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The Acceleration of the Iron(II)–(III) Exchange by Tartaric Acid[1]

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The iron(II)–(III) reaction has been studied in the presence of tartaric acid at an ionic strength of 0.55 M and at several hydrogen ion concentrations. Analysis of the data at 0, 5, and 10° with $[H^+] = 0.11\ M$ indicates catalysis due to the reaction between Fe^{+2} and $Fe(HTar)_2^+$. The rate law is

$$R = k_1[Fe^{+2}][Fe^{+3}] + k_2[Fe^{+2}][FeOH^{+2}] + k_4[Fe^{+2}][Fe(HTar)_2^+]$$

The rate constant k_4 could not be calculated due to the lack of the necessary formation constant values. In the presence of fumaric acid at 0° and $[H^+] = 0.55\ M$ no acceleration of the rate was observed.

The iron(II)–(III) exchange reaction has been the subject of several investigations since Silverman and Dodson[2] showed that measurable rates were obtained using 2,2′-bipyridine to quench the reaction.[3–5] Recent work has included studies of the acceleration of the exchange by sulfate, oxalate, and phosphate anions.[6–8]

Since, in this laboratory, we have been interested in the role of organic oxyacid anions as possible bridging groups between the oxidizing and reducing species in these reactions,[9–11] it was decided to extend our investigations to the iron system. One previous study of this type was that of Duke and Wolf,[12] who indicated catalysis in the presence of *p*-phthalic acid.

Experimental

Reagents.—Iron(III) perchlorate tracer stock solutions were prepared from a hydrochloric acid solution of Fe^{55}–Fe^{59}, obtained from Oak Ridge National Laboratory. Two sets of stock solutions were made. In the first, the radioactive iron was extracted in isopropyl ether to remove any metal contaminants and then was back extracted into water. Iron wire (Baker and Adamson 99.90% assay) was dissolved in approximately 1 M nitric acid and oxidized to the +3 state with hydrogen peroxide. After the excess peroxide was destroyed by prolonged boiling, the solution was mixed with the purified radioactive solution and the iron(III) hydroxide was then precipitated with ammonia. The precipitate was washed with de-ionized water until washings gave a negative test for chloride. It was then taken up in perchloric acid and the solution was diluted to the required concentration. The second set of solutions was prepared in a manner identical with that described above, except that there was no extraction of the radioactive iron(III) portion. Identical kinetic experiments over a series of concentrations showed no detectable differences in the stock solutions.

Hydrated iron (II) perchlorate (G. F. Smith and Co., reagent grade) was recrystallized three times from a 5 M perchloric acid solution. No attempt was made to exclude oxygen and about 25% of the iron in the solid was in the +3 state. Stock solutions which were about 0.05 M in iron(II) perchlorate and about 0.1 M in perchloric acid were stored at 0°. Determination of concentrations of iron(II) and (III) and of perchloric acid were made by the method of Silverman and Dodson.[2]

Sodium perchlorate solutions were prepared from recrystallized material (G. F. Smith and Co., reagent grade). The salt concentration was determined by evaporation of aliquots of solution to dryness at 165°. Perchloric acid, 70–72% (J. T. Baker Chemical Co.), was used without further purification. Reagent grade tartaric acid was used. Fumaric acid (practical grade) was recrystallized three times from water and dried at 80°. Lanthanum nitrate (Fischer Scientific Co.) was reagent grade.

