Chlorosulphuric Acid as a Non-aqueous Solvent: Part VI— Conductometric & Spectral Studies of Various Inorganic & Organic Acid Anhydrides in Chlorosulphuric Acid

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Conductometric and spectral studies of the solutions of acid anhydrides in chlorosulphuric acid indicate that nitric and nitrous oxides behave as non-electrolytes, whereas dinitrogen trioxide, dinitrogen tetroxide and dinitrogen pentoxide form nitrosonium and nitronium ions. Phosphorous pentoxide gives a mixture of various sulphur oxychlorides which behave as non-electrolytes. Arsenic trioxide, antimony trioxide and bismuth trioxide get solvolysed whereas boric anhydride forms tetrachlorosulphato boric acid when dissolved in chlorosulphuric acid. Organic acid anhydrides behave as bases. From the extent of protonation of these solutes, it has been inferred that chlorosulphuric acid is a stronger acid than sulphuric acid.

SYSTEMATIC physico-chemical investigations of the solutions of various anhydrides of inorganic and organic acids in fluorosulphuric acid[1] have shown that the acid gets dehydrated and hydronium (H_3^+O) ions are formed. Such an investigation is lacking in chlorosulphuric acid as a non-aqueous solvent. As chlorosulphuric acid is weaker than disulphuric and fluorosulphuric acids, investigations on the solution behaviour of the inorganic and organic acid anhydrides shall be of greater help in differentiating the basicities of these anhydrides.

Materials and Methods

The design of the conductivity cells used has been described earlier[2]. Conductance measurements were made as described previously[3]. Chlorosulphuric acid (BDH technical) was first fractionally distilled according to Robinson and Ciruna[4] at 151°/746 mm pressure and redistilled under nitrogen atmosphere before use.
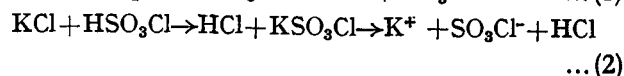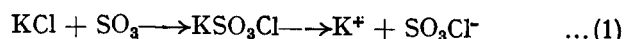
Nitrous oxide, nitric oxide, dinitrogen trioxide, dinitrogen tetroxide and dinitrogen pentoxide were prepared and purified by the well established methods[5]. Arsenic trioxide, antimony trioxide, antimony pentoxide, bismuth trioxide, phosphorous pentoxide and boric anhydride were commercially available samples and were used without further purification. Succinic anhydride was washed with dry ether and then dried over phosphorous pentoxide for 24 hr. Commercially available samples of acetic anhydride (b.p. 140°/740 mm), isobutyric anhydride (b.p. 182°/745 mm) and dichloroacetic anhydride (b.p. 101°/16 mm) were distilled in an inert atmosphere before use. Maleic anhydride was recrystallized from chloroform and dried over phosphorous pentoxide. Potassium chlorosulphate was prepared by the literature method[4] and used

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as such. Antimony pentachloride (BDH) was used without further purification.

Results and Discussion

It has already been shown that (SO_3Cl^-) ions are responsible for the conductance of these solutions and (SO_3Cl^-) is the strongest monoacid base[4]. Specific conductance versus molality curves of various solutes in chlorosulphuric acid are given in Fig. 1. The conductometric factor, γ (the number of SO_3Cl^- ions produced per mole of solute) has been obtained by comparing the observed conductance curves with those of potassium chlorosulphate (a fully ionized base). Acid-base titration curves in chlorosulphuric acid medium are given in Fig. 2.

When sulphur trioxide is added to chlorosulphuric acid the conductance of the solution decreases. This decrease in conductance may be assigned to the formation of higher chloropolysulphuric acids of the type HS_2O_6Cl, HS_3O_9Cl and probably $HS_4O_{12}Cl$ and even higher polyacids which further behave as non-electrolytes in chlorosulphuric acid. Higher polyacids of chlorosulphuric and disulphuric acids have already been reported by Gillespie and Robinson[6]. The non-electrolytic behaviour of these higher acids in chlorosulphuric acid has been confirmed by the fact that on addition of potassium or sodium chloride there is always an increase in conductance; at no stage there is any decrease. The reaction occurring could be represented by Eq. (1) or (2).

$$KCl + SO_3 \longrightarrow KSO_3Cl \longrightarrow K^+ + SO_3Cl^- \qquad ...(1)$$

$$KCl + HSO_3Cl \rightarrow HCl + KSO_3Cl \rightarrow K^+ + SO_3Cl^- + HCl \qquad ...(2)$$

