

Solvolytic of Various Niobium(V), Tantalum(V), Molybdenum(V) & Molybdenum(VI) Compounds in Chlorosulphuric Acid

R. C. PAUL†, (Miss) JASWINDER KAUR, D. KONWER & J. K. PURI*

Department of Chemistry, Panjab University, Chandigarh 160 014

Received 20 November 1980; revised and accepted 15 June 1981

Pentoxides, chlorides, bromides and oxychlorides of niobium and tantalum, and ammonium metaniobate and tantalate solvolyse in HSO_3Cl to form $\text{H}[\text{Nb}(\text{SO}_3\text{Cl})_4]$ and $\text{H}[\text{Ta}(\text{SO}_3\text{Cl})_4]$ which behave as non-electrolytes in it. Potassium molybdate and molybdenum pentoxide solvolyse in HSO_3Cl to form an orange solid of composition $\text{MoO}_2(\text{SO}_3\text{Cl})_2$. Molybdenum pentachloride solvolyse in HSO_3Cl to form $\text{H}_2[\text{Mo}(\text{SO}_3\text{Cl})_6]$ which behaves as a non-electrolyte in this medium.

SULPHUR trioxide is known^{1,2} to form adducts of the composition $\text{Nb}_2\text{O}_5 \cdot 4\text{SO}_3$ and $\text{Ta}_2\text{O}_5 \cdot 5\text{SO}_3$ which have been described as oxygenated derivatives of polysulphuric acids, $(\text{NbO}_2)_2\text{S}_4\text{O}_{13}$ and $(\text{TaO}_2)_2 \cdot \text{S}_5\text{O}_{16}$. Goroshenko and coworkers^{3,4} isolated the compounds $\text{Nb}_2\text{O}_4(\text{SO}_4)$, $\text{Nb}_2\text{O}_3(\text{SO}_4)_2$ and $\text{Nb}_2\text{O}_2(\text{SO}_4)_3$ which lost sulphur trioxide on heating. Crystal structures of these compounds are lacking, but in view of the readiness with which niobium(V) and tantalum(V) form metal-oxygen bonds, they may be regarded as sulphate complexes rather than sulphates of oxygenated

cations. It is therefore, of some interest to investigate the behaviour of niobium(V), tantalum (V) and molybdenum(V) and molybdenum(VI) compounds in chlorosulphuric acid.

Conductance measurements were made according to the method reported earlier⁵. Chlorosulphuric acid (BDH, technical grade) was used as reported earlier⁶.

Pentoxides of niobium, tantalum and molybdenum (BDH) were commercially available samples and were used as such. Commercially available samples of niobium, tantalum and molybdenum pentahalides were further purified by sublimation in an atmosphere of dry chlorine gas. Commercially available samples of niobium and tantalum pentabromides (Fluka) were used as such without further purification. Niobium and tantalum oxychlorides (BDH) were used as such. Commercial samples of ammonium metaniobate and tantalate and potassium molybdate were used without further purification.

Interpolated values of specific conductance of various compounds at different concentrations in HSO_3Cl are shown in Fig. 1. The conductometric factor γ (the number of SO_3Cl^- ions produced per mole) of the solute for various solutes has been determined by the method already reported and the values are given in Table 1.

Niobium and tantalum(V) oxides have very little solubilities in HSO_3Cl . Even on heating upto 45°C , the solubility could only be increased upto 0.14 molality. These solutions have very low con-

