ibid.*, **64**, 2514 (1942).

[5] B. E. Warren, H. Krutter and O. Morningstar, *J. Am. Ceram. Soc.*, **19**, 202 (1936).

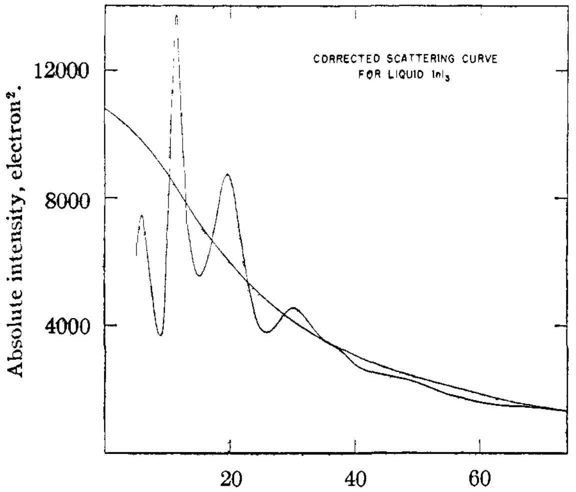

Fig. 1.—Fully corrected intensity curve for liquid InI_3. The superposed monotonic curve is the calculated scattering for independent In and I atoms.

Discussion

The radial distribution curve shows only two well-defined peaks (Fig. 2), occurring at atomic separations of 2.70 and 4.52 Å. There are also two poorly resolved peaks at 3.15 and 5.85 Å. and very slight bumps at about 7.6 and 9.0 Å.

The separation of 2.70 Å. must be assigned to the length of the covalent In–I bond. Pauling[6] gives 2.72 Å. as the sum of the covalent radii for In and I. Brode[2] reported 2.67 and Stevenson and Schomaker[4] gave 2.76 Å. for this distance in gaseous InI_3. The second peak at 4.52 Å. represents the I–I separation for which Brode reports 4.50 Å. The ratio of the interatomic distances corresponding to the first two peaks is 1.674. The ratio of edge-length to center-to-apex distance for a regular tetrahedron is 1.633 whereas the corresponding ratio for an equilateral triangle is 1.732. The area under the first peak is estimated to be 24000 electron². If the coördination number of indium is n, this area should be $2nK_{In}K_I$. The apparent coördination number is thus calculated to be 4.7. This number may be interpreted as either 4 or 5. It is too far from 3 for trigonal coördination to be likely; and a coördination number of 6 is out of the question because the ratio of edge-length to center-to-apex distance for a regular octahedron is only 1.414. It is to be expected that the average number of near neighbors in a molecular liquid be rather larger than the molecular coördination number because of intermolecular interference. On this basis, tetrahedral coördination of I atoms around In seems most likely in liquid InI_3.

A comparison of the radial distribution curve for InI_3 with that for $AlCl_3$ reveals both similarities and differences. In the first place, there is a great difference in the degree of resolution of all but the first two peaks. None of the remaining peaks up to 10 Å. is resolved in the case of InI_3 while all are resolved in the case of $AlCl_3$. This difference may be due to a much lower concentration of polymer in liquid InI_3 than in $AlCl_3$ or to a much greater rigidity of the Al_2Cl_6 dimer than of the polymeric InI_3. In the latter case, the longer interatomic distances in the relatively rigid Al_2Cl_6 molecule are preserved in the radial distribution curve while the corresponding distances in In_2I_6 may range over such large amplitudes that the smearing out nearly removes the peaks. As nearly as they can be fixed, however, the positions of the peaks in the indium iodide distribution show a considerable similarity to the positions of corresponding peaks for aluminum chloride.[7] Thus the ratios of the r-values for corresponding peaks in the two distributions are: 2.70/2.20 = 1.23; 4.52/3.60 = 1.26; 5.85/5.57 = 1.05; 7.60/6.52 = 1.16. The ratios of the covalent radii,[6] furthermore, are In/Al = 1.14 and I/Cl = 1.29. The over-all agreement among these ratios strongly suggests that fused indium iodide contains a dimeric species that is similar in structure to the double tetrahedron of the Al_2Cl_6 molecule, differing principally in being some 15–20% larger.

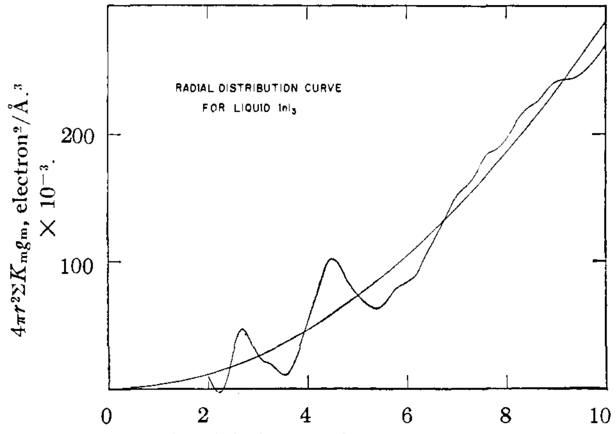

Fig. 2.—The radial distribution curve for liquid InI_3. The superposed monotonic curve is the average density function.