The sulphur trioxide dissolved in HSO_3Cl may convert KCl to KSO_3Cl or KCl may be solvolysed by chlorosulphuric acid to KSO_3Cl. In both the cases SO_3Cl^- ions are produced which are responsible
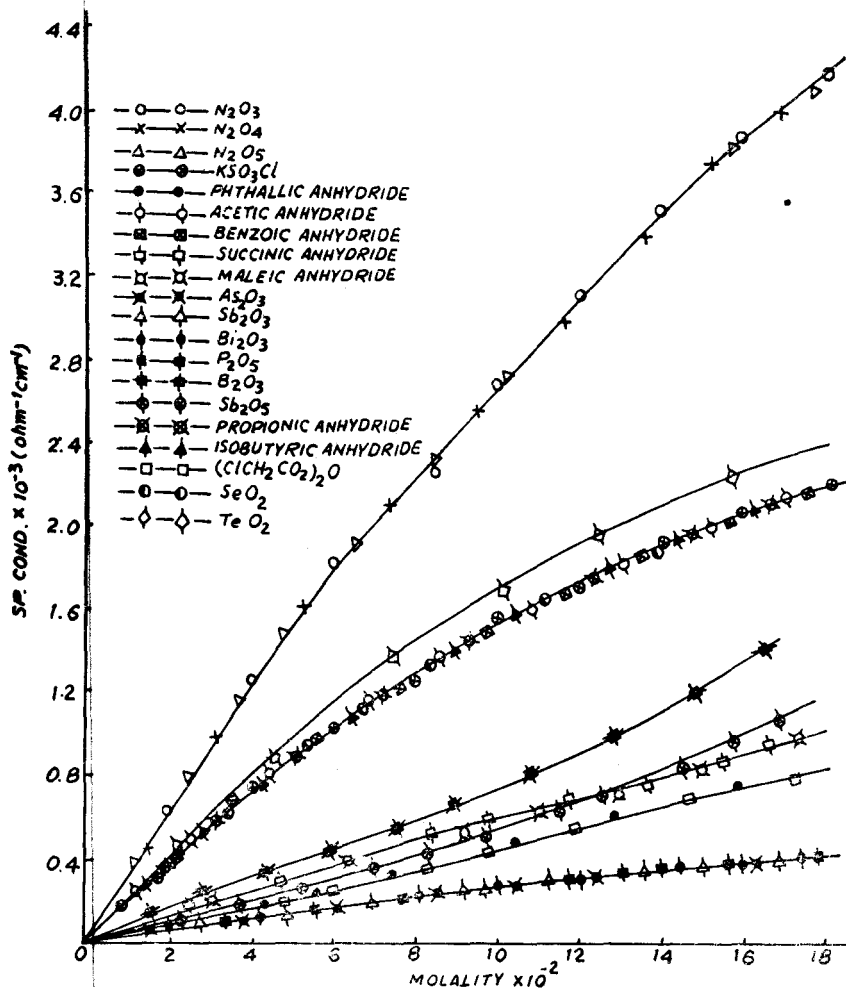
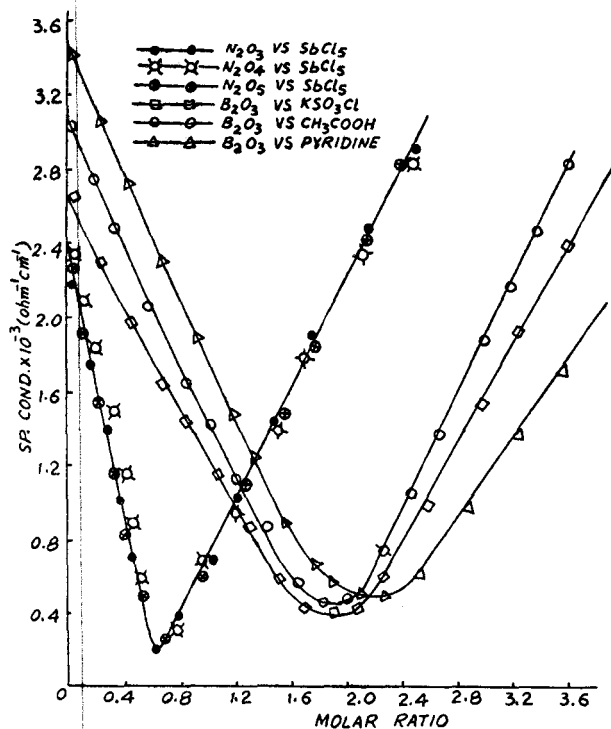Fig. 1 — Conductance of various inorganic and organic acid anhydrides in chlorosulphuric acid at 25°