Electron Exchange Measurements.—Solutions of iron(II) and (III) perchlorate, tartaric or fumaric acid, perchloric acid, and sodium perchlorate of ionic strength 0.55 M were allowed to equilibrate in a thermostatic bath for at least 3 hr. The reaction was started by injection of a small aliquot of radioactive iron(II) solution into the reaction mixture and mixing was achieved by bubbling air through the solution for 10 sec. No oxidation of the iron(II) was detected in the mixing procedure. During the course of the reaction, eight 5-ml. aliquots were removed at measured time intervals and quenched by injection into a solution of 5 ml. of 2 M sodium acetate, 1 ml. of 0.1 M lanthanum nitrate, and 5 ml. of 0.1% 2,2′-bipyridine. The final two samples were taken after ten half-lives had elapsed. To the quenched solutions was added a 1-ml. portion of 15 M ammonium hydroxide and, after a few minutes to allow for formation of the lanthanum hydroxide, the solutions were centrifuged. Aliquots (5 ml.) of the supernatant solutions were transferred to screw-cap, lusteroid counting tubes and the iron(II) 2,2′-bipyridine fraction was counted in a well-type scintillation counter. Reproducibility of counting rates was better than 1%.

At higher temperatures the quench solutions were composed of 3 ml. of sodium acetate, 0.5 ml. of lanthanum nitrate, and 5 ml. of 2,2′-bipyridine. This was to minimize iron(II) tartrate formation, which interfered with the quenching.

Initially, the reaction was followed using the method of Silverman and Dodson.[2] Although good reproducibility was achieved with only iron present, when tartaric acid was added, formation of iron(III) tartrate took place in the quench, leading to reduced amounts of the iron(III) hydroxide. In order to overcome this difficulty, the procedure just described was adapted from the method of Sheppard and Brown.[7]

Results

Experiments performed under conditions similar to those of Silverman and Dodson[2] indicated that the reaction was first order in each of iron(II) and (III) con-

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[1] This work is supported by Grant AT(11-1)-1001 from the U. S. Atomic Energy Commission.

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[3] (a) J. Hudis and A. C. Wahl, *J. Am. Chem. Soc.*, **75**, 4153 (1953); (b) G. S. Lawrence, *Trans. Faraday Soc.*, **53**, 1326 (1957).

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[6] W. L. Reynolds and S. Fukushima, *Inorg. Chem.*, **2**, 176 (1963).

[7] J. C. Sheppard and L. C. Brown, *J. Phys. Chem.*, **67**, 1025 (1963).

[8] R. L. Willix, *Trans. Faraday Soc.*, **59**, 1315 (1963).

[9] C. H. Brubaker, Jr., and C. Andrade, *J. Am. Chem. Soc.*, **81**, 5282 (1959).

[10] L. P. Quinn, Ph.D. Thesis, Michigan State University, 1961.

[11] C. H. Brubaker, Jr., "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 117.

[12] F. R. Duke and E. Wolf, *Iowa State J. Sci.*, **34**, 157 (1959).

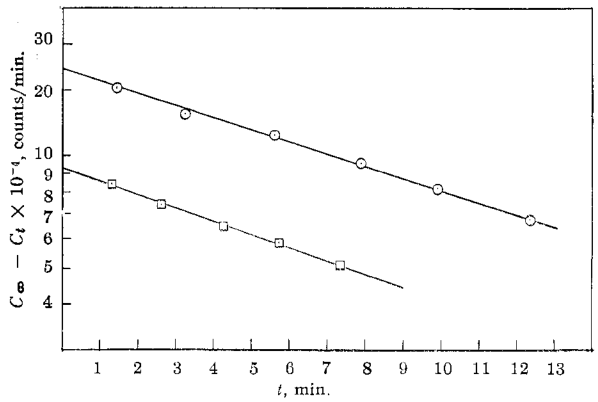

Fig. 1.—Typical rate data: 0°, $[H^+] = 0.55$ *M*; C_∞ and C_t are radioactivities at "infinite" time and at time *t*. Upper curve: $[Fe^{+2}] = 3.746 \times 10^{-4}$ *M*, $[Fe^{+3}] = 3.931 \times 10^{-4}$ *M*, [tartaric acid] $= 1.023 \times 10^{-3}$ *M*. Lower curve: $[Fe^{+2}] = 5.195 \times 10^{-4}$ *M*, $[Fe^{+3}] = 4.322 \times 10^{-4}$ *M*, [fumaric acid] $= 3.270 \times 10^{-3}$ *M*.

centrations. The specific rate constant, '*k*', was derived using the expression

$$'k' = \frac{0.693}{t_{1/2}([Fe^{+2}] + [Fe^{+3}])}$$

and values of $t_{1/2}$ were obtained from plots of log $(C - C_t)$ against *t* as shown in Fig. 1. Duplicate experiments were reproducible to ±3%. Apparent zero-time exchange varied from 10 to 25%.

