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Studies on Molybdenum(III)-Halomine Titrations in Aqueous Hydrochloric Acid Medium

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The quantitative reduction of N-halo- and N,N-dihaloarylsuphonamides with molybdenum(III) in aqueous hydrochloric acid medium has been studied in detail. The analytical utility of these redox systems for titrimetric analysis has also been tested.

INTRODUCTION

Molybdenum(III) is a biologically active metal which is involved in the functioning of enzymes causing reduction of nitrogen to ammonia and nitrates. It has been identified as an excellent reagent in the reduction of organic compounds like nitro, nitroso and sulphoxides[1–3]. It is a mild reductant as vanadium(II) but stronger than titanium(III). Molybdenum(III) can be prepared in aqueous hydrochloric acid medium from ammonium molybdate by chemical reduction under nitrogen atmosphere[4].

The chemistry of N-halo- and N,N-dihaloarylsuphonamides is of interest due to their diverse behaviour and wide applications[5, 6]. Detailed survey of literature shows that essential details regarding the molybdenum(III) reduction of halomines is scanty[7–9]. Hence in the present study the redox titrations of molybdenum(III) with chloramine-T (CAT), bromamine-T (BAT), chloramine-B (CAB) and bromamine-B (BAB), and N,N-dihaloarylsulphonamides such as dichloramine-T (DCT), dibromamine-T (DBT) and dibromamine-B (DBB) were investigated.

Sulphoxides have been often used as intermediates in the production of pharmaceuticals. In the crop protection many sulphoxides are used as insecticides and acaricides[10, 11] and as bactericides and fungicides[12, 13]. As a part of the present analytical work, CAT was used as a back titrant in the reductive estimation of sulphoxides.

EXPERIMENTAL

About 1.2 g of ammonium molybdate (GS Chemicals, Mumbai) dissolved in 2 dm^{-3} of 2 mol dm^{-3} hydrochloric acid was chemically reduced with about 80 g of zinc amalgam under nitrogen blanket to get approximately 0.01 mol dm^{-3} of molybdenum(III) solution. An assembly of apparatus similar to that suggested by Siggia and Hanna[14] but slightly modified was used for the reduction.

The molybdenum(III) solution obtained was standardised by titration with standard cerium(IV) sulphate solution using ferroin indicator under nitrogen

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blanket[4]. Molybdenum(III) solutions of different concentrations were prepared similarly by taking appropriate amounts of ammonium molybdate and amalgamated zinc.

CAT (SD Fine Chemicals, Mumbai) was used after recrystallisation. DCT, BAT and DBT were prepared by literature methods[15]. CAB, BAB, DCB and DBB were prepared from benzene sulphonamide (Koch Light Laboratory) by reported methods[15]. The purity of these compounds was checked by chemical analysis and active halogen content[16]. Approximately 0.01 mol dm^{-3} solutions of these were prepared by literature methods[15] and standardised iodometrically[16] as and when required. Solutions of lower concentrations were prepared by proper dilution (CAT) or by taking appropriate weights of the halomines.

Determination of Stoichiometry of the Reactions

(I) *Volumetric Method:* The titration flask used consisted of a flat-bottomed closed vessel of 100 mL capacity with five vents of IC joints for free flow of oxygen-free nitrogen, for introduction of reductant, for oxidants and for other solutions.

A known volume of molybdenum(III) solution (V_1 mL, 0.01 mol dm^{-3}) was transferred from the microburette to the titration flask. A known excess of N-halo/N,N-dihaloarylsulphonamide solution (20 mL, 0.01 mol dm^{-3}) was pipetted out. 25 mL of 1 mol dm^{-3} hydrochloric acid was added to this mixture and stirred continuously by means of a magnetic stirrer. Then 20 mL of 5% potassium iodide solution was added and the liberated iodine was titrated against standard sodium thiosulphate solution using starch indicator (V_2mL). The whole experiment was carried out under nitrogen blanket.

A blank titration was carried out in the absence of molybdenum(III) but by taking the same aliquots of sulphonamides and potassium iodide solution and titrating against the same standard sodium thiosulphate solution (V_3 mL).

The number of electrons, n, involved in the reaction was calculated as under:

$$n = \frac{\text{no. of equivalents of reductant}}{\text{no. of moles of oxidant}} = \frac{(V_1M_1 2/3)}{[(V_3 - V_2)M_2/X]}$$

$X = 2$, for monohalosulphonamides

$X = 4$, for dihalosulphonamides

where M_1 and M_2 are molar concentrations of molybdenum(III) and sodium thiosulphate solutions, respectively.

(II) *Potentiometric Method:* The titration cell consisted of a flat-bottomed vessel of 100 mL capacity with five vents of IC joints for free flow of oxygen-free nitrogen, for Pt-SCE assembly and for the introduction of the titrant. An Equip-Tronics model EQ-600 digital potentiometer was used to measure the potential across the Pt-SCE assembly.

