(2) partial decomposition of the ethyl acetate, producing ethyl chloride and titanium acetate. The second factor seems more probable, since refluxing a solution of titanium tetrachloride in ethyl acetate resulted in a partial loss of chlorine. No explanation is made concerning the fact that but three of the chlorine atoms had been replaced.

Summary

The reaction between titanium tetrachloride and hydrogen peroxide in dry ethyl acetate has been studied in some detail. A white compound containing titanium, chlorine and hydrogen peroxide in the approximate ratio of 1:1:1 can be prepared. This material is unstable toward water, as well as slightly elevated temperatures. In decomposing, it becomes yellow-orange in color. It is very soluble in water, producing orange-red clear solutions.

URBANA, ILL. RECEIVED SEPTEMBER 16, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Use of Iodine and of Potassium Iodate as Volumetric Oxidizing Agents in Solutions Containing Mercuric Salts. I. The Effect of Mercuric Salts upon the Stoichiometry of Various Oxidation–Reduction Reactions. New Procedures for the Titration of Arsenite and Antimonite with Standard Solutions of Iodine or of Potassium Iodate

BY N. HOWELL FURMAN AND CLARK O. MILLER[1]

Introduction

The stoichiometry of certain reactions between powerful oxidizing agents and halides, or between the halogens or their oxy acids and reducing agents, is modified when mercuric salts are present in excess. Several situations may arise, depending upon particular halide that is present, the total acidity and the relative concentrations of mercuric salt, halide and acid. There are two principal kinds of behavior which are of interest here: (a) the failure of free halogen to appear when a limited quantity of a halide, an excess of mercuric ion and an excess of nitric, sulfuric or perchloric acid is treated with a powerful oxidizing agent, as for example, potassium bromate or permanganate; (b) the reduction of bromate to bromide, of iodate to iodide and of iodine to iodide by various reducing agents in the presence of an excess of mercuric salt and acid. The former case will be reviewed briefly with presentation of some experimental observations, and the latter will be treated more fully, especially with regard to the reactions of potassium iodate and of iodine and the application of these reactions in volumetric analysis.

(a) The Non-appearance of Free Halogen when Mercuric Salt is Present in Excess.—G. F. Smith[2] described a series of experiments in which solutions of bromides, chlorides or iodides containing mercuric nitrate or perchlorate and the corresponding free acid were heated with an excess of potassium bromate solution. He reported that no reaction was observed and that the solution after the heating liberated an amount of iodine equivalent to the original potassium bromate when an excess of potassium iodide was added to the cold solution. He found similar results for mixtures of a bromide, mercuric salt, potassium permanganate and acid, and attributed this "preventive effect" to the formation of slightly ionized mercuric halides.

We have repeated experiments of the type described by Smith upon mixtures containing potassium iodide, excess of mercuric sulfate and sulfuric acid. Potassium bromate or permanganate was added. After heating there was no loss of oxidizing power toward potassium iodide. Reactions had occurred, however, for the potassium bromate had been reduced and an equivalent amount of iodate had been formed, as was indicated by the presence of bromide and iodate in mixtures that were examined qualitatively and by quantitative experiments. The potassium permanganate was decolorized and iodate was formed. Smith's explanation[2] of the "protective action" of mercuric salts is contradicted by these qualitative experiments.

In the case of iodide, which is of principal inter-

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[2] G. F. Smith, THIS JOURNAL, 45, 1417 (1923).

est in this paper, the oxidation proceeds to the iodate stage without visual evidence of the intermediate formation of free iodine when mercuric salts are present in sufficient excess. In the absence of mercuric salts the oxidation of iodide usually leads to the quantitative liberation of iodine in solutions that are 1–2 *N* in acid. The explanation of the effect of mercuric salts seems clear from the evidence that is available in the literature. In the oxidation of iodide to higher states we are concerned with the effect of mercuric ion and acidity upon the equilibria

$$2I^- + 2e \rightleftharpoons I_2 \qquad (1)$$

$$I_2 + H_2O \rightleftharpoons I^- + IO^- + 2H^+ \qquad (2)$$

$$3IO^- \rightleftharpoons IO_3^- + 2I^- \qquad (3)$$

Measurements are presented in this paper regarding the effect of mercuric ions and acidity upon process (1). Mercuric ions tend to bind iodide ions in the form of complex and undissociated molecules. It is thus more difficult to liberate iodine from an iodide in the presence of a mercuric salt than in its absence. Mercuric ions tend to aid processes (2, 3) by removing one of the products of the reaction, namely, iodide. Some of the evidence previously published regarding processes (2, 3) in the presence of mercury will be summarized briefly. Brückner[3] found that iodine in the presence of mercuric oxide undergoes autoxidation

$$6HgO + 6I_2 = 5HgI_2 + Hg(IO_3)_2 \qquad (4)$$

A similar autoxidation occurs if mercuric sulfate is added to a solution of iodine. A complex white precipitate that contains mercuric sulfate, iodide and iodate, is formed. Hovorka[4] observed a similar process when mercuric perchlorate was used.

$$6Hg(ClO_4)_2 + 6I_2 + 6H_2O = 5HgI_2 + Hg(IO_3)_2 + 12HClO_4 \qquad (5)$$

This type of autoxidation is not limited to iodine, for Chateau[5] has demonstrated similar autoxidation of bromine and chlorine, respectively, in the presence of mercuric mercury, to form hypochlorite or hypobromite. The change of hypoiodous acid to an equivalent mixture of iodate and iodide (equation 3) is rapid according to Skrabal.[6] Reaction (2) is also rapid, for a solution of iodine is rapidly decolorized when added to a solution of mercuric sulfate.

The binding or removal of iodide ions is the important factor in promoting the change of iodine to iodate. A similar autoxidation occurs when silver is used instead of mercuric ion[7] and the mechanism has been shown to involve reactions (2, 3).

