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The Cerimetric Determination of Hypophosphite after Oxidation with Iron(III)

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Because hypophosphite has come to have a number of commercial applications as a reducing agent, and because phosphite is frequently an intermediate product in the oxidation of hypophosphite, it is desirable to establish an analytical procedure for the determination of hypophosphite in the presence of phosphite. For this purpose, volumetric methods with iodometric or cerimetric procedures have been described by Jones and Swift,[1] Bernhart,[2] and Rao and Rao.[3] These procedures, however, are all inapplicable to rapid analyses because of their complexity and difficulty. On the other hand, Sastri and Radhákrishnamurthi[4] found that an excess of hypophosphite reduces iron(III) quantitatively in hydrochloric acid solutions upon boiling:

$$H_3PO_2 + 2Fe^{3+} + H_2O \rightarrow H_3PO_3 + 2Fe^{2+} + 2H^+ \quad (1)$$

Sastri and Kalidas[5] later applied this reaction to the determination of hypophosphite in the presence of phosphite; their procedure consisted of boiling, for 20 min, hypophosphite with approximately twice as much iron(III) as was required for the stoichiometric reaction in a 1.0-to-2.0 N hydrochloric acid medium and of titrating the iron(II) thus formed with a standard solution of cerium(IV) sulfate. This Sastri-Kalidas procedure has the advantages of simplicity and rapidity, for it requires only one standard solution which is very stable. However, it has been observed in preliminary experiments that the reaction does not reach quantitative completion, even when the Sastri-Kalidas procedure is followed completely. In this paper, therefore, the reaction between hypophosphite and iron(III) at the boiling temperature is re-examined, and the applicability of this reaction to the determination of hypophosphite in the presence of phosphite is discussed.

Experimental

Reagents. All the chemicals were of a reagent grade. The standard solutions of hypophosphite and phosphite were prepared by dissolving monosodium hypophosphite monohydrate and disodium phosphite pentahydrate respectively in distilled water. The concentrations of these solutions were determined by the Rao-Rao procedure.[3] A standard solution of cerium(IV) sulfate was prepared and standardized by the conventional method. A solution of iron(III) was prepared by dissolving ammonium iron(III) sulfate in distilled water. For the detection of the end point of titration, one drop of a 0.025 M ferroin indicater solution was used.

Procedure. A solution containing hypophosphite alone or both hypophosphite and diverse salts was transferred to a 300-*ml* flask equipped with a reflux cooler. The calculated volumes of the iron(III) solution and of the hydrochloric acid were added, and then the whole was diluted to about 100 *ml*. The resulting solution was boiled on an electric heater for the required time. After cooling, the solution was titrated with the standard solution of cerium(IV) sulfate to the blue-yellow end point of the ferroin indicator.

Results and Discussion

Conditions for the Determination of Hypophosphite. The effects of the mole ratio of iron(III) to hypophosphite on the oxidation of hypo-

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[1] R. T. Jones and E. H. Swift, *Anal. Chem.*, **25**, 1272 (1953).

[2] D. N. Bernhart, *ibid.*, **26**, 1798 (1954).

[3] K. B. Rao and G. G. Rao, *Z. anal. Chem.*, **147**, 274, 279 (1955).

[4] M. N. Sastri and Ch. Radhákrishnamurthi, *ibid.*, **147**, 16 (1955).

[5] M. N. Sastri and Ch. Kalidas, *Rec. trav. chim.*, **75**, 1122 (1956).

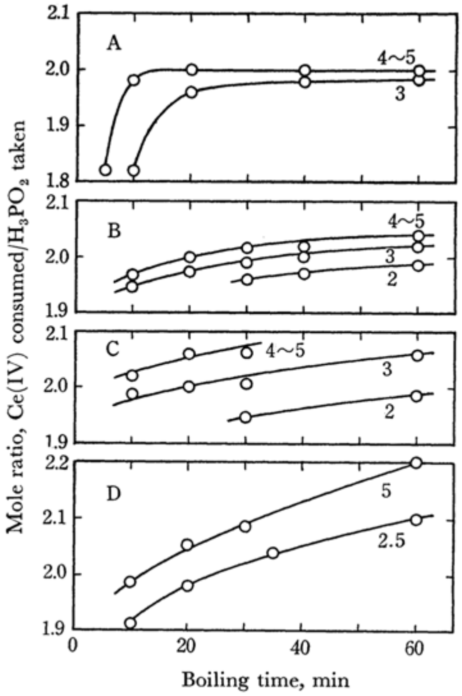

Fig. 1. Oxidation of 0.25 mmol of hypophosphite in (A) 1.6, (B) 1.2, (C) 0.8 and (D) 0.4N hydrochloric acid solutions. Numericals on curves represent amounts of iron(III) added in mmol.

phosphite at the boiling temperature were observed at different concentrations of hydrochloric acid; the results are shown in Fig. 1. When a hydrochloric acid concentration between 0.4 and 1.2N is selected, the oxidation of hypophosphite is greatly affected by the boiling time; if the solution is boiled to excess, some hypophosphites may be oxidized beyond phosphite to phosphate, while if boiling is insufficient, the oxidation to phosphite does not reach quantitative completion. In a 1.6N hydrochloric acid medium, however, 0.25 mmol of hypophosphite can be quantitatively oxidized to phosphite, without being oxidized to phosphate, with 5 mmol of iron(III) by boiling it for at least 20 min.

For the determination of hypophosphite, therefore, approximately ten times as much iron(III) as the amount required for the stoichiometric reaction was added, the final acidity was adjusted with hydrochloric acid to approximately 1.6N, and the mixture was boiled for about 20 min.

The Effects of Phosphate, Acetate, and Citrate on the Determination of Hypophosphite. Sample solutions containing about 0.2 mmol of hypophosphite and from 0.1 to 2 mmol of phosphite, acetate, or citrate were analyzed by the proposed procedure. The data in Tables 1 and 2 show an accuracy and precision of better than one percent in the presence of these anions.

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TABLE 1. EFFECTS OF PHOSPHITE ON THE DETERMINATION OF HYPOPHOSPHITE

Hypophosphite taken mmol	Phosphite added mmol	Cerium(IV) soln. required m*l*	Hypophosphite found mmol	Error %
0.273	0.103	5.60[*1]	0.274	+0.4
0.273	0.205	5.54[*1]	0.271	−0.7
0.273	0.308	5.59[*1]	0.274	+0.4
0.269	0.410	5.52[*1]	0.270	+0.4
0.269	0.513	5.56[*1]	0.272	+1.1
0.277	0.939	5.58[*2]	0.281	+1.4
0.277	1.409	5.57[*2]	0.280	+1.1

[*1] 0.0980N cerium(IV) solution.
[*2] 0.1007N cerium(IV) solution.

TABLE 2. EFFECTS OF ACETATE AND CITRATE ON THE DETERMINATION OF HYPOPHOSPHITE[*]

Sodium salt added mmol	0.1073N Cerium(IV) soln. required m*l*	Hypophosphite found mmol	Error %
Acetate; 1	3.67	0.197	+0.5
Acetate; 2	3.63	0.195	−0.5
Citrate; 0.2	3.64	0.195	−0.5
Citrate; 1	3.66	0.196	0
Citrate; 2	3.65	0.196	0

[*] The amount of hypophosphite taken in each case was 0.196 mmol.