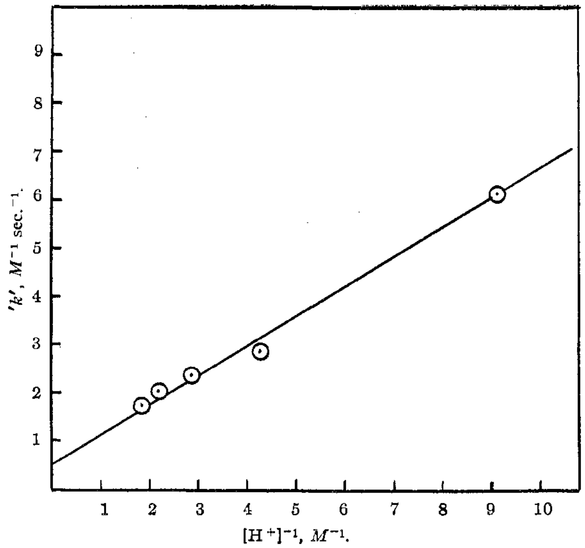

Fig. 3.—Rate *vs.* reciprocal hydrogen ion concentration.

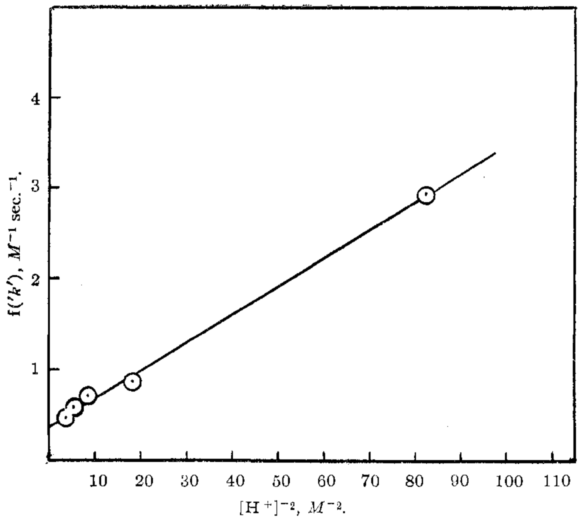

Fig. 4.—f('k') *vs.* $[H^+]^{-2}$.

In previous investigations of catalysis in this system, most authors[7] have assumed that the iron(III) is responsible for bringing the anion into the activated complex. There are, however, other paths which might be included in the general reaction scheme. For example, mechanisms such as

$$\mathrm{FeTar} + {}^*\mathrm{FeTar}^+ \xrightarrow{k_2} {}^*\mathrm{FeTar} + \mathrm{FeTar}^+ \tag{8}$$

might have been used to interpret the present data, but the H(+) dependence tends to argue against this or any path which requires (Tar^{-2}), *e.g.*, Fe^{+2} + *$Fe(Tar)_2^-$. Also, Kirschner[15] has shown that in the crystalline state, copper tartrate dihydrate is tridentate, and it is reasonable to assume this structure for the corresponding iron complexes. On steric grounds it would seem unlikely that close attack by the iron(II) complex on the iron(III) tartrate could take place.

Where bitartrate ions are involved, bidentate coordination seems more reasonable, rendering the complex ion open to close attack or to remote attack at the second carboxyl group. A reaction such as that between $Fe(HTar)^+$ and *$Fe(HTar)^{+2}$ probably should be discounted for steric reasons.

In their study, Reynolds and Fukushima[6] found that the rate constants for exchange paths involving sulfate (corresponding to k_3 and k_4 in this work) were considerably larger than k_1 and that the rate involving $Fe(SO_4)_2^-$ was thirty times greater than that due to 1:1 complex formation. In the present system, where the rates are not much greater than in the uncatalyzed path, it might be expected that the catalytic effect was due mainly to reaction 4, as is observed.

(15) S. Kirschner, *J. Am. Chem. Soc.*, **82**, 4174 (1960).

Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

The Formation of the Monoiodobismuth(III) Ion

BY ADRIAN J. EVE[1] AND DAVID N. HUME

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The reaction between bismuth and iodide ions in acidic medium has long been the basis of a colorimetric method for the determination of small amounts of bismuth.[2] A spectrophotometric study of the analytical method has led to results which are incompatible with the published values[3] of the formation constants presumed to be involved. A systematic spectrophotometric investigation of the nature and stability of the bismuth iodide complexes has therefore been undertaken. The present report gives the results for the lowest complex, which had previously been studied by Frolen, Harris, and Swinehart.[4] In attempting to repeat the work of those authors, we have confirmed the formula of the lowest complex to be BiI^{+2} but have found a much lower formation constant and observed a number of the solutions to be unstable with respect to precipitation.

Experimental

All solutions were prepared from reagent grade chemicals and water which had been distilled and subsequently passed through

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(1) On leave from the Department of Chemistry, University College of Rhodesia and Nyasaland, Salisbury, Southern Rhodesia.

(2) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1950.

(3) S. Ahrland and I. Grenthe, *Acta Chem. Scand.*, **11**, 1111 (1957).

(4) L. F. Frolen, W. S. Harris, and D. F. Swinehart, *J. Phys. Chem.* **61**, 1672 (1957).

a mixed-bed ion-exchange column. Experiments in which hypophosphorous acid was not added to prevent the formation of iodine were conducted under a nitrogen atmosphere, solutions being transferred from one vessel to another by hypodermic syringes fitted with Teflon-coated needles.

Measurements were made in 10-mm. quartz cells on a Cary Model 14 spectrophotometer kept in a room at a constant temperature of 24 ± 1°. No other attempt was made to thermostat solutions. In each series of experiments, the iodide concentration was kept constant while the bismuth concentration was varied between 10^{-1} and 10^{-5} M. All concentrations are expressed in gram-moles per liter.

Results

One series of measurements was carried out in the presence of 0.01 M hypophosphorous acid to reproduce the conditions of Frolen, *et al.*, and another using nitrogen to exclude all traces of oxygen which might otherwise oxidize iodide (Table I). In the latter series, the ionic strength was held constant at 2 M by addition of sodium perchlorate. The absence of iodine or triiodide, which would give an interfering absorption, was established spectrophotometrically.

TABLE I

ABSORBANCE OF BISMUTH–IODIDE MIXTURES

	Initial bismuth concn., M	Initial iodide concn., M	Absorbance at 282 mμ[a]
	A. With hypophosphorous acid		
1	0.10	4.00×10^{-4}	[b]
2	0.010	4.00×10^{-4}	[b]
3	0.0010	4.00×10^{-4}	0.778
4	0.00010	4.00×10^{-4}	0.119
5	0.000010	4.00×10^{-4}	0.024
6	0.010	4.00×10^{-5}	0.262
	B. Without hypophosphorous acid		
7	0.10	8.00×10^{-5}	0.633
8	0.010	8.00×10^{-5}	0.519
9	0.0010	8.00×10^{-5}	0.197
10	0.00010	8.00×10^{-5}	0.028

[a] All solutions were 1 M in $HClO_4$. The absorbance was measured with respect to a blank of 1 M $HClO_4$ and, in the case of the first six solutions, 0.01 M H_3PO_2. [b] Precipitate formed.

The absorbance values obtained in the first series were higher than those obtained by Frolen, *et al.*, by factors of 2.5 to 3.5. Precipitation in the more concentrated solutions prevented estimation of a limiting value of the absorbance of the complex, and therefore calculation of the formation constant, by their method. The measurements in the second series could be used, however, and their method of calculation was applied with the following refinements. The measured absorbance was corrected for the contribution due to uncomplexed bismuth, using the value of 0.186 M^{-1} cm.$^{-1}$ for the molar absorptivity (extinction coefficient) at 282 mμ. The initial value of the formation constant, derived from the assumption of complete conversion of I^- to BiI^{+2} in the most concentrated bismuth solution, was used to calculate a more accurate value of the concentration of the complex in the most concentrated solution, and from it corrected values of the molar absorptivity of the complex and the formation constant were obtained. The process was then repeated, and it was found that after the second approximation, constant values of the molar absorptivity, ϵ_1, and formation constant, β_1, were obtained. The final results are summarized in Table II. The molar absorptivity of the BiI^{+2} ion was found to be 7.84×10^3 M^{-1} cm.$^{-1}$ at 282 mμ.

