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.

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[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

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

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

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

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).

accord with the equation of von Meyer.[4] First, no liberation of nitrogen was observed in the early stages of the reaction, and second, no monoiodobenzene was detected. Nitrogen was evolved slowly toward the end of the titration. Upon treatment of the partially oxidized solution with alkaline beta-naphthol, a red dye was formed, indicating the presence of a diazonium salt. Equations for the three types of iodate processes may then be written:

(a) In 1-3 *N* HCl with mercuric chloride present

$$3C_6H_5NHNH_2 + 2KIO_3 + 3HCl = 3C_6H_5NNCL + \underset{\underset{HgI_2}{\downarrow}}{2KI} + 6H_2O \quad (3)$$

(b) In 1-3 N HCl

$$5C_6H_5NHNH_2 + 4KIO_3 + 9HCl = 5C_6H_5NNCl + 2I_2 + 12H_2O \quad (4)$$

(c) In 4-6 *N* HCl

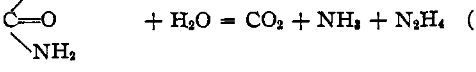
$$C_6H_5NHNH_2 + KIO_3 + 3HCl = C_6H_5NNCl + ICl + KCl + 3H_2O \quad (5)$$

The quantitative oxidation appears to be concerned with the formation of the diazonium salt, and the reaction of the latter with the medium to give nitrogen and phenol is a secondary process. The presence of phenol was confirmed by evaporating the solution to a small volume and coupling with phthalic anhydride.

The formation of the diazonium salt was also observed when phenylhydrazine was titrated with iodine. If a large excess of iodine-potassium iodide solution were used, both phenol and iodobenzene probably would be formed.

Chattaway[9] has shown that primary aromatic amines are transformed into diazonium salts by the action of other halogens (Cl_2 or Br_2) in glacial acetic acid solution.

Semicarbazide.—Prior studies of the determination of semicarbazide have been along the same lines as in the case of hydrazine. It was shown by Maselli[10] that semicarbazide is hydrolyzed with the formation of hydrazine by boiling in dilute sulfuric acid solution



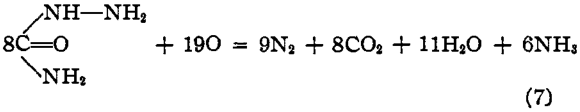
$$C(=O)(NH{-}NH_2)(NH_2) + H_2O = CO_2 + NH_3 + N_2H_4 \quad (6)$$

The general concept that the hydrolysis of the compound must precede its oxidation apparently persists.[11]

Kurtenacker and Kubina[8] suggested two procedures for the determination of semicarbazide with potassium iodate. One consisted in adding a measured excess of standard potassium iodate, boiling to expel iodine and back-titration of the excess of the iodate. The other method was the conventional direct titration to the iodine monochloride end-point; few test analyses were given.

Hovorka[12] devised an indirect procedure for the determination of semicarbazide, using mercuric perchlorate and iodate. Thirty minutes are usually required for the oxidation to reach completion, after which the excess of iodate is determined by adding an excess of potassium iodide and titrating the iodine with standard thiosulfate solution. The chief advantage that this method offers is that the necessity of boiling iodine out of the solution is eliminated.

The oxidation of semicarbazide with either chlorate, bromate or iodate was investigated by Datta and Choudhury[13,14] with the object of developing a gasometric method for estimating the compound. The equation that was given for the reaction is

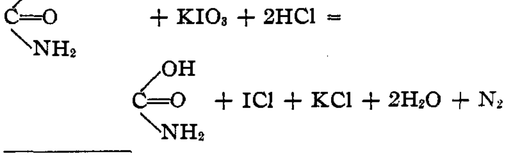


$$8C(=O)(NH{-}NH_2)(NH_2) + 19O = 9N_2 + 8CO_2 + 11H_2O + 6NH_3 \quad (7)$$

The results deviate as much as 3.0% from the theoretical. The carbon dioxide must be absorbed. The fact that a functional group, $-NH_2$, is partially oxidized seems to make this type of procedure uncertain.

Bartlett[15] reported that 99.9% of the semicarbazide present was oxidized by excess of iodine in three seconds in a phosphate buffer of *p*H 7.

From a consideration of the various facts, the rapid reaction of semicarbazide with iodine in neutral solution or with iodate in acid solution is not due to hydrolysis, but depends upon direct attack of the hydrazine group with intermediate formation of unstable carbamic acid, which immediately breaks down to give carbon dioxide and ammonia



$$C(=O)(NH{-}NH_2)(NH_2) + KIO_3 + 2HCl = C(=O)(OH)(NH_2) + ICl + KCl + 2H_2O + N_2 \quad (8)$$

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[9] Chattaway, *J. Chem. Soc.* (London), **93**, 852 (1908).

[10] Maselli, *Gazz. chim. ital.*, **35**, I, 267 (1905).

[11] V. Harlay, *J. Pharm. Chem.*, **123**, 199 (1936); through *C. A.*, **30**, 4789 (1936). The first step of the method here proposed is the heating of the semicarbazide with 10, 20 or 30% hydrochloric acid in a sealed tube to hydrolyze it, after which the conventional iodometric titration is used.

