

Potentiometric Determinations using Bromochlorohydantoin as a New Oxidimetric Titrant

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A new oxidimetric titrant, bromochlorohydantoin (1-bromo-3-chloro-5,5-dimethylhydantoin) is introduced for use in non-aqueous media. Direct potentiometric determinations of a variety of diverse types of reductants, viz. arsenic(III), antimony(III), tin(II), iron(II), thallium(I), ferrocyanide, iodide, hydrazine, phenylhydrazine, semicarbazide, hydroquinone, aniline, ascorbic acid, oxine, thiosulphate, thiourea thiosemicarbazide, thiocyanate, Reinecke's salt, mercury(II) tetrathiocyanatocobaltate(II) and mercury(II) tetrathiocyanatozincate(II) have been carried out using this titrant.

In the course of our investigations on new organic oxidimetric titrants in non-aqueous media¹⁻³, it has been found that a solution of bromochlorohydantoin (1-bromo-3-chloro-5,5-dimethylhydantoin) (hereafter abbreviated as BCH) in acetic acid has good stability to meet the requirements for an ideal redox titrant in non-aqueous media. In this note we describe our successful attempts towards the determination of a variety of reductants, such as As(III), Sb(III), Sn(II), Fe(II), Tl(I), hexacyanoferrate(II), iodide, hydrazine, phenylhydrazine, semicarbazide, hydroquinone, aniline, ascorbic acid, oxine, thiosulphate, thiourea, thiosemicarbazide, thiocyanate, Reinecke's salt, Hg(II) tetrathiocyanatocobaltate(II) and Hg(II) tetrathiocyanatozincate(II) using the BCH in acetic acid as the redox titrant in potentiometry.

A Toshniwal titration potentiometer type CL 06A with a 'nullmeter' indicator, a platinum indicator electrode and an aqueous saturated calomel reference electrode was used. All the titrations were carried out at room temperature (32 ± 2 C). Equivalence points were determined by drawing normal, first derivative and second derivative curves and these were checked by the Hostetter-Roberts equation⁴ or the Yan equation⁵.

All the reagents employed were either BDH Analar, or Merck G R or any other analytical reagent grade chemicals. Distilled water and dry acetic acid were used as solvents for the reductants and oxidant respectively unless otherwise specified.

BCH was prepared by standard method given in literature⁶. It is practically insoluble in water, but is fairly soluble in glacial acetic acid (61.5 g/kg at 32°C)

and other common organic solvents. An approximately 0.025 M (0.1 N) solution of BCH was prepared in dry glacial acetic acid and the solution was kept in an amber coloured bottle. It was found to be stable for two or three days and thereafter the strength of the solution gradually decreased at a rate of 0.1% per day. BCH solution decomposes appreciably when kept in colourless bottles, the rate being over 1.0% per day. For accurate work fresh solutions should be used. The stock solution of BCH was standardised by adding aqueous potassium iodide solution and titrating the liberated iodine with standard thiosulphate solution using starch as indicator.

Approximately 0.1 N solutions of antimony(III), ferrocyanide, iodide, hydrazine, semicarbazide, hydroquinone, ascorbic acid, thiosulphate, thiourea, thiosemicarbazide and thiocyanate were prepared in distilled water. Solution of As(III) was prepared by dissolving known weight of As_2O_3 in 1N sodium hydroxide, neutralising it with 1N sulphuric acid and making upto definite volume with distilled water. Stock solution of thallium(I) was prepared by dissolving known weight of thallos carbonate in acetic acid and diluting it with distilled water. Iron(II) solution was prepared in 2N sulphuric acid. Stock solutions of tin(II), phenylhydrazine, aniline, mercury(II), tetrathiocyanatocobaltate(II) and mercury(II) tetrathiocyanatozincate(II) were prepared by dissolving weighed amounts of the samples in conc. hydrochloric acid and then diluting with distilled water. Solution of oxine was prepared in 50% aqueous-acetic acid. Solution of Reinecke's salt was prepared in distilled water, and an aliquot of this solution was digested with 5N sodium hydroxide and acidified with conc. hydrochloric acid before the titration. The strength of these solutions were checked by standard methods^{7,8}.

Measured aliquots (5-10 ml) of the reductant solutions were taken in the titration cells. To these, 10 ml portions of acetic acid and other reagents such as KBr, HCl etc. (if required) were added. The solutions were diluted to 50 ml with water. Standard solution of BCH was added in 0.1 ml portions from a microburette. After each addition of the oxidant the reaction mixture was stirred for 1 min and the steady potential noted. The titration was continued until there was no significant change in potential on further addition of the titrant.

