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Titrimetric Determinations using Dichlorohydantoin & Dibromohydantoin in Aqueous Acetic Acid Medium

M P RADHAMMA & P INDRASENAN*
Department of Chemistry,
University of Kerala, Trivandrum 695 034

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Dichlorohydantoin and dibromohydantoin are found to be suitable oxidimetric titrants for mercury(I), sulphite, thiosulphate, thiourea, thiosemicarbazide, ascorbic acid, aniline, phenol, isonicotinic acid hydrazide, mercury(II) tetrathiocyanatocobaltate(II) and mercury(II) tetrathiocyanatozincate(II).

Dichlorohydantoin (DCH) and dibromohydantoin (DBH) have recently been introduced as new oxidimetric titrants for use in aqueous acetic acid medium[1]. Direct potentiometric titrations of (i) Hg(I), (ii) sulphite, (iii) thiosulphate, (iv) thiourea, (v) thiosemicarbazide, (vi) ascorbic acid, (vii) aniline, (viii) phenol, (ix) isonicotinic acid hydrazide, (x) $Hg[Co(CNS)_4]$ and (xi) $Hg[Zn(CNS)_4]$ using DBH have now been developed. With DCH, direct potentiometric titrations are successful only for thiourea and the two complex thiocyanates. The remaining reductants could be determined only by excess-back method using DCH. These determinations form the subject of the present note.

The apparatus and electrode assemblies were the same as described earlier[2]. Both potentiometric[2] and excess-back titrations[3] were carried out by the reported methods at room temperature ($30 \pm 2°C$).

Both DCH and DBH were prepared by halogenation of 5,5-dimethylhydantoin as per the method suggested by Okada *et al*[4]. Standard solutions ($\sim 0.1N$) of DCH and DBH were prepared in anhydrous acetic acid and were kept in amber coloured bottles[1,2].

Standard solutions ($\sim 0.1N$) of the reductants (i-ix) were prepared in water. Solutions of the complex thiocyanates (x and xi) were prepared in $2N$ hydrochloric acid. The strengths of these solutions were checked by standard methods[5,6].

Both DCH and DBH undergo reduction, yielding 5,5-dimethylhydantoin[1]. The conditional redox potentials in glacial acetic acid at 30°C are found to be +1.19 and 1.13V for DCH and DBH, respectively. These values indicate that both are moderately strong oxidants.

In the direct potentiometric titrations of thiourea and the two complex thiocyanates using DCH, presence of potassium bromide (0.5 g) is found essential. Moreover, for the two complex thiocyanates prior decomposition of the complexes and addition of conc. hydrochloric acid (5 ml) are also needed. The remaining 8 reductants can only be determined by excess-back titrations using DCH within a period of 10 min. For ascorbic acid, aniline and phenol addition of potassium bromide (0.5 g) is found essential. In these cases the actual oxidant is the bromine produced *in situ* by the reaction of DCH with the added bromide. The other 5 reductants, for which only excess-back method is possible, simple titrations without adding any other reagents are possible.

All the 11 reductants can be determined by direct potentiometric method using DBH as the titrant (Table 1). Simple titrations without adding any other reagents are successful for sulphite, thiosulphate, ascorbic acid, aniline and isonicotinic acid hydrazide. In the cases of the two complex thiocyanates, prior decomposition and addition of conc. hydrochloric acid (5 ml) are required. For Hg(I), thiourea, thiosemicarbazide and phenol addition of potassium

Table 1—Titrimetric Determinations with Dichlorohydantoin Dibromohydantoin.