The first series of reactions, studied at 0°, was performed at fairly high acidity ($[H^+] = 0.545$ *M*). The results are given in Table I. The value of 1.44 ± 0.03 for '*k*' in the absence of tartaric acid is slightly higher than Silverman and Dodson's[2] 1.35 ± 0.02.

TABLE I

TARTARIC ACID EXPERIMENTS, 0°, $\mu = 0.55$ *M*, $[H^+] = 0.545$ *M*

$10^4[Fe^{+2}]$, *M*	$10^4[Fe^{+3}]$, *M*	10^3[tartaric acid], *M*	$t_{1/2}$, sec.	'*k*', M^{-1} sec.$^{-1}$	
3.746	3.931	. . .	642	1.42	1.44 ± 0.03
5.368	4.756	. . .	483	1.42	
2.684	7.471	. . .	462	1.48	
3.746	3.931	0.05115	591	1.53	
3.746	3.931	0.1238	612	1.47	
3.746	3.931	0.2476	636	1.42	
3.746	3.931	0.6194	597	1.51	
3.746	3.931	1.023	563	1.61	
5.198	4.313	1.871	438	1.50	
3.746	3.931	3.095	490	1.84	
5.198	4.313	4.688	423	1.72	

Increase of the reaction rate in the presence of tartaric acid was not great, and even with a tartaric acid concentration five times that of total iron, the rate was only 25% greater than in the uncatalyzed reaction. This was thought to be due to the very small amounts of free tartrate or bitartrate anion in the solution, and experiments were conducted at the same ionic strength and temperature but at $[H^+] = 0.11$ *M*. Results are shown in the first part of Table II and catalysis is seen with increasing tartaric acid concentrations. Analogous experiments were carried out at 5 and 10° and, when the data could be compared with those of Silverman and Dodson,[2] agreement was found to be good (Table II and Fig. 2). It may be noted that at higher temperatures, the range of concentrations where experiments could be conducted was limited due to interference in the quenching procedure. Apparently, iron(II) tartrate was formed in the quench solution, the 2,2'-bipyridine complex being formed only after some time. (This was seen as a gradual deepening of the solution color to the intense red of the iron(II) complex.)

TABLE II

TARTARIC ACID EXPERIMENTS, $\mu = 0.55$ *M*, $[H^+] = 0.110$ *M*

$10^4[Fe^{+2}]$, *M*	$10^4[Fe^{+3}]$, *M*	10^3[tartaric acid], *M*	$t_{1/2}$, sec.	'*k*', M^{-1} sec.$^{-1}$	
		0°			
2.602	2.155	. . .	471	3.09	mean[a] 3.08 ± 0.08
2.598	3.173	. . .	371	2.96	
2.598	4.695	. . .	297	3.20	
5.083	5.581	0.467	209	3.11	
5.185	5.581	1.870	181	3.56	
2.556	4.603	2.576	211	4.59	
5.100	5.679	3.748	105	6.14	
5.185	5.581	4.670	81	7.96	
		5°			
3.062	3.957	. . .	166	5.92	mean[a] 5.82 ± 0.10
4.078	4.336	. . .	144	5.72	
3.062	3.957	0.9355	159	6.21	
3.062	3.957	1.471	143	6.90	
3.062	3.957	1.873	136	7.25	
		10°			
3.062	3.957	. . .	105	9.41[a]	
3.062	3.957	0.1871	98	10.08	
3.062	3.957	0.2806	94	10.50	
3.062	3.957	0.3678	90	10.94	
3.062	3.957	0.5506	84	11.89	

