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Department of Chemistry, Andhra University, Waltair (India)

Dichrometric Estimation of Phosphite and Hypophosphite Silver Salt Catalysis

By
G. GOPALA RAO and K. BHASKARA RAO

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Phosphite and hypophosphite must be powerful reducing agents in both acid and basic solutions from theoretical considerations. According to LATIMER[13] the standard potentials of the reactions involved are given in Table 1. The American convention is followed in assigning the sign to the potential values.

Table 1

Reaction	Potential
1. (a) $H_3PO_2 + H_2O = H_3PO_3 + 2\,H^+ + 2e^-$	$E^\circ = +0.5$ acid solution
(b) $H_2PO_2^- + 3\,(OH)^- = PO_3^{2-} + 2\,H_2O + 2e^-$	$E^\circ_B = +1.57$ basic solution
2. (a) $H_3PO_3 + H_2O = H_3PO_4 + 2\,H^+ + 2e^-$	$E^\circ = +0.276$ acid solution
(b) $HPO_3^{2-} + 3\,(OH)^- = PO_4^{3-} + 2\,H_2O + 2e^-$	$E^\circ_B = +1.12$ basic solution

Although the oxidation potentials of most oxidising agents are much higher than the values given in the table, hypophosphite and phosphite are only slowly oxidised. Even a powerful oxidant like potassium permanganate (standard redox potential—1.51) oxidises hypophosphite only very slowly. According to KOLTHOFF[12] the oxidation of hypophosphite to phosphate by potassium permanganate, in 0.05 N sulphuric acid takes 24 hours for completion at the room temperature, while the oxidation of phosphite to phosphate takes 2 hours. KŐSZEGI[10] and POUND[16] state that the oxidation of hypophosphite is not complete even in 24 hours. ZIVY[22] reported the complete oxidation of hypophosphite to phosphate only when it is heated for 25 minutes under reflux in a medium 0.7 N with respect to sulphuric acid and containing a large concentration of manganous sulphate. Even with the use of bromide as catalyst POUND[16] observed that 2—3 hours' time is necessary for the completion of the oxidation of hypophosphite with permanganate. Schwicker[19] found that the reaction is complete in 30 minutes at 50° C only when ammonium molybdate is employed as a catalyst. The oxidation of hypophosphite and phosphite with ceric sulphate (standard redox potential—1.44 in 1 M H_2SO_4) is also difficult to achieve. Complete oxidation is possible only when heated on the hot plate for 30 mts. at 109° to 112° C according to Bhaskara Rao and Gopala Rao[1] or at 93° C for 30 mts. in the presence of silver sulphate catalyst. Gopala Rao and Gowda[5] found that heating for 20 mts. on the boiling water bath in 10 N H_2SO_4 in the presence of silver sulphate catalyst is necessary to accomplish the complete oxidation of hypophosphite to phosphate with sodium vanadate (formal redox potential—1.3 volts in 8 N H_2SO_4). The reaction of hypophosphite with potassium iodate, bromate—bromide, bromine and iodine are also slow[2, 3, 4, 6, 7, 8, 9, 11, 14, 15, 17, 18, 20, 21].

The use of potassium dichromate has not been investigated for the determination of hypophosphite and phosphite. As potassium dichromate is a cheap and readily available primary standard, we have undertaken the present investigation.

Preliminary experiments have shown that the oxidation of hypophosphite or phosphite by dichromate is not quantitatively complete even by heating the mixture in 5.0 N sulphuric acid at temperatures ranging from 93° to 110° C. Hence we resorted to the use of silver sulphate as a catalyst. This catalyst has already been employed by Gopala Rao and Gowda[5] in the oxidation of hypophosphite and phosphite by vanadate and by Bhaskara Rao and Gopala Rao[1] for the oxidation with ceric sulphate.

Experimental

The solutions of potassium dichromate, potassium phosphite, sodium hypophosphite and silver sulphate employed in our investigations have been prepared from Merck›s "Pro Analysi" samples. Phosphite and hypophosphite solutions are standardised by Jenkins' and Bruening›s[7] bromate method and verified by the cerimetric method reported by us previously. In the present study phosphite or hypophosphite was allowed to react with excess dichromate under different conditions and the unreacted dichromate estimated by titration with standard Mohr's salt solution using diphenylbenzidine as indicator.

Reaction of Phosphite with Potassium Dichromate

The reaction between dichromate and phosphite in acid medium is very slow at the room temperature. Even in the presence of silver sulphate, the reaction is not rapid enough to serve as a basis for the estimation of phosphite. This will be evident from the results recorded in Table 2.

Table 2

Reaction between Dichromate and Phosphite in Acid Medium at the Room Temperature.

10 ml. of about 0.02 M phosphite solution + 10 ml. of about 0.075 N dichromate solution + acid to keep the overall acidity at 2 N + water to make up to 50 ml.

