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A Study of the Reaction Between Bismuth(III) Iodide and Amine Hydriodides

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Received August 31, 1967

Twenty seven compounds were prepared by the reaction of amine hydriodide salts with bismuth(III)-iodide. The melting point, densities and qualitative solubilities of the compounds were determined. Absorption spectra of the compounds were observed in a number of solvents. Analytical data indicated that four of the compounds had iodine to bismuth ratios of 4 to 1; three of the compounds had iodine to bismuth rations of 6 to 1; twenty of the compounds had iodine to bismuth ratios of 9 to 2.

Introduction

The synthesis of compounds of the type $R_xBi_yI_z$, where R represents an amine cation, were first reported by Kraut.[1] He reported the preparation of the following different species: $RBiI_4$; R_2BiI_5; $R_3Bi_2I_9$; $R_4Bi_3I_{13}$; $R_5Bi_3I_{12}$. Kraut also believed a number of different compounds could be made by varying the proportion of the reactants. The following compounds were reported by the reaction of dimethylanilinium iodide and bismuth iodide: $RBiI_4$; R_2BiI_5; $R_3Bi_2I_9$; $R_4Bi_3I_{13}$; $R_6Bi_5I_{21}$. Francios and Blanc[2,3] reacted bismuth(III)-iodide with a number of organic bases (primarily alkaloids) and reported the following different species: RBi_3I_{10}; $R_2Bi_3I_{11}$ and $R_3Bi_4I_{15}$. Four compounds with empiricial formulas of $RBiI_4$ were synthesized by Datta and Sen.[4] Quinoliniumtetraiodobismuthate(III) and tris-pyridiniumnonaiodobismuthate(III) were prepared by Vanino and Hauser.[5] The hexaiodobismuthate(III) salts of aniline, N,N-dimethylaniline, p-toludine and pyridine were reported by Bartholomew and Burrows.[6] The aniline and toluidine were yellow and the other two were red.

Pugh[7] reported the preparation of four tetraiodobismuthate(III) salts of different hydrazines. The tetraiodobismuthate(III) salt of hexamethyldiamino-isopropanol as reported by Aurisicchio.[8] The 8-hydroxyquinoline salt and four substituted derivatives of 8-hydroxyquinoline were reported to react with acid solutions of bismuth(III)iodide to form the tetraiodobismuthate(III) compounds by Laskar.[9] Orthophenanthroline was found to form a tetraiodobismuthate(III) salt when reacted with an acid solution of BiI_3 by Sutton.[10] Ahrland and Grenthe[11] calculated formation constants for the BiI_4^-, BiI_5^{2-} and BiI_6^{3-} ions. Their work also indicated there were no polymeric bismuth ions in solution.

Experimental Section

Materials. Bismuth(III)iodide solutions were prepared from reagent grade bismuth trioxide. The amines were the highest grade commercially available and were used without purification. All solvents used were reagent grade.

Synthetic procedure. The method of preparation was almost identical for the different compounds. A solution of bismuth(III)iodide, 0.5 molar with respect to hydrodic acid, was prepared by dissolving bismuth-(III) oxide in 47% hydriodic acid. The amine hydriodide salts were each prepared by addition of an excess of hydriodic acid to 0.25 moles of the particular amine. The amine salt was diluted to 200 ml. and a 50 ml. aliquot (0.25 mole) of the bismuth(III)iodide solution was added slowly with constant stirring.

The solid products were separated from the reaction medium by filtration with sintered glass crucibles, rinsed twice with 2-propanol and with diethyl ether and dried in a vacuum desiccator. The compounds were recrystallized from a 50% (in volume) solution of 2-propanone and 1 molar aqueous hydriodic acid.

Analytical procedures. Bismuth was determined by titration with EDTA using xylenol orange as an indicator. Approximately 0.2 g of the accurately weighed sample was placed in an erlenmeyer flask with 5 ml. of concentrated nitric acid and digested at low temperature until all the free iodine as removed and the remaining solutions were clear. The solution was diluted to 100 ml. with distilled water, the pH adjusted to 1.7 and titrated with standard EDTA solutions. The samples used for iodine determination were placed in

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(8) G. Aurisicchio, *Ind. Chim.* (Roma), 7, 1358 (1932).
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(11) S. Ahrland and I. Grenthe, *Acta Chem. Scand.*, *11*, 1111 (1957).
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25 ml. of 0.5 molar tartaric acid. Excess sodium hydroxide was added and the samples heated until the free amine was expelled. The pH of the solution was adjusted to 6 by the addition of tartaric acid and diluted to 200 ml. with distilled water. The iodine content was then determined by potentiometric titration with standard silver nitrate, using a silver indicating electrode and a mercury-mercurous sulfate reference electrode. The results of the analysis are shown in Table I.

Table 1.

