[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Studies on Hydrolyzed Bismuth(III) Solutions. Part I. E.m.f. Titrations[1]

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The hydrolysis of the aquo Bi(III) ion has been studied in solutions with $[ClO_4^-] = 1.00$ *M* by a *p*H titration method. The data agree with the results of investigations on solutions with $[ClO_4^-] = 3.00$ *M* in that one main complex, $Bi_6O_6^{+6}$, is formed in solutions where less than 2 hydroxide ions are bound per bismuth atom. At high *p*H values, there is evidence for the formation of a more basic complex, $Bi_6O_6(OH)_3^{+3}$. The values for the equilibrium constants obtained were

$$6Bi^{+3} + 6H_2O \rightleftharpoons Bi_6O_6^{+6} + 12H^+ \qquad \log \beta_{12,6} = -0.53$$

$$Bi_6O_6^{+6} + 3H_2O \rightleftharpoons Bi_6O_6(OH)_3^{+3} + 3H^+ \qquad \log K_{15.6} = -8.1$$

The value of $\beta_{12,6}$ reported for solutions with $[ClO_4^-] = 3.00$ *M* is slightly greater than the value found for solutions with $[ClO_4^-] = 1.00$ *M* because of the lowering of the free energy of the hexameric species in solutions of high ionic strength.

The question of just what species are present in hydrolyzed solutions of Bi(III) salts has led to several investigations during approximately the last decade. In 1947, Granér and Sillén[3] reported that the hydrolysis proceeded by a continuous polymerization process yielding a highly polydisperse system. Souchay and Peschanski[4] studied the hydrolysis reaction by a spectrophotometric technique and proposed that one complex predominated and that this complex contained more than 3 bismuth atoms. Faucherre[5] has reported the existence of a more basic complex than that corresponding to a (OH^-):Bi ratio of 2 and has proposed the formula $Bi_8(OH)_{20}^{+4}$. Potentiometric titrations with a glass electrode were used to study the reaction. Holmberg, Kraus and Johnson[6] found a degree of polymerization[7] of 5 or 6 using sedimentation equilibrium measurements in the ultracentrifuge. Olin,[8] using bismuth amalgam and glass electrodes, studied the hydrolysis in solutions with $[ClO_4^-] = 3.00$ *M* over a wide range of total bismuth concentrations and explained the data in terms of the existence of a single polymer $Bi_6O_6^{+6}$ together with small amounts of the monomer $BiOH^{+2}$.

During the course of an investigation of the light scattering by highly hydrolyzed $Bi(ClO_4)_3$ solutions, it was necessary to make a detailed study of the variation, at high *p*H, of the average number of hydroxide ions bound per bismuth atom, *Z*, all in the constant ionic medium with $[ClO_4^-] = 1.000$ *M*. This investigation was made to obtain more information on the hydrolysis reaction at high *p*H values where $Z \simeq 2.0$, in particular to determine whether complexes more basic than those with 2 OH^- per Bi(III) are formed.

Experimental

Materials.—Bismuth(III) perchlorate solutions were prepared by dissolving weighed amounts of reagent grade Bi_2O_3 in warm concentrated perchloric acid. The solutions were filtered and the bismuth was determined as the oxyiodide and the phosphate. The results of the determinations agreed within 0.1%. The total perchlorate content of the stock solutions was determined by passing a definite volume of the solution, which contained a sufficiently large hydrogen ion concentration to reduce the hydrolysis to a negligible amount, through the hydrogen ion form of the cation exchange resin Dowex-50W-X8. The eluate was titrated with standard NaOH which gives the total perchlorate ion concentration and the analytical excess of H^+, denoted by *H*, was calculated from $H = [ClO_4^-] - 3[Bi^{+3}]$. Standard sodium hydrogen carbonate and perchloric acid solutions were prepared from reagent grade chemicals. Sodium perchlorate and silver perchlorate solutions were prepared as described elsewhere.[9] Nitrogen gas was purified by washing with 10% H_2SO_4, 10% NaOH, distilled water and finally 1 *M* $NaClO_4$.