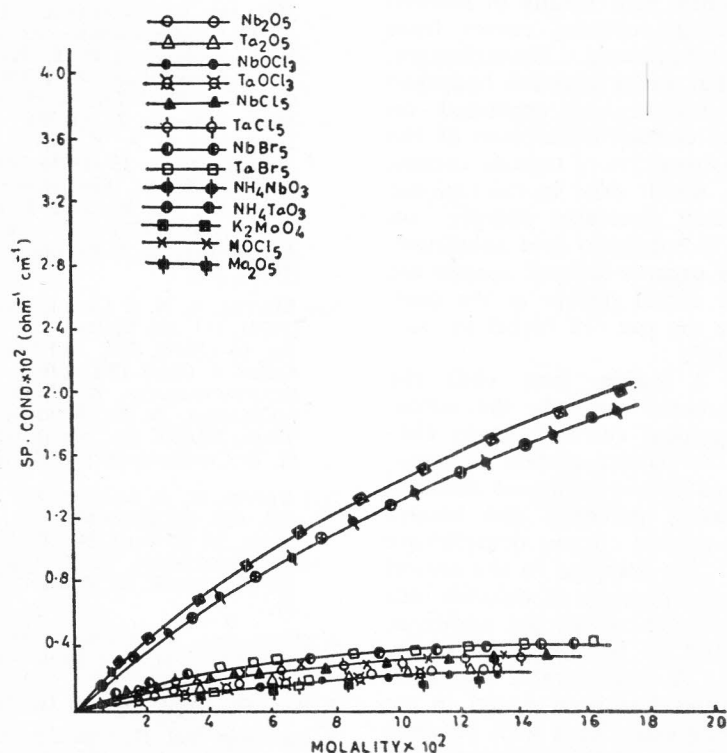


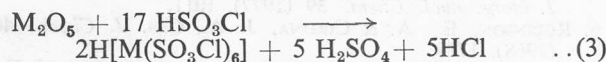
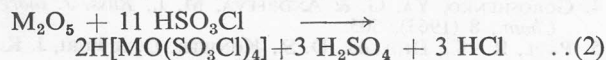
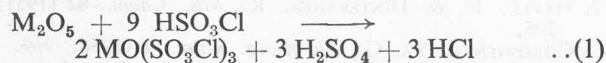
Fig. 1 — Specific conductances of some Nb(V), Ta(V) and Mo(V & VI) compounds in chlorosulphuric acid at 25°C .

†Present address : Vice-Chancellor, Panjab University, Chandigarh 160 014.

TABLE 1 — γ -VALUES OF SOME NIOBIUM(V), TANTALUM(V), MOLYBDENUM(V) AND MOLYBDENUM(VI) COMPOUNDS IN CHLOROSULPHURIC ACID

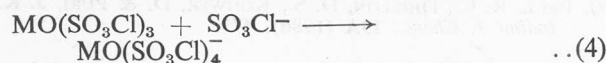
Compound	γ -Value at concentration			
	0.02M	0.05M	0.10M	0.15M
Nb ₂ O ₅	0.25	0.21	0.17	—
Ta ₂ O ₅	0.25	0.21	0.17	—
NbOCl ₃	0.20	0.17	0.15	—
TaOCl ₃	0.20	0.17	0.15	—
NbCl ₅	0.34	0.30	0.25	0.21
TaCl ₅	0.34	0.30	0.25	0.21
NbBr ₅	0.50	0.43	0.31	0.26
TaBr ₅	0.50	0.44	0.31	0.26
NH ₄ NbO ₃	1.16	1.07	1.04	1.00
NH ₄ TaO ₃	1.15	1.07	1.04	1.00
K ₂ MoO ₄	1.33	1.20	1.16	1.09
MoCl ₅	0.34	0.31	0.26	0.22
Mo ₂ O ₅	0.16	0.15	0.13	—

ductances which further indicates that both these solutes behave as non-electrolytes in HSO₃Cl. However, from the conductance data (Fig. 1), the possible modes of reaction may be suggested as given in Eqs (1-3).



(where M = Nb, Ta)

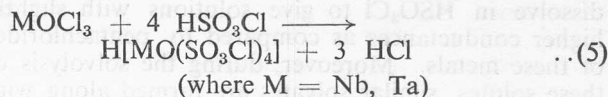
If reaction (1) is valid, there should be a decrease in conductance on the addition of KSO₃Cl to the above solutions according to the reaction (4),



But no decrease in conductance is observed at any stage. Therefore, reaction (1) can easily be ruled out. It is very difficult to differentiate between the reactions (2) and (3). However, UV spectra of these solutes in chloro-sulphuric acid show a band at 350nm which is located at a slightly higher wavelength as compared to that observed for vanadium in HSO₃Cl (ref. 7) where species of the type H [VO(SO₃Cl)₄] is postulated to exist. Therefore, it is reasonable to assume that both niobium and tantalum behave similarly as vanadium and the solvolytic reaction should be represented by Eq. (2) rather than Eq. (3). Moreover, the formation of the species H[NbO(SO₃Cl)₄] and H[TaO(SO₃Cl)₄] in chlorosulphuric acid is quite reasonable since species H[NbO(HSO₄)₄] and H[TaO(HSO₄)₄] are observed in other strong acids⁸. A slightly higher conductance of these solutions may be due to the weak basic⁶ behaviour of H₂SO₄ and HCl in this solvent.

