

## Titanium(III)-haloamine titrations in aqueous sulphuric acid medium: Titrimetric and potentiometric methods

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Titanium(III) species, generated from cathodic reduction of titanium(IV) sulphate using a perforated cylindrical copper cathode under nitrogen cover, have been characterised by UV-visible spectra and by determination of redox potential of Ti(IV)-Ti(III) couple. Redox titrations of chloramine T, chloramine B, bromamine B, bromamine T, dichloramine T, dichloramine B, dibromamine B and dibromamine T with titanium(III) sulphate by volumetry with both visible and potentiometric end points, have been carried out. The monohalo- and dihalo-sulphonamides undergo 2 and 4 electron reductions respectively. These halo-sulphonamides have been used as back titrants for establishing the probable number of electrons involved in the titanium(III) sulphate reduction of certain typical compounds like hydroxylamine, cyclohexanoneoxime and *p*-nitrotoluene. Utility of titanium(III) as a reductant in the electro reduction processes and in analytical and kinetic studies have been highlighted.

Titanium(III) salts have been shown to be very good reducing agents for aromatic nitro, nitroso and hydroxylamine compounds<sup>1</sup>. The kinetics of reduction of nitro compounds and its substituted products by titanium(III) chloride was studied by Hinshelwood and coworkers<sup>1</sup>. Indirect electrochemical reduction of nitro compounds with titanium(III) sulphate were reported in previous years<sup>2</sup>. Reported literature lacks essential details for using titanium(III) sulphate for reduction of aromatic halosulphonamides. Hence the present investigation was undertaken.

Chemistry of N-halo-N metallo and N-N-dihalo-aromatic sulphonamides is of interest due to their diverse behaviour and wide applications<sup>3-5</sup>.

As a part of analytical, and kinetic studies with transition metal ion redox systems<sup>6-8</sup> we present

herein the results of the reduction of N-halo and N-N-dihalo sulphonamides with electrolytically generated titanium(III) sulphate in aqueous sulphuric acid medium under deaerated conditions. Use of N-halosulphonamide as a back titrant for reduction of hydroxyl amine hydrochloride, cyclohexanoneoxime and *p*-nitrotoluene is also discussed.

### Experimental

Titanium(IV) sulphate was prepared by the gradual addition of titanium dioxide (Glaxo, special quality) to hot concentrated sulphuric acid (Glaxo, Excellar grade). Yellowish green solid of titanium(IV) sulphate was dissolved in water boiled well and filtered to get clear solution.

The electrolytic cell assembly consisted of 500 cm<sup>3</sup> glass beaker fitted with electrodes, diaphragm and a gas vent. A porous pot was used as diaphragm in which 2 mol dm<sup>-3</sup> sulphuric acid (50 cm<sup>3</sup>) was taken as anolyte. A lead or platinum foil was used as anode. The cathode was a perforated copper cylinder and titanium(IV) sulphate (250 cm<sup>3</sup> acidic solution) was used as catholyte. Pure nitrogen gas was passed continuously over the catholyte to prevent aerial oxidation of titanium(III) sulphate, that was generated in cathodic compartment. The cell voltage was 4.5V and cathodic current density 1-3 A/dm<sup>2</sup> was maintained and the catholyte was stirred continuously.

The UV-visible spectrum of titanium(III) sulphate in aqueous sulphuric acid medium was recorded in Beckmann DU-6 spectrophotometer. The absorption maximum ( $\lambda_{\max}$ : 480 nm) was found to be in agreement with that reported in literature<sup>1</sup>.