Apparatus and Procedure.—The hydrogen ion concentration of the solutions was determined with the cell

Glass electrode|solution S||1 *M* $NaClO_4$||15 m*M* Ag^+,
985m*M* Na^+ 1000 m*M* ClO_4^-|AgCl|Ag (1)

The general design of the cell has been described earlier.[9] The hydrogen ion concentration was obtained from the measured e.m.f. values using the relation

$$E = E' - 59.16 \log h \tag{2}$$

where *h*, the hydrogen ion concentration, is in m*M*/l. The empirical constant *E'* was obtained by titrating standard perchloric acid with sodium hydrogen carbonate solutions and *vice versa* covering the range of hydrogen ion concentrations from the neutral point to 300 m*M*. The experimental values of *E'* were plotted as a function of *E* for use in solving (2). Up to hydrogen ion concentrations of *ca.* 150 m*M*, *E'* could be described as a linear function of *h*, *i.e.*, $E' = E^0 + kh$. The values of E^0 were reproducible from day to day to about 0.05 mv. The factor *k* corrects for variations in $\gamma_\pm$ and liquid–liquid junction potentials and for deviations of the glass electrode from the Nernst slope. This was found to be considerably larger than the value for similar cells with $[ClO_4^-] = 3.00$ *M*, as is to be expected. The value of *k* was 0.060 mv./m*M* and was reproducible to *ca.* ±5%, while the value with 3 *M* ClO_4^- is about 0.0167 mv./m*M*.[9,10] The day to day reproducibility of *k* is the limiting factor determining the accuracy with which *h* can be measured. At values of *h* greater than 150 m*M*, the value of *k* gradually decreased, and at *h* = 300 m*M*, the uncertainty in *E'* approaches ±0.3 mv.

A Beckman Type 40498 glass electrode was used, and the potentials of the cell were read to 0.01 mv. with a Leeds and Northrup K-2 potentiometer using a Cary Model 31 Vibrating Reed Electrometer as a null point indicator. All measurements were carried out in an oil thermostat controlled to 25 ± 0.1°. The entire apparatus including the thermostat was enclosed within an aluminum box to provide electrostatic shielding for the high impedance circuit, and this equipment was located in a room thermostated at approximately 25°.

The titrations were made in the following manner. Exactly 50.00 ml. of a solution with [Bi(III)] = *B*, *H* the

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[3] F. Granér and L. G. Sillén, *Acta Chem. Scand.*, **1**, 631 (1947).

[4] P. Souchay and D. Peschanski, *Bull. soc. chim. France*, 439 (1948).

[5] J. Faucherre, *ibid.*, 253 (1954).

[6] R. W. Holmberg, K. A. Kraus and J. S. Johnson, THIS JOURNAL, **78**, 5506 (1956).

[7] The degree of polymerization is the number of metal atoms in the complex in a monodisperse system and the weight average number of metal atoms in the complexes in a polydisperse system.

[8] (a) Å. Olin, *Acta Chem. Scand.*, **11**, 1445 (1957); (b) F. Granér, Å. Olin and L. G. Sillén, *ibid.*, **10**, 476 (1956).

[9] R. S. Tobias, *ibid.*, **12**, 198 (1958).

[10] G. Biedermann and L. G. Sillén, *Arkiv Kemi*, **5**, 425 (1953).

analytical hydrogen ion concentration = 0, and $[ClO_4^-]$ = 1.00 *M* was pipetted into the titration flask. This solution, designated S in (1), then was titrated with either a bismuth solution also of concentration *B* but with $H = 600$ to 800 m*M* or with equal volumes of standard sodium hydrogen carbonate and a bismuth solution of concentration 2*B* and $H = 0$. In this way, the hydrolysis could be studied over a wide range of hydrogen ion concentrations. A strong stream of nitrogen was passed through the solutions during the titrations. Steady values of the cell e.m.f. were obtained within a few seconds and remained constant to within ±0.1 mv. over a period of 24 hr. At high *p*H values, the solutions were checked carefully for the presence of a Tyndall effect. It was observed that the potentials began to drift as soon as the first traces of a solid phase appeared, and no measurements were made under these conditions.