[12] Hovorka, *Coll. Czechoslov. Chem. Commun.*, **3**, 285 (1931).

[13] Datta, THIS JOURNAL, **36**, 1014 (1914).

[14] Datta and Choudhury, *ibid.*, **38**, 2736 (1916).

[15] Bartlett, *ibid.*, **54**, 2853 (1932).

In solutions that are lower than 3 N in hydrochloric acid the iodate is reduced to iodine if mercuric salt is absent, or to iodide if mercuric chloride is present in concentration sufficient to bind the iodide. The latter stoichiometry has not been realized hitherto in a direct titration.

Experimental

Since the researches of Ardagh, *et al.*[16] have shown that solutions of phenylhydrazine are relatively unstable, even when acidified, and must be preserved under an inert atmosphere, it was found desirable in our work to weigh samples of purified phenylhydrazine hydrochloride for each experiment. Samples of an Eastman product were recrystallized from hot water after decolorizing them with charcoal. The crystals were washed thoroughly with alcohol, then with ether and were dried by vacuum desiccation overnight. Drying for short intervals at 100° is also permissible, but at higher temperatures discoloration occurs and partial rearrangement to *p*-phenylenediamine takes place.

The purity of the crystals was tested by titration of samples with sodium hydroxide that had been standardized against pure benzoic acid, using phenolphthalein indicator. At the equivalence point the solution contains sodium chloride and free phenylhydrazine, $K_b = 1.6 \times 10^{-9}$. Hence for solutions between 0.1 and 0.01 N the *p*H at the end-point is from 9.1–8.6. In a series of nine titrations the maximum error was ±0.25% and the average was +0.03%, on the assumption of a pure product.

The standard potassium iodate and the mercuric chloride solutions were prepared as in the preceding investigation,[2] where the nature of the electrical apparatus is also mentioned.

Semicarbazide hydrochloride, from the G. F. Kahlbaum Co., was purified by dissolving in distilled water, filtering, and precipitating by the addition of 1–2 volumes of ethyl alcohol. The crystals were filtered, washed repeatedly with 95% alcohol, then with ether. After vacuum desiccation overnight the material was suitable for weighing. The tested technique of purification together with the titrations to the iodine monochloride point with iodate served to establish the purity of the material.

The Titration of Phenylhydrazine Hydrochloride with Standard Potassium Iodate in the Presence of Hg^{++}.—Portions of the purified substance ranging from 0.08 to 0.26 g. were titrated in solutions of various acidities as shown in Table I. In each case 15–25 ml. of saturated mercuric chloride was present, and the final volume after titration was about 150 ml. In neutral or feebly acid solution phenylhydrazine reduces mercuric ion; it is therefore desirable to acidify the solution before adding the phenylhydrazine. No reduction occurred when the acidity was at least 2 N. If only a small amount of mercurous chloride is formed, the solution need not be discarded because the iodate oxidizes the mercurous chloride to mercuric, during the titration.

At the end of the titration to the first end-point (iodide) the potential jump is 0.06 to 0.08 volt per 0.05 ml. of 0.1 N KIO_3; either classical or simplified methods may be used. The use of carbon tetrachloride for the "iodide" end-point is not very satisfactory.

TABLE I

POTENTIOMETRIC TITRATION OF PHENYLHYDRAZINE WITH POTASSIUM IODATE SOLUTION IN THE PRESENCE OF MERCURIC CHLORIDE

1	2	3	4	5	6	7
Sample, g.	KIO_3 to iodide end-pt., ml.	$C_6H_5N_2$-H_3HCl found from 2, g.	KIO_3 to ICl end-pt., ml.	Subst. found from 4	Concentration of HCl, N Init.	Final
0.1831	35.55	0.1833	53.30	0.1832	1.1	3.6
.1119	21.73	.1120	32.53	.1118	2.8	4.0
.1447	28.05	.1446	42.05	.1446	2.6	4.2
.1328	25.70	.1325	38.59	.1326	2.8	3.9
.1590	30.77	.1587	46.08	.1584	1.6	5.0
.1099*	21.28	.1098	32.05	.1101	3.2	4.1
.1219*	23.63	.1218	35.50	.1220	3.6	4.2
.1159*	22.45	.1158	33.66	.1157	2.4	3.9

The KIO_3 solution was 0.02378 M and the normality is, respectively, 6 or 4 times molarity for the iodide and iodine monochloride end-points. In the last three determinations, marked (*), from 0.5 to 1 ml. of aniline was present.

After finding the first end-point, the stoichiometry of equation (5) may be realized by continuing the titration after adding hydrochloric acid to 4–6 M concentration. Potential break: 0.12–0.16 volt per 0.05 ml. of 0.1 N KIO_3. Care must be taken to avoid the accumulation of nitrogen bubbles on the platinum indicator electrode.

It is of interest that potassium iodate oxidizes the hydrazine group selectively in the presence of an aromatic amine (aniline), whereas more powerful oxidants attack the latter under similar conditions.