We have shown qualitatively that the presence of an excess of a mercuric salt does not inhibit the oxidation of a limited quantity of halide ion by a powerful oxidizing agent like potassium permanganate or potassium bromate. Evidence from the literature has been cited to show the mechanism of the formation of oxy-halogen acids by spontaneous autoxidation of the halogens in the presence of mercuric or silver ions. In a particular case such as the reaction between bromate and iodide, the presence of mercuric salt tends to establish an equilibrium between iodate, iodide, bromate and bromide such that the total oxidizing power of the solution toward a powerful reductant remains constant.

(b) **The Action of Reducing Agents upon Bromate and Iodate in the Presence of Mercuric Salts.** (1) **In the Presence of Mercuric Sulfate, Perchlorate or Nitrate and the Corresponding Acid.**—Under these conditions bromate is reduced to bromide or iodate to iodide by a reductant that is sufficiently powerful. The following are some typical reactions

$$6Mn^{++} + 2BrO_3^- + 6H_2O + Hg^{++} = 6MnO_2 + HgBr_2 + 12H^+ \qquad (6)$$

$$4Cr^{+++} + 2BrO_3^- + 10H_2O + Hg^{++} = 4HCrO_4^- + HgBr_2 + 16H^+ \qquad (7)$$

$$6NO_2^- + 2BrO_3^- + Hg^{++} = 6NO_3^- + HgBr_2 \qquad (8)$$

$$6C_2O_4^{=} + 2BrO_3^- + Hg^{++} + 12H^+ = 12CO_2 + HgBr_2 + 6H_2O \qquad (9)$$

In the absence of mercuric ion, the bromate is reduced to free bromine in each instance (6–9).

Hovorka[4] determined the lower acids of phosphorus and also certain hydrazine derivatives by adding a measured excessive quantity of standard potassium iodate, mercuric perchlorate and acid. After oxidation was complete the excess of oxidant was determined.

(2) **Reactions in the Presence of Mercuric Chloride.**—When chloride is present in excess, and mercuric ion is present, there is competition between iodide and chloride ion for association with mercuric ion in the form of complexes or nonionized molecules. There is also a distribution of any elementary iodine that may be present be-

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(3) K. Brückner, *Monatsh.*, **27**, 341 (1906); **28**, 961 (1907).

(4) Hovorka, *Collect. Czechoslovak Chem. Comm.*, **2**, 559, 608 (1930); **3**, 285 (1931).

(5) Chateau, *Bull. soc. chim.*, [4] **17**, 121 (1915).

(6) Skrabal, *Chem.-Ztg.*, **33**, 1184 (1909).

(7) Josien, *Ann.*, **11**, 5, 147 (1936); *cf.* also Kolthoff and Furman, "Potentiometric Titrations," J. Wiley & Sons, Inc., New York, 1931, p. 192.

tween combination with iodide ion and mercuric chloride, respectively. The net result of these various tendencies is that iodate tends to be reduced to iodide and iodine to iodide by the majority of reductants (those of E_0 values less than 0.5–0.6 volt). Iodine under these conditions shows no tendency to undergo autoxidation to form iodate and iodide. Mercuric iodide is readily soluble in a sufficient excess of hydrochloric acid, and it dissolves without decomposition according to Kohler.[8]

In the absence of chloride ion, mercuric salts such as the sulfate tend to form complex basic salts, most of which are insoluble.[9]

The presence of chloride ion and acid tends to diminish the "protective effect" that Smith[2] observed. The following table indicates the extent to which loss of halogen occurs under various conditions.

TABLE I

THE EFFECT OF CHLORIDES UPON THE REACTION BETWEEN IODIDE AND BROMATE IN THE PRESENCE OF MERCURIC NITRATE

20.00 ml. of approximately 0.1 N $KBrO_3$ used, equivalent to 23.15 ml. of approximately 0.1 N $Na_2S_2O_3$. Mercury added as HgO dissolved in HNO_3. Time of boiling five minutes. Dilution 100 ml. 10.0 ml. 0.1 N KI added. 2.0 g. of mercury in soln.

Expt.	NaCl added, g.	Nitric acid, N	Iodine value of boiled solns., ml. of $Na_2S_2O_3$	Difference ml. of $Na_2S_2O_3$
1	0.0	1.0	23.13	−0.02
2	.1	1.0	23.05	− .10
3	.2	1.0	22.95	− .20
4	.7	0.5	22.60	− .55
5	1.0	1.0	22.90	− .25
6	1.5	2.0	17.90	−5.25
7	2.0	1.0	20.25	−2.90
8	5 ml. 6 N HCl	0.5	20.20	−2.95
9	10 ml. 6 N HCl	1.0	17.75	−5.40

In expts. 1–5 there was insufficient chloride to bind the mercury completely as mercuric chloride (2 g. mercury is equivalent to 1.17 g. sodium chloride). The formation of a mercuric iodate precipitate was noted in expts. 1–3. Solutions 6–9 became brown showing the liberation of iodine.

If error were introduced by the action of nitric acid upon the iodide to liberate iodine it would be in the direction opposite to that found by experiment. After the heating, the solution was cooled and diluted to 250 ml. before the addition of excess of potassium iodide to avoid the liberation of excess iodine by the action of nitric acid after the protective action of the mercuric ion had been removed. Experiment 1 indicates that this procedure is adequate.

We attribute the loss in oxidizing power (expts. 2–8, Table I) to the fact that the iodine does not undergo immediate autoxidation in such solutions, and hence escapes as vapor.

The following differences between the behavior of iodine in neutral and acidified mercuric chloride solutions are rather striking, and confirm the view that hydrochloric acid prevents autoxidation of iodine.