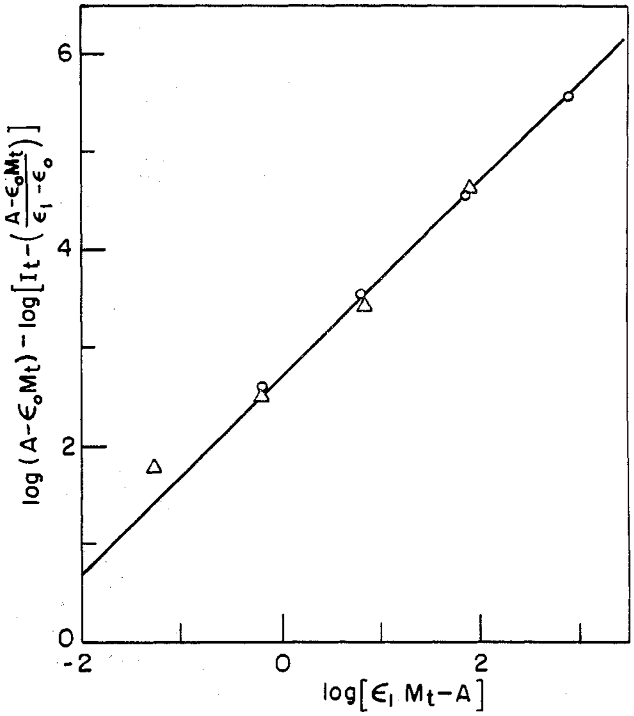

Fig. 1.—Determination of the formation constant of BiI^{+2} from data at 282 mμ: Δ in the presence of hypophosphorous acid, and O in the absence of hypophosphorous acid.

TABLE II

CALCULATION OF FORMATION CONSTANT, β_1

$(Bi^{+3})_{orig.}$, M	A[a]	$(BiI^{+2}) \times 10^5$, M	(Bi^{+3}), M	$(I^-) \times 10^5$, M	$\beta_1 \times 10^{-2}$
0.1	0.614	7.84	9.99×10^{-2}	0.164	4.78
0.01	0.517	6.60	9.93×10^{-3}	1.40	4.74
0.001	0.197	2.51	9.75×10^{-4}	5.49	4.70
0.0001	0.028	0.357	9.64×10^{-5}	7.64	4.85

[a] Corrected for absorption by free bismuth ions.

A second method of calculation, the graphical approach of Newman and Hume,[5] has been applied to all the results in Table I for comparison. The rearranged form of their equation E12 as used in the case of the chloride complexes of bismuth[6]

$$\log(A - \epsilon_0 M_t) - q \log\left[I_t - q\frac{(A - \epsilon_0 M_t)}{\epsilon_q - \epsilon_0}\right] = \log(\epsilon_q M_t - A) - \log \beta_q$$

relates the measured absorbance, A, to the total ligand and metal ion concentrations I_t and M_t, and the molar absorptivities of the metal and complex ions, ϵ_0 and ϵ_q. An assumption as to the number of ligands, q, involved in the complex has to be made. If the assump-

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(5) L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4571 (1957).
(6) L. Newman and D. N. Hume, *ibid.*, **79**, 4576 (1957).

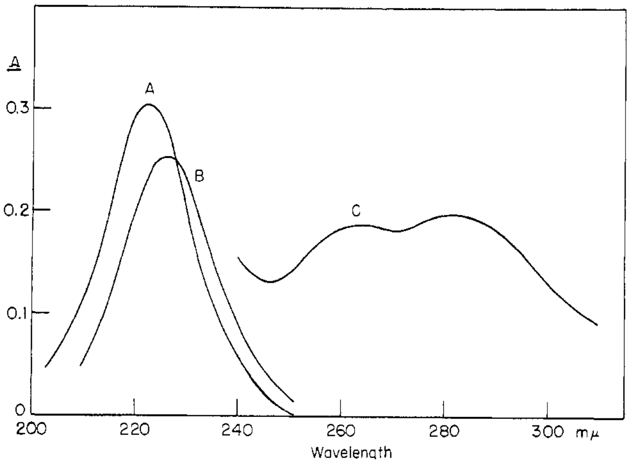

Fig. 2.—Spectra of 2.5 × 10^{-5} *M* Bi(III) in 1-cm. cells: A, in 1 *M* $HClO_4$: B, in 1 *M* $HClO_4$ and 0.45 *M* H_3PO_2; C, as BiI^{-2} in 1 *M* $HClO_4$.

tion is correct, a straight line of unit slope results with an intercept of log β_q.