The results of the titrations are presented in Table I. BCH gets reduced to 5,5-dimethylhydantoin during the reaction in accordance with Eq.(1).

Table 1—Potentiometric Titrations using Bromochlorohydantoin as Titrant

| Reductant | Range studied mmol | Reductant taken mmol | Max. error % | Stand. dev.* |
|---------------------------|-----------------------|-------------------------|-----------------|----------------------|
| As(III) | 0.25-0.45 | 0.2706 | 0.23 | 7.1×10^{-5} |
| Sb(III) | 0.25-0.41 | 0.2530 | 0.40 | 4.1×10^{-4} |
| Sn(II) | 0.16-0.33 | 0.1638 | 0.25 | 3.8×10^{-4} |
| Fe(II) | 0.20-0.61 | 0.2012 | 0.40 | 4.3×10^{-4} |
| Tl(I) | 0.08-0.26 | 0.0836 | 0.39 | 5.8×10^{-5} |
| Ferrocyanide | 0.20-0.63 | 0.2096 | 0.47 | 2.4×10^{-4} |
| Iodide | 0.38-0.77 | 0.4850 | 0.45 | 7.9×10^{-4} |
| Hydrazine | 0.19-0.29 | 0.2436 | 0.29 | 1.4×10^{-4} |
| Phenyl hydrazine | 0.07-0.16 | 0.0754 | 0.36 | 9.6×10^{-5} |
| Semicarbazide | 0.09-0.19 | 0.0919 | 0.38 | 1.8×10^{-4} |
| Hydraquinone | 0.22-0.46 | 0.2280 | 0.22 | 1.9×10^{-4} |
| Aniline | 0.07-0.18 | 0.0965 | 0.41 | 9.2×10^{-5} |
| Ascorbic acid | 0.26-0.53 | 0.2654 | 0.40 | 4.0×10^{-4} |
| Oxine | 0.10-0.21 | 0.1320 | 0.38 | 2.1×10^{-4} |
| Thiosulphate | 0.04-0.14 | 0.0459 | 0.35 | 3.7×10^{-5} |
| Thiourea | 0.06-0.12 | 0.0600 | 0.46 | 1.2×10^{-4} |
| Thiosemicarbazide | 0.03-0.10 | 0.0574 | 0.23 | 6.3×10^{-5} |
| Thiocyanate | 0.06-0.15 | 0.0623 | 0.40 | 9.5×10^{-5} |
| Reinecke's salt | 0.01-0.03 | 0.0150 | 0.40 | 4.4×10^{-5} |
| Hg[Co(CNS) ₄] | 0.01-0.03 | 0.0152 | 0.39 | 2.5×10^{-5} |
| Hg[Zn(CNS) ₄] | 0.02-0.04 | 0.0199 | 0.40 | 2.8×10^{-5} |

*Six replicates

$RN_2(Cl)(Br) + 2H^+ + 4E^- \rightleftharpoons RN_2H_2 + Cl^- + Br^- \dots (1)$
 where $R = C_5H_6O_2$. The formal redox potential of the couple BCH/hydantoin in glacial acetic acid at room temperature (34) is + 1.15V. A steady potential is attained in each case very quickly and a potential jump of 100-350 mV is obtained at the equivalence point for the addition of 0.1 ml of 0.1N oxidant.

The results show that all the titrations are very accurate and precise. The potential break is very sharp. All the 21 reductants undergo usual oxidations as reported earlier¹⁻³. Simple titrations without adding any other reagents are possible for thiocyanate and iodide only. For the determinations of oxine, thiosemicarbazide, thiosulphate, hexacyanoferrate(II), aniline and thiourea, addition of 0.5 g of KBr is essential. In these systems KBr reacts with the oxidant and the bromine produced *in situ* reacts with the reductants. For As(III), Sb(III), Tl(I), ascorbic acid, hydrazine, phenylhydrazine, semicarbazide, hydroquinone, Reinecke's salt, Hg[Co(CNS)₄] and Hg[Zn(CNS)₄], addition of both KBr (0.5 g) and conc. HCl (5 ml) is needed to get a sharp break in potential at the equivalence point. For Sn(II) addition of a pinch of

sodium bicarbonate is necessary to maintain an inert atmosphere in the system to eliminate aerial oxidation of the reductant. In the case of Fe(II) addition of orthophosphoric acid (5 ml) is essential for the success of the titration. Orthophosphoric acid removes Fe(III) formed during the reaction via complexation resulting in the lowering of the potential of the couple Fe(III)/Fe(II) and thereby causing sharp break at the equivalence point.

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