Studies on the Use of meta-Periodic Acid as an Oxidant for the Estimation of following Inorganic Compounds: Thallous Nitrate, Stannous Chloride, Hydroxyl-amine, Hydrochloride and Antimonious oxide

P. V. Verma and K. C. Grover

Periodic acid has been used for the estimation of both Inorganic and Organic compounds. Here, thallous ion is oxidised to thallic ion, using equivalent quantities of reagents, stannous ion is oxidised to stannic ion, using at least 3 equivalents of periodate, Hydroxyl-amine hydrochloride can be quantitatively estimated by periodate, using at least 3 equivalents of the latter and antimonious ion is oxidised to antimonic ion, using equivalent quantities of reagents.

Periodic acid has been used for the selective oxidation of organic compound[1] since 1928. The first type of periodate oxidation is the well known—glycol cleavage discovered by Malaprade and initially developed by Fleury and J. Lange[2]. The second type of periodate oxidation was noted to take place in malic, malonic and aceto-acetic acid[3].

A survey of the literature revealed that no work have been done on the oxidations of the above compounds by periodic acid.

EXPERIMENTAL

The chemicals employed were B.D.H. Analar products or Merck A. G. products and were used without further purification.

Determination of the Excess of Periodate : The procedures adopted were the same as given earlier in cases of Mandelic acid[4], Hydrazine Sulphate[4] or Tartaric acid[5].

Thallous Nitrate : Thallium (I) has been estimated by a number of oxidants, *e.g.*, KIO_3, Bromine and Iodine.

$$Tl^+ - 2e^- \longrightarrow Tl^{+++}$$
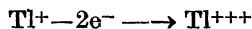
The prepared solution of thallous nitrate (B.D.H. Analar product) contains 0·6660 gm. of it/100 ml as standardised against potassiumiodate solution[6].

1. L. Malaprade, *Compt. rend.*, 1928, **186**, 382.
2. Fleury and J. Lange, *Compt. rend.*, 1932, **195**, 1395.
3. P. Fleury and J. Courtois, *Bull. Soc. Chim.*, 1947, **14**, 358; (5), 1948, **15**, 190.
4a. P. S. Verma and K. C. Grover, *Jour. Indian Chem .Soc.*, 1969, No. 2, **46**, 141-147.
4b. P. S. Verma and K. C. Grover, *Aust. J. Chem.*, 1967, **20**, 1533-7.
5. P. S. Verma and K. C. Grover, *Aust. J. Chem.*, 1968, **21**, 1531-4.
6. A. J. Berry, *Analyst.*, 1926, **51**, 137.

TABLE 1

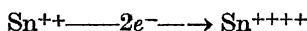*(All reagents 0·05N) pH = 5·60*

Time = 15-20 min.   Temperature = 32°.

1 ml. of 0·05 NHIO$_4$ = 0·00666 gm. thallous nitrate.

No.	Thallous Nitrate Taken (ml)	Periodic acid added (ml)	Periodic acid consumed (ml)	Thallous Nitrate Present (gm.)	Thallous Nitrate found (gm.)	% recovery	% error ±
1.	5.00	6.00	5.02	0.03330	0.03343	100.38	+0.38
2.	5.00	10.00	5.01	0.03330	0.03336	100.17	+0.17
3.	6.00	10.00	6.02	0.03996	0.04009	100.32	+0.32
4.	8.00	15.00	8.03	0.05328	0.05348	100.38	+0.38
5.	10.00	15.00	10.03	0.06660	0.06679	100.28	+0.28
6.	12.00	20.00	12.02	0.07992	0.08005	100.16	+0.16

Thus, thallous ion is oxidised to thallic ion using periodate as an oxidant under the conditions[4a], using equivalent quantities of reagents.

Stannous Chloride : Stannous chloride has been estimated by different oxidants, *e.g.*, with KIO$_3$ in presence of a mineral acid[7].

$$Sn^{++} \underline{\qquad} 2e^- \underline{\qquad} \rightarrow Sn^{++++}$$

The prepared solution of A.R. stannous chloride (SnCl$_2$.2H$_2$O) contains 1·4044 gm of it/250 ml. (as standardised against KIO$_3$ solution in presence of a mineral acid).