The formal redox potential of the Ti(IV)-Ti(III) couple  $E_{\text{Ti(IV)-Ti(III)}}^0$  is a measure of the reducing properties of reductant. Different known amounts of titanium(III) were cathodically generated and the electrode potential measured each time under deaerated condition. The Nernst equation in which E (mV versus SCE) indicates the equilibrium potential of the dynamic equilibrium between the reduced and oxidized forms which established rapidly at the platinum indicator electrode can be represented by:

$$E_{(\text{mV versus SCE})} = E_{\text{Ti(IV)-Ti(III)}}^0 + \frac{2.303RT}{nF} \log \frac{[\text{Ti(IV)}]}{[\text{Ti(III)}]} \dots (1)$$

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Table 1—Titrimetric and potentiometric determination of probable number of electrons involved in the reduction of N-halo and N,N-dihalo aromatic sulphonamides and certain other compounds by titanium(III) sulphate in aqueous sulphuric acid medium at 298 K

Compounds	Range (mg)	Electrons Participating in Reaction			Standard Deviation
		Calc.	Volumetry <sup>a</sup>	Potentiometry <sup>a</sup>	
CAT	1.41-14.08	2.0	2.04	2.00	0.02
CAB	1.12-12.21	2.0	2.00	2.05	0.02
BAT	1.11-11.30	2.0	1.97	1.99	0.03
BAB	1.22-12.16	2.0	2.00	2.00	0.02
DCT	1.20-11.95	4.0	4.04	4.00	0.03
DCB	1.01-10.00	4.0	4.02	4.01	0.05
DBT	1.55-15.52	4.0	3.96	3.99	0.04
DBB	1.23-12.32	4.0	4.01	4.00	0.03
HAH <sup>b</sup>	1.73-6.95	2.0	—	1.99	0.02
CHO <sup>b</sup>	1.21-8.69	4.0	—	3.95	0.04
PNT <sup>b</sup>	1.92-10.68	6.0	—	5.95	0.03

<sup>a</sup>Average of six trials.

<sup>b</sup>by back-titration method

where  $R = 8.314 \text{ J mol}^{-1}$ ;  $T = 298 \text{ K}$ ;  $n = 1$  and  $F = 96500 \text{ C mol}^{-1}$ . Plot of  $E_{(mV \text{ versus SCE})}$  against  $\log[Ti(IV)]/[Ti(III)]$  was linear with intercept equal to  $E_{cal} - (E_{Ti(IV)}^0 - E_{Ti(III)}^0)$ . Taking  $E_{cal}$  for saturated KCl at 298 K as 0.241 V,  $E_{Ti(IV)-Ti(III)}^0$  could be found. The measurements were carried out at different concentrations of sulphuric acid. The formal redox potential of Ti(IV)-Ti(III) was found to be 0.0595V.

Titanium(III) sulphate was standardised volumetrically by back titrating it with ammonium ferric sulphate under nitrogen blanket and it was stable for more than 8 h. Chloramine-T (CAT) (SD Fine Chem), was used after recrystallisation with water. Chloramine-B (CAB), dichloramine-T (DCT), dichloramine-B (DCB), dibromamine-T (DBT), dibromamine-B (DBB), bromamine-T (BAT) and bromamine-B (BAB) were prepared by literature methods<sup>9</sup>.

The purity of all the compounds were checked by the elemental analysis of N, S and X and by estimating the amounts of active halogen present in them by iodometric method<sup>10</sup>. They were further characterised by their IR and FT NMR spectra<sup>11</sup>. Even though the solutions were quite stable for several days, aqueous solutions of monohalosulphonamides and partially aqueous solutions, (1:1 (v/v) water-acetic acid) of dihalosulphonamides were prepared and standardised as and when needed.

#### Volumetric method

To a known volume ( $V_1 \text{ cm}^3$ ) of the substance ( $5.0 \text{ cm}^3$  of  $0.001 \text{ mol dm}^{-3}$  in water or 1:1 (v/v)

water-acetic acid) titanium(III) sulphate ( $5 \text{ cm}^3$  of  $0.005 \text{ mol dm}^{-3}$ ) was added ( $V_2 \text{ cm}^3$ ). To this deaerated ammonium ferric sulphate ( $5 \text{ cm}^3$   $0.025 \text{ mol dm}^{-3}$ ) was added. Resulting solution was titrated against standard titanium(III) sulphate ( $0.05 \text{ mol dm}^{-3}$ ) stored under nitrogen atmosphere ( $V_3 \text{ cm}^{-3}$ ) using 10% ammonium thiocyanate as indicator. A blank titration was carried out by taking same aliquot of titanium(III) sulphate and ammonium ferric sulphate and titrating against standard titanium(III) sulphate ( $V_4 \text{ cm}^{-3}$ ). Experiment was done under deaerated condition. The number of electrons involved in this reaction is given by Eq. 2.

$$n = \frac{[V_2 - (V_4 - V_3)] M_1}{V_1 \times M_2} \quad \dots (2)$$

where  $M_1$  and  $M_2$  are the molarities of titanium(III) sulphate and the substrate respectively. The results are given in Table 1.

