which received 250 mg. per Kg. of cystine, while the controls show a still higher percentage of survival at the end of the twenty-three day period of observation. With 7.5 mg. per Kg. of neoarsphenamine the results from the two cystine experiments are anomalous but here again the controls show a definitely higher percentage of survival at the end of the observation period. At the 9.0 mg. per Kg. dose the percentage of survivals is not very different for animals receiving 250 mg. per Kg. of cystine and the controls are somewhat higher for those receiving 500 mg. per Kg. of cystine. However, since the 9.0 mg. per Kg. dose of neoarsphenamine is almost the Minimal Sterilizing Dose in rats infected with *T. equiperdum* it would be expected that the effect of cystine would be less noticeable. Further, the number of animals tested at this dosage was smaller than at 5.0 mg. and 7.5 mg. per Kg. greatly increasing the possibility of error.

The results show clearly that the trypanocidal effectiveness of neoarsphenamine is materially reduced by the administration of cystine during the period of neoarsphenamine therapy.

We gratefully acknowledge the assistance of the Biological Laboratories of E. R. Squibb & Sons in conducting the biological tests reported herein.

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THE CHEMICAL NATURE OF IODOBISMUTHIC ACID AND ITS RELATION TO THE CHEMISTRY OF THE ALKALI IODIDE. COMPOUNDS OF BISMUTH IODIDE.*

BY A. E. JURIST AND W. G. CHRISTIANSEN.[1]

Recently Motard (1), François (2), Delwaulle (3) and François and Delwaulle (4) have identified a number of alkali metal iodide compounds of bismuth iodide and antimony iodide. While studying the chemistry of Iodobismitol, which is a solution of sodium iodobismuthite and sodium iodide in a glycol, preferably propylene glycol, the structural characteristics of the compound sodium iodobismuthite have been investigated. A compound which might be an iodobismuthic acid, having the formula BiI_3, HI, 3 H_2O, has already been isolated by Arppe (5) but no relation between it and the alkali metal iodide-bismuth iodide compounds has yet been shown.

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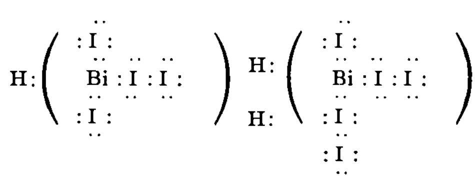
Noyes, Hall and Beattie (6) studied the solubility of bismuth oxychloride in hydrochloric acid and thereby reached the conclusion that there were probably chlorobismuthic acids having the formulas $HBiCl_4$ and H_2BiCl_5. Similarly, by studying the solubility of bismuth oxyiodide in hydriodic acid, applying the method of Noyes, Hall and Beattie, we have determined that there are two iodobismuthic acids of the formula $HBiI_4$ and H_2BiI_5 analogous to the two chlorobismuthic acids described above. It is not unlikely that the corresponding chloro- and iodo-antimonic acids could be demonstrated.

If the results of this work are combined with the demonstrated fact that bismuth is in the anion in sodium iodobismuthite (7) it is quite probable that sodium iodobismuthite as used in Iodobismitol is a salt of the iodobismuthic acid H_2BiI_5. Similarly it is probable that all the alkali metal iodide compounds of bismuth and antimony iodides described by François and Delwaulle (*loc. cit.*) represent alkali metal salts of iodobismuthic acids or iodoantimonic acids. If we consider the structure of the two iodobismuthic acids in the light of modern theories the following arrangements appear possible for $HBiI_4$ and H_2BiI_5.



In these two acids bismuth iodide remains unaltered. In the acid $HBiI_4$ it, together with the iodide ion from one molecule of hydriodic acid, yields the complex anion, BiI_4; the hydrogen atom from the hydriodic acid is attached to this entire anion—the latter has one free electron which is set free when the two iodine atoms become attached as indicated above. Similarly in the acid H_2BiI_5 two iodine atoms from two molecules of hydriodic acid together with the molecule of bismuth iodide, yield the anion BiI_5, and two electrons are set free so that this acid has two ionizable hydrogen atoms, instead of one, as in $HBiI_4$. In both cases the electronic character of the bismuth is unchanged from that in bismuth iodide. A distinction is being made between the electrical character of the bismuth atom and the character of the group containing it.

These two structures would then readily account for the existence of salts in which alkali metals occupy the positions indicated above for hydrogen atoms. In the salts such as the sodium iodobismuthites the bismuth is, as in the case of the acids, part of an anion which is electronegative in character. The presence of the bismuth in the complex anion such as shown here accounts for the fact that bismuth in Iodobismitol upon electrolysis migrates as a part of the anion without itself being electronegative.

EXPERIMENTAL.

The method used was to place two Gm. of bismuth oxyiodide in an ampul with 10 cc. of hydriodic acid, varying the concentration of the latter with each experiment. The ampuls were sealed and rotated in a constant temperature bath for 72 hours or longer at 25° C. The ampuls were then opened and specific gravity, iodine and bismuth determinations were made on the clear supernatant layer. The solid phase was also assayed for its bismuth and iodine content in order to determine whether any changes in its composition had taken place. These assays showed that the solid phase changed gradually from bismuth oxyiodide to bismuth iodide with increasing acid concentrations and that the major portion of the solid phase was bismuth iodide in all experiments in which the bismuth concentration in solution became considerable.