If the distances 3–6 and 3–7 (Fig. 3) are taken as 7.60 and 5.85 Å., respectively, the I–I distance 3–4 is fixed at 4.85 Å. The distance between the centers of a regular tetrahedron of edge-length about 4.5 Å. is about 3.2 Å. It is therefore reasonable to assign the observed peak at 3.15 Å. in the radial distribution curve to the distance between In atoms in the double tetrahedron. Placing In atoms at 1 and 2 in Fig. 3, distant 3.15 Å. apart, fixes the In–I distance 1–6 at 2.78 Å. and the In–I distance 1–3 at 5.12 Å. The former of these presumably forms a part of the peak at 2.70, the latter falls in the broadened right-hand side of the peak at 4.52.

There are four In–I distances of the type 1–6 and four of the type 1–5. The average of all eight is the observed value of 2.70. If the distance 1–6 is taken as 2.78 Å., the distance 1–5 would be about 2.62 Å. This assignment fixes the I–I distance 5–8 at 4.18 Å., also a part of the second broad peak.

The positions of all eight atoms of the dimer are now known, and all the interatomic separations may be computed. They are listed in Table I.

The weighted average of the four distances assumed to fall in the 4.52 Å. peak is 4.60 Å. The

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(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y.

(7) This circumstance was pointed out by one of the referees.

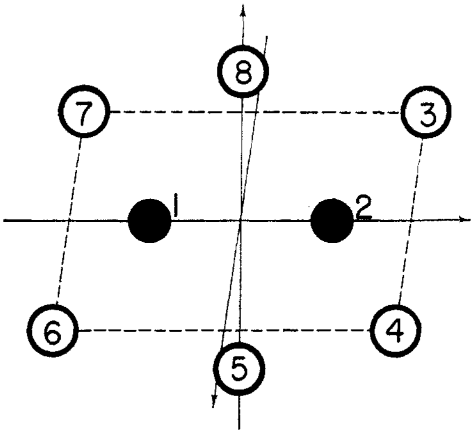

Fig. 3.—Model of dimeric In_2I_6 patterned after the structure of Al_2Cl_6. The open circles are iodine atoms and the full circles are indium atoms.

agreement here is quite satisfactory, since the weight of the 5.11 Å. distance in fixing the position of this peak is probably considerably less than its frequency would indicate; and more important, much of the peak is the result of intermolecular interference. For the contributions of 11 I–I distances and 4 In–I distances, the area under this peak should be

$$4K_{\text{In}}K_{\text{I}} + 11K_{\text{I}}^2 = 41300 \text{ electron}^2$$

The actual area is estimated to be about 99,000 electron². The difference, of course, is due to the large amount of intermolecular scattering, mostly between I atoms of adjacent molecules. The radius-sum for iodine atoms in van der Waals contact is about 4.3 Å., and interferences between such atoms would fall in the same peak. Such intermolecular scattering would increase the area under the peak but probably would not shift greatly the position of its maximum, since the total of all intermolecular interferences in this region occur over a wide range of distances with no strongly preferred separation.

Table I

Interatomic Distances in Fused Indium Iodide

Atoms	Type	Frequency	Distance	Observed peak
In–I	1–5	4	2.62	2.70
In–I	1–6	4	2.78	
In–In	1–2	1	3.15	3.15
I–I	5–8	1	4.18	4.52
I–I	5–6	8	4.34	
I–I	3–4	2	4.85	
In–I	1–3	4	5.11	
I–I	3–7	2	5.85	5.85
I–I	3–6	2	7.60	7.60

The dimeric structure whose geometry is detailed in Fig. 3 and in Table I will account for all of the prominences in the observed radial distribution curve except that at about 9 Å. The latter is believed to be due entirely to intermolecular scattering. It should be noted, however, that the uncertainty of the value 7.60 Å. assigned to the diagonal I–I distance 3–6, is reflected in all the distances listed in Table I except the I–I distance 3–7. The over-all reliability of these calculated distances is probably not better than about 0.1 Å. The reliability of the measured separations, when completely resolved in the radial distribution curve, we believe to be within 0.03 Å.

The resolution of all but the first two peaks in the radial distribution curve for InI_3 is very much poorer than in Al_2Cl_6. This circumstance seems to indicate that the proportion of dimer, In_2I_6, is relatively very low. No numerical estimate of the proportion of dimer (that is, of the value of the equilibrium constant for the dimerization) can reasonably be made from the X-ray data. It is interesting to note that the calculated scattering curves for monomeric InI_3 and for the dimeric structure In_2I_6 proposed above agree about equally well with the observed scattering curve. There is scarcely a choice between the structures on the basis of this agreement alone. Agreement between observed scattering pattern and the pattern calculated for a proposed model is normally used as a criterion of reliability of the proposed model in investigations using diffraction by gases. The criterion is much less suitable for the diffraction of X-rays by liquids because of the larger scattering contribution due to molecular interference.

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