[a] These values may be compared with 3.26, 5.80, and 9.70 obtained from the data of Silverman and Dodson.[2]

Since it was believed that catalysis was due to the formation of complexes between the organic acid and the iron species, experiments were carried out with fumaric acid present. In this case, although there would be a conjugated double-bond, conduction path between the oxidizing and reducing species, chelation is not likely. (There is no hydroxyl on the carbon α to the bound carboxyl group which would allow ring formation.) The results of experiments carried out over a 25-fold range of fumaric acid concentrations are given in Table III and no acceleration of the rate is seen. It would seem, then, that fumarate is effective in reactions such as Taube's[13] due to its being bound to the oxidizing agent, $(NH_3)_5CoL^{+2}$, so that a much higher concentration of complex occurs than with Fe^{+3} plus fumarate.

TABLE III

FUMARIC ACID EXPERIMENTS, $\mu = 0.55$ *M*, $[H^+] = 0.545$ *M*, 0°

$10^4[Fe^{+2}]$, *M*	$10^4[Fe^{+3}]$, *M*	10^3[fumaric acid], *M*	'*k*', M^{-1} sec.$^{-1a}$
2.581	2.605	0.2102	1.52
3.804	3.622	0.1813	1.48
3.629	2.539	2.180	1.39
4.322	5.195	3.270	1.46
3.475	5.195	4.355	1.48

[a] Mean = 1.48 ± 0.03.

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(13) H. Taube, *Advan. Inorg. Chem. Radiochem.*, 1, 1 (1959).

Discussion

In their investigation into the catalysis of the exchange by oxalic acid, Sheppard and Brown[7] found a linear relationship between 'k' and oxalic acid concentrations, which they were able to ascribe to the formation of iron(III) oxalate. Similar analysis of the present data showed no such relationship, but it was found that plots of 'k' vs. [tartaric acid]^2 were linear. Although the mechanism of catalysis by the anions is by no means certain in this system, previous workers have assumed that the reaction paths most favored would be dependent on the nature of the complexes formed. In the present work, if we assume that the only complexes present are those of iron(III), reaction paths could be written as (tartaric acid = H_2Tar)

$$Fe^{+2} + {}^*Fe^{+3} \xrightarrow{k_1} {}^*Fe^{+2} + Fe^{+3} \qquad (1)$$

$$Fe^{+2} + {}^*FeOH^{+2} \xrightarrow{k_2} {}^*Fe^{+2} + FeOH^{+2} \qquad (2)$$

$$Fe^{+2} + {}^*FeHTar^{+2} \xrightarrow{k_3} {}^*Fe^{+2} + FeHTar^{+2} \qquad (3)$$

$$Fe^{+2} + {}^*Fe(HTar)_2{}^{+} \xrightarrow{k_4} {}^*Fe^{+2} + Fe(HTar)_2{}^{+} \qquad (4)$$

The reaction rate may be represented by

$$R = k_1[Fe^{+2}][Fe^{+3}] + k_2[Fe^{+2}][FeOH^{+2}] + k_3[Fe^{+2}][FeHTar^{+2}] + k_4[Fe^{+2}][Fe(HTar)_2{}^{+}] \qquad (5)$$