Amount of phosphite taken = 0.1775 millimoles

Time: hours	Amount of phosphite oxidised in millimoles	
	without catalyst	with catalyst: 2 ml. of 5% silver sulphate solution
1	nil	0.0050
3	0.0075	0.0325
6	0.0250	0.0600
12	0.0335	0.0950
24	0.0800	0.1400

It is evident from the Table 2 that phosphite cannot be oxidised completely to phosphate by potassium dichromate at the room temperature. Although silver sulphate catalyses the reaction to some extent it does not enable the reaction to reach completion even in 24 hours. Hence experiments have been carried out at the temperature of the boiling water bath, and the results are recorded in the Table 3.

Table 3. *Reaction between Dichromate and Phosphite at 93° C.*

10 ml. of about 0.02 M phosphite solution + 20 ml. of about 0.05 N dichromate solution + H_2SO_4 to keep the overall acidity at 2 N + water to make up to 5.0 ml. Heated in the boiling water bath for varying times.

Amount of phosphite taken = 0.2080 millimoles

Time of reaction minutes	Amount of phosphite oxidised in millimoles	
	without catalyst	with catalyst: 2 ml. of 5% Ag_2SO_4
15	0.0575	0.1525
30	0.0775	0.1852
40	0.1075	0.2035
50	0.1265	0.2076
60	0.1510	0.2075
90	0.1625	0.2077
120	0.1905	0.2078

It can be seen from the results in Table 3 that the oxidation of phosphite to phosphate by dichromate is completed in about 50 minutes at the temperature of the boiling water bath in the presence of silver sulphate catalyst. In the absence of the catalyst the reaction is not completed even in two hours. The useful catalytic effect of silver sulphate is thus evident. We have noted that the relative proportion of dichromate and phosphite has a considerable effect on the speed of reaction. Hence experiments have been carried to find out the optimum proportion of dichromate to be added. The results are given in Table 4.

Table 4. *Effect of Variation of Dichromate Concentration.*
X ml. of about 0.05 N dichromate + Y ml. of about 0.02 M phosphite + acid to keep the overall acidity at 2 N + 2 ml. of 5 percent silver sulphate + water to make up to 50 ml. — Heated on the boiling water bath for 60 mts.

Amount of phosphite taken in millimoles	Amount of dichromate added in milli Eqts	Amount of phosphite oxidised in millimoles
0.2078	0.5140	0.1850
0.2078	0.7710	0.2005
0.2078	1.0280	0.2075
0.1039	0.2570	0.0975
0.1039	0.5140	0.1036
0.1039	0.5140	0.1036
0.4156	1.0280	0.3975
0.4156	2.0560	0.4150

It is evident from the results of the Table 4 that the oxidation of phosphite to phosphate by dichromate is quantitatively completed at the temperature of boiling waterbath in presence of silver sulphate catalyst in about one hour, only when the dichromate is present at a stoichiometric concentration twice in excess of the phosphite taken. Further, we have carried out experiments to see the effect of variation in the concentration of the silver sulphate catalyst and found that 2 ml. of 5% silver sulphate is the minimum amount required. Varying the concentration of sulphuric acid from 2 to 5 N has been found to be without any effect on the time required for the reaction. A large number of determinations of phosphite have been done under the optimum conditions prescribed and some typical results are given in Table 5.

Table 5. *Dichrometric Estimation of Phosphite with Silver Sulphate as Catalyst*

Amount of phosphite taken in millimoles	Amount of phosphite found in millimoles
0.0520	0.0518
0.1040	0.1036
0.2080	0.2075
0.3120	0.3120
0.3640	0.3632
0.4160	0.4152

Determination of Hypophosphite

Like phosphite, hypophosphite also reacts with dichromate very slowly. This is evident from the results of our experiments conducted at the room temperature and recorded in Table 6.

Even the silver catalysed reaction is not rapid enough to reach quantitative completion at the room temperature. Hence experiments have been conducted at the temperature of the boiling water bath and the results are recorded in Table 7.

From the results in Table 7, it is evident that hypophosphite is quantitatively oxidised to phosphate by potassium dichromate in

Table 6. *Reaction between Dichromate and Hypophosphite at 28° C.*
10 ml. of about 0.01 M hypophosphite + 20 ml. of about 0.05 N dichromate + H_2SO_4 to keep the overall acidity at 2 N + water to make upto 50 ml.
Amount of hypophosphite taken = 0.0902 millimoles

Time of reaction in hours	Amount of hypophosphite oxidised in millimoles	
	without catalyst	With catalyst: 2 ml. of 5 percent Ag_2SO_4
1	0.0024	0.0324
3	0.0108	0.0408
6	0.0156	0.0504
12	0.0228	0.0588
24	0.0480	0.0756

Table 7. *Reaction between Dichromate and Hypophosphite at the Temperature of the boiling Water Bath.*
10 ml. of about 0.01 M hypophosphite + 20 ml. of about 0.05 N dichromate + H_2SO_4 to keep the overall acidity at 2 N + water to make upto 50 ml. — heated on boiling water bath for varying times.
Amount of hypophosphite taken = 0.1034 millimoles.

