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# Solvolysis of Various Vanadium(V) and Chromium(VI) Compounds in Chlorosulphuric Acid. Part XIII

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*Vanadium(V) oxide, vanadium oxotrichloride and ammonium metavanadate solvolyse to the non-electrolyte H[VO(SO$_3$Cl)$_4$] in chlorosulphuric acid, whereas chromium dioxo-dichloride and potassium mono, and dichromates and chromium trioxide solvolyse to CrO$_2$(SO$_3$Cl)$_2$. Polymerization of these species is indicated at higher concentrations. The solvolysed product CrO$_2$(SO$_3$Cl)$_2$ has been isolated and characterized.*

## Introduction

Various solvolysis in $HSO_3Cl$ have been reported [1–7] but not for vanadium or chromium compounds. The species $VO(HS_2O_7)$ is reported in 65% oleum; $(VO)_2(SO_4)_3$ [8, 9] as well as $VO(OH)(HSO_4)_2$, $VO(HSO_4)_3$ and $V(OH)_2(HSO_4)_3$ [10] and $H[VO(HSO_4)_4]$ in 100% $H_2SO_4$ [11] and also in $H_2S_2O_7$ [12]. Here we report on solvolysis in the stronger acid $HSO_3Cl$ [13].

## Experimental

Measurements of conductivities were carried out as described previously [14]. A.R. grade $V_2O_5$, $NH_4VO_3$, $K_2Cr_2O_7$ and $CrO_3$ were used. $VOCl_3$, $CrO_2Cl_2$ and $SbCl_5$ fractionated under reduced pressure.

Chlorosulphuric acid (BDH technical grade) was used as reported in literature [15].

The conductance values (γ) for various solutes have been obtained by comparing the observed data with the calibration curves as described earlier (*loc. cit.*) and are reported in Table I. Ultra violet spectroscopic measurements were recorded on a Beckmann Model Du spectrophotometer over the range 240–720 nm. Magnetic susceptibility measurements were carried out at room temperature by the standard Guoy method using a permanent magnet and a sample tube calibrated with a standard nickel dichloride solution. The usual corrections for the susceptibility of the sample were applied. Wherever possible transference were carried out in a dry box. Infrared spectra were recorded in nujol mulls prepared in an inert atmosphere using silver chloride cells on a Perkin-Elmer 337 Spectrophotometer in the range 1500–400 cm$^{-1}$.

TABLE I. Summary of the γ-Values at Different Concentrations of some Vanadium(V) and Chromium(VI) Compounds in Chlorosulphuric Acid.

| Compound | 0.02 *M* | 0.05 *M* | 0.10 *M* | 0.15 *M* |
|---|---|---|---|---|
| $V_2O_5$ | 0.12 | 0.12 | | |
| $VOCl_3$ | 0.11 | 0.07 | 0.05 | 0.05 |
| $NH_4VO_3$ | 1.16 | 1.00 | 0.98 | 0.97 |
| $K_2Cr_2O_7$ | 1.33 | 1.07 | 1.07 | 1.00 |
| $K_2CrO_4$ | 1.30 | 1.15 | 1.10 | 1.00 |
| $CrO_2Cl_2$ | 0.12 | 0.07 | 0.05 | 0.05 |
| $CrO_3$ | 0.12 | 0.08 | 0.05 | |

## Results and Discussion

Vanadium pentoxide has very limited solubility in chlorosulphuric acid at room temperature. Even on heating to 45 °C, only 0.08 molal concentration could be obtained. The dissolution of this solute in chlorosulphuric acid is always accompanied by the evolution of HCl. There is only a slight increase in the conductance of the solution. The colour of the solution is reddish brown. From conductance data (Fig. 1), the following modes of solvolytic reactions may be proposed.

$$V_2O_5 + 9HSO_3Cl \longrightarrow 2VO(SO_3Cl)_3 + 3H_2SO_4 + 3HCl \quad (1)$$

$$V_2O_5 + 11HSO_3Cl \longrightarrow 2H[VO(SO_3Cl)_4] + 3H_2SO_4 + 3HCl \quad (2)$$

If reaction (1) is valid, there should be a decrease in conductance, when $KSO_3Cl$ is added to the solution of vanadium pentoxide in chlorosulphuric acid, according to the reaction $VO(SO_3Cl)_3 + SO_3Cl^- \longrightarrow VO(SO_3Cl)_4^-$, but no decrease in conductance is observed at any stage and therefore reaction (1) is