Results and Discussion

The titration curves are presented in Fig. 1. The *p*H of the solutions is plotted as a function of the degree of neutralization $n = -H/B$, *i.e.*, the equivalents of base added per gram atom Bi(III). Since Olin[8] has made a detailed study of the variation of $[Bi^{+3}]$ with *p*H in solutions with $[ClO_4^-]$ = 3.00 *M*, it is of interest to compare the results of this experiment with his in the *p*H range where the measurements overlap. A plot was made of the average number of hydroxide ions bound per bismuth atom, $Z = (h - H)/B = n + h/B$, as a function of log *h* with *B* as a parameter for $0 \leqslant Z \leqslant 2.0$. A family of parallel curves $Z(\log h)_B$ was obtained with constant displacements along the abscissa corresponding to the difference ratio $(\Delta \log B/\Delta \log h)_Z = t = 2.3 \pm 0.15$.

The experimental curves $Z(X)$, where $X = \log B - t \log h$, were compared with theoretical curves $Z(\mathbf{X})$ calculated for the reactions producing only one polymer with an OH:Bi(III) ratio of 2.[11] The theoretical curves were obtained as follows. The new variable **X** is defined by the relation

$$\mathbf{X} = X - X_{Z=1} + \alpha \qquad (3)$$

where $X_{Z=1}$ is the value of X at $Z = 1$ and α is an arbitrary parameter, as yet undefined, which establishes the position of the curves along the abscissa, *i.e.*, they pass through the point $Z = 1$, $\mathbf{X} = \alpha$. Considering the general reaction with equilibrium constant β_n

$$n\mathrm{Bi}^{+3} + 2n\mathrm{H_2O} \rightleftharpoons \mathrm{Bi}_n(\mathrm{OH})_{2n}{}^{+n} + 2n\mathrm{H}^+ \qquad (4)$$

$$B = b + nh^{-2n}b^n\beta_n \text{ where } b = [\mathrm{Bi}^{+3}] \qquad (5)$$

$$\text{and } Z = (h - H)/B = \frac{2nh^{-2n}b^{n-1}\beta_n}{1 + nh^{-2n}b^{n-1}\beta_n} = \frac{2n(h^{-t}b)^{n-1}\beta_n}{1 + n(h^{-t}b)^{n-1}\beta_n} \qquad (6)$$

where $t = (\partial \log B/\partial \log h)_Z = 2n/(n - 1)$

By definition

$$X = \log B - (2n/(n - 1)) \log h = \log Bh^{-2n/(n-1)} \qquad (7)$$

Solving equation 6 for *b* as a function of *Z* and *h* and substituting this into equation 5 gives B as a function of *Z* and *h*. This expression is then substituted into equation 7 giving

$$X = \frac{1}{(n-1)} \log Z - \frac{1}{(n-1)} \log (n(2 - Z)\beta_n) + \log (2/(2 - Z)) \qquad (8)$$

$$\text{At } Z = 1,\ X_{Z=1} = \log 2 - \frac{1}{(n-1)} \log n\beta_n \qquad (9)$$

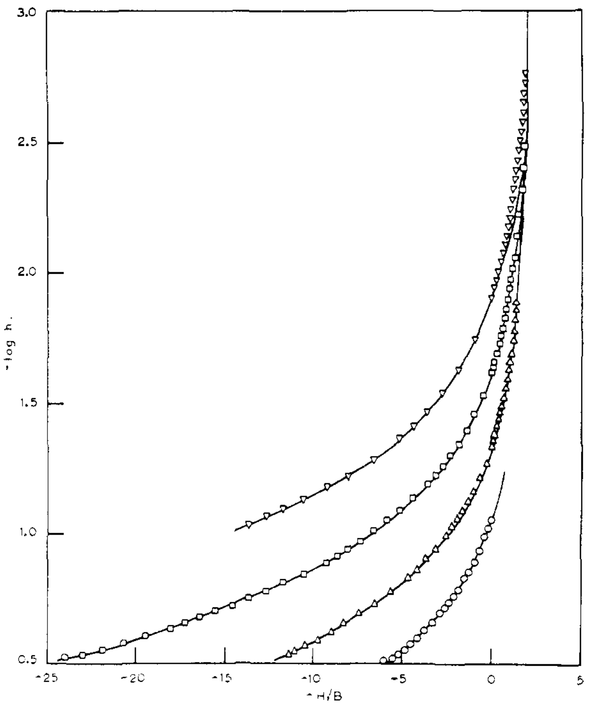

Fig. 1.—Log *h* as a function of $-H/B$, the degree of neutralization. Concentrations are in moles per liter. The curves are calculated for $\log \beta_{12,6} = -0.53$. B = 50 m*M* ○, 25 m*M* △, 12.5 m*M* □ and 6.25 m*M* ▽.