A series of eight determinations under conditions similar to those indicated in Table I, but with omission of the mercuric salt, proved that it was possible to realize the stoichiometry of equation (4); after adding hydrochloric acid to 4–6 M concentration the titration may be continued to a second end-point corresponding to equation (5). The maximum errors were +0.20 and −0.30%. Only three determinations were in error by more than 0.2%.

A critical experimental study of the conventional iodine method yielded the following conclusions: low results are obtained in alkaline solution; the reaction is incomplete in strongly acid solution; correct results are obtained when the *p*H of the solution is between 2 and 5. We found the iodine method to be tedious due to the sluggishness of the reaction near the end-point. We regard the various iodate procedures that have been described as far superior to the titration with iodine.

The Oxidation of Semicarbazide in the Presence of Mercuric Chloride.—The weighed samples were dissolved in water and hydrochloric acid (see Table II) and 15–30 ml. of saturated mercuric chloride solution was added. The initial volume ranged from 40–80 ml. The progress of the reaction was followed potentiometrically or by noting the readings of a sensitive galvanometer in series with a high resistance. The reaction is slow near the "iodide" end-point, so that the last 0.2 ml. of reagent must be added in drops at about thirty-second intervals. Each drop produces a potential rise which diminishes rapidly prior to the end-point, but does not diminish at the end-point; change, 0.08 volt per 0.05 ml. of 0.1 N KIO_3. Up to a certain limit the addition of more mercuric chloride makes the process more rapid.

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[16] Ardagh, *et al.*, THIS JOURNAL, **54**, 721 (1932).

The iodine monochloride equivalence point is very sharp and must be recommended as the most satisfactory for ordinary titrations. If a carbon tetrachloride layer is used for indication, very thorough stirring or shaking is necessary near the end-point. The break in e. m. f. is about 0.13 volt per 0.05 ml. of 0.1 *N* reagent. The data in Table II are fairly representative of 22 determinations that were made.

TABLE II

POTENTIOMETRIC TITRATION OF SEMICARBAZIDE HYDROCHLORIDE WITH STANDARD POTASSIUM IODATE IN THE PRESENCE OF MERCURIC CHLORIDE

1	2	3	4	5	6	7
Sample, g.	KIO_3 to "iodide" end-pt., ml.	Subst. found from 2 g.	KIO_3 to ICl end-point, g.	Subst. found from 4 g.	Concn. of HCl, *N*	
					Initial	Final
0.1263	31.80	0.1264	47.50	0.1266	1.1	6.1
.1026	25.76	.1025	38.68	.1026	0.8	3.7
.1362	34.73	.1362	52.04	.1361	.8	3.4
.1514	38.48	.1509	57.84	.1514	1.7	4.3
.0627	15.95	.0626	24.00	.0627	1.3	5.0
.1070	27.20	.1066	40.82	.1067	1.2	4.0
.0874*			33.42	.0874		4.65
.1612*			61.70	.1613		4.3
.1055			40.40	.1058		4.8

The potassium iodate solution was 0.02378 *M* for the first two determinations and 0.02344 for the others. The normalities for the iodide and iodine monochloride reactions are, respectively, 6 and 4 times the molarity. In the determinations marked (*) the solution contained 0.1 to 0.5 g. of urea. Potassium iodate oxidizes the aliphatic hydrazine derivative selectively in presence of the corresponding amino compound just as was the case with the aromatic substances.

A number of experiments proved that it was impractical to base a direct titration on the process involving the reduction of the iodate to iodine in dilute hydrochloric acid solution (less than 3 *N*) in the absence of mercuric chloride. The reaction was extremely slow in the neighborhood of the end-point.

Of the determinations made to the iodine monochloride point only four deviated as much as 0.21–0.27% from the theoretical value, and the average deviation was −0.05%. Semicarbazide could therefore serve as a standard substance since it is purified and preserved easily. The substance has suitable characteristics for the removal of an excess of an oxidizing agent that is not powerful enough to attack the amino group. The nature of the products (CO_2, N_2, ammonium salt and water) is favorable for such application.

Summary

1. The oxidation of phenylhydrazine in acidic solution by potassium iodate or by iodine has been shown to result in the formation of the diazonium salt which slowly hydrolyzes giving off nitrogen and forming phenol in the absence of an excess of potassium iodide.

2. The iodate procedures have been compared with the iodine method and they offer decided advantages of rapidity and ease of execution.

3. Potassium iodate does not attack aniline readily in cold acidified solutions and correct results are obtained for phenylhydrazine in the presence of the former.

4. The optimum conditions for the stoichiometric reduction of iodate to iodide, with mercury present, or to iodine monochloride in 3–6 *N* hydrochloric acid solution by both phenylhydrazine and semicarbazide have been investigated. In the case of phenylhydrazine it was also found possible to obtain an end-point corresponding to the reduction of the iodate to iodine, at low acid concentration.

5. The mechanism of the oxidation of semicarbazide has been considered and it has been pointed out that hydrolysis need not precede the oxidation process.

6. Potassium iodate attacks urea very slowly in cold acidified solutions and semicarbazide may therefore be titrated selectively in the presence of the former substance.

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