		Bismuth (%)		Iodine (%)		m.p.
	Density g/cm³	Calcd.	Found	Calcd.	Found	Range °C
$(\text{iso-}C_3H_7)_2NH_2BiI_4$		25.52	25.5±0.1	62.00	62.2±0.2	182-186
$(\text{n-}C_3H_7)_3NHBiI_4$	2.96	24.28	24.5±0.1	58.97	58.9±0.1	146-147
$2\text{-}NH_2.C_5H_4NHBiI_4$	3.76	24.74	25.7±0.1	62.54	62.5±0.1	270-281
$2\text{-}CH_3.C_5H_4NHBiI_4$	3.65	25.78	25.9±0.1	62.61	62.3±0.2	199-201
$(CH_3)_4N_3BiI_6$	2.78	17.52	17.6±0.1	63.83	63.9±0.2	310 d
$(\text{n-}C_3H_7NH_3)_3BiI_6$	3.07	18.16	18.4±0.1	66.16	66.2±0.1	265-267
$((\text{iso-}C_3H_7)_2NH_2)_3BiI_6$	3.66	.6137	16.5±0.1	59.63	60.8±0.3	211-213
$((CH_3NH_3)_3Bi_2I_9)$	3.84	25.24	25.4±0.1 [a]	68.97	69.1±0.1 [a]	300 d
			25.3±0.1 [b]		68.8±0.1 [b]	
$((CH_3)_2NH_2)_3Bi_2I_9$	3.20	24.62	24.9±0.1 [a]	67.25	67.0±0.1 [a]	306 d
			25.0±0.1 [b]		67.3±0.1 [b]	
$(C_2H_5NH_3)_3Bi_2I_9$		24.62	25.0±0.1	67.25	67.1±0.2	311 d
$((C_2H_5)_2NH_2)_3Bi_2I_9$	3.19	23.45	23.6±0.1	64.09	64.1±0.2	259-262
$(C_2H_5)_3NH_3Bi_2I_9$	2.81	22.40	22.2±0.1	61.20	60.7±0.2	133-135
$((\text{n-}C_3H_7)_2NH_2)_3Bi_2I_9$	2.54	22.40	22.4±0.1	61.20	61.2±0.2	180-182
$(\text{n-}C_4H_9NH_3)_3Bi_2I_9$	2.97	23.46	23.8±0.1	64.10	64.0±0.3	274-275
$(\text{iso-}C_4H_9NH_3)_3Bi_2I_9$	3.02	23.46	23.7±0.1	64.10	63.8±0.2	241-249
$(H_3CCH(CH_3)CH_2CH(CH_3)NH_3)_3Bi_2I_9$	2.75	22.40	22.6±0.1	61.20	61.2±0.2	210-213
$(C_6H_5NH_3)_3Bi_2I_9$	3.25	22.69	22.2±0.1	62.00	62.6±0.3	171-175
$(\text{N-}C_2H_5.C_6H_5NH_2)_3Bi_2I_9$	3.16	21.70	21.7±0.1	59.29	58.9±0.2	179-181
$(C_5H_5NH)_3Bi_2I_9$	3.60	23.21	23.4±0.1	63.44	63.2±0.2	270-274
$(C_6H_{11}NH_3)_3Bi_2I_9$	2.92	23.00	23.2±0.1	62.81	62.6±0.2	301-305
$(3\text{-}CH_3.C_5H_4NH)_3Bi_2I_9$	3.55	22.69	23.0±0.1	62.00	62.0±0.2	150-156
$(4\text{-}CH_3.C_5H_4NH)_3Bi_2I_9$	3.10	22.69	22.9±0.1		61.9±0.3	203-205
$(C_2H_5)_4N_3Bi_2I_9$	2.85	21.42	21.6±0.1	58.55	59.1±0.2	287 d

Physical properties of the compounds. Each of the three types of compounds prepared in this work have a distinctive color. The R_3BiI_6 compounds are orange red, the $RBiI_4$ compounds are a dark red and the $R_3Bi_2I_9$ species are all crimson red. The compounds are all decomposed by water but are not hygroscopic and can be kept indefinitely in normal atmospheres. They are soluble in methanol, N,N-dimethyl formamide, acetonitrile, acetone and are somewhat less soluble in ethanol and 2-propanol. All of the compounds have slight solubility in diethyl ether and are practically insoluble in benzene chloroform and carbon tetrachloride.

The melting points or decomposition temperatures of the compounds were determined using a modified Thiele-Dennis melting point tube containing Dow Corning 550 silicone oil. The densities of the compound were measured with calibrated pcynometers by a displacement technique using carbon tetrachloride as the displaced liquid. The melting point and density data are shown in Table I.