Substituting the expressions for X and $X_{Z=1}$ into equation 3 and setting $\alpha = \log 2$, we obtain

$$\mathbf{X} = \frac{1}{(n-1)} \log (Z/(2 - Z)) + \log (2/(2 - Z)) \qquad (10)$$

The theoretical curves $Z(\mathbf{X})$ are plotted on a separate sheet of coördinate paper for comparison with the experimental data. From the difference $\mathbf{X} - X$ between the abscissas of the experimental and theoretical curves, we obtain the value of β_n using equations 3 and 9 which give

$$\mathbf{X} - X = \frac{1}{(n-1)} \log \beta_n + \frac{\log n}{(n-1)}$$

The experimental curves $Z(X)$ were compared with the theoretical curves computed for $n = 5$ and 6. Since the shapes of these curves differ by very little, it is impossible to determine the predominating reaction from these data alone. Since the spacing between the curves $\eta\ (\log h)_B$, where $\eta = \log B/b$, can be determined more accurately than that for the $Z(\log h)_B$ curves, and since Olin's analysis of the $\eta\ (\log h)_B$ data gave $t = 2.40$ corresponding to the formation of $\mathrm{Bi_6(OH)}^{+6}$, the best fit was determined for the mechanism giving the hexamer. The value obtained for the equilibrium constant $\beta_{12,6}$ for the reaction

$$6\mathrm{Bi}^{+3} + 12\mathrm{H_2O} \rightleftharpoons \mathrm{Bi_6(OH)_{12}}^{+6} + 12\mathrm{H}^+$$

was $\log \beta_{12,6} = -0.53$ for the best over-all fit of the data. This is shown in Fig. 2 where the solid line is drawn for $\log \beta_{12,6} = -0.53$. Since the probable error of the points in the plot $Z(X)_B$ varies greatly with both X and B, and the probable error in Z is generally much greater than the error in *h*, this has been depicted by vertical lines drawn through *ca.*

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[11] For detailed discussions of the analysis of the curves $Z(\log h)_B$ and general curve fitting methods, see the papers of Sillén and coworkers, *e.g.*, (a) ref. 9, (b) L. G. Sillén, *Acta Chem. Scand.*, **8**, 299 (1954). (c) *ibid.*, **8**, 318 (1956).

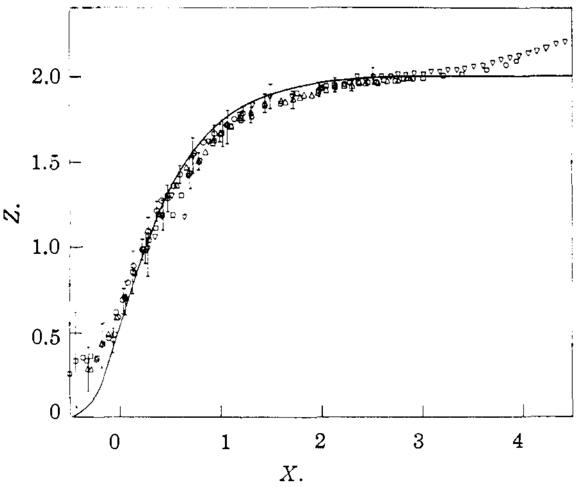

Fig. 2.—The average number of OH^- bound per Bi(III), $Z = (h - H)/B$, as a function of X. Concentrations are in moles per liter. The curve is calculated for log $\beta_{12,6} = -0.53$. B values are the same as in Fig. 1.

$^1/_4$ of the points. Within the experimental error, the points for $0 \leqslant Z \leqslant 2.0$ describe a single curve in agreement with the results of Olin. It should be noted that while e.m.f. methods are very useful in studying dimerization and trimerization reactions, it becomes progressively more difficult to determine unequivocally what products are formed for higher degrees of polymerization. It is therefore desirable to supplement the e.m.f. measurements by the measurement of some property of the polymeric species themselves.