The cell was charged with 20 mL of 1 mol dm^{-3} of KCl solution (KBr for bromosulphonamide) and 50 mL of 1 mol dm^{-3} of hydrochloric acid. Purified nitrogen gas was bubbled slowly. Molybdenum(III) (10 mL, 0.01 mol dm^{-3}) was introduced into the cell and stirred continuously by means of a magnetic stirrer. Deaerated N-halo/N,N-dihaloarylsulphonamide solution was added from a microburette in small quantities and the emf values were noted after each increment of titrant. The end point was obtained graphically from E *vs.* V, ($\Delta E/\Delta V$) *vs.* V and ($\Delta^2E/\Delta V^2$) *vs.* V plots. The electron change involved in the reaction was given by

$$n = \frac{V_2M_2}{V_1M_1}$$

where V_1, M_1 and V_2, M_2 are the volumes and the molar concentrations of the reductant and the oxidants, 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.

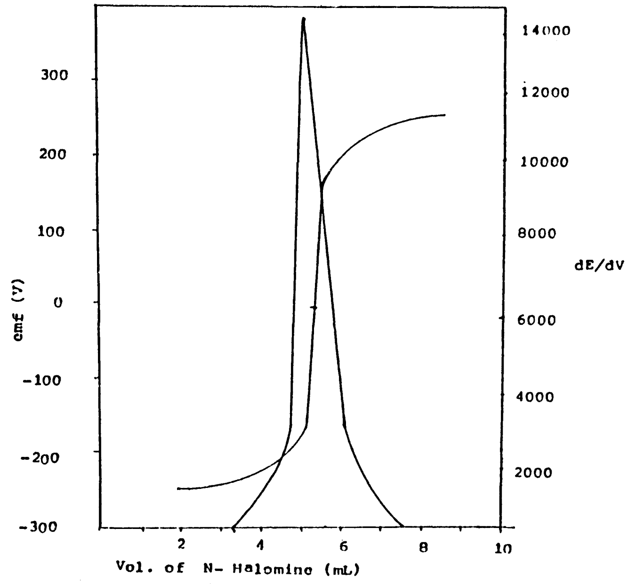


Fig. 1 Typical output of the result (emf *vs.* V and dE/dV *vs.* V) for Mo(III)-CAT titration.

Estimation of Sulphoxides: Dimethyl sulphoxide (DMSO) and diphenyl sulphoxide (DPSO) of AnalaR grade were obtained from SISCO Fine Chemicals, Mumbai, India and used without further purification.

About 0.1 g of sulphoxide was accurately weighed into the cell; 10 mL of tetrahydrofuran and 25 mL of hydrochloric acid (1 mol dm^3) were added. Nitrogen gas was bubbled through the solution. A known excess of molybdenum(III) solution (V_1 mL, M_1 mol dm^{-3}) was transferred into the cell and the mixture was heated to 60°C for about 30 min. After cooling to room temperature, the mixture was titrated potentiometrically against standard CAT solution (V_2 mL, M_2 mol. dm^{-3}). A blank experiment was carried out under identical conditions in the absence of suphoxide. The volume of CAT consumed for blank (V_3 mL) was noted. The number of electrons, n, involved in the reaction was given by

$$n = \frac{(V_3 - V_2)2M_2}{M}$$

where V_2 and V_3 are the volumes (in mL) of CAT in back and blank titrations respectively and M = number of moles of sulphoxide taken. M was calculated using the formula,

$$M = \frac{\text{Wt of sample} \times \text{Purity}}{\text{m.w. of sample} \times 100}$$

The percentage of sulphoxide was also determined titrimetrically using titanium(III) chloride as reductant by the assay method of Barnard and Hargrave[17].

For the identification of products, the reaction was carried out on a macro scale. The products were isolated and identified by reported methods[18].

RESULTS AND DISCUSSION

Reduction of molybdenum(VI) to molybdenum(III) in 2 mol. dm^{-3} hydrochloric acid medium has been reported to proceed in two steps[19].

$$\text{(i)}\quad Mo(VI) + e^- \longrightarrow \underset{\text{(brown)}}{Mo(V)}, \quad E = +0.53\ V$$

$$\text{(ii)}\quad Mo(V) + 2e^- \longrightarrow \underset{\text{(green)}}{Mo(III)}, \quad E = +0.25V$$

The molybdenum(III) has been shown to be present as $[Mo(OH)_2]^+$ in aqueous acid medium. Its solutions in 2 mol dm^{-3} hydrochloric acid have been found to be stable for about 5 days over zinc amalgam under nitrogen blanket.