Time of reaction in minutes	Amount of hypophosphite oxidised in millimoles	
	without catalyst	with catalyst: 2 ml. of 5 percent Ag_2SO_4
15	0.0520	0.0864
30	0.0588	0.0966
40	0.0672	0.1014
50	0.0704	0.1032
60	0.0738	0.1030
90	0.0804	0.1031
120	0.0948	0.1032

Table 8. *Effect of Variation of Dichromate Concentration.*
X ml. of about 0.01 M hypophosphite + Y ml. of about 0.05 N dichromate + H_2SO_4 to keep the overall acidity at 2 N + 2 ml. of 5 percent silver sulphate + water to make up to 50 ml. — Heated on the boiling water bath for 60 minutes.

Amount of hypophosphite taken in millimoles	Amount of dichromate added in milli Eqts.	Amount of hypophosphate oxidised in millimoles
0.0517	0.2560	0.0445
0.0515	0.5120	0.0516
0.1034	0.5120	0.0840
0.1034	0.7680	0.0924
0.1034	1.0240	0.1032
0.2068	1.0240	0.1650
0.2068	2.0480	0.2065

presence of silver sulphate catalyst in about 50 minutes at the temperature of boiling water bath; whereas in the absence of the catalyst the reaction is not complete, even in two hours. Hence the need for the silver sulphate catalyst becomes evident. We have also carried out some experiments to determine the effect of the variation of the dichromate. The results are given in Table 8 (p. 337).

It can be seen from the results in Table 8 that, just as in the case of phosphite, the oxidation of hypophosphite by dichromate is not complete quantitatively even in the presence of the silver sulphate (at the temperature of boiling water bath) in about 60 minutes, unless the dichromate is taken twice in excess of the hypophosphite taken. Experiments have shown us that the minimum amount of catalyst required corresponds to about 2 ml. of 5% silver sulphate for 50 ml. of the reaction mixture. A large number of determinations of hypophosphite have been carried out by this catalysed dichromate method and some typical results are recorded in Table 9.

Table 9. *Dichrometric Estimation of Hypophosphite with Silver Sulphate as Catalyst*

Amount of hypophosphite taken in millimoles	Amount of hypophosphite found in millimoles
0.0259	0.0256
0.0518	0.0514
0.1036	0.1032
0.1295	0.1290
0.1554	0.1550
0.2072	0.2065

Summary

1. It has now been shown that it is possible to determine accurately phosphite and hypophosphite with potassium dichromate. The method consists in heating the hypophosphite or phosphite with a known excess of dichromate in 2 N sulphuric acid with 2 ml. (per 50 ml. of reaction mixture) of 5% silver sulphate as a catalyst on the boiling water bath for one hour; and estimating the unreacted dichromate with a standard solution of ferrous ammonium sulphate.

2. The method has the advantage that potassium dichromate is by itself an excellent primary standard.

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Prof. G. GOPALA RAO, Head of the Chemistry Department, Andhra University,
Waltair (India)

National Research Council, Dokki, Cairo (Ägypten)

Über einen neuen, hochselektiven Nachweis von Zirkonium mittels Brenzcatechinvioletts in Gegenwart von Komplexon

Von
H. FLASCHKA und **F. SADEK**

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Brenzcatechinviolett (nachfolgend als Bcv. abgekürzt) wurde von MALÁT u. Mitarb.[2,5] als metallspezifischer Indicator in die Komplexometrie eingeführt. Sein hauptsächlicher Vorteil lag bisher in der Verwendung zur hochselektiven Titration von Wismut und Thorium in saurem Medium. Die Bestimmung dieser beiden Metalle wird nur durch ganz wenig andere Metalle gestört, darunter auch Zirkonium. Dieses bildet mit Bcv. einen Chelatkomplex, der stabiler ist, als das Zirkoniumkomplexonat, so daß die Titration anderer Metalle durch Blockieren des Indicators unmöglich wird[1,4]. Dieses Verhalten eröffnet jedoch die Möglichkeit einen empfindlichen und nahezu spezifischen Nachweis für Zirkonium auszuarbeiten, da Störungen durch andere Metalle mittels Komplexons ausgeschaltet werden können. Im nachstehenden wird über die Ergebnisse von Untersuchungen in dieser Richtung Mitteilung gemacht. Versuche, die Reaktion zu einer photometrischen Zirkoniumbestimmung auszuwerten, sind im Gange; es wird gegebenenfalls später darüber berichtet werden.

Als günstigste Bedingung zur Entwicklung der Blaufärbung des Zirkon-Bcv.-Komplexes hat sich ein p_H-Bereich von etwa 4—6,5 erwiesen (in Gegenwart von Komplexon), was mittels Acetatpufferung unschwer einzustellen ist. Unterhalb 4 ist die Farbe des Komplexes Rot bis Violett. Oberhalb 6,5 ist der Zirkonkomplex zwar ebenfalls blau, aber auch das freie, gelbe Bcv. beginnt sich zu verfärben; es wird bei 7 graustichig, bei 7,5 blaugrau und bei 8 blauviolett. Die p_H-Grenzen für den Farbwechsel