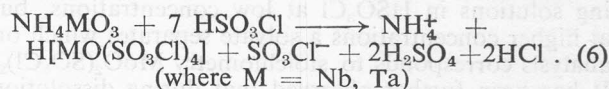
Oxychlorides of niobium and tantalum form orange-coloured solids in HSO₃Cl. The solids dissolve with some difficulty to give solutions with low conductances (Fig. 1). There is no indication of the formation of cations of the type NbO₂⁺ and

TaO₂⁺ in solutions. However, the conductance data indicate the following possible mode of solvolytic reaction :



In order to confirm the non-electrolytic behaviour of H[NbO(SO₃Cl)₄] and H[TaO(SO₃Cl)₄] in HSO₃Cl, some acid-base titrations have been carried out in it. On the addition of KSO₃Cl (a strong base of the system⁶) to the solutions of niobium and tantalum oxychlorides in HSO₃Cl, there is always an increase in conductance and the conductance-composition curve is almost similar to that of KSO₃Cl in this solvent.

Both ammonium metaniobate and tantalate give yellow coloured highly conducting and stable solutions in chlorosulphuric acid. UV and visible spectra of these solutions are similar to those of Nb₂O₅, NbOCl₃, Ta₂O₅ and TaOCl₃ solutions in HSO₃Cl, suggesting that similar type of species are present in the solution. However, the conductance data indicate the following mode of solvolytic reaction :

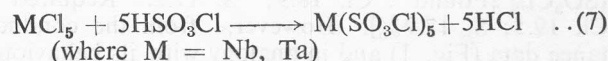


To further investigate the solvolysis of ammonium metaniobate and tantalate in HSO₃Cl, the solutions of these solutes in HSO₃Cl have been titrated against SbCl₅ (a strong acid of this system⁹). On the addition of SbCl₅ there is always a decrease in conductance which passes through a minimum and then increases again. The decrease in conductance may be due to the reaction,

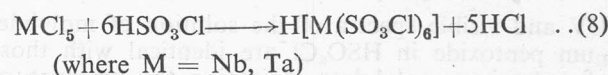


The break in the conductance curves at the 1:1 molar ratio of acid/base shows that the species H[MO(SO₃Cl)₄] formed during solvolysis does not take part in the titrations. Only one SO₃Cl⁻ ion produced takes part in the titrations and thus supports the above mode of reaction (Eq. 6).

Pentachlorides of niobium and tantalum dissolve in chlorosulphuric acid with difficulty even on warming to give low-conducting and stable solutions. But at higher concentrations, a solvate separated out which was analysed and found to correspond to the composition M(SO₃Cl)₅. In analogy with the behaviour of these compounds in other strongly acidic media⁸, the following possible mode of solvolytic reaction may be proposed :

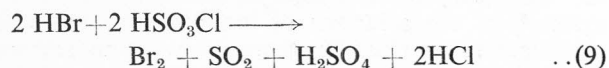


It may be further assumed that these solvolyzed products, once formed, react further with the solvent to form the species of the types H [M(SO₃Cl)₆]. Thus, the overall reaction may be proposed as :

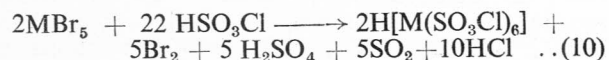


The species $H[M(SO_3Cl)_6]$ behaves as a non-electrolyte in this solvent, where HCl is a very weak base.

Similarly, pentabromides of niobium and tantalum dissolve in HSO_3Cl to give solutions with slightly higher conductances as compared to pentachlorides of these metals. Moreover, during the solvolysis of these solutes, similar solvates are formed along with free Br_2 and SO_2 . Hydrobromic acid produced during the reactions is oxidized by SO_3 (obtained by the self-dissociation of the solvent) to liberate free bromine (Eq. 9) :

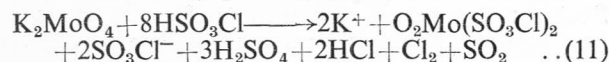


Bromine and SO_2 , so produced, behave as non-electrolytes¹⁰ in this solvent while H_2SO_4 and HCl behave as weak bases⁶. However, the conductance data show the overall possible mode of solvolytic reaction as :