(a) Concentrated mercuric chloride solution plus iodine.	(b) A mixture of 5 ml. saturated iodine solution, 10 ml. saturated $HgCl_2$ soln. and 40 ml. of 6 N HCl.
1. The color of iodine disappears, unless a rather large amount is added.	1. The iodine color is evident, but faint.
2. No iodine is extracted from *the colorless solution* by carbon tetrachloride.	2. Iodine is extracted, but with much greater difficulty than from water. After 4 extractions with 5 ml. portions of CCl_4 only half of the iodine had been removed from the soln.
3. Upon addition of HCl, iodine is liberated.	3. After extraction, no iodide could be detected in the aqueous layer. (Evidence of non-formation of ICl which should leave iodide in the aqueous layer, $I_2 + Cl^- = ICl + I^-$)
4. After the removal of iodide from the aqueous layer by silver ion, the remaining solution[a] was able to oxidize iodide when acidified with HCl.	4.[a] The iodine that remained in the aqueous layer could be titrated to iodine monochloride with standard iodate.

[a] At this point the solution contained iodate.

[a] At this point the solution contained iodine and not iodate.

In both cases (a, b) we are concerned with the gross process

$$6I_2 + 6H_2O + 6HgCl_2 = 5HgI_2 + Hg(IO_3)_2 + 12HCl \qquad (10)$$

but in case (a) the equilibrium conditions are such that the formation of iodate is favored, whereas with excess of acid (case b) the interaction of iodate and iodide to form free iodine is favored. There is a further competing reaction that must be considered

$$HgCl_2 + I_2 \rightleftharpoons HgCl_2I_2 \qquad (11)$$

as was found in distribution experiments by Herz and Paul.[10] This process accounts for the great difficulty with which iodine is extracted from solutions containing mercuric chloride and hydrochloric acid.

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(8) Kohler, *Ber.*, **12**, 608 (1879).

(9) In Gmelin-Kraut, "Handbuch der anorganische Chemie," Vol. V^2, pp. 804–805, many compounds of the type $(3HgO \cdot 2SO_3)_x \cdot HgI_2 \cdot yH_2O$ are reported.

(10) Herz and Paul, *Z. anorg. Chem.*, **85**, 214 (1914).

In the foregoing considerations the formation of iodine monochloride has been neglected, although it might be an intermediate step in certain of the autoxidations that occur.[11]

Explanation of the Varied Stoichiometry of Iodate Reactions in the Presence of Mercuric Chloride and Hydrochloric Acid.—It has been demonstrated by Schoonover and Furman[12] that in addition to the customary iodate processes

$$IO_3^- + 6H^+ + Cl^- + 4e = ICl + 3H_2O \quad (12)$$

(In 4–6 N HCl; Hg may be either present or absent)

and

$$IO_3^- + 6H^+ + 5e = {}^1/_2I_2 + 3H_2O \quad (13)$$

(dilute acid, 1–3 N; Hg^{++} absent)

a third type of stoichiometry may be realized in the oxidation of arsenite by iodate ion

$$IO_3^- + 6H^+ + 6e = I^- + 3H_2O \quad (14)$$

The last process (14) occurs in the presence of a sufficient excess of mercuric chloride and at acidities between 1 and 3 N. In the subsequent section an attempt will be made to explain the latter type of stoichiometry upon the basis of electrode potential measurements.

The Effect of Mercuric Salts upon the Iodine–Iodide Potential

We now present measurements of the effect of mercuric salts upon the iodine–iodide potential, and make application of the effect to the titration of arsenite and antimonite by iodine at acidities not used hitherto.

In the measurements of potentials an attempt has been made to reproduce the conditions that prevail during titrations and to obtain data showing how the potentials of the various systems change relative to each other as a function of acidity. From such data it is possible to choose the most favorable range of acidity. No attempt has been made to correct for liquid junction potentials, since the calculation of the corrections at the high concentrations in question presents difficulties,[13,14] and for the present purposes relative potential values are adequate. As has been pointed out by Brönsted and Pedersen[15] high precision in measuring relative potentials is obtained when the concentration of the oxidation–reduction system is small relative to that of the other electrolytes.

As a test of our technique we have repeated the determination of the potential of the arsenate–arsenite systems as a function of acidity and have obtained good agreement with the data of Foerster and Pressprich[16] as is shown by the graph of the values on Fig. 1, curve 2, where points from both sets of measurements are plotted.

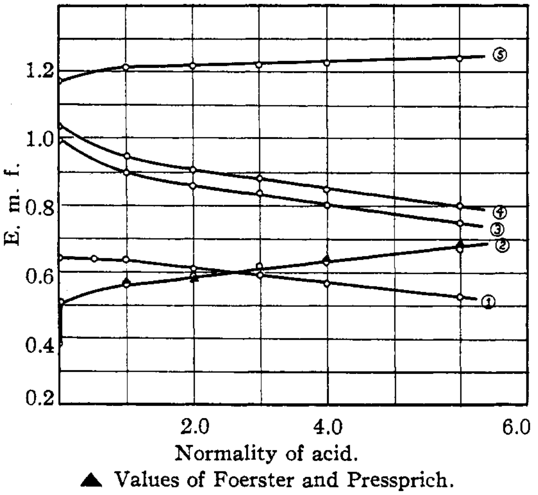

Fig. 1.—The abscissas represent normalities of hydrochloric acid, curves 1–5, or of sulfuric acid, curve 6. The ordinates represent oxidation–reduction potentials relative to the normal hydrogen electrode as zero, without correction for liquid junctions: (1), oxidation–reduction potentials of solutions 0.01 N in both iodine and iodide; (2), data for the arsenic system; solutions 0.01 N or 0.005 M in both forms of arsenic. The solid triangles are from measurements of Foerster and Pressprich;[7] (3), graph of potentials for the solutions used in (1) after adding 2 g. of mercuric chloride per 50 ml; (4), graph of potential values after adding 2 g. of mercuric chloride per 50 ml. of the solutions used in (3); (5), graph of potential values obtained upon adding 2 to 4 g. of solid mercuric sulfate to 50-ml. portions of solutions approx. 0.01 N in both iodine and potassium iodide and containing sulfuric acid as given on the abscissa axis.

