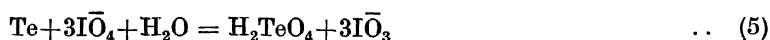
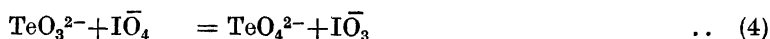
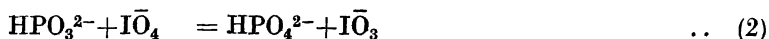
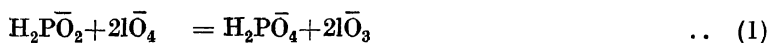


Periodate as an Analytical Reagent. Part II. Estimation of Hypophosphite, Phosphite, Selenite, Tellurite and Tellurium

R. L. Kaushik and Rajendra Prosad

Sodium metaperiodate has been used for the determination of hypophosphite, phosphite, selenite, tellurite and tellurium present alone or in a mixture of two of the compounds.

Hypophosphite, phosphite, selenite, tellurite and tellurium are oxidised quantitatively by metaperiodate in presence of borax according to the following reactions :—



In all the above reactions, metaperiodate is reduced to iodate. The reaction has been found to be considerably slow in cold in each case and, therefore, an excess of metaperiodate has always been used. After a suitable period of heating, the residual metaperiodate has been determined iodometrically in a buffered solution¹.

From equations 1 and 2, it is clear that metaperiodate oxidises hypophosphite and phosphite to dihydrogen phosphate and monohydrogen phosphate respectively. Monohydrogen phosphate can be titrated to the neutralization of primary stage of phosphoric acid which corresponds to the amount of phosphite present. By a combination of the above two methods, analysis of mixtures of hypophosphite and phosphite present together in a solution has been done. Since the reaction has been found to be sluggish in the neutral medium and fast in the alkaline medium, a known volume of standard alkali has been added to the mixture solution along with known standard metaperiodate before heating the reaction mixture to oxidise hypophosphite and phosphite. The alkali content in the oxidised mixture has been determined. The increase in the amount of alkali corresponds to the amount of

1. I. M. Kolthoff, R. Belcher, V. A. Stenger and G. Matsuyama, *Volumetric Analysis*, Vol. III, (Interscience Publishers, Inc., New York, 1957), p 273.

phosphite present in the mixture. From the same solution, the unreacted metaperiodate has been determined as before. The net titre of metaperiodate corresponds to both hypophosphite and phosphite. From these estimations, the amounts of hypophosphite and phosphite have been determined.

Selenite and tellurite both are oxidised by metaperiodate according to the equations 3 and 4 respectively. Dichromate, in acidic medium, has been used for the determination of tellurite². Selenite does not interfere in this determination. Mixtures of selenite and tellurite can, therefore, be estimated by a combination of the above two methods. An aliquot of the mixture is first heated with metaperiodate when both selenite and tellurite are oxidised. Another aliquot is then treated with dichromate when tellurite alone is oxidised. The quantities of selenite and tellurite can now be calculated easily by the reagents consumed in the above two estimations.

Tellurite and tellurate both are reduced to metallic tellurium by Bougault's Reagent³ ($\text{HCl} + \text{NaH}_2\text{PO}_2$) which can be oxidised to tellurate by metaperiodate (eq. 5). This fact has been utilized for the analysis of mixtures of tellurite and tellurate. Tellurite alone has been determined by metaperiodate (eq. 4). Tellurite and tellurate both have been reduced to metallic tellurium which has been again oxidised to tellurate by metaperiodate (eq. 5). From the titre values of metaperiodate in the above two estimations, the amounts of tellurite and tellurate have been calculated.

EXPERIMENTAL

Estimation of hypophosphite, phosphite, selenite, tellurite and tellurium: A known volume of the solution of the substance to be estimated was pipetted into a conical flask containing an excess of standard sodium metaperiodate solution and saturated borax solution (20 ml.). The contents of the flask were boiled for a suitable period of time and the reaction mixture was cooled to room temperature. The unreacted metaperiodate was determined iodometrically from the buffered solution¹. The net titre of the metaperiodate corresponded to the oxidation of the material taken. The results are recorded in Table I.