The absorption spectra of the three types of complex iodo-bismuth salts were measured in the following solvents: methanol, nitromethane, acetone, N,N-dimethylformamide and acetonitrile. The spectra of a given salt are similar but not identical in the different solvents. The initial spectra of the different types of salts in a given solvent are different and vary with time. If sufficient time is allowed for the system to come to equilibrium the spectra are quite similar. The successive spectra of solutions, measured before sufficient time has elapsed to achieve equilibrium, are complex and show several different maxima. The nonaiodobismuthate(III) salts dissolve in acetonitrile to give red solutions which change relatively slowly through shades of orange and finally are clear yellow solutions. At different times the following maxima can be observed in the spectra of these solutions: 465, 360, 281, 242 and 226 mμ. The system does not follow Beer's law at any of these wavelengths. The same compounds will dissolve in methanol to give red solutions which very rapidly become yellow. The spectra of these salts after equilibrium has been achieved is practically identical to the spectra of BiI_3 in the same solvent. Apparently the variations of the spectra with time are due to solvation reactions in which solvent molecules are displacing the iodide ions from the complex. The rates of these reactions vary with the solvents and are dependent upon the Lewis base and/or the dielectric constant of the solvents. All three types of compounds have identical spectra in the presence of a large excess of iodide ion. They have a distinct maximum at a wavelength of 455 mμ with a molar absorbance of $8.5(\pm 0.1)\times 10^3$l/M-cm in methanol solution containing 0.1M/l of NaI. Aqueous solutions of the compounds with (HI) greater than 1.0M/l have a sharp absorption maximum at a wavelength of 465 mμ with a molar absorbance of 1.21 (± 0.05) $\times 10^4$l/M-cm. Beer's law is obeyed under both of these conditions.

Results and Discussion

The isolation of three different types of compounds in this work was an unexpected result. A procedure was followed which resulted in practically identical concentrations of bismuth, iodide and amine cations in the different preparations. Calculations, using the constants of Ahrland and Grenthe,[11] indicated that more than 90% of the total bismuth was in the form of BiI_6^{3-} with small amounts of BiI_5^{2-} and BiI_4^- present. A very large excess of both amine cation and iodide ion was maintained during and after the reaction, as the bismuth solution was added to the hydriodide solution and was precipitated almost immediately.

The reaction of di-iso-propyl amine hydriodide with the solution of bismuth(III)iodide was the only one which exhibited a tendency to form two different solid products from the common solution. The first product was in the form of dark red needle-like crystals. After standing a considerable period of time orange red flaky crystals were deposited. The dark red crystals were di-iso-propylammoniumtetraiodobismuthate(III) and the orange crystals were tris-di-iso-propylammoniumhexaiodobismuthate(III).

Tris-di-n-butylammoniumnonaiodobismuthate(III), tris-di-iso-butylammoniumnonaiodobismuthate(III) and tris-N-ethylaniliniumnonaiodobismuthate(III) formed heavy dark red oils as initial reaction products. After vigorous stirring in the reaction mixture the usual bright red crystalline solids were formed.

The reactions between methylammonium hydriodide and dimethylammonium hydriodide with bismuth(III)-iodide solutions were performed by two different methods in an attempt to determine the effect of the variation in the concentration of the amine salt on the reaction products. Data concerning the analysis of these products are listed in Table I as parts (a) and (b) for the respective compounds. Products corresponding to the (a) parts of these data were prepared from a 2 to 1 mole ratio of the ammonium salt to bismuth-(III)iodide, with the addition of the bismuth(III)-iodide to the salt solution. Compounds corresponding to the (b) parts of these data were prepared using a 1 to 2 mole ratio of ammonium salts to the bismuth-(III)iodide, with the addition of the salt solution to the bismuth(III)iodide solution. The analytical results indicate that the same compounds were prepared by both procedures. The only significant difference was in the quantity of product produced. The preparations with greater amounts of amine salt gave higher yields of product.

The final yield varied from 86 to approximately 100%, calculated in terms of the bismuth(III)iodide. The large excess of amine salt apparently causes the reaction to go nearly to completion. The variations in final yields were probably due to losses in the washing and recrystallization processes.

There is limited information concerning the geometry of these compounds in either the solid state or as ions in solution. The BiI_6^{3-} is probably octahedral. McPherson[12] *et al.,* reported the structure of 2-picoliniumtetraiodobismuthate(III) as determined by x-ray diffraction methods. The unit cell is composed of four molecules and each bismuth atom is surrounded by an irregular distorted octahedron of iodine atoms. Two iodine atoms in the octahedron are joined to a single bismuth atom with Bi-I bond lengths of 2.85 and 2.87 Å. Due to the distorted structure the Bi-I bond lengths of the other four are not equal, two having lenghts of 3.12 Å and the others with bond lengths of 3.25 and 3.49 Å. According to Ahrland and Grenthe[11] the $Bi_2I_9^{3-}$ ion does not exist in solution and no studies of its structure in the solid state have been published. Its structure could be postulated as binuclear with bismuth atoms at the center of two octahedra with a bridge of three bromine atoms. The analogous compounds $K_3W_2Cl_9$[13,14] and $K_3Cr_2Cl_9$[15] have been reported to have this structure.

The formation of a particular solid compound from solution is governed by a number of factors. The final product is the specific form which produces the greatest change in the free energy of the total system. The relative concentration of reacting species is the primary factor in determining the amounts of different complex ions at equilibrium in a given solution. The assumption is often made that a solid product in equilibrium with a solution will, to a great extent, be controlled by the relative concentration of species in solution. However, if the rate of change from one form to another is rapid the solution can adjust to furnish a minor constituent to a second phase. This is apparently the case in the systems studied, as three types of solid products were obtained from almost identical concentrations of reacting species. Also, attempts to alter the species by variations of concentration failed. Apparently the lattice free energy is the most important factor in determining the stoichiometry of the final product.

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