Experimental

Apparatus and Materials.—Potentials were measured with a student-type assembly. Two spirals of bright platinum were used and averages of concordant readings of these relative to a saturated calomel electrode have been recorded. The side arm of the electrode terminated in a sintered porcelain plate. The cell was maintained at 25 ± 0.1° in a thermostat.

Potentiometric titrations were made by the classical

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[11] Faull and Forbes, THIS JOURNAL, **55**, 1809 (1933), postulate the formation of iodine monochloride in 6 N HCl solution by the action of air and light upon iodine. Hübl (cited in Beckurts "Methoden der Massanalyse," F. Vieweg and Sohn Braunschweig, 1931, p. 162) inferred that iodine monochloride was formed by the interaction of mercuric chloride and iodine in alcoholic solution.

[12] Schoonover and Furman, *ibid.*, **55**, 3123 (1933).

[13] Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

[14] Guggenheim, *ibid.*, **33**, 842 (1929).

[15] Brönsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922).

[16] Foerster and Pressprich, *Z. Elektrochem.*, **33**, 176 (1927).

method[17] or by the Furman and Wilson[18] continuous reading method. The calibrations of measuring vessels, standard cells and weights were checked against the secondary laboratory standards. Arsenious oxide from the Bureau of Standards was the basis of standardization of the volumetric solutions.

A solution approximately 0.02 *N* in iodine and in potassium iodide was prepared by dissolving 2.8806 g. of resublimed iodine and an equivalent amount (3.7678 g.) of dried reagent grade potassium iodide and diluting to 1 liter. An arsenate-arsenite solution of similar concentration was prepared from 1.0682 g. of reagent grade arsenious oxide dissolved in a minimum amount of sodium hydroxide, plus an equivalent amount (4.337 g.) of recrystallized sodium arsenate ($Na_2HAsO_4 \cdot 12H_2O$). The solution was made faintly acid to phenolphthalein and diluted to 1 liter.

Solutions of arsenite and antimonite for testing new titration procedures were prepared from Merck reagent grade arsenious oxide or from tartar emetic from the J. T. Baker Chemical Co., and analyzed iodometrically. Mercuric chloride was added in the form of a saturated solution in *N* hydrochloric acid.

Potential Measurements.—Twenty-five-ml. portions of the iodine–iodide solution were pipetted into the cell and the solution was diluted to 50 ml. with acid of the proper concentration to make the final concentrations as indicated in Table II. No attempt has been made to introduce corrections for triiodide ion formation because mercuric chloride is capable of binding both iodide ion and free iodine (or triiodide) to varying extents at various acidities. After making measurements on various mixtures of iodine–potassium iodide–acid, in each case 2 g. of solid mercuric chloride was added, and the mixture was stirred to constant composition and potential. The process was then repeated with the addition of 2 g. more of mercuric chloride. The data are recorded in Table II.

TABLE II

THE EFFECT OF HYDROCHLORIC ACID AND OF MERCURIC CHLORIDE UPON THE IODINE–IODIDE SYSTEM AT 25°

HCl, *N*	Potential, Pt *vs.* satd. calomel, v. 1 Soln. 0.01 *N* in I_2 & KI	2 As in 1 plus 2 g. $HgCl_2$ per 50 ml.	3 As in 2 plus 2 g. $HgCl_2$ per 50 ml.
0.0	0.400	0.760[a]	0.787[a]
.5	.400	.687[a]	.721[a]
1.0	.395	.662	.692
2.0	.376	.628	.649
3.0	.362	.607	.625
4.0	.345	.586	.604
6.0	.294	.531	.546

[a] In these instances a little solid iodine was observed. To each of the values (col. 1–3) 0.246 volt has been added in plotting Fig. 1.

A similar series of measurements was made upon solutions containing mercuric sulfate and sulfuric acid. Under these conditions mercuric iodide was first precipitated, but dissolved upon the addition of more mercuric sulfate. A fine white precipitate that separated was known to contain mercuric iodate bound in a complex compound.

TABLE III

THE EFFECT OF SULFURIC ACID AND MERCURIC SULFATE UPON THE OXIDATION–REDUCTION POTENTIAL OF EQUIVALENT MIXTURES OF IODINE AND IODIDE AT 25°

H_2SO_4 *N*	Potential, pt. *vs.* satd. calomel, v. 1 Soln. approx. 0.01 *N* in I_2 and KI	2 Soln. as in 1 plus 2 g. $HgSO_4$ per 50 ml.	3 As in 2 plus 2. g. $HgSO_4$
0.0	0.404	0.939	0.937
1.0	.404	.971	.966
2.0	.397	.980	.977
4.0	.379	.994	.996
6.0	.351	1.008	1.006

In this case it is evident that a reaction has occurred that has produced a system of very high potential (*iodate–iodide* system). The values are somewhat higher than the normal potential of the iodate–iodide–acid system because iodide ions are bound in the form of undissociated or complex substances. A mixture of mercuric sulfate, potassium iodide, potassium iodate and sulfuric acid of composition within the range of the measurements gave a potential in the measured range.

Foerster and Pressprich[16] have shown that arsenate–arsenite mixtures approach equilibrium potentials slowly and that a small quantity of iodide hastens the process. They observed that the iodine–iodide potential did not interfere with the measurements as long as the amount of this system added was equivalent to less than 10% of the arsenate–arsenite system. In our measurements a very minute crystal of potassium iodide was added to each solution so that the ratio of the two forms of arsenic was practically 1:1 at 0.01 *N* for each form.