It should be noticed that the equation only applies to the case of two species being present, both absorbing, and so allows for absorption due to bismuth ions but does not allow for any contribution to the absorbance by iodide ions. It has been verified, by experiment, that iodide does not absorb at this wave length when present at this low concentration.

The plot of the results is shown in Fig. 1, in which the best straight line of unit slope has been drawn. This line agrees very well with the data, confirming that the complex is indeed BiI^{+2}. From the intercept, β_1 was found to be 4.79 × 10^2, in good agreement with the previous method of calculation.

Discussion

A comparison of the results reported here and those reported by previous authors reveals a number of important differences.

The value of the stability constant is tenfold smaller than that reported previously (4.35 × 10^3), which suggests that an error may have been made by previous workers in recording the concentration of iodide. A comparison of the sixth solution in Table I where the iodide concentration was 4.0 × 10^{-5} *M* and a solution in the previous paper where this concentration was given as 3.9 × 10^{-4} *M* reveals approximately the same value for the absorbance.

The failure of previous authors to observe precipitation from the more concentrated bismuth solutions cannot be as readily explained. From the solubility product of bismuth iodide, which has been reported as 8.1 × 10^{-19},[3] one would expect precipitation from some of the solutions in Table I where none appeared and from the solutions prepared by Frolen. We have observed two effects due to the presence of hypohosphorous acid: first, a marked decrease in the *rate* of precipitation of bismuth iodide from supersaturated solutions and, secondly, the formation of a similar-appearing precipitate even in the absence of iodide ions. The latter appears to be mainly metallic bismuth resulting from the reduction of the uncomplexed ion by hypophosphorous acid. Bomberger[7] has, in fact, shown it possible to obtain a quantitative precipitation of metallic bismuth from perchloric acid medium by heating with hypophosphorous acid. It has been our experience that hypophosphorous acid, once opened to the atmosphere, deteriorates rapidly, and this might be the cause of its reactivity having been overlooked.

Experiments have also shown that hypophosphorous acid reacts with dilute solutions of bismuth without precipitation. The absorption band of bismuth is shifted to longer wave lengths and the absorbance is decreased (Fig. 2), suggesting that a weak complex is formed. It was because of this that the second series of measurements of the formation of BiI^{+2} was carried out in the absence of hypophosphorous acid. The good agreement between the results obtained in the two series of experiments, as evidenced by Fig. 1, confirms the suggestion that the complex between bismuth and the acid is very weak. The absorption spectrum of the ion BiI^{+2} has been found to have two peaks above 240 mμ, as shown in Fig. 2, with a maximum absorbance at 282 mμ.

In Fig. 1 the deviation of the lowest result from the line is suggestive of the formation of a second species, presumably BiI_2^+. The narrowness of the range of concentrations which are high enough to permit an appreciable fraction of this species to be formed and still low enough to avoid precipitation of bismuth iodide makes study of this species exceedingly difficult, and no confirmation of its formula or estimate of its formation constant could be made from our data.

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(7) D. R. Bomberger, *Anal. Chem.*, **30**, 1321 (1958).

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The Kinetics of the Chromate–Dichromate Reaction as Studied by a Relaxation Method

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In recent years the application of relaxation techniques to the study of fast reactions has received considerable attention. Eigen and deMaeyer[2] have developed the theory and experimental techniques for studying such reactions. However, little attention has been

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(2) M. Eigen and L. deMaeyer, "Techniques of Organic Chemistry," A. Weissberger, Ed., Interscience Publ., New York, N. Y., 1963, Vol. VIII, Part II, Chapter XVIII.