TABLE 2

(All reagents 0·05N)

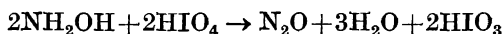1 ml. of 0·05 NHIO$_4$ = 0·00564/Stannous chloride

Time = 20–25 min., Temperature = 35°, pH = 4·86

No.	Stannous chloride taken (ml)	Periodic acid added (ml)	Periodic acid consumed (ml)	Stannous chloride present (gm.)	Stannous chloride found (gm.)	% recovery	% error ±
1.	5.00	5.00	* could not be recorded				
2.	5.00	10.00					
3.	5.00	15.00	5.00	0.02809	0.02820	100.39	+0.39
4.	6.00	20.00	6.00	0.03371	0.03840	100.38	+0.38
5.	8.00	25.00	8.00	0.04495	0.04512	100.37	+0.37
6.	10.00	30.00	10.01	0.05618	0.05640	100.39	+0.39

* Readings 1 and 2 could not be recorded due to the reaction of iodine with residual stannous salt.

Thus, stannous ion can be quantitatively estimated with periodate in an atmosphere of carbon dioxide and that, at least, three equivalents of periodate are needed in this case under the conditions[4a].

7. G. S. Jamieson, *Ind. Eng. Chem.*, 1916, 8, 500.

Hydroxyl-amine hydrochloride :   Hydroxyl-amine hydrochloride has been estimated with Ceric sulphate.   The method is too slow for direct titration but a back titration method is described by Cooper and Morris[8].

$$2NH_2OH + 2HIO_4 \rightarrow N_2O + 3H_2O + 2HIO_3$$

The prepared hydroxyl-amine hydrochloride (Johnson Analytical grade product) solution contains 0·4344 gm. of it/250 ml. as standardised against NaOH using methyl red as indicator.

TABLE 3

(All reagents 0·05 N)

1 ml. of 0·05 NHIO$_4$ = 0·001737 gms.   Hydroxyl-amine Hydrochloride

Time = 1 hour.,   Temperature = 30°, pH = 6·20

Exp. No.	Hydroxyl-amine hydro-chloride taken (ml)	Periodic acid added (ml)	Periodic acid consumed (ml)	Hydroxyl-amine hydro-chloride present (gm.)	Hydroxyl-amine hydro-chloride found (gm.)	% recovery	% error ±
1.	5.00	5.00					
2.	5.00	10.00	* could not be recorded.				
3.	5.00	15.00	4.99	0.008685	0.008668	99.79	—0.21
4.	8.00	25.00	7.98	0.013896	0.013861	99.74	—0.26
5.	10.00	30.00	9.99	0.017370	0.017353	99.89	—0.11
6.	12.00	40.00	11.97	0.020844	0.020791	99.74	—0.26
7.	14.00	45 00	13.98	0.024318	0.024283	99.85	—0.15
8.	16.00	50.00	15.98	0.027792	0.027757	99.87	—.013

* The readings 1 and 2 could not be recorded due to the development of the colour on account of the presence of residual hydroxyl-amine hydrochloride.

The results show that hydroxyl-amine hydrochloride can be quantitatively estimated by periodate, using at least, three equivalents of the latter[4a].

Antimoniousoxide

Antimony in oxide has been oxidised by oxidants like iodine and bromine

$$Sb_2O_3 + 2HIO_4 \longrightarrow Sb_2O_5 + 2HIO_3$$
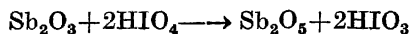
The prepared solution of antimonious oxide (B.D.H. Analar) contains 1·8220 gms. of it/ 500 ml. and is standardised against the standard solution of iodine.

8. S. P. Cooper and J. B. Morris, *Anal. Chem.*, 1952, **24**, 1360.

TABLE 4

(*All reagents* 0·05 *N*)

1 ml. of 0·05 NHIO$_4$ = 0·003644 gms. antimonious oxide.

Time = 10–15 min., Temperature = 32°, pH = 6·30

Exp. No.	Antimonious oxide taken (ml)	Periodic acid added (ml)	Periodic acid consumed (ml)	Antimonious oxide present (gm.)	Antimonious oxide found (gm.)	% recovery	% error ±
1.	5.00	5.00	5.00	0.018220	0.018220	100.00	±0.00
2.	5.00	10.00	5.01	0.018220	0.018256	100.22	+0.22
3.	6.00	10.00	6.01	0.021864	0.021900	100.15	+0.15
4.	8.00	15.00	8.02	0.029152	0.029225	100.21	+0.21
5.	10.00	15.00	10.01	0.036440	0.036476	100.10	+0.10
6.	12.00	20.00	12.02	0.043728	0.043800	100.15	+0.15
7.	14.00	20.00	14.01	0.051016	0.051052	100.05	+0.05

Thus, antimonious ion is oxidised to antimonic ion using periodic acid as an oxidant under the conditions[4a] using equivalent quantities of the reagents.

Chemistry Department,
Jodhpur University,
Jodhpur.