Fig. 2 — Conductometric acid-base titrations of different anhydrides in chlorosulphuric acid at 25°

for an increase in the conductance (HCl produced in the latter case behaves as a very weak electrolyte[4]). Even the addition of potassium chlorosulphate directly does not bring about a fall in the conductance of the solution which confirms the observation recorded above.
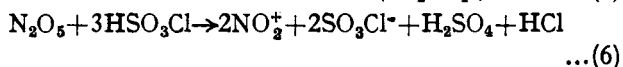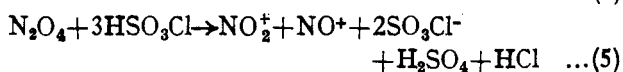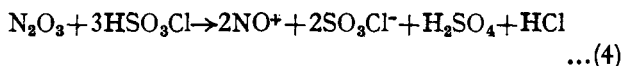
In the case of selenium trioxide, however, there is no significant change in the conductance of the solution indicating thereby that it behaves as a non-electrolyte, probably due to the formation of a compound of the type $HSeSO_6Cl$, analogous to the species $HSeSO_6F$ in fluorosulphuric[7] acid which behaves as a non-electrolyte. Both selenium and tellurium dioxides are highly soluble in chlorosulphuric acid and give highly conducting solutions. From the conductometric factor (Υ), it is seen that in the case of selenium dioxide monoprotonation takes place whereas in the case of tellurium dioxide incomplete diprotonation takes place. It seems to be quite reasonable to suggest the following mode of protonation (Eq. 3) in the case of selenium dioxide.

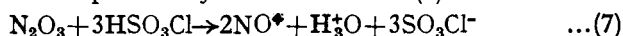$$SeO_2 + HSO_3Cl \rightarrow \overset{+}{H}O = Se = O + SO_3Cl^- \qquad ...(3)$$
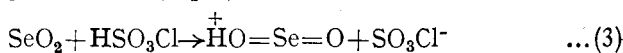
In the case of tellurium dioxide the second incomplete protonation may take place at the other oxygen atom.

Both nitrous and nitric oxides are quite soluble in chlorosulphuric acid, but behave as non-electrolytes in it.

Dinitrogen trioxide, dinitrogen tetroxide and dinitrogen pentoxide are readily soluble in chlorosulphuric acid forming highly conducting solutions. At lower concentrations these solutions are colourless but when the concentrations are increased yellow colour develops. From the conductance data and the Υ values obtained (Fig. 1), the following modes of reactions (4-6) may be represented:

$$N_2O_3+3HSO_3Cl \rightarrow 2NO^+ + 2SO_3Cl^- + H_2SO_4 + HCl$$
$$\dots(4)$$

$$N_2O_4+3HSO_3Cl \rightarrow NO_2^+ + NO^+ + 2SO_3Cl^- + H_2SO_4 + HCl \quad \dots(5)$$

$$N_2O_5+3HSO_3Cl \rightarrow 2NO_2^+ + 2SO_3Cl^- + H_2SO_4 + HCl$$
$$\dots(6)$$

The possibility of the reaction (7)

$$N_2O_3+3HSO_3Cl \rightarrow 2NO^+ + H_3^+O + 3SO_3Cl^- \quad \dots(7)$$

has been ruled out as the Υ value obtained is 2. Chlorosulphuric acid is molecularly self-dissociated according to Eq. (8)

$$HSO_3Cl \rightarrow HCl + SO_3 \quad \dots(8)$$

and the water formed during the above reaction combines with SO_3 to produce sulphuric acid rather than getting protonated as hydronium ions. When the concentration of these anhydrides is increased light yellow solids separate out. IR spectrum of the solid obtained from N_2O_5 in silver chloride plates show a strong band at 2310 cm^{-1} indicating the presence of NO_2^+ ions. The other frequencies of NO_2^+ ion and those for the anions could not be resolved as the solvent itself covers the whole region. In the case of solid obtained from N_2O_4, the bands at 2280 and 2145 cm^{-1} may be assigned to the species NO_2^+ and NO^+ respectively. Similarly in the case of the solid obtained from N_2O_3 a sharp peak at 2165 cm^{-1} indicates the presence of NO^+ ion and supports the modes of ionization as shown in Eqs. (4-7).

Further, to check the validity of the above modes of ionization some acid-base titrations between antimony pentachloride (a strong acid of the system) and the solutions of these anhydrides in chlorosulphuric acid have been