#### Potentiometric method

(a) *Direct titration*: A Digisum (India) model 801 digital potentiometer equipped with a platinum-calomel electrode assembly was used for the potentiometric studies throughout this work.

Titanium(III) sulphate ( $10 \text{ cm}^3$  of  $0.217 \text{ mol dm}^{-3}$ ) was placed in a beaker ( $100 \text{ cm}^3$ ) fitted with platinum electrode, calomel electrode and a gas vent for nitrogen. The cell emf,  $E_{(mV \text{ versus SCE})}$  was noted. In the case of dihalosulphonamides reaction mixture contained 1:1 (v/v) water-acetic

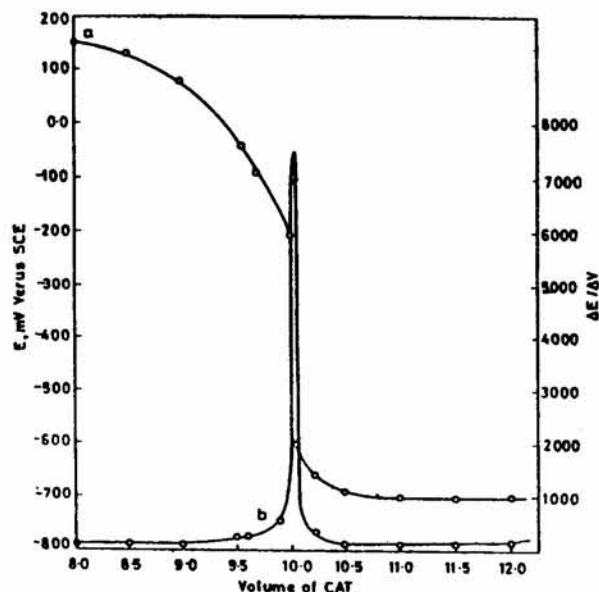


Fig. 1—A typical potentiometric titration curve of titanium(III) [10 cm<sup>3</sup>, 0.217 M] with CAT (0.0108 M); a, titration curve; b, first derivative curve.

acid as solvent. Deaerated halosulphonamide (0.0106 mol dm<sup>-3</sup>) was added from micro burette in small quantities. The emf,  $E_{(mV \text{ versus SCE})}$  value was noted after each addition. A potential jump at the equivalence point ranged from 200-400 mV per 0.05 cm<sup>3</sup> of the titrant. The end point was determined graphically by plotting the first derivative curve ( $\Delta E/\Delta V$ ) versus volume ( $V$  cm<sup>3</sup>). The number of electrons involved in the reaction is given by Eq. 3.

$$n = \frac{V_2 \times M_2}{V_1 \times M_1} \quad \dots (3)$$

where  $V_1$ ,  $M_1$ ,  $M_2$ ,  $M_2$  are volume and molarity of the oxidant and reductant respectively. A typical potentiometric plot is shown in Fig. (2).

In the second part, aromatic halosulphonamide was used as back titrant for establishing the stoichiometry of titanium(III) sulphate reduction of certain compounds like hydroxylamine hydrochloride (HAH), cyclohexanoneoxime (CHO) and *p*-nitrotoluene (PNT). Hydroxylamine hydrochloride (Rudi point, Industria Chemical SPA, Torino-Italy) and *p*-nitrotoluene (Glaxo) were used as such. Cyclohexanoneoxime was prepared and recrystallised by literature method.

