Vanadium(II)-Halomine Titrations in Aqueous Sulphuric Acid Medium: Titrimetric and Potentiometric Methods

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Vanadium(II) in aqueous sulphuric acid has been used for the quantitative reduction of N-halo sulphonamides. Monohalosulphonamides and dihalosulphonamides undergo two and four electron change respectively. Other reducible compounds like hydroxylamine and nitrobenzene also undergo quantitative reduction. The analytical utility of the redox systems for titrimetric analysis has also been tested.

Vanadium(II) species have been shown to be very good reducing agents for a variety of inorganic cations and complexes in aqueous solutions [1-8]. They have also been identified as excellent and efficient in the reduction of organic compounds like nitro, nitroso, azo, hydrazo, diazonium and hydroxylamines [9]. The standard redox potential of vanadium(II) in aqueous sulphuric acid has been reported to be -0.255V [10] and hence it is milder reductant than chromium(II) but stronger than titanium(III). Vanadium(II) in aqueous sulphuric acid solution can be prepared from the vanadium salts of higher oxidation states by electrolytic reduction [11] or by chemical reduction using zinc-amalgam under nitrogen atmosphere [12]. Being a typical d^3 ion, it is kinetically inert but undergoes ready electron transfer reaction.

Reported literature lacks details regarding vanadium(II) reduction of N-halo- and N,N-dihalo- sulphonamides. The chemistry of of these oxidants is of interest due to their diverse behaviour and wide applications [13,14]. Hence, as a part of electrochemical studies with transition metal-ion redox systems [15,16] redox titrations of vanadium(II) with chloramine-T(CAT), bromamine-T(BAT), chloramine-B(CAB) and bromamine-B(BAB) and N,N-dihalosulphonamides such as dichloramine-T(DCT), dichloramine-B(DCB), dibromamine-T(DBT) and dibromamine-B(DBB) were investigated. Further, the use of these halosulphonamides as back titrants for establishing the number of electrons involved in the vanadium(II) reduction of certain typical compounds like nitrobenzene and hydroxylamine hydrochloride were also studied.

EXPERIMENTAL

An approximately 0.05 $mol.dm^{-3}$ solution of vanadium(II) sulphate in 1 $mol.dm^{-3}$ sulphuric acid was prepared from about 2.25 g of vanadyl sulphate (GSC Chemicals, Bombay) by chemical reduction with about 80 g of zinc amalgam under nitrogen blanket. An assembly of apparatus was similar to that suggested by Siggia and

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Hanna [17] but slightly modified and used for the purpose.

The vanadium(II) solution was standardised by volumetric titration under nitrogen blanket with standard ammonium iron(III) sulphate solution using thiocyanate as indicator [12]. The vanadium(II) species was characterised by UV-VIS spectra (two intense bands of 570 and 849 nm) and measuring the redox potential of V(II)-V(III) system. Vanadium(II) solutions of lower concentrations were prepared similarly by taking appropriate amounts of vanadyl sulphate and zinc amalgam.

CAT (Sd fine Chemicals, Bombay) was used after recrystalisation. DCT, BAT and DBT were prepared by literature methods [18]. CAB, BAB, DCB and DBB were prepared from benzene sulphonamide (Koch-Light Laboratory) by reported methods [18]. The purity of these compounds were checked by chemical analysis and active halogen content [19]. Approximately 0.05 mol.dm^{-3} solutions of these were prepared by literature methods [18] and stndardised iodometrically [19] as and when required. Lower concentrations of the above solutions were prepared by appropriate dilution.