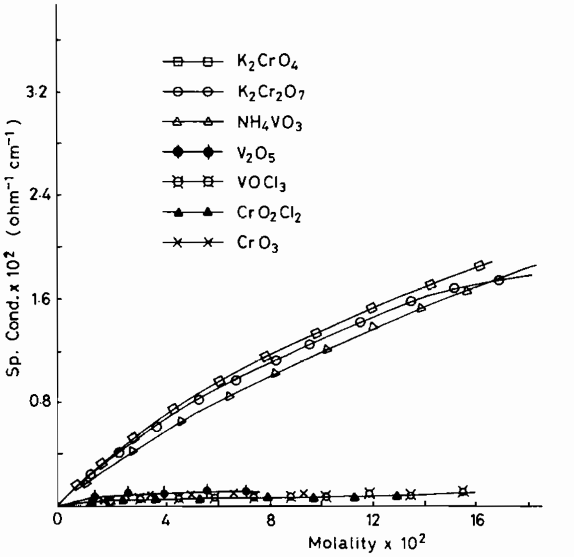

Fig. 1. Specific conductances of some vanadium and chromium compounds in chlorosulphuric acid at 25 °C.

ruled out. The possibility of reaction (2) is quite reasonable as the formation of the analogous species $H[VO(HSO_4)_4]$ has already been reported in other strong acids [11, 12]. Since there is no significant decrease in conductance on addition of $KSO_3Cl$ to the solution of Vanadium pentoxide in chlorosulphuric acid, it may further be concluded that the specie $H[VO(SO_3Cl)_4]$, either behaves as a non-electrolyte or a very weak acid, but its acidity could not be determined because of the weakly basic nature of $H_2SO_4$ [16] and HCl [15] produced during the solvolytic reaction. At low concentration, the solutions are clear, but at higher concentrations a solvate separates out which indicates a further polymerization of the species $H[VO(SO_3Cl)_4]$. The polymeric nature of similar species $H[VO(HSO_4)_4]$ has already been reported by Gillespie and coworkers [11].

Hayek and Engelbrecht [17] have reported that vanadyl chloride when heated with sulphur trioxide, forms $V_2O(SO_4)_4$. Woolf [18] has suggested an ionic structure $(VO_2)_2S_4O_{13}$ for this compound. Recently Paul and coworkers [12] have shown that vanadyl chloride when dissolved in disulphuric acid form species of the type $H[VO(HSO_4)_4]$. It is therefore of interest to investigate the behaviour of vanadium oxotrichloride in chlorosulphuric acid to check whether it forms some addition compound of the type $V_2O(SO_4)_4$ with the free sulphur trioxide obtained from the self-dissociation of the solvent as ($HSO_3Cl \longrightarrow HCl + SO_3$) or whether it gets solvolysed to form the species $H[VO(SO_3Cl)_4]$.

Vanadium oxotrichloride when dissolved in chlorosulphuric acid initially forms a yellow solvate, which, on shaking, goes into solution. The resulting solutions are of low conductivity. However, the conductance data (Fig. 1) indicate the possible mode of solvolytic reaction to be;

$$VOCl_3 + 3HSO_3Cl \longrightarrow VO(SO_3Cl)_3 + 3HCl \qquad (3)$$

$$VOCl_3 + 4HSO_3Cl \longrightarrow H[VO(SO_3Cl)_4] + 3HCl \qquad (4)$$

As discussed earlier, reaction (3) is ruled out. A slight increase in conductance of the solutions is due to the presence of HCl produced during the solvolytic reaction. Moreover, since the solutions are found to be only very slightly conducting, there is no possibility of the formation of $VO^{3+}$ or $VO_2^{2+}$ ions in solutions, which would have produced the corresponding $SO_3Cl^-$ ions. Ultraviolet and visible spectra of the solutions of $V_2O_5$ and $VOCl_3$ in chlorosulphuric acid show a broad band at 340 nm which is similar to those of $V_2O_5$, as already reported in 100 percent sulphuric [17] and disulphuric [12] acids, thereby indicating the presence of $H[VO(SO_3Cl)_4]$ in chlorosulphuric acid analogous to the species $H[VO(HSO_4)_4]$ in other strong acids.