Olin, from the analysis of η (log $h)_B$ data, gave the value log $\beta_{12,6} = 0.330$ in the ionic medium with $[ClO_4^-] = 3.00$ M. Sufficient data are given in Olin's paper to calculate $Z(X)$ for the single concentration $B = 10$ mM. These points describe a curve very similar in shape to the one in Fig. 2, and these are best fitted by log $\beta_{12,6} = 0.03$. The cause of the discrepancy between the values of the constant obtained from Olin's data by the two methods is not known; however, this corresponds to a rather small displacement of the curves along the abscissa. The value obtained in this work, log $\beta_{12,6} = -0.53$ is, at any rate, smaller indicating that the change from the medium with $[ClO_4^-] = 1.00$ M to $[ClO_4^-] = 3.00$ M leads to an increase in the hydrolysis constant. This is to be expected, since the higher concentration of ClO_4^- should lower the free energy of the species $Bi_6(OH)_{12}^{+6}$. The solid curves in Fig. 1 are drawn for the value of the constant $\beta_{12,6}$ determined in this work.

The question of the stabilization of the more highly charged species by solutions of very high ionic strength is one deserving further investigation, since it is generally assumed that the distribution of the complexes is similar in solutions of high and low ionic strength. The dimerization reaction of the Fe(III) ion may be cited as an example of the effect of high salt concentration on polymer formation.[12,13] The constant for the dimerization of $FeOH^{+2}$ to give $Fe_2(OH)_2^{+4}$ determined in solutions with 3 M $NaClO_4$ was 2.2 times greater than in 1 M $NaClO_4$ and 550 times greater than the value obtained by extrapolation to infinite dilution.

In highly hydrolyzed solutions, where $Z > 2.0$, the data Z(log $h)_B$ are considerably more sensitive to the appearance of further reactions leading to products more basic than $Bi_6(OH)_{12}^{+6}$ than are the log B/b data. Although the data indicate the formation of one or more species with OH:Bi ratios of greater than 2 at high pH in the solutions with $B =$ 12.5 and 6.25 mM, precipitation soon ensues. At bismuth concentrations greater than 12.5 mM, the solid phase appears before Z has increased measurably above 2.0. Since bismuth forms many basic salts of the type BiOX, it is not surprising that precipitation tends to occur at $Z = 2$ in the presence of 1 M ClO_4^-. It is difficult, however, to perform measurements on solutions with lower anion concentrations and still be able to make reasonable assumptions about the constancy of activity coefficients and the variation of junction potentials.

The complex with $Z > 2.0$ has been described as $Bi_4O_3(OH)_4(ClO)_4)_2$[14]; however, this was based on the premise that the species with $Z = 2$ was a dimer $Bi_2(OH)_4^{+2}$ and that further polymerization occurred as the basicity of the complex increased. Faucherre[5] gave the formula for the complex as $Bi_8O_{10}^{+4}$ again based on the assumption of further polymerization of the $Bi_4O_4^{+4}$ proposed by Souchay[4] as the basicity of the complex increased. Since it now appears that the hydrolysis of Bi(III) up to $Z = 2$ results in the formation of one predominant complex $Bi_6(OH)_{12}^{+6}$ or $Bi_6O_6^{+6}$, it would appear more logical to propose that the more basic complex still has 6 bismuth atoms. This configuration seems to have a rather great stability, and the Z(log $h)_B$ curves all approach 2 asymptotically. Finally at high pH an inflection occurs in the curves for low bismuth concentrations and they rise again. Since solid compounds corresponding to the formula $Bi_2O(OH)_3ClO_4$ have been prepared,[14,15] it seems reasonable to assume that the species is $Bi_6(OH)_{15}^{+3}$ or some less hydrated form, *e.g.*, $Bi_6O_6(OH)_3^{+3}$. The few available data can be fitted fairly well by assuming one additional reaction

$$Bi_6O_6^{+6} + 3H_2O \rightleftharpoons Bi_6O_6(OH)_3^{+3} + 3H^+$$

with a constant log $K_{15,6} = -8.1$.

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(14) M. Prytz and P. Nagel, *Z. anorg. u. allgem. Chem.*, **227**, 65 (1936).

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