Pre-oxidation by Iodine Monochloride—Potassium Hydroxide and Use of Iodine Monochloride End Point in the Determination of Hydrazine, Thiocyanate, Thiosulfate and Glucose

By Bechu SHARMA

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Iodate procedures introduced by Andrews[1] and later developed by Jamieson[2] and Lang[3], involve essentially the formation of iodine (+). Although applicable to a variety of common reductants, in a number of cases, iodate is not capable of bringing about direct oxidation. Thus ferrous iron and ferrocyanide bring about an apparent state of equilibrium which changes only slowly. Lang[3-4] proposed for such reductants a preoxidation by iodine monochloride solution prepared from iodide and iodate in the presence of chloride. Lang further found applicability of this method to an alkaline medium, wherein some cases hypoiodite acts more efficiently, e. g. for the determination of hydrogen peroxide[4] and formaldehyde[5]. An additional advantage of this procedure is that the back titrations can as well be followed with permanganate and ceric sulfate which are standared volumetric oxidizing agents. This point has been emphasized by Swift[6] and his coworkers in the determination of arsenic(III) wherein excessive iodine monochloride was followed in an acid medium. An earlier communication described the "iodine monochloride + sodium hydroxide" oxidation and iodine monochloride end point using iodate, permanganate and ceric sulfate for the determination of thiourea and its derivatives[7]. Subsequent investigations revealed that thiosulfate which is oxidized by alkaline hypoiodite could as well be determined. In an alkaline medium, thiosulfate is oxidized to sulfate which provides an advantage of a high conversion factor. The direct oxidation of thiocyanate by iodate, stops at cyanide stage alone while by alkaline hypoiodite it is converted into cyanate. Herein then, the modified procedure would provide an advantage of higher molecular ratio. Again, the oxidation of hydrazine sulfate, which is an ideal primary standard on account of its stability, ease of purification and various acidimetric and oxidimetric applications, was subjected to restricted conditions of acidity when titrated by iodine monochloride procedure. On the other hand, however, it could be easily oxidized by hypoiodite. Glucose is not oxidized by iodate in an acid medium, but iodine in weakly alkaline medium is capable of oxidizing it to gluconic acid. This principle was therefore applied to the determination of glucose as well. It may be pointed out that there are no direct titrimetric procedures for glucose, whose oxidation, except by iodine, hardly stops at the gluconic acid stage and the complete oxidation by drastic oxidants like permanganate and ceric sulfate in an acid medium and by ferricyanide in an alkaline medium, requires critical operative conditions for quantitative conversion into carbon dioxide and water.

1) L. W. Andrews, *J. Am. Chem. Soc.*, **25**, 756 (1903).
2) G. S. Jamieson, *Am. J. Sci.*, **33**, 352 (1912).
3) R. Lang, *Z. anorg. u. allgem. Chem.*, **142**, 229 (1925).
4) R. Lang, ibid., **142**, 280 (1925).
5) R. Lang, *Z. anal. Chem.*, **106**, 12 (1936).
6) E. H. Swift and C. H. Gregory, *J. Am. Chem. Soc.*, **52**, 901 (1930).
7) G. S. Deshmukh and M. G. Bapat, *Z. anal. Chem.*, **156**, 276 (1957).

Experimental

A 0.5 M iodine monochloride solution was prepared by dissolving 17.5 g. of potassium iodate, and 22.7 g. of potassium iodide in 250 ml. of water to which 150 ml. 12 M hydrochloric acid was added. The solution was titrated with iodate or iodide solution using carbon tetrachloride till the organic layer was colorless. A 0.1 M potassium thiocyanate solution was prepared and standardized as usual by titration with standard silver nitrate solution. Sodium thiosulfate solution was standardized against potassium dichromate as well as with 0.1 N potassium iodate using iodine monochloride end point. The latter was found to be a better check due to the oxidation of thiosulfate to sulfate, which was subsequently achieved by hypoiodite oxidation. A 0.1 N hydrazine sulfate solution was prepared from British Drng House (L.R.) reagent recrystallized from water twice and dried at 140°C. A 1% glucose solution was prepared from E. Merck (L.R.) sample and was standardized by iodimetric determination. Potassium permanganate and ceric sulfate solutions were prepared and standardized as usual. Except for glucose the following

TABLE I. OXIDATION OF HYDRAZINE BY IODINE MONOCHLORIDE+POTASSIUM HYDROXIDE

ml. 0.1 N (0.025 M) hydrazine sulfate	ml. 0.5 M iodine monochloride	Overall alkali %	Reaction time in min.	ml. 0.025 M iodate	Diff. %
(*a*) *Effect of excessive oxidant*					
10	3	1	5	9.60	4.00
10	4	1	5	9.80	2.00
10	5	1	5	9.95	0.50
15	10	1	5	14.95	0.33
(*b*) *Effect of hydrazine concentration*					
10	5	2	5	10.00	—
15	8	2	5	14.95	0.33
20	10	2	5	20.00	—
(*c*) *Test analysis*					
				ml. 0.1 N permanganate	
5	2	1	5	4.95	1.00
10	5	1	5	9.95	0.50
15	7	2	5	15.00	0.00
25	10	2	10	24.90	0.04

In all the experiments, hydrazine sulfate+iodine monochloride+potassium hydroxide was the order followed, in order to utilize the oxidant both in an acid and an alkaline medium.