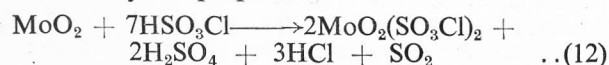
(where M = Nb, Ta)

Potassium molybdate forms clear highly conducting solutions in HSO_3Cl at low concentrations, but at higher concentrations a solvate separates which on analysis corresponds to stoichiometry $MoO_2(SO_3Cl)_2$. It has been further observed that during dissolution of the solute in HSO_3Cl , sufficient amount of chlorine gas is evolved which shows that some oxidation reaction is taking place (Eq. 11) :



UV and visible spectra of the above solution are similar to those⁷ of CrO_2Cl_2 solution in HSO_3Cl and hence the species $O_2Mo(SO_3Cl)_2$ analogous to the species $O_2Cr(SO_3Cl)_2$, is present in the solution. Both these species are known to behave as non-electrolytes in HSO_3Cl . But H_2SO_4 and HCl present in the above reaction contribute very little towards the conductance values making the γ value for reaction (11) slightly more than one. Chlorine and SO_2 produced during the reaction behave as non-electrolytes in this solvent.

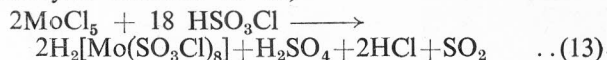
Molybdenum pentoxide forms yellowish-red solution in HSO_3Cl accompanied by the evolution of SO_2 gas which show that oxidation to molybdenum (VI) has taken place. But at higher concentrations, an orange solid separates out. It was isolated, washed with anhydrous methylene chloride and finally dried *in vacuo*. Elemental analysis of the compound corresponds to the composition $MoO_2(SO_3Cl)_2$ [Found : Cl, 18.9; S, 17.2. Required : Cl, 19.5; S, 17.9%]. However, from the conductance data (Fig. 1) and in analogy with its behaviour in other strong acids⁸, the possible mode of solvolytic reaction may be proposed as :



UV and visible spectra of the solution of molybdenum pentoxide in HSO_3Cl are identical with those of potassium molybdate indicating the presence of

species of the type $MoO_2(SO_3Cl)_2$ in solution supporting the above mode of reaction.

Molybdenum pentachloride when dissolved in HSO_3Cl , initially gives yellow solution which finally changes to reddish-yellow without any significant change in conductance. This indicates that molybdenum(VI) is present in solution. It is further observed that during the dissolution of the solute, SO_2 gas is evolved. Conductance data indicate the solvolytic reaction to be,



Formation of $H_2[Mo(SO_3Cl)_8]$ is quite reasonable as the formation of analogous species $H_2[Mo(HSO_4)_8]$ in other strong acids has been already reported⁸. Addition of KSO_3Cl to the above solution does not cause any decrease in conductance of the solution which further indicates that $H_2[Mo(SO_3Cl)_8]$ behaves as a non-electrolyte in this solvent. Both H_2SO_4 and HCl in the above reaction behave as weak bases⁶ in this solvent.

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Studies on Thallium Oxalates : Part VII—Thermal Decomposition of Strontium Bis(oxalato)diaquothallate-(III) Monohydrate

S. R. SAGI, KARRI V. RAMANA* & M. S. PRASADA RAO
Department of Chemistry, Andhra University, Waltair 530 003

Received 5 November 1980; revised 2 February 1981; accepted 23 June 1981

A crystalline precipitate with an empirical formula $SrTi_2(C_2O_4)_4 \cdot 5H_2O$ is obtained by adding 0.1M oxalic acid solution to a 0.01 M thallium(III) salt solution in the presence of 0.025 M $Sr(NO_3)_2$ and 0.125 M HNO_3 . Thermal analysis of the compound indicates the formation of $SrTi_2(C_2O_4)_2$ (stable from 150°-290°C) which finally decomposes to a mixture of strontium carbonate and oxides of thallium(I) and thallium(III). The thermal data along with infrared, microscopic and X-ray diffraction data suggest the structural formula of the complex as $Sr[Tl(C_2O_4)_2(H_2O)_2]_2 \cdot H_2O$.

SUITABLE conditions for the formation of bis(oxalato)diaquothallate(III) complex in which the metal-ligand ratio is 1:1.5 have been reported¹.