(b) *Potentiometric back titration*: Known volume of substrate (2.5 cm<sup>3</sup> of 0.01 mol dm<sup>-3</sup>) and titanium(III) sulphate (10 cm<sup>3</sup> of 0.028 mol dm<sup>-3</sup>) were placed in 100 cm<sup>3</sup> beaker, provided with platinum and standard calomel electrode. Nitrogen

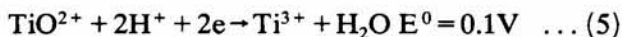
was passed continuously. Deaerated chloramine-T solution (0.432 mol dm<sup>-3</sup>) was added from micro burette and the solution was stirred. A blank titration was carried out under similar conditions in the absence of the substrate. End point was determined graphically. The number of electrons participated in the reaction is given by Eq. 4.

$$n = \frac{[V_2 - V_3] M_2}{V_1 M_1} \quad \dots (4)$$

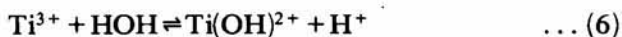
where  $M_1$  and  $M_2$  are the molarities of substrate and halosulphonamide (CAT) respectively;  $V_1$ , volume of substrate;  $V_2$ , volume of halosulphonamide (CAT) used for blank titration and  $V_3$ , volume of halosulphonamide (CAT) in back titration.

### Results and discussion

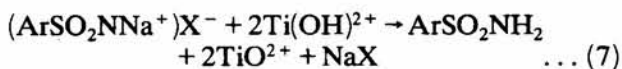
On reduction of titanium(IV) sulphate, violet solution containing  $Ti(H_2O)_6^{3+}$  ions were obtained.



The major reactive species in reduction was assumed to be hydrolysed form of titanous ion<sup>1</sup>, the equilibrium can be represented as follows:



Monohalosulphonamides (CAT, CAB, BAT, BAB) underwent reductions by titanium(III) with 1:2 stoichiometry as in Eq. 7.

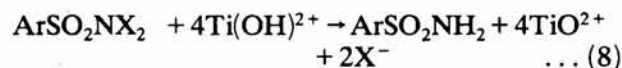


where



Toluene *para*-sulphonamide (TSA), the reduced product was detected by paper chromatography<sup>3</sup>.

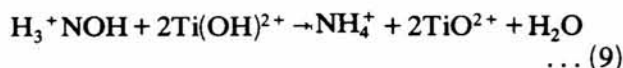
Dihalosulphonamides (DCT, DCB, DBT, DBB) got reduced by titanium(III) with 1:4 stoichiometry as follows:



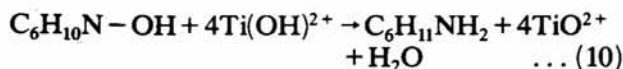
where



While using chloramine-T (CAT) as back titrant for titanium(III) sulphate reduction of hydroxylamine hydrochloride, the reduction was spontaneous involving 2 electron change. This can be represented as:

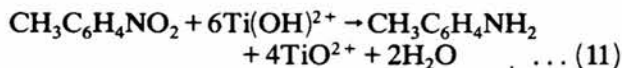


The reduction product,  $\text{NH}_4^+$ , was detected by Nessler's test. The reaction between cyclohexanoneoxime and titanium(III) sulphate was complete within 15 minutes yielding 1:4 stoichiometry.



The reduction product, cyclohexylamine, was isolated and characterised by determination of boiling point, which is in good agreement with that reported in literature  $134^\circ\text{C}$ .

*p*-Nitrotoluene required 30 minutes for completion of reduction to yield *p*-aminotoluene, corresponding to 1:6 stoichiometry as shown in Eq. (11)



*p*-aminotoluene was isolated and the melting point ( $45^\circ\text{C}$ ), agreed with that reported in literature. Further it was verified that halosulphonamides which were used as back titrants, did not react with reac-

tion product of the above reactions under the experimental conditions in less than 10 minutes.

Common anions such as  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{PO}_4^{3-}$  and  $\text{Cl}^-$  did not interfere, while  $\text{ClO}_4^-$ ,  $\text{NO}_4^{2-}$ ,  $\text{H}_2\text{N-NH}_2$ , quinone and anthraquinone interfered even when present in trace amounts as they were reduced by titanium(III) sulphate.

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