TABLE IV

THE EFFECT OF ACIDITY UPON THE OXIDATION–REDUCTION POTENTIAL OF THE ARSENATE–ARSENITE SYSTEM, AT 25°

Medium	E. m. f. Pt. *vs* satd. calomel electrode, v.
$NaHCO_3$ *p*H 7	0.06–0.08 Unsteady
Buffer, *p*H 5	.23–0.24 Unsteady
Buffer, *p*H 3	.28
N HCl	.334
2 *N* HCl	.358
3 *N* HCl	.382
4 *N* HCl	.400
6 *N* HCl	.446

(In Fig. 1, curve 2, 0.246 volt has been added to these values)

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[17] Kolthoff and Furman, "Potentiometric Titrations," 2d ed., John Wiley & Sons, Inc., New York, 1931, p. 71 ff.

[18] Furman and Wilson, THIS JOURNAL, **50**, 288 (1928).

Discussion

The graphs (1, 2, Fig. 1) for the arsenic and iodine systems represent the oxidizing power of equivalent mixtures of the two forms in each case. At the beginning of the titration of a solution 0.01 N in arsenite and 1–2 N hydrochloric acid, the arsenate–arsenite ratio would be small and the potential would lie about 0.0885 volt below curve 2, while the potential of an iodine–iodide system, formed by the momentary *liberation of iodine* by interaction of iodate and the small amount of iodide derived from the iodate that had been added up to this point, would lie 2 or 3 times 0.059 volt above curve 1, Fig. 1. The iodine would be immediately reduced by the arsenite. This simple explanation in terms of oxidation–reduction potentials seems to account more adequately for the non-appearance of iodine in the early stages of such a titration than the qualitative interpretation in terms of relative reaction rates that were given by Schoonover and Furman.[12] In the latter a slow rate was attributed to the interaction of iodate, iodide and acid. As the titration proceeds, the relative positions of the two systems on the potential scale are reversed, and there is a sharp equivalence point corresponding to the oxidation of arsenite to arsenate and the reduction of iodate to iodine.

Figure 1 also indicates that the iodine–iodide system with mercuric chloride added is above the arsenate–arsenite system over the range of acidity that was studied. An increase in the concentration of mercury tends to bind the iodide more completely and the potential of a 1:1 mixture is raised still further by the increase.

The considerations that have been presented indicate clearly that new applications of iodine as an oxidizing agent may be made if mercuric chloride is added to the acidified solution that is to be titrated. Hitherto iodine has been used to titrate only the more powerful reductants such as stannous tin in acid solution. The latter may be titrated with iodate, which is reduced to iodide.[19] The steadiness of potentials at the end-points indicates that the presence of mercuric chloride tends to eliminate the troublesome autoxidation of iodide by air, which is catalyzed by many ions.

The potentials measured for the iodine–iodide system in the presence of mercuric sulfate and sulfuric acid are very much higher than for mixtures containing comparable amounts of mercuric chloride and hydrochloric acid. In contrast with the latter, doubling of the quantity of mercuric sulfate had practically no effect upon the potential. The iodine color disappeared in the sulfate case, and both electrical and chemical evidence points to the formation of iodate and iodide. It is difficult to make use of this high potential for titration purposes because of the appearance of insoluble products containing iodate.

The Iodometric Determination of Arsenic and Antimony in Acid Solution in the Presence of Mercuric Chloride

The preceding sections have indicated that the determination of trivalent arsenic or antimony may be made with standard iodine in a new range of acidity if mercuric chloride is added. The obvious advantages are the elimination of buffer mixtures and the possibility of operating in the presence of substances which would give undesirable precipitates or undergo oxidation at the *p*H which prevails in the usual iodometric method. It is necessary to use an excess of mercuric chloride that is sufficient to bind both the iodide introduced as potassium iodide in the standard solution and that which is formed by reduction of iodine.

The end-points of the oxidations may be determined either potentiometrically or with the aid of a suitable organic solvent for iodine, like carbon tetrachloride. The interference of mercuric chloride with the starch–iodide indicator for iodine is well known, and is probably to be attributed to binding of iodide and iodine by mercuric ion.[20] Mylius[21] proved that an iodide concentration of at least 10^{-6} g. is necessary. If an excess of potassium iodide is added, mercuric salts no longer interfere.[22] The early explanation by Millon[23] that mercuric chloride caused iodine to rearrange to iodine monochloride and iodide appears untenable because iodine may be extracted by carbon tetrachloride from solutions which fail to develop the color with starch.

Titration of Known Solutions.—Solutions of arsenite and antimonite were titrated with standard iodine solution in bicarbonate medium using starch as indicator. The titrations were repeated in solutions of various acidities with mercuric chloride present. In the latter case excel-

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(19) Ramsey and Blann, THIS JOURNAL, **56**, 815 (1934).

(20) Kolthoff, "Volumetric Analysis," Vol. II, J. Wiley & Sons, Inc., New York, 1929, p. 350.

(21) Mylius, *Ber.*, **28**, 388 (1896).

(22) Mahr, *Z. anal. Chem.*, **104**, 241 (1936).

(23) Millon, *Ann. chim. phys.*, **18**, 389 (1846).

lent agreement was obtained between potentiometric methods and the appearance of a permanent iodine color in a layer of carbon tetrachloride.

Table V

Comparison of the Determination of Arsenic and Antimony by Iodine in Bicarbonate Medium with that in Mercuric Chloride–Acid Medium

Solution usd (As or Sb) ml.	Standard iodine required In $NaHCO_3$ medium, av. ml.	In $HgCl_2$ acid medium, ml.	$HgCl_2$ soln., ml.	HCl concn., *N*
		A. Arsenic		
10.00	11.09	11.08	25	2.9
10.00	11.09	[a]	25	5.0
10.00	11.09	11.12	25	3.8
10.00	11.09	[a]	25	4.4
24.96	27.68	27.67	25	3.0
20.00	22.18	22.15	20	3.0
34.96	38.77	38.73	50	2.6
		B. Antimony		
10.00	13.40	13.40	25	2.7
10.00	13.40	[a]	25	4.2
24.96	33.37	33.40	50	2.6
24.96	33.37	33.32	50	3.0[a]
20.00	26.80	26.70	25	2.8

[a] Indicates that the reaction was too slow to be practical at the acidity in question.