It has been established that the N-halo and N,N-dihaloarylsulphonamides are reduced to arylsulphonamides involving two and four electron change respectively[9]. The experimental results with molybdenum(III) reduction of these sulphonamides also show similar result. Hence, molybdenum(III) reduction of monohalo and dihaloarylsulphonamides proceeds with 1 : 1 and 1 : 2 stoichiometry respectively (Table-1).

TABLE-1
TITRIMETRIC AND POTENTIOMETRIC DETERMINATION OF THE NUMBER OF ELECTRONS (PROBABLE) INVOLVED IN THE REDUCTION OF N-HALO-AND N,N-DIHALOARYLSULPHONAMIDES BY Mo(III) IN AQUEOUS HYDROCHLORIC ACID MEDIA (T = 298 K)

Compound	Range studied in mg	Value of *n* in the reaction			
		Theor.	Titri.	Poten.	± σ
CAT	1.40–14.06	2	2.006	2.001	0.018
CAB	1.10–11.20	2	2.011	2.005	0.019
BAB	1.21–12.12	2	2.034	2.011	0.029
BAT	1.12–11.21	2	2.010	1.998	0.039
DCB	1.00–10.10	4	3.988	4.010	0.034
DCT	1.21–12.10	4	4.015	4.002	0.028
DBT	1.56–15.56	4	4.012	3.998	0.031
DBB	1.24–12.34	4	3.987	3.989	0.032

$$\underset{\text{(monohalo)}}{(\mathrm{ArSO_2NNa^+})\mathrm{X}} + [\mathrm{Mo(OH)_2}]^+ \longrightarrow \underset{\text{(sulphonamide)}}{\mathrm{ArSO_2NH_2}} + \mathrm{NaX} + \mathrm{MoO_2^+}$$

$$\underset{\text{(dihalo)}}{\mathrm{ArSO_2NX_2}} + 2[\mathrm{Mo(OH)_2}]^+ \longrightarrow \underset{\text{(sulphonamide)}}{\mathrm{ArSO_2NH_2}} + 2\mathrm{MoO_2^+} + 2\mathrm{X^-}$$

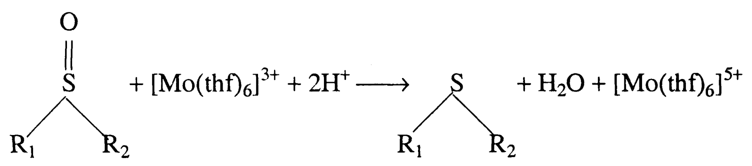
The cerium(IV) has been shown to oxidise molybdenum(III) to molybdenum(VI) involving a three electron change[4]. However, in the present work the halosulphonamides were found to effect the oxidation of Mo(III) to Mo(V) with a two electron change. Further, they did not oxidise the other reaction products under the experimental conditions within 15 min.

The common ions such as SO_4^{2-}, HSO_4^-, PO_4^{3-}, Cl^- and Br^- did not interfere with the reaction. In potentiometric titration, the presence of appropriate sodium or potassium halides (20 mL of 1 mol dm^{-3} for a total volume of 85 mL) have been found to stabilise the potentials. A potential jump of nearly 300–750 mV (−ve to +ve potential) per 0.05 mL or 0.01 mol dm^{-3} of the titrant was observed at the end point.

The reduction of sulphoxides with molybdenum(III) in the presence of tetrahydrofuran (thf) yield corresponding sulphides with 1 : 1 stoichiometry. (Table-2)

TABLE-2
POTENTIOMETRIC DETERMINATION OF SULPHOXIDES USING MOLYBDENUM(III)-CAT SYSTEM

Compound	Weight of the sample (in g.)		
	Actual weight taken	Found	
		Std. method	Mo(III)-CAT method
1. DMSO	(a) 0.1026	0.1018	0.1010
	(b) 0.1332	0.1329	0.1325
	(c) 0.1534	0.1528	0.1525
	(d) 0.1811	0.1809	0.1805
2. DPSO	(a) 0.1014	0.1008	0.1006
	(b) 0.1202	0.1200	0.1202
	(c) 0.1406	0.1399	0.1396
	(d) 0.1704	0.1700	0.1698



Hence, a two electron transfer is involved in this process. The results obtained compare well with the standard methods[17, 20]. The substances reducible by molybdenum(III) like nitro, amine oxide, azo, diazo, etc., interfere and hence must be avoided.

Effect of Temperature: The reduction of sulphoxide at the laboratory temperature required 3 h for completion. However, at the temperature of 60°C the reduction was completed in 30 min.

Effect of Solvent: The molybdenum(III) reduction of sulphoxide was quantitative in tetrahydrofuran-hydrochloric acid. Best results were obtained with a solvent composition of 10 mL of tetrahydrofuran and 25 mL of 1 mol. dm^{-3} hydrochloric acid for a total volume of 75 mL.

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