Ammonium metavanadate readily dissolves in chlorosulphuric acid, to form reddish brown solutions, which are highly conducting. UV and visible spectra of the solution are similar to those of $V_2O_5$ and $VOCl_3$ in chlorosulphuric acid suggesting the presence of similar type of species as $H[VO(SO_3Cl)_4]$ in solution. From the $\gamma$ values obtained and the spectral studies, the possible modes of solvolytic reaction may be proposed as;

$$NH_4VO_3 + 3HSO_3Cl \longrightarrow NH_4^+ + VO_2^+ + 2SO_3Cl^- + H_2SO_4 + HCl \qquad (5)$$

$$NH_4VO_3 + 7HSO_3Cl \longrightarrow NH_4^+ + H[VO(SO_3Cl)_4] + SO_3Cl^- + 2H_2SO_4 + 2HCl \qquad (6)$$

Reaction (5) requires a $\gamma$ value of two, but our experimental $\gamma$ value is only slightly more than one. Therefore the possibility of the reaction (5) is ruled out. Hence in a manner analogous to the behaviour of ammonium metavanadate in other strong acids [11, 12], its behaviour may be represented by eqn. (6) which agrees very well with our experimental data.

To throw more light on the solvolysis of ammonium metavanadate and on the nature of $H[VO(SO_3Cl)_4]$ in chlorosulphuric acid, some acid-base titrations have been carried out using antimony pentachloride (an acid of this system [19]). On addition of antimony pentachloride to the solution containing ammonium metavanadate in chlorosulphuric acid, there is always a decrease in conductance which may be due to the reaction, $H_2^+SO_3Cl + SO_3Cl^- \longrightarrow 2HSO_3Cl$. The break in the conductance composition curve at the molar ratio acid/base of 1:1 suggests that the species $H[VO(SO_3Cl)_4]$, formed during the reaction, practically does not take part in the titration, only one $SO_3Cl^-$, which is produced as a result of solvolysis, takes part and thus supports the mode of reaction already expressed by the eqn. (6).

Hayek and Engelbrecht [17] have reported that chromyl chloride reacts with $SO_3$ to form $CrO(SO_4)_2$. Woolf [18] has suggested the formation of an ionic compound $(CrO_2)^{2+} \cdot S_2O_7^{2-}$. Even the existence of the species $H_2CrSO_7$ and $H_2Cr_4O_{13}$ have been postulated in solutions of chromates in 30–80 percent sulphuric acid [2]. Mishra and Symons [10] have studied the behaviour of potassium chromate in 100 percent sulphuric acid and have postulated the formation of $O_2Cr(OH)(HSO_4)$ and have excluded the formation of the cation $CrO_2^{2+}$. However Gillespie and coworkers [20] and recently Paul and coworkers [12] have supported the formation of $O_2Cr(HSO_4)_2$ when potassium chromate dissolves in sulphuric and disulphuric acids respectively.

Potassium chromate dissolves in chlorosulphuric acid to give light yellow conducting solutions. However from the conductance data the following possible modes of solvolytic reactions may be proposed;

$$K_2CrO_4 + 2HSO_3Cl \longrightarrow 2K^+ + H_2CrO_4 + 2SO_3Cl^- \qquad (7)$$

$$K_2CrO_4 + 3HSO_3Cl \longrightarrow 2K^+ + H_3^+CrO_4 + 3SO_3Cl^- \qquad (8)$$

$$K_2CrO_4 + 6HSO_3Cl \longrightarrow 2K^+ + CrO_2^{2+} + 4SO_3Cl^- + 2H_2SO_4 + 2HCl \qquad (9)$$

$$K_2CrO_4 + 4HSO_3Cl \longrightarrow 2K^+ + CrO_2SO_4 + 2SO_3Cl^- + H_2SO_4 + 2HCl \qquad (10)$$

$$K_2CrO_4 + 6HSO_3Cl \longrightarrow 2K^+ + CrO_2(SO_3Cl)_2 + 2SO_3Cl^- + 2H_2SO_4 + 2HCl \qquad (11)$$

Possibility of reactions (7) to (10) can easily be ruled out since our experimental $\gamma$ value is slightly more than one and fits very well in equation (11).

Further support in favour of reaction (11) has been found in the ultraviolet and visible spectra of the above solution which show absorption bands at 250, 340, 420 and 780 nm which are similar to those of potassium chromate in $H_2SO_4$ and $H_2S_2O_7$ [12] indicating the presence of $CrO_2(SO_3Cl)_2$ analogous to $CrO_2(HSO_4)_2$ in other strong acids. $H_2SO_4$ and HCl thus formed during the reactions contribute very little towards the $\gamma$ values. In support of the formation of $CrO_2(SO_3Cl)_2$ acid-base titrations with $SbCl_5$ and potassium chromate in chlorosulphuric acid have been carried out. Addition of $SbCl_5$ to the solution of potassium chromate in chlorosulphuric acid causes a decrease in the conductance of the solution, while a further addition of $SbCl_5$ again causes an increase in conductance of the solution. A minimum in the conductance composition curve at a molar ratio 1:1 (Fig. 2) suggests that only one $SO_3Cl^-$ ion is being produced as a result of solvolysis and the species $CrO_2(SO_3Cl)_2$ behaves as a non-electrolyte in chlorosulphuric acid.