There are several factors which determine the range of acid concentration that is permissible. At low acidities mercuric iodide tends to precipitate, and at high acidities the rate of reaction diminishes. At high acidities the potentials of the two systems tend to converge. The best condition is the lowest acidity that prevents the precipitation of mercuric iodide. An increase in the amount of mercuric chloride often permits the use of less acid.

The range of acidity is more restricted for antimony than for arsenic. The oxidation–reduction potential of the antimony system lies higher throughout the range than that of the arsenic system although exact data are not available. Latimer and Hildebrand[24] give 0.75 volt as the E_0 value for the antimony system.

If carbon tetrachloride is used as an indicating medium the mixture must be stirred quite vigorously as there is a tendency for iodine to accumulate in this solvent prior to the end-point. In the potentiometric titration there is no tendency for the potential to drift to lower values at the end-point after violent stirring for several minutes.

Applications.—The new method was further tested upon weighed samples of pure arsenious oxide. End-points were found with good concordance both potentiometrically[18] and with carbon tetrachloride. The solutions contained 50 ml. of saturated mercuric chloride solution and were 1.2–1.7 *N* in hydrochloric acid.

	1	2	3	4
As_2O_3 present, g.	0.0453	0.0739	0.0697	0.1203
As_2O_3 found, g.	$.0453_5$	.0740	.0696	.1202

Substances of antimony content unknown to the operator (M) were examined. Weighed samples of tartar emetic were dissolved in 20 ml. of water and 50 ml. of *N* hydrochloric acid saturated with mercuric chloride. Found: 37.48, 37.52 and 37.57% Sb. Value established by other investigators and other methods, av. 37.54% Sb.

One-gram samples of an alloy were dissolved in sulfuric acid (10 ml. concn.) with the usual precautions to remove sulfur dioxide and to prevent oxidation by air. After addition of 2 g. of sodium and potassium tartrate and 10 ml. of concd. hydrochloric acid and 50 ml. of the mercuric chloride, and proper dilution, potentiometric titrations were made. Found: 7.29 and 7.27% Sb, Bureau of Standards Certificate value 7.31% Sb. Owing to the presence of copper and other ions the use of carbon tetrachloride is not recommended for indication in the analysis of antimony alloys.

THE DETERMINATION OF ANTIMONY WITH STANDARD POTASSIUM IODATE

Introduction

Potassium iodate was first used by Andrews[25] for the determination of trivalent antimony, and the application of the method was extended by Jamieson.[26] The conditions employed were concentrated hydrochloric acid medium 4–6 *N*, in which the iodate is reduced to iodine monochloride. Lang[27] also used potassium iodate for the determination of antimony, but under conditions that result in the formation of iodine cyanide in a solution 1.2 *N* in hydrochloric acid; this method has the advantage that starch indicator may be used.

In the present investigation the reaction between antimonite and iodate has been studied with the object of testing the various stoichiometric processes that are possible, particularly at low acidities, with or without the addition of mercuric chloride.

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(24) Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, 1934, Appendix II.

(25) Andrews, This Journal, **25**, 756 (1903).

(26) Jamieson, *Ind. Eng. Chem.*, **3**, 250 (1911).

(27) Lang, *Z. anorg. allgem. Chem.*, **142**, 242 (1925).

The Effect of the Concentration of Hydrochloric Acid upon the Stoichiometry of the Reaction between Antimonite and Iodate.—The acidity is the important factor in determining the stoichiometry of this reaction, as was observed by Schoonover and Furman[12] in the analogous reaction between arsenite and iodate. At a low range of acidities a definite equivalence point was detected corresponding to the reduction of iodate to iodine

$$5H_3SbO_3 + 2KIO_3 + 2HCl = I_2 + 5H_3SbO_4 + 2KCl + H_2O \quad (15)$$

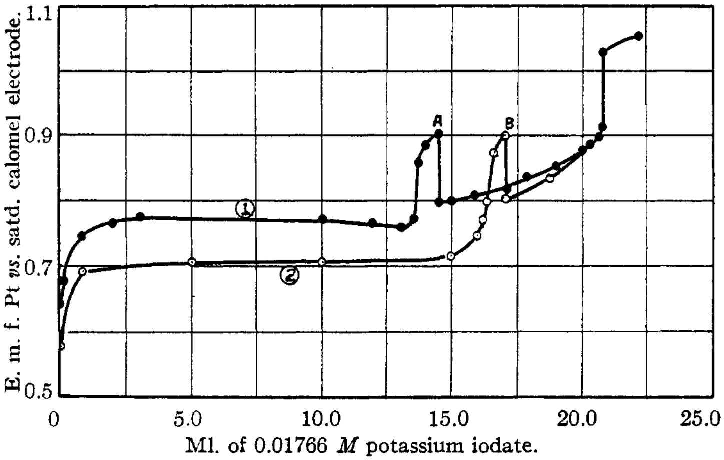

Fig. 2.—Curve 1: Graph of e. m. f. during titration of 0.0889 g. of antimony with 0.01766 M KIO_3 in the presence of mercuric chloride. Initial HCl concentration 2.7 N. At point A, HCl is added to bring its concentration above 5 N. Curve 2: repetition of titration as given in 1, with no mercuric chloride present.

In the absence of tartrates this "iodine" end-point is obtained over the narrow range of 2.4–3.5 N acid; with tartrates present the acidity may be as low as 1 N. Theoretically it might be possible to realize the stoichiometry of reaction (15) at somewhat higher acidities. The change in potential at the end-point would depend upon a transition from the iodine–iodide level to the iodine–iodine monochloride level which is less favorable for observation than a change to the iodine–iodate level.