Reductant	Range of reductant studied mmol	Standard deviation* μmol	Maximum error %
(a) With dichlorohydantoin			
Mercury(I)	0.38-2.11	1.90	0.29
Sulphite	0.18-0.56	1.80	0.36
Thiosulphate	0.06-0.28	2.20	0.28
Thiourea	0.06-0.13	0.17	0.47
Thiosemicarbazide	0.05-0.16	2.10	0.32
Ascorbic acid	0.09-0.55	2.20	0.45
Aniline	0.05-0.16	2.40	0.41
Phenol	0.05-0.21	1.80	0.34
Isonicotinic acid hydrazide	0.09-0.31	2.70	0.44
$Hg[Co(CNS)_4]$	0.03-0.06	0.04	0.43
$Hg[Zn(CNS)_4]$	0.03-0.07	0.09	0.45
(b) With dibromohydantoin			
Mercury(I)	0.15-0.47	0.11	0.43
Sulphite	0.12-0.25	0.32	0.35
Thiosulphate	0.04-0.12	0.06	0.45
Thiourea	0.04-0.11	0.04	0.29
Thiosemicarbazide	0.03-0.08	0.08	0.46
Ascorbic acid	0.25-0.52	0.10	0.41
Aniline	0.06-0.15	0.04	0.45
Phenol	0.04-0.15	0.08	0.27
Isonicotinic acid hydrazide	0.02-0.08	0.08	0.39
$Hg[Co(CNS)_4]$	0.02-0.06	0.09	0.43
$Hg[Zn(CNS)_4]$	0.02-0.07	0.10	0.41

*Six replicates

bromide (0.5 g) is found essential for the titrations. It is interesting to note that aniline does not require any added bromide for its bromination with DBH, while phenol requires added bromide. This may be due to the fact that aniline, being a base, facilitates the decomposition of DBH and the resulting bromide ions react with DBH to afford sufficient bromine for the bromination of aniline. In the case of phenol the decomposition of DBH is very slow. Therefore, in the case of phenol addition of potassium bromide (0.5 g) is essential.

The results show that all the titrations using both DCH and DBH as titrants are very accurate and precise. The reductants undergo oxidation by either of the oxidants according to Eqs. (1-10):

$$Hg^{+} \rightarrow Hg^{2+} + e^{-} \quad \ldots (1)$$

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^{+} + 2e^{-} \quad \ldots (2)$$

$$S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^{+} + 8e^{-} \quad \ldots (3)$$

$$CS(NH_2)_2 + 5H_2O \rightarrow SO_4^{2-} + CO(NH_2)_2 + 10H^{+} + 8e^{-} \quad \ldots (4)$$

$$NH_2CSNHNH_2 + 4H_2O \rightarrow SO_4^{2-} + CN^{-} + N_2 + 13H^{+} + 10e^{-} \quad \ldots (5)$$

$$C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^{+} + 2e^{-} \quad \ldots (6)$$

$$C_6H_5NH_2 + 3Br_2 \rightarrow C_6H_2Br_3NH_2 + 3HBr \quad \ldots (7)$$

$$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr \quad \ldots (8)$$

$$C_5H_4NCONHNH_2 + H_2O \rightarrow C_5H_4NCOOH + N_2 + 4H^{+} + 4e^{-} \quad \ldots (9)$$

$$CNS^{-} + 4H_2O \rightarrow SO_4^{2-} + CN^{-} + 8H^{+} + 6e^{-} \quad \ldots (10)$$

It is clear that one equivalent of oxidant (either DCH or DBH) is consumed per mol of Hg(I); 2 equivalents for sulphite and ascorbic acid; 4 equivalents for isonicotinic acid hydrazide; 6 equivalents for aniline and phenol; 8 equivalents for thiosulphate and thiourea; 10 equivalents for thiosemicarbazide; and 24 equivalents for $Hg[Co(CNS)_4]$ and $Hg[Zn(CNS)_4]$.

Both DCH and DBH can be used for the determination of more reductants by direct potentiometric method as compared to those using dichloroamine-T (DCT)[7] and dibromamine-T (DBT)[8]. For example, thiourea and the two complex thiocyanates can be determined potentiometrically with DCH and DBH and these can be determined only by excess-back method using both DCT and DBT. Although DCH has a higher redox potential (+1.19 V) than DBH (+1.13 V), DBH is more reactive than the former. The higher reactivity of DBH may be attributed to its lesser stability in comparison to DCH.

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