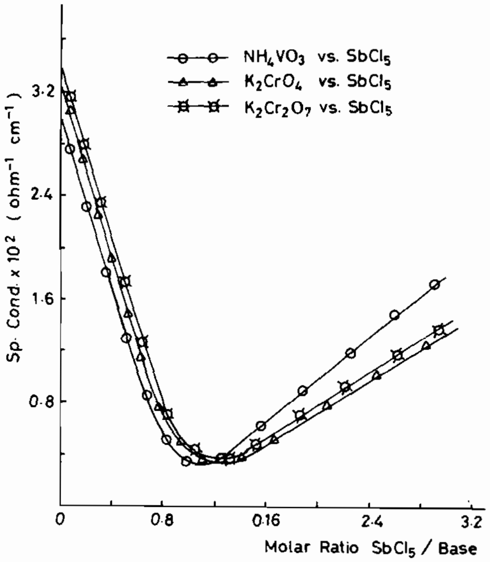

Fig. 2. Acid/base titrations of various solutes in chlorosulphuric acid at 25 °C.

Chromyl chloride when added to chlorosulphuric acid initially forms a yellowish-green solvate which on shaking dissolves and gives orange-red coloured solution of low conductivity. It has been observed that at higher concentration this solid solvate remains undissolved even on warming with hot water for few hours with continuous shaking, but the colour of the solid solvate changed to dark green. This green solid was then filtered under a nitrogen atmosphere and washed first with thionyl chloride and finally dried under vacuum. This compound fumes in moist air. Its composition is supported by elemental analysis and infra-red spectroscopy; the elemental analysis corresponding to $CrO_2(SO_3Cl)_2$ [Analysis of $CrO_2(SO_3Cl)_2$: Found: Cr = 15.9; S = 19.7; Cl = 21.9. Required: Cr = 16.5; S = 20.3; Cl = 22.5%].

This dark green compound was found to be insoluble in various aprotic solvents and therefore it was very difficult to find its molecular weight and the molar conductance. Magnetic susceptibility measurements of this green solid indicate it to be diamagnetic in nature and thus supports the formation of $CrO_2(SO_3Cl)_2$ solvate. Further support in favour of the formation of above solvate has been obtained from its infra-red absorption spectra which give peaks at 960, 320, 345, 442, 560, 580, 640, 1075 and 1170 $cm^{-1}$. The strong bands at 960 $cm^{-1}$ may be assigned to Cr=O stretching mode as well as to the $SO_3Cl^-$ group in a manner reported earlier [22–24]. The free chlorosulphate ion as in alkali metal chlorosulphates [25] has a $C_3V$ symmetry and shows six infrared active fundamental vibrations, three of which are degenerate. The degenerate modes, however undergo splitting as a result of lowering of the symmetry of chlorosulphate group in the transition metal chlorosulphates as reported earlier [5]. The other bands shown may be assigned as 320 $cm^{-1}$ (S–Cl wag), 345 ($\nu_6$E), 442 (S–Cl stretch), 560 $cm^{-1}$ ($\nu_2$(A) symmetric $SO_3$ deformation), 580 $cm^{-1}$ ($\nu_3$(A) Asym. $SO_3$ deformation), 640 $cm^{-1}$ ($\nu_5$(E)), 1075 ($\nu_1$(A) symmetric $SO_3$ stretch) and 1170 $cm^{-1}$ ($\nu_4$(E), Asym. $SO_3$ stretch) also indicate the splitting of the degenerate $\nu_5$(E) and $\nu_6$(E) modes and also the symmetric $SO_3$ stretching vibration $\nu_1$(A) is about 30 $cm^{-1}$ higher [25] than the corresponding ionic potassium chlorosulphate indicating covalent bonding in the $CrO_2(SO_3Cl)_2$ compound. Thus on the basis of above studies the mode of solvolytic reaction for the $CrO_2Cl_2$ in $HSO_3Cl$ may be proposed as;

$$CrO_2Cl_2 + 2HSO_3Cl \longrightarrow CrO_2(SO_3Cl)_2 + HCl \qquad (12)$$

The slight increase in conductance is due to the presence of HCl produced during the reaction.