The change in potential at the latter transition is only of the order of 0.03–0.07 volt per 0.05 ml. of 0.1 N potassium iodate. The classical potentiometric method rather than simplified methods was used for this small change. At acidities of 4–6 N the iodine that is liberated in the first reaction (15) is oxidized to iodine monochloride

$$2I_2 + KIO_3 + 6HCl = 5ICl + KCl + 3H_2O \quad (16)$$

and a second end-point is realized by adding hydrochloric acid and titrating to a second break in potential. The addition of the acid produces a drop in potential point B, curve 2, Fig. 2. At the latter end-point 0.05 ml. of 0.1 N iodate produces a rise of 0.07–0.12 volt. The presence of tartrate does not interfere with the detection of either end-point.

It was observed[12] that the presence of an immiscible organic solvent for iodine increases the potential change at the iodine equivalence point. Benzene is more effective than carbon tetrachloride and is to be recommended if the iodine end-point alone is to be determined. If the iodine monochloride end-point is also to be found, carbon tetrachloride offers mechanical advantages: ease of stirring from its position below the aqueous layer, and prevention of loss of iodine by volatilization.

The potassium iodate was 0.01766 M. The normalities for the iodide, iodine or iodine monochloride end-points are, respectively, 6, 5 or 4 times the molarity.

The iodine end-point was also obtained by titrating antimonite with iodate in sulfuric acid solutions from 2.7 to 6.0 N. In twelve determinations the maximum error was 0.2%. Only the iodine end-point is obtained in this medium.

The Oxidation of Trivalent Antimony in Hydrochloric Acid Solution with Mercuric Chloride Present.—In the presence of mercuric chloride there is a sharp end-point at the completion of the reduction of the iodate to iodide

$$3H_3SbO_3 + KIO_3 \xrightarrow[(HgCl_2)]{(HCl)} 3H_3SbO_4 + KI \quad (17)$$

TABLE VI

THE TITRATION OF ANTIMONITE WITH POTASSIUM IODATE IN HYDROCHLORIC ACID SOLUTIONS

Expt.[a]	Antimony present, g.	KIO_3 to iodine end-pt., ml.	Antimony found from 3, g.	KIO_3 to ICl end-pt., ml.	Antimony found from 5, g.	HCl concn. Init. N	HCl concn. Final N
2	0.0889	16.54	0.0889	20.70	0.0891	2.7	5.3
3	.0889	16.53	.0889	20.68	.0890	3.7	5.3
4	.0889	16.55	.0890	20.70	.0891	3.4	7.0
9	.0889	16.53	.0889	20.67	.0890	2.9	4.4
7[b]	.1555	28.81	.1549			1.4	
10[b]	.1779	33.31	.1781	41.43	.1782	0.8	4.7
25[b]	.0777	14.43	.0776	18.05	.0777	1.2	5.0

[a] The few experiments that have been selected include a fair sampling of the most and least accurate results of the whole series.

[b] Low initial acidity possible because tartrate was present.

We have explained the mechanism of this process on the basis of the formation of undissociated mercuric iodide which is soluble in hydrochloric acid. The iodine–iodide potential is so far increased by this process that iodine formed momentarily during the reaction is immediately reduced to iodide by the antimonite. The relative levels of the iodine and antimony systems under these conditions have been discussed (p. 158).

The first small increment of standard iodate beyond the iodide end-point produces free iodine which may be detected readily by extraction to a layer of carbon tetrachloride, and this simple visible indication agrees with the potentiometric end-point within about 0.02 ml. of 0.1 *N* solution. At acidities below 3.5 *N* the change in e. m. f. is of the order of 0.25 volt per 0.05 ml. of 0.1 *N* iodate at the end-point. The continuous-reading circuit was used for most of the determinations that are represented in Table VII. In many cases carbon tetrachloride was also present and a double indication was obtained. After the finding of this first end-point, increase of hydrochloric acid concentration to 4–6 *N* again causes a drop in potential (A, curve 1, Fig. 2) and the titration may be carried to the iodine monochloride point.

TABLE VII

THE DETERMINATION OF ANTIMONY WITH POTASSIUM IODATE IN THE PRESENCE OF MERCURIC CHLORIDE

1	2	3	4	5	6	HCl	
Expt.[a]	Antimony present, g.	KIO_3 to iodide end-pt., ml.	Antimony found from 3, g.	KIO_3 to ICl end-pt., ml.	Antimony found from 5 g.	Concentration Init. N	Final N
1	0.0889	13.80	0.0890	20.67	0.0889	2.6	5.3
2	.0889	13.79	.0890	no break		2.8	2.0
13	.1779	27.57	.1778	41.34	.1779	3.0	5.9
26	.1779	27.59	.1780	41.37	.1789	3.0	3.5
8[b]	.1555	24.05	.1552	36.06	.1551	1.8	4.0
15[b]	.0777	12.03	.0776	18.05	.0777	2.0	4.4
32[b]	.0889	13.78	.0889	20.67	.0889	1.4	3.8

[a] See notes below Table VI regarding selection of experiments, and normality of potassium iodate.

[b] Tartrates present.

Discussion

The general conclusions of these studies of the stoichiometry of the antimony reactions are similar to those in the investigation of the determination of arsenic;[12] the rather obvious conclusion that both arsenic and antimony if present together would be determined simultaneously according to any of the three possible reactions, has been verified by experiments which need not be detailed here.

The possibility of visual estimation of the iodide end-point has been pointed out; this applies to the determination of arsenic as well, although it was not noted in the former investigation.[12] We believe the mechanism of the oxidations by iodate in the presence of mercuric chloride to be essentially the same as those by iodine. The use of iodate rather than iodine offers the advantage of detecting the iodine monochloride end-point if the first end-point is overstepped.