Estimation of mixtures of hypophosphite and phosphite: To an aliquot of the mixture was added known volumes of standard sodium metaperiodate and standard sodium hydroxide. The reaction mixture was boiled for about 10 min. and cooled to room temperature. The alkali present in the oxidised mixture was determined by titrating against a standard solution of hydrochloric acid using methyl orange as the indicator. The increase in the alkali content corresponded to the amount of phosphite present. The same solution was buffered with borax and boric acid and the unreacted metaperiodate was determined as before. The net titre of metaperiodate corresponded to both hypophosphite and phosphite present in the solution. From these estimations, the amounts of hypophosphite and phosphite were calculated. The results are recorded in Table II.

2. V. Lenher and H. F. Wakefield, *J. Amer. Chem. Soc.*, 1923, **45**, 1423.

3. L. Vignoli and Ben Khaled, *J. Pharm. Chim.*, 1938, **27**, 443.

TABLE I

Reaction time : 10 minutes at boiling temperature.

| Substance | Amount taken (mg.) | Amount found (mg.) |
|---------------------------|-----------------------|-----------------------|
| KH_2PO_2 | 69.0 | 69.2 |
| | 46.5 | 46.8 |
| | 37.4 | 37.3 |
| | 18.5 | 18.6 |
| | 9.2 | 9.2 |
| Na_2HPO_3 | 92.8 | 92.6 |
| | 66.2 | 66.0 |
| | 54.7 | 55.3 |
| | 46.4 | 46.7 |
| | 37.0 | 37.3 |
| Na_2SeO_3 | 207.7 | 208.0 |
| | 166.1 | 165.6 |
| | 124.6 | 124.9 |
| | 116.6 | 116.6 |
| | 87.4 | 87.7 |
| K_2TeO_3 | 220.0 | 219.7 |
| | 165.0 | 165.1 |
| | 151.4 | 151.1 |
| | 110.0 | 110.5 |
| | 75.7 | 76.2 |
| Te* | 58.8 | 59.2 |
| | 44.0 | 44.3 |
| | 30.0 | 30.0 |
| | 24.4 | 24.4 |
| | 11.6 | 11.9 |

* Reaction mixture was boiled till whole of Te was completely oxidised.

TABLE II

Reaction time : 10 minutes at boiling temperature.

| Mix No. | Na_2HPO_3 taken (mg.) | KH_2PO_2 taken (mg.) | 0.1N NaIO_4 consumed (ml.) | 0.1N NaOH liberated (ml.) | Na_2HPO_3 found (mg.) | KH_2PO_2 found (mg.) |
|------------|---|--|---|--|---|--|
| 1. | 33.1 | 45.5 | 22.7 | 2.6 | 33.1 | 45.5 |
| 2. | 66.2 | 36.4 | 24.55 | 5.25 | 66.4 | 36.6 |
| 3. | 99.3 | 27.3 | 26.25 | 7.85 | 99.0 | 27.5 |
| 4. | 132.3 | 18.2 | 28.0 | 10.5 | 132.3 | 18.2 |
| 5. | 165.4 | 9.1 | 29.75 | 13.0 | 165.7 | 9.1 |

Estimation of mixtures of selenite and tellurite : A known volume of the mixture was added to an excess of standard sodium metaperiodate and saturated borax solution (20 ml). The reaction mixture was boiled for about 10 min, cooled to room temperature and the

unreacted metaperiodate was determined as before. The metaperiodate consumed corresponded to both selenite and tellurite. From another suitable aliquot of the mixture, tellurite alone was determined by potassium dichromate in acid medium². From the net titre values of the reagents consumed in the above two estimations, the amounts of selenite and tellurite were determined (Table III).

TABLE III

Reaction time : 10 minutes at boiling temperature.

| Mix No | K ₂ TeO ₃ taken (mg.) | Na ₂ SeO ₃ taken (mg.) | 0.1N NaIO ₄ consumed (ml.) | 0.1N K ₂ Cr ₂ O ₇ consumed (ml.) | K ₂ TeO ₃ found (mg.) | Na ₂ SeO ₃ found (mg.) |
|--------|---|--|---------------------------------------|---|---|--|
| 1. | 171.5 | 15.5 | 15.2 | 13.45 | 171.0 | 15.2 |
| 2. | 137.2 | 31.1 | 14.4 | 10.8 | 137.2 | 31.1 |
| 3. | 102.9 | 46.7 | 13.55 | 8.1 | 102.8 | 47.1 |
| 4. | 68.6 | 62.3 | 12.55 | 5.4 | 68.6 | 62.0 |
| 5. | 34.3 | 77.8 | 11.7 | 2.7 | 34.3 | 77.9 |