Inclusion of the formation constants, β_1 and β_2, of the tartrate complexes

$$\beta_1 = \frac{[FeHTar^{+2}]}{[Fe^{+3}][HTar^{-}]} \qquad \beta_2 = \frac{[Fe(HTar)_2{}^{+}]}{[Fe^{+3}][HTar^{-}]^2}$$

and $k_1{}^a$ and K_h, the dissociation constant and hydrolysis constant of the tartaric acid and the aquated iron(III) ion, respectively, yields the expression

$$R = [Fe^{+2}]_T[Fe^{+3}]_T \times \left\{ \frac{k_1 - \frac{k_2K_h}{[H^+]} + \frac{k_3k_1{}^a\beta_1[H_2Tar]}{[H^+]} + \frac{k_4\beta_2k_1{}^{a2}[H_2Tar]^2}{[H^+]^2}}{1 + \frac{K_h}{[H^+]} + \frac{\beta_1k_1{}^a[H_2Tar]}{[H^+]} + \frac{\beta_2k_1{}^{a2}[H_2Tar]^2}{[H^+]^2}} \right\} \qquad (6)$$

where 'k' corresponds to the factor in the braces. $[Fe^{+2}]_T$ and $[Fe^{+3}]_T$ are total iron(II) and (III).

It is possible to estimate the size of the last three terms of the denominator. Under conditions of $[H^+] = 0.11\ M$ and at 0°, $K_h/[H^+] \approx 10^{-3}$. Previous work involving complexes of transition metal ions with the hydrogen succinate anion[14] yielded β values of the order 10^1–10^2. A similar order of magnitude is to be expected in the case of the bitartrate ion, and, although in this case a trivalent cation is involved, β values may not differ much from those cited. Calculation of the last two terms in the denominator shows them to be about 10^{-3} and 10^{-6}, respectively. Each of these terms is smaller than unity and may thus be neglected.

The importance of reaction path 3 above may be examined by plotting the function

$$\frac{'k' - \left(k_1 + \frac{k_2K_h}{[H^+]}\right)}{[H_2Tar]}$$

against tartaric acid concentration. Such a plot, from the data at 0° in Table II, gives the intercept $(k_3k_1{}^2\beta_1)/[H^+]$ as nearly zero, indicating that path 4 predominates.

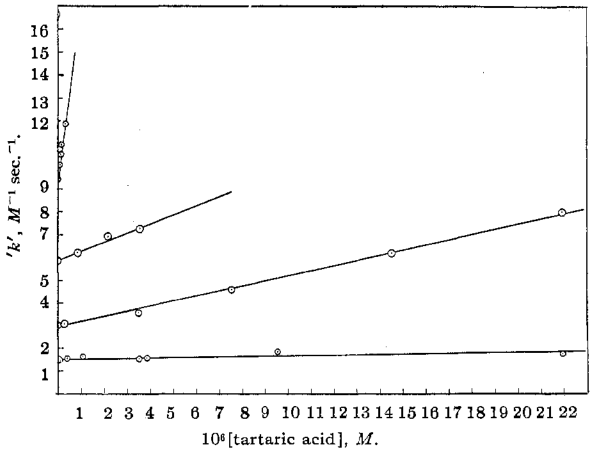

Fig. 2.—'k' vs. [tartaric acid]^2: Bottom curve: 0°, $[H^+] = 0.55\ M$. Other curves: $[H^+] = 0.11\ M$; second from bottom, 0°; third, 5°; fourth, 10°.

At low tartaric acid concentrations and at constant ionic strength and hydrogen ion concentration, from eq. 6, 'k' may be written in the form

$$'k' = k_1 + \frac{k_2K_h}{[H^+]} + \frac{k_4k_1{}^{a2}\beta_2[H_2Tar]^2}{[H^+]^2} \qquad (7)$$

TABLE IV

EXPERIMENTS AT VARYING ACIDITIES, 0°, μ = 0.55 M

$[H^+]$, M	$10^4[Fe^{+2}]$, M	$10^4[Fe^{+3}]$, M	$10^3[H_2Tar]$, M	'k', M^{-1} sec.$^{-1}$
0.545	5.198	4.313	3.800	1.72[a]
0.454	5.172	5.758	3.802	2.04
0.347	5.271	5.979	3.865	2.38
0.233	5.271	5.979	3.865	2.84
0.100	5.100	5.679	3.748	6.14

[a] Interpolated from data in Table I.