Summary

1. The fact that the addition of iodine to solutions of mercuric salts in sulfuric, perchloric and nitric acids produces an immediate rearrangement into equivalent quantities of iodide and iodate has been confirmed.

2. The apparent failure of strong oxidizing agents to oxidize halides in the presence of highly ionized mercuric salts has been explained by showing that an oxidation does occur, but that the total oxidizing power of the solution toward a strong reducing agent like potassium iodide is preserved due to the autoxidation of the halogen under these conditions.

3. The effect of chlorides upon mixtures of bromate, iodide and mercuric nitrate has been observed, and the peculiar properties of solutions of iodine in mercuric chloride have been pointed out.

4. The ability to obtain the iodide equivalence point in the reaction between iodate and arsenite in the presence of mercuric chloride and hydrochloric acid has been attributed to an increase in the iodine–iodide potential due to the removal of iodide ions from solution as un-ionized mercuric iodide which is soluble in hydrochloric acid.

5. The oxidation–reduction potentials of equivalent mixtures of arsenate and arsenite and of iodine and iodide have been measured at various concentrations of hydrochloric and sulfuric acids. The very marked effect of mercuric chloride and mercuric sulfate upon the potentials of the iodine–iodide mixtures has been determined, and the increase has been attributed to binding of iodide by mercuric ions when chlorides are present and to the formation of iodate in the solutions containing sulfates.

6. It has been shown that a standard iodine solution may be used to titrate arsenite in solutions 1.2–3.8 *N* in hydrochloric acid, or antimonite in solutions 2–2.8 *N* in the acid, provided mercuric chloride is added to increase the iodine–iodide potential to a sufficient extent. This new

mode of titrations has been applied to the determination of arsenic and antimony in a few of the materials that are encountered in practice.

7. It is possible to determine antimony with standard potassium iodate under conditions such that the iodate may be reduced, as desired, to iodide, iodine or iodine monochloride. The first and third, or the second and third of the possible stoichiometric processes may be realized to give two end-points in a single titration. The new procedures involving the reduction of iodate to iodine at low acidities, or to iodide at low acidities in the presence of mercuric chloride, give results which compare favorably in accuracy with those obtained by other procedures.

PRINCETON, N. J. RECEIVED JULY 31, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Use of Iodine and of Potassium Iodate as Volumetric Oxidizing Agents in Solutions Containing Mercuric Salts. II. The Oxidation of Phenylhydrazine and of Semicarbazide by Means of Potassium Iodate

BY CLARK O. MILLER AND N. HOWELL FURMAN

Introduction

The nature and proportions of the end-products of the oxidation of hydrazine and its derivatives vary with the specific nature and the oxidation–reduction potential of the oxidizing system and with the *p*H of the medium. These facts have been established by various investigators.[1] It is a striking fact that hydrazine is oxidized quantitatively to nitrogen and water only by iodine, bromine or certain halogen oxyacids or salts;[1a,c] in other cases variable amounts of hydrazoic acid and ammonium salts are formed.

The determination with iodine must be made in buffered neutral or alkaline solutions since the reaction is too slow in acid medium for direct titrations. Hydrazine and its derivatives, especially phenylhydrazine, are readily oxidized by air under these conditions and hence the iodine method is of limited applicability.

We have shown[2] that the addition of mercuric chloride to the acidified solution that is to be titrated makes it possible to realize the stoichiometry of the reduction of iodate to iodide or of iodine to iodide smoothly in a range of acidity that would not be possible in the absence of the mercuric salt. This development increases the scope of iodine and iodate methods. We have chosen the oxidation of phenylhydrazine and of semicarbazide, respectively, as further illustrations of the application of potassium iodate under the new conditions of titration.

Phenylhydrazine.—Emil Fischer[3] stated that an emulsion of phenylhydrazine and water reacted as follows with iodine

$$2C_6H_5NHNH_2 + 2I_2 = 3HI + C_6H_5NH_2 \cdot HI + C_6H_5N_3 \quad (1)$$

If an excess of hydrazine is used (2 moles per mole of $C_6H_5NHNH_2$) the reaction that occurs is

$$C_6H_5NHNH_2 + 2I_2 = 3HI + C_6H_5I + N_2 \quad (2)$$

according to von Meyer.[4] A volumetric process was based upon reaction (2) by adding a measured excess of standard iodine to the slightly alkaline solution, followed by back-titration with standard thiosulfate.

Fehling's solution oxidizes phenylhydrazine to nitrogen, water and benzene, and the nitrometric method of Watson Smith[5] is based on this reaction.

Seide, Scherlin and Bras[6] state that iodic acid reacts with phenylhydrazine in benzene–water emulsion to give a 25% yield of monoiodobenzene. Rimini[7] noted that hydrazine was oxidized by iodic acid, and Kurtenacker and Kubina[8] stated that direct titration of phenylhydrazine and semicarbazide with iodate to the iodine monochloride end-point is possible, but gave experimental evidence only for the latter compound. They also studied the determination of both substances with standard potassium bromate.

Mechanism of the Oxidation.—In our studies, two observations were made which do not seem in

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[1] (a) Browne and Shetterly, THIS JOURNAL, **30**, 53 (1908); (b) Hale and Redfield, *ibid.*, **33**, 1353 (1911); (c) Bray and Cuy, *ibid.*, **46**, 858 (1924).

[2] Furman and Miller, *ibid.*, **59**, 152 (1937).

[3] Fischer, *Ber.*, **10**, 1335 (1887).

[4] E. von Meyer, *J. prakt. Chem.*, **36**, 115 (1887).

[5] Watson Smith, *Chem. News*, **93**, 83 (1906).

[6] Seide, Scherlin and Bras, *J. prakt. Chem.*, **138**, 225 (1933).

[7] Rimini, *Gazz. chim. ital.*, **35**, I, 267 (1905).

[8] Kurtenacker and Kubina, *Z. anal. Chem.*, **64**, 388 (1924).