The method of calculating the mass action constants at the different acid concentrations follows that of Noyes, Hall and Beattie (6). Briefly, it is as follows. The reaction between the bismuth oxyiodide and hydriodic acid is expressed by the following three equations.

$$BiOI + 2HI = BiI_3 + H_2O \quad (1)$$
$$BiOI + 3HI = HBiI_4 + H_2O \quad (2)$$
$$BiOI + 4HI = H_2BiI_5 + H_2O \quad (3)$$

In order to set up from these equations the formulas representing the mass-action constants it is necessary to assume that $HBiI_4$ and H_2BiI_5 have the same degree of ionization as hydriodic acid. The concentration of hydrogen ion is calculated by subtracting three times the bismuth concentration from the iodine concentration since the concentration of hydrogen ion from hydriodic acid must equal the iodide ion from the same source while the concentration of iodide ion from hydriodic acid must equal the total iodine content minus that present as bismuth iodide (BiI_3). The actual hydrogen ion is then calculated by multiplying the latter difference by the degree of ionization of hydriodic acid at the concentration determined. The three mass-action equations corresponding to (1), (2) and (3) are respectively:

$$\frac{\Sigma Bi}{(\Sigma H)^4\gamma^4} = K \quad (4)$$

$$\frac{\Sigma Bi}{(\Sigma H)^2(\Sigma H - \Sigma Bi)^3\gamma^4} = K_1 \quad (5)$$

$$\frac{\Sigma Bi}{(\Sigma H)^2(\Sigma H - 2\Sigma Bi)^4\gamma^4} = K_2 \quad (6)$$

In these equations ΣBi and ΣH represent the total dissolved bismuth and total hydrogen-ion concentrations in atomic weights per 1000 Gm. of water and the term γ represents the degree of ionization of hydriodic acid at the hydrogen-ion concentration existing in the experiment. The calculation of the mass-action constants K, K_1 and K_2 would have been more accurate had the activity coefficient for hydriodic acid been available, substituting it in these equations for the degree of ionization. The degree of ionization of hydriodic acid was calculated for the different concentrations from the conductivity data for hydriodic acid given in "International Critical Tables," Volume 6.

The data obtained in these solubility studies and the constants calculated from them are given in the following table. All concentrations are expressed in terms of atomic weights per 1000 Gm. of water.

TABLE I.

Experiment Number.	Density of Solution at 25° C.	Iodine Concentration.	Bismuth Concentration ΣBi.	Hydrogen Concentration ΣH.	Degree of Ionization of HI γ.	K.	K_1.	K_2.
1	0.9952	0.1802	0.0260	0.1022	0.930	318.6	7521.4	563470.0
2	0.9934	0.1847	0.0189	0.1280	0.920	98.23	1240.0	22920.0
3	0.9953	0.1528	0.0076	0.1300	0.920	37.14	342.3	3928.5
4	0.9955	0.1877	0.0170	0.1367	0.920	69.54	740.4	12407.0
5	1.0349	0.4971	0.0546	0.3333	0.885	7.212	37.01	359.0
6	1.0955	0.9809	0.1624	0.4937	0.868	4.816	21.11	1661.7
7	1.1731	1.5945	0.2886	0.7287	0.837	2.085	12.99	2511.4
8	1.1924	1.8206	0.3286	0.8348	0.820	1.497	8.041	1278.5
9	1.2451	2.3571	0.4590	0.9801	0.810	1.155	7.844	92142.0
10	1.3070	2.7756	0.5489	1.1289	0.788	0.877	5.725	1515300.0

All concentrations are given in terms of atomic weights per 100 Gm. of water.

The foregoing data show that an equilibrium exists between two acids of the formula $HBiI_4$ and H_2BiI_5. When the results obtained for K, K_1 and K_2 as given in the foregoing table are plotted using the logarithms of K, K_1 and K_2 against ΣH, the hydrogen concentration, this will become apparent. These curves show that the reaction between bismuth oxyiodide and hydriodic acid is neither a fourth order reaction nor a fifth order reaction but an equilibrium between the two.

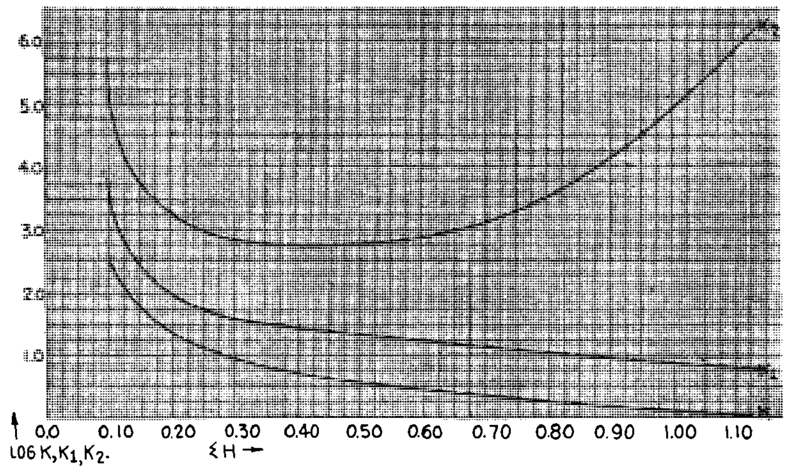


Fig. 1.

This means, then, that iodobismuthic acid is a mixture of two acids $HBiI_4$ and H_2BiI_5. Therefore salts of both acids can exist.

SUMMARY.

By studying the solubility of bismuth oxyiodide in hydriodic acid the existence of two iodobismuthic acids, $HBiI_4$ and H_2BiI_5, has been demonstrated. This indicates that the sodium iodobismuthites are salts of these acids. The bismuth in these salts is anionic in that the bismuth iodide molecule has become part of a complex anion.

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OUR RESPONSIBILITIES.

As one looks around we are concerned with the status of personal character, the disregard of responsibility. Education is essential for all, but personal character shapes the results of education. No age nor time has been free from selfish motives nor individual yield to self-gratification.

Perfection cannot be credited to any one group nor all imperfections charged to the other—that is secondary to coöperation for results.