Estimation of mixtures of tellurite and tellurate : A known volume of the mixture was added to an excess of sodium metaperiodate and saturated borax solution (20 ml.). The reaction mixture was boiled for about 10 min., cooled to room temperature and the unreacted metaperiodate was determined as before. The net titre of metaperiodate corresponded to tellurite only. From another aliquot of the mixture, both tellurite and tellurate were reduced to metallic tellurium by Bougault's reagent³ (HCl+NaH₂PO₂). The precipitated tellurium was filtered, washed and oxidised to tellurate by metaperiodate in borax medium (eq. 5). The unreacted metaperiodate was determined as before. The net titre of metaperiodate corresponded to both tellurite and tellurate. From these estimations, the amounts of tellurite and tellurate were calculated. The results are given in Table IV.

TABLE IV

| Mix No. | K ₂ TeO ₃ taken (mg.) | K ₂ TeO ₃ taken (mg.) | 0.1N NaIO ₄ consumed by | | K ₂ TeO ₃ found (mg.) | K ₂ TeO ₄ found (mg.) |
|---------|---|---|---------------------------------------|----------|---|---|
| | | | K ₂ TeO ₃ (ml.) | Te (ml.) | | |
| 1. | 70.5 | 33.1 | 5.55 | 24.0 | 70.5 | 33.1 |
| 2. | 48.2 | 82.7 | 3.90 | 29.95 | 48.2 | 82.2 |
| 3. | 39.4 | 66.2 | 3.1 | 23.95 | 39.3 | 66.0 |
| 4. | 29.5 | 49.6 | 2.35 | 18.0 | 29.6 | 49.8 |
| 5. | 19.7 | 33.1 | 1.55 | 12.0 | 19.6 | 33.2 |

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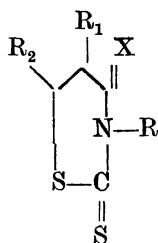
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and residual solution was evaporated on waterbath. The resulting product was immediately added to acetic anhydride (50 ml.) containing sulphuric acid (0.5 ml.), when an exothermic reaction took place. Reaction mixture was stirred at 80–90° for 3 hr. and then was poured on crushed ice (200 g.) and left overnight. This mixture was extracted with benzene and the benzene extract was dried over anhydrous sodium sulphate. Benzene was distilled away and residual oily liquid was chromatographed over silica gel with benzene as eluent. The product obtained on chromatography was crystallised from benzene-hexane; yield 60–65% m.p. 80° (lit.⁴ m.p. 80.5–81.5°).

Following this procedure and reacting sodium methyldithiocarbamate with crotonic acid and methacrylic acid, II and III were synthesised respectively. Also prepared by the same procedure were 3-allyl-2-thiono-4-oxo-1,3-thiazanes IV, V and VI by reacting sodium allyldithiocarbamate with acrylic acid, crotonic acid and methacrylic acid respectively.

Method (B): Sodium methyldithiocarbamate (16 g.) was dissolved in water (30 ml.) and cooled to 0°. An alcoholic solution of β -bromopropionic acid (15.3 g.) was added dropwise with mechanical stirring and the reaction mixture was left overnight. Water and alcohol were evaporated on waterbath. The residual product was put in acetic anhydride (50 ml.) containing a few drops of sulphuric acid. The reaction mixture was stirred at 80–90° for 3 hr., then poured on crushed ice and left overnight, and worked up following the procedure in method A. As a result a compound identical with compound obtained by method A was obtained.