Volumetric method

To a known volume of N-halo- / N,N-dihalo-sulphonamide solution (V_1 cm^3, M_1 mol.dm^{-3}), 25 cm^3 of 1 mol dm^{-3} sulphuric acid was added. A known excess of vanadium(II) solution (V_2 cm^3 0.005 mol.dm^{-3}) was run down from a burette to this mixture. Deareated ammonium iron(III) sulphate (V_3 cm^3, 0.05 mol.dm^{-3}) was pipetted out and the resulting mixture was titrated against standard vanadium(II) solution using 10% ammonium thiocyanate as the indicator. The reddish orange colour changed to clear light green at the end point. A blank titration was carried out by taking the same aliquot of vanadium(II) and ammonium iron(III) sulphate solutions and tirating against the same standard vanadium(II) solution (V_4 cm^3). The whole experiment was carried out under nitrogen blanket. The number of electrons involved in the reaction was calculated as under

$$n = \frac{\text{no of moles of V(II) species reacted}}{\text{no of moles of the substrate reacted}}$$

$$n = \frac{[V_2 + V_4 - V_3]\, M_2}{V_1\, M_1}$$

where M_1 and M_2 are the molar concentrations of substrate and the vanadium(II) respectively. The results are presented in Table 1.

Potentiometric method

The titration cell consisted of a flat bottomed closed vessel of 100 cm^3 capacity with five vents of IC joints - for the free flow of oxygen-free nitrogen, for Pt-SCE assembly and for the introduction of the titrant. An Equip-Tronic model EQ-600 digital potentiometer was used to measure the potential across Pt-SCE assembly.

The cell was charged with 20 cm^3 of 1 mol.dm^{-3} of KCl solution (KBr for bromosulphonamides) and 50 cm^3 of 1 mol.dm^{-3} sulphuric acid. Purified nitrogen gas was bubbled slowly. Vanadium(II) sulphate (10 cm^3, 0.01 mol.dm^{-3}) was introduced into the cell and stirred

Table 1

Titrimetric and Potentiometric Determination of the Number of electrons (Probable) involved in the reduction of N-halo- and N,N-dihalo- sulphonamides by V(II) in Aqueous sulphuric acid media
T = 298 °K

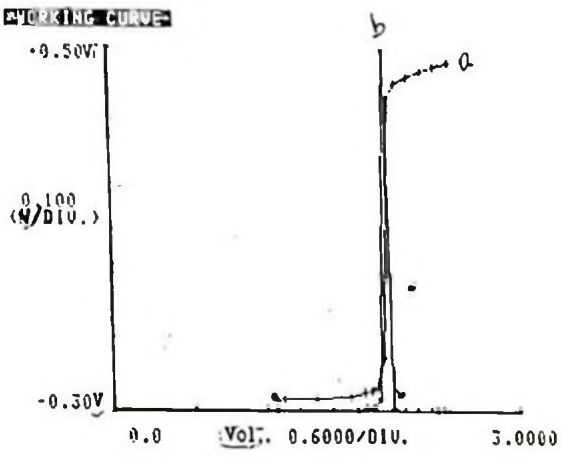
Compound	Range Studied in mg	Value of n in the reaction			
		Theor.	Titri.	Poten.	± σ
CAT	1.408 - 14.08	2	2.036	2.010	0.019
CAB	1.12 - 11.21	2	2.011	2.005	0.019
BAT	1.11 -11.2	2	1.988	2.000	0.026
BAB	1.2 - 12.1	4	2.001	2.006	0.029
DCT	1.2 - 12.0	4	2.002	4.010	0.030
DCB	1.00 -10.0	4	3.998	4.010	0.035
DBT	1.55 - 15.55	4	4.002	4.015	0.029
DBB	1.23 - 12.32	6	4.001	3.988	0.036
HAH	1.7 - 6.00	6	-	1.98	0.033
NB	1.2 - 12.0	6	-	5.99	0.028

Titrimetric result is average of 6 trials; Potentiometry is back titration method

continuously by means of a magnetic stirrer. Deareated N-halosulphonamide / N,N-dihalosulphonamide solution was added from a micro-burette in small quantities and the emf values were noted after each increament of titrant. A potential jump of about 350-750 mV (-ve potential to +ve) per 0.05 cm^3 of the titrant was observed at the end point. The first order ($\Delta E/\Delta V$) and second order ($\Delta^2E/\Delta V^2$) derivative curves were used to determine the end points. The electron change involved in the reaction was given by

$$n = V_2M_2 / V_1M_1$$

where V_1 and M_1, V_2 and M_2 are the volume and the molar concentrations of the reductant and the oxidant, respectively. The experiment was repeated in the presence of common anions such as SO_4^{-2}, HSO_4^-, PO_4^{-3}, ClO_4^- and NO_3^-. Typical potentiometric plots are shown in Fig. 1.