Plots of 'k' against $[H_2Tar]^2$ yielded straight lines under these conditions, and data at the three temperatures studied are shown in Fig. 2. Due to the fact that $k_4k_1{}^{a2}\beta_2$ is a composite of terms for which literature values are not available, the calculation of activation parameters could not be justified.

A final set of experiments was performed at varying acidities with iron(II), (III), and tartaric acid concentrations approximately constant. The results are shown in Table IV. A plot of 'k' against $[H^+]^{-1}$ was seen to be linear (Fig. 3). This is explained by assuming that the second term in eq. 7 predominates. Since, however, the values for k_1 and k_2 are known, it is possible to evaluate the first two terms and, from the data in Table IV, plots were made of $'k' - [k_1 + (k_2K_h/[H^+])]$ vs. $[H^+]^{-2}$. Reasonable linearity was found (Fig. 4). This is taken as further proof the reaction paths 1, 2, and 4 are operative. In Fig. 4, however, the curve should pass through the origin. The nonzero intercept probably is due, in part at least, to the sensitivity of the calculation to 'k' and k_1 values. At higher acidities there may be a contribution from reaction path 3.

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(14) A. McAuley and G. H. Nancollas, *J. Chem. Soc.*, 4458 (1961).

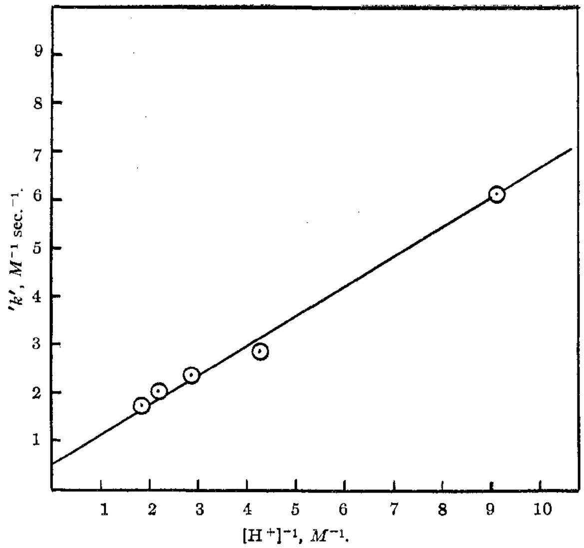

Fig. 3.—Rate *vs.* reciprocal hydrogen ion concentration.

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

$$\mathrm{FeTar} + {}^*\mathrm{FeTar}^+ \xrightarrow{k_2} {}^*\mathrm{FeTar} + \mathrm{FeTar}^+ \qquad (8)$$

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.

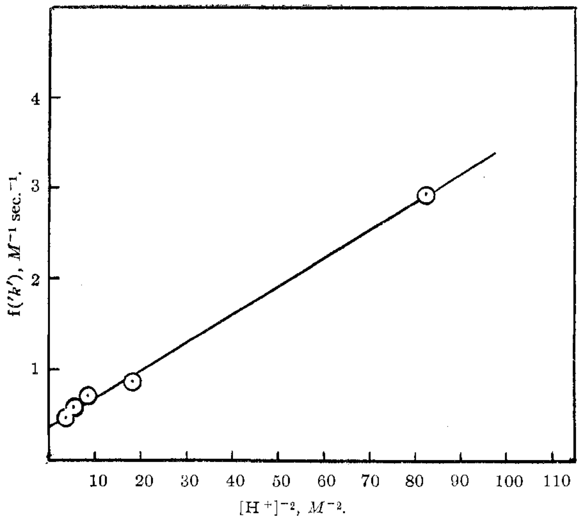

Fig. 4.—f('k') *vs.* $[H^+]^{-2}$.

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.

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

Notes

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The Formation of the Monoiodobismuth(III) Ion

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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).