TABLE I



X = O for I to VI
X = S for VII to XII

| | R | R ₁ | R ₂ | m.p. °C or b.p. °C (mm) | n _D at 27°C | Formula | C% | | H% | | N% | |
|------|-----------------|-----------------|-----------------|----------------------------|------------------------------|---|-------|-------|-------|-------|-------|-------|
| | | | | | | | Calc. | found | Calc. | found | Calc. | found |
| I | CH ₃ | H | H | 80° | — | C ₅ H ₇ NOS ₂ | 37.3 | 37.5 | 4.4 | 4.5 | 8.7 | 8.7 |
| II | CH ₃ | H | CH ₃ | 99°(0.1) | 1.6345 | C ₆ H ₉ NOS ₂ | 41.1 | 41.2 | 5.2 | 5.1 | 8.0 | 8.0 |
| III | CH ₃ | CH ₃ | H | 88° | — | C ₆ H ₉ NOS ₂ | 41.1 | 40.8 | 5.2 | 5.3 | 8.0 | 7.8 |
| IV | Allyl | H | H | 108°(0.3) | 1.6355 | C ₇ H ₉ NOS ₂ | 44.9 | 44.8 | 4.8 | 4.8 | 7.5 | 7.2 |
| V | Allyl | H | CH ₃ | 99–100°(0.1) | 1.6070 | C ₈ H ₁₁ NOS ₂ | 47.8 | 47.8 | 5.5 | 5.3 | 7.0 | 7.0 |
| VI | Allyl | CH ₃ | H | 90°(0.1) | 1.6164 | C ₈ H ₁₁ NOS ₂ | 47.8 | 48.2 | 5.5 | 5.6 | 7.0 | 7.0 |
| VII | H | H | H | 106° | — | C ₄ H ₆ NS ₃ | 29.4 | 29.5 | 3.0 | 3.1 | 8.6 | 8.3 |
| VIII | H | H | CH ₃ | 142–143° | — | C ₅ H ₇ NS ₃ | 33.9 | 34.1 | 4.0 | 4.0 | 7.9 | 7.8 |
| IX | H | CH ₃ | H | 93–94° | — | C ₅ H ₇ NS ₃ | 33.9 | 34.2 | 4.0 | 3.8 | 7.9 | 8.0 |
| X | CH ₃ | H | H | 115°(0.06) | — | C ₅ H ₇ NS ₃ | 33.9 | 34.1 | 4.0 | 3.9 | 7.9 | 8.1 |
| XI | CH ₃ | H | CH ₃ | 120°(0.06) | — | C ₆ H ₉ NS ₃ | 37.7 | 37.4 | 4.7 | 4.7 | 7.3 | 7.5 |
| XII | CH ₃ | CH ₃ | H | 114–115°(0.1) | — | C ₆ H ₉ NS ₃ | 37.7 | 37.7 | 4.7 | 4.7 | 7.3 | .1 |

Similar procedure was followed for preparation of II and III by reacting sodium methyl-dithiocarbamate with β -bromobutyric acid and methyl- β -bromoisobutyrate respectively. Following the above procedure IV, V, VI were also synthesised by the treatment of sodium allyldithiocarbamate with β -bromopropionic acid, β -bromobutyric acid and methyl- β -bromoisobutyrate respectively.

Preparation of 2,4-dithiono-1,3-thiazanes : 2-Thiono-4-oxo-1,3-thiazane (2.9 g.) was dissolved in xylene (100 ml.) and to this phosphorus pentasulphide (3 g.) was added. The mixture was heated to reflux for 3 hr. The reaction mixture was filtered and xylene was distilled away. The residual solid was crystallised from benzene to give 2,4-dithiono-1,3-thiazane m.p. 106° (lit³ m.p. 109°). The other 2,4-dithiono-1,3-thiazanes (VIII, IX, X, XI and XII) were likewise prepared from the corresponding 2-thiono-4-oxo-1,3-thiazanes.

TABLE II

| | IR (cm ⁻¹) | UV (m μ) | | | |
|------|------------------------|------------------|----------------|------------------|----------------|
| | | λ_{\max} | log ϵ | λ_{\max} | log ϵ |
| I | 1700, 1455, 1280, 1090 | 310 | 4.07 | 267 | 4.16 |
| II | 1700, 1450, 1280, 1090 | 310 | 4.07 | 267 | 4.11 |
| III | 1700, 1455, 1240, 1090 | 310 | 4.06 | 267 | 4.13 |
| IV | 1705, 1650, 1330, 990 | 313 | 3.97 | 267 | 4.10 |
| V | 1705, 1645, 1335, 990 | 312 | 3.96 | 267 | 3.99 |
| VI | 1705, 1650, 1325, 980 | 313 | 4.06 | 267 | 4.10 |
| VII | 3125, 1495, 1235, 1205 | 344 | 4.27 | 317 | 4.21 |
| VIII | 3125, 1495, 1215, 1200 | 345 | 4.02 | 317 | 4.00 |
| IX | 3150, 1495, 1220, 1200 | 345 | 4.13 | 317 | 4.09 |
| X | 1450, 1280, 1255 | 335 | 4.06 | 325 | 4.09 |
| XI | 1450, 1265, 1250 | 339 | 4.07 | 323 | 4.10 |
| XII | 1450, 1255, 1230 | 340 | 4.07 | 325 | 4.08 |

The physical and analytical data of the compound I to XII are given in Table I. The U.V. maxima and prominent IR absorption bands of these compounds are listed in Table II.