TABLE II. OXIDATION OF THIOCYANATE BY IODINE MONOCHLORIDE+POTASSIUM HYDROXIDE

ml. 0.01 M thiocyanate	ml. 0.5 M iodine monochloride	Overall alkali %	Reaction time in min.	ml. 0.025 M iodate	Diff. %
(*a*) *Effect of excessive oxidant*					
10	2	1	5	7.20	−10.00
10	5	1	5	7.80	− 2.50
10	5	1	10	7.80	− 2.50
10	10	1	10	7.85	− 1.88
(*b*) *Effect of alkali concentration*					
10	2	3	10	7.50	− 6.25
10	4	4	10	7.80	− 2.50
10	5	4	10	7.90	− 1.25
10	5	6	10	7.95	− 0.62
(*c*) *Test analysis*					
5	3	4	10	3.95	− 1.25
7.5	5	5	10	5.90	− 1.56
10	10	5	10	7.95	− 0.62
10	10	5	10	7.95	− 0.62

The order of mixing was thiocyanate, iodine monochloride and alkali, in order to utilize the oxidant in acid and alkali medium.

general procedure was adopted. An aliquot of the reductant solution was taken in an Erlenmeyer flask to which an amount of iodine monochloride (at least 3/2 times that calculated on the reduction to iodide) and finally 25% (potassuim hydroxide solution were added to render the solution 1~2 N in alkali. Advantage of the addition of iodine monochloride was that the oxidant was available in an acid as well as in an alkaline medium. However, with thiosulfate, sulfur precipitates and the oxidation hardly goes to completion. The addition of alkali prior to iodine monochloride avoided this and the oxidation was found to be smooth. After being kept for 5~10 min. the solution was transferred to a 150 ml. beaker, acidified with 12 M hydrochloric acid to give an overall 5~6 N acidity and was titrated with iodate, permanganate or ceric sulfate by

TABLE III. OXIDATION OF THIOSULFATE BY IODINE MONOCHLORIDE+POTASSIUM HYDROXIDE

ml. 0.01 M thiosulfate	ml. 0.5 M iodine monochloride	Overall alkalinity %	Reaction time in min.	ml. 0.025 M iodate	Diff. %
(*a*) *Effect of excessive oxidant*					
5	2	1	5	3.80	− 5.00
5	3	1	5	3.80	− 5.00
5	4	1	5	3.85	− 3.75
10	10	1	10	7.85	− 1.88
(*b*) *Effect of alkali concentration*					
5	2	1	10	3.90	− 2.50
5	2	2	10	3.95	− 1.25
5	2	4	10	3.95	− 1.25
10	5	4	10	7.95	− 0.62
(*c*) *Test analysis*					
				ml. 0.1 M ceric sulfate	
5	2	4	15	3.95	− 1.25
7.5	4	4	10	5.95	− 0.83
10	8	4	10	7.95	− 0.62
10	10	4	10	7.95	− 0.62

Order of mixing.—Iodine monochloride+thiosulfate+alkali.—On slow addition of iodine monochloride to thiosulfate, part of sulfur separates, due to high acidity in contact with thiosulfate.

TABLE IV. OXIDATION OF GLUCOSE BY IODINE MONOCHLORIDE+POTASSIUM HYDROXIDE

ml. of 1% glucose	ml. 0.5 M iodine monochloride	Overall alkalinity %	Reaction time in min.	ml. 0.025 M iodate	Diff. %
(*a*) *Effect of excessive oxidant*					
10	3	Just alkaline to dissolve iodine*	5	10.70	3.17
10	5	〃	5	10.95	0.90
15	7	〃	10	16.40	1.05
15	8	〃	10	16.55	0.15
(*b*) *Effect of alkali concentration*					
10	3	1	5	10.60	4.07
10	5	2	5	10.75	2.71
10	5	2	10	10.75	2.71
(*c*) *Test analysis*					
10	5	as in (*a*)	10	10.95	0.90
15	10	〃	10	16.55	0.15
20	10	〃	10	22.00	0.45
20	10	〃	5	21.70	1.81

10 ml. of 1% glucose require 11.05 ml. 0.025 M iodate.

* As in the presence of excess of alkali, hypoiodite does not act smoothly on glucose, the order of mixing was "glucose+iodine monochloride", to which only just sufficient alkali was added to dissolve the liberated iodine. Finally little more alkali was added to convert iodine into hypoiodite.

the amperometric "Dead Stop End Point". The unit was the simple form of the one described by Foulk and Bawden[8]. One tenth volt was the impressed potential across the indicator electrodes between which a mechanical stirrer served to mix thoroughly the reaction mixture. The current measurements were made by a sensitive galvanometer with a lamp-and-scale arrangement. The current increased to a maximum and then decreased to a minimum where the conversion of iodine and iodide to iodine (+) was complete. In the oxidation of glucose, the control of alkalinity was most critical. This was achieved by careful addition of alkali to the mixture of glucose and iodine monochloride to the point where the iodine that separated just dissolved. The reverse order glucose-alkali-iodine-monochloride was found to give variable results. In glucose determination, the final titration was possible only with iodate because other oxidants, permangante and ceric sulfate, attacked the gluconic acid. The results of one typical series of experiments are summarized in Tables I—IV.

8) C. W. Foulk and A. T. Bawden, *J. Am. Chem. Soc.*, 48, 2045 (1926).

Summary

The principle of hypoiodite (iodine monochloride+potassium hydroxide) pre-oxidation and iodine monochloride end point has been adopted to the determination of hydrazine, thiocyanate, thiosulfate and glucose. The availability of alternative standard titrating solutions (iodate, permanganate and ceric sulfate) and applicability over a range of reductant concentrations are essential features of this procedure.

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Chemical Laboratories
Banaras Hindu University
India