Titration Curve (First Differential

As a part of the present analytical work, the aromatic sulphonamides were used as back titrants for establishing the reaction stoichiometry of vanadium(II) reduction of hydroxylamine hydrochloride (HAH) and nitrobenzene (NB). The solution of HAH (Sd fine chemicals) was prepared in water and NB (SISCO, fine chemicals) was used in methanol.

Potentiometric Back Titration

The titration cell was charged with 50 cm^3 of 1 $mol.dm^{-3}$ sulphuric acid and 20 cm^3 of 1 $mol.dm^{-3}$ KCl solution. Nitrogen gas was bubbled through this solution continuously. Vanadium(II) sulphate (10 cm^3, 0.025 $mol.dm^{-3}$) was introduced into the cell, followed by a known volume of the substrate (2.5 cm^3, 0.01 $mol.dm^{-3}$). The mixture was stirred magnetically and titrated with deareated CAT solution (0.06 $mol.dm^{-3}$) from a microburette as earlier. A blank titration was carried out under identical conditions in the absence of the substrate. The end point was determined graphically. The number of electrons involved in the reactions were obtained from

$$n = \frac{(V_2 - V_3)\, M_2}{V_1 M_1}$$

where M_1 and M_2 are the molar concentrations of the substrate and CAT respectively. V_1 = volume of the substrate, V_2 = volume of CAT for blank titration and V_3 = volume of CAT in back titration.

RESULTS AND DISCUSSION

Reduction of vanadyl sulphate ($VOSO_4$) to vanadium(II) proceeds in two steps [20].

$$VO^{+2} + 2H^+ + e \longrightarrow V^{+3} + H_2O,\ E^0 = +0.361\ V$$

$$V^{+3} + e \longrightarrow V^{+2},\qquad E^0 = +0.255\ V$$

(Purple blue)

The vanadium(II) exists as hexa aquo ion $[V(H_2O)_6]^{+2}$ in aqueous acid media and the presence of acid prevents the reduction of water by the highly reactive Vanadium(II) [21]. Its solutions in 1 $mol.dm^{-3}$ sulphric acid have been found to be stable for about seven days over zinc amalgam under nitrogen blanket.

The monohalosulphonamides (CAT, BAT, CAB and BAB) are reduced by vanadium(II) with 1:2 stoichiometry (Table 1).

$$(Ar.SO_2NNa^+)\ X^- + 2V^{+2} + 2H^+ \longrightarrow ArSO_2NH_2 + 2V^{+3} + NaX$$

where Ar = C_6H_4-CH_3 or C_6H_5, X=Cl^- or Br^-.

Dihalosulphonamides (DCT, DBT, DCB and DBB) undergo reduction by vanadium(II) with 1:4 stoichiometry (Table 1).

$$ArSO_2NX_2 + 4V^{+2} + 2H^+ \longrightarrow ArSO_2NH_2 + 4V^{+3} + 2X^-$$

The reduction of hydroxylamine hydrochloride involving 2 electron change can be represented as

$$H_3{}^+NOH + 2V^{+2} + 2H^+ \longrightarrow NH^+_4 + 2V^{+3} + H_2O.$$

The formation of ammonium ion was detected by Nessler's test.

The reduction of nitrobenzene required 15-20 minutes and corresponded to 1:6 stoichiometry.

$$C_6H_5NO_2 + 6V^{+2} + 6H^+ \longrightarrow C_6H_5NH_2 + 4V^{+3} + 2H_2O$$

The product, aniline was isolated and identified by reported methods [22].