Similarly chromium oxide at low concentration in chlorosulphuric acid gives orange-red coloured solution of low conductivity. At higher concentrations, again, a dark green solid is formed after shaking the solutions for a few hours. The green solid was isolated and analysed in a manner discussed earlier and corresponds to the composition $CrO_2(SO_3Cl)_2$. It was interesting to note that when the mixture of this green solid and chlorosulphuric acid are heated at 100 °C with continuous shaking the colour of the solid changed to dark brown after two hours. This dark brown solid was separated and analysed and gave the same results as the green solid reported in case of the solvolysis of $CrO_2Cl_2$ in chlorosulphuric acid. The infrared spectra of this brown solid was identical to that reported for the green solid. Therefore the mode of solvolysis of $CrO_3$ in $HSO_3Cl$ may be proposed as;

$$CrO_3 + 3HSO_3Cl \longrightarrow CrO_2(SO_3Cl)_2 + H_2SO_4 + HCl \qquad (13)$$

The slight increase in conductance is due to the weak basic behaviour of $H_2SO_4$ and HCl in this solvent [15, 16].

Potassium dichromate readily dissolves in chlorosulphuric acid to form yellow coloured solutions which are highly conducting. Ultraviolet and visible spectra of the solution of potassium dichromate in $HSO_3Cl$ are similar to those of potassium chromate and chromyl chloride in this acid and molar extinction coefficient is approximately double to that of potassium chromate confirming the presence of the species $O_2Cr(SO_3Cl)_2$ in solutions. From the conductance data and the UV and visible spectral studies, the solvolytic reaction may be proposed to be:

$$K_2Cr_2O_7 + 9HSO_3Cl \longrightarrow 2K^+ + 2[CrO_2(SO_3Cl)_2] + 2SO_3Cl^- + 3H_2SO_4 + 3HCl \qquad (14)$$

The conductometric titration curve of potassium dichromate with antimony pentachloride in chlorosulphuric acid shows a minimum at a molar ratio of 1:1 (Fig. 2) indicating that in this case also only one $SO_3Cl^-$ ion is likely to be produced as a result of solvolysis.

## References

1 R. C. Paul, D. S. Dhillon, Vijay Sharma, D. Konwer and J. K. Puri, *J. Inorg. Nucl. Chem., 41*, 825 (1979).
2 R. C. Paul, D. S. Dhillon, D. Konwer and J. K. Puri, *J. Inorg. Nucl. Chem., 43*, 1071 (1981).
3 R. C. Paul, Miss Jaswinder, Kaur, D. Konwer and J. K. Puri, *Indian J. Chem., 20*, 1212 (1981).
4 R. C. Paul, D. S. Dhillon and J. K. Puri, *J. Inorg. Nucl. Chem., 39*, 1011 (1977).
5 E. Buncel, *Chem. Rev., 70*, 336 (1970).
6 R. C. Paul, D. S. Dhillon, D. Konwer and J. K. Puri, *J. Inorg. Nucl. Chem., 44*, 55 (1979).
7 J. K. Puri, Pritpal Singh and Jack M. Miller, *Inorg. Chim. Acta*, in press (1983).
8 J. W. Mellor, 'A Comprehensive Treatise of Inorg. Chemistry and Theoretical Chemistry, Vol. IV, p. 821, Longmans Green, London (1939).
9 Ephraim, 'Inorganic Chemistry', Gurney and Jackson, London, p. 608 (1960).
10 H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 4411 (1962).
11 R. J. Gillespie, R. Kapoor and E. A. Robinson, *Can. J. Chem., 44*, 1203 (1966).
12 R. C. Paul, J. K. Puri and K. C. Malhotra, *J. Inorg. Nucl. Chem., 33*, 4191 (1971).
13 R. C. Paul, D. S. Dhillon and J. K. Puri, *Indian. J. Chem., 10*, 1058 (1975).
14 R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc. (A)*, 1994 (1967).
15 E. A. Robinson and J. A. Ciruna, *Can. J. Chem., 46*, 1719 (1968).
16 T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 2332 (1960).
17 E. Hayek and A. Engelbrecht, *M. Chem., 80*, 640 (1949).
18 A. A. Woolf, *Chem. Industry*, 4113 (1954).
19 E. A. Robinson, Paper presented at the International Conference on non-aqueous solvents, June 1967, Canada.
20 N. Bailey, A. Carrington, K. A. K. Lott and M. C. R. Symons, *J. Chem. Soc.*, 290 (1960).
21 Kapoor Ph.D. Thesis, McMaster University, Canada 1968.
22 W. E. Hobbs, *J. Chem. Phys., 28*, 1220 (1958).
23 W. V. Rochat and G. L. Gard, *Inorg. Chem., 158* (1969).
24 E. K. Mooney and K. R. Seddon, *T. Met. Chem., 2*, 215 (1977).
25 E. A. Robinson and J. A. Ciruna, *Can. J. Chem., 46*, 1716 (1968).