The above stoichiometry was observed when subsrate was used as titrant. When V(II) was used as the titrant, it has been found that the vanadium(II) is oxidised to vanadium(IV). However, the halo-sulphonamides did not further oxidise the reaction product of the above (V^{3+}) under experimental conditions within 10 minutes.

The common ions such as SO_4^{-2}, HSO_4^-, PO_4^{-3}, Cl^- and Br^- did not interfere with the reaction but ClO_4^- and NO_3^- interfered even when present in trace amounts; they were reduced by vanadium(II).

In potentiometric titrations, the presence of appropriate sodium or potassium halides (20 cm^3 of 1 $mol.dm^{-3}$ for a total volume of 85 cm^3) have been found to stablise the potentials.

The results obtained show that the vanadium(II) reductions of N-halosulphonamides, N,N- dihalo-sulphonamides, hadroxylamine, hydrochloride and nitrobenzene are quantitative. A comparison of the results with those standard methods [19] show that these are accurate and precise.

REFERENCES

1. M.J.Burkhart, and T.W.Newton, *J.Phys. Chem.* **73** (1969) 1741.
2. B.R.Baker, M.Orthanovic and N.Sutin, *J.Amer. Chem. Soc.*, **89** (1967) 722.
3. C.A.Jacks and L.E.Bennet, *Inorg. Chem.*, **13** (1974) 2035.
4. P.H.Dodel and H.Taube, *Z. Phys. Chem. Frnkf. Ausg.* **44** (1965) 92.
5. P.R.Guenther and R.G.Linck, *J.Amer.Chem.Soc.*, **A 91** (1969) 3769.
6. R.N.F.Thorneley and A.G.Sykes, *J.Chem.Soc.*, **(1970) A** 1036.
7. M.Green and A.G.Sykes, *Chem. Commun.*, **(1970)** 241.
8. A.J.Parker and J.H.Espenson, *Inorg. Chem.*, **8** (1969) 185.
9. HO.Tse-Lok (Review) *Synthesis.* 0039-7881/ **79** (1979).
10. A.F.Clifford *Inorganic Chemistry of Qualitative Analysis.* **Prentice-Hall** (1961) p476.
11. G.Venkateshwaran, A.S.G khale and P.N.Moorthy, A.C.Division, B.A.R.C. **(personal communication).**
12. A.I.Vogel, *Quantitative Inorganic Analysis.* **ELBS edition Longman** (1975) p 337-339.
13. K.K.Banerge, B.Jayarama and D.S.Mahadevappa, *J.Sci.Ind.Res.*, **46** (1987) 65.
14. M.M.Cambell, & G.Johnson, *Chem. Rev.*, **78** (1978) 65.
15. Padmalatha, B.S.Sherigara, H.V.K.Udupa, *J.Electrochem. Soc.India*, 34-A (1995). 326
16. B.S.Sherigara and Padmalatha, *Ind.J.Chem.*, **33A** (1995) 396.
17. Sidney Siggia and Gordon Hanna, *Quantitative Organic Analysis via Functional Groups*, **John Wiley, 4th ed.** (1979) p 660.
18. A.Chrzazewska, *Bull.Soc.Sci. Left Lo Dz. el 3 (1952); through Chemical Abst.* **49** (1955) 212.
19. I.M.Kolthoff and R.Belcher, *Volumetric Analysis Vol.III*, **InterScience Publishers** (1957).
20. R.B.Fischer and D.G.Peters, *Quantitative Chemical Analysis* 3rd ed. **W.B. Saunders Co and Toppan Co. Tokyo,** (1968) p-513.
21. L.F.Larkworthy, K.C.Patel and D.J.Phillips, *J.Chem.Soc.*, **A (1971)** 1347-50.
22. A.I.Vogel, *Practical Organic Chemistry* 3rd ed. ELBS and **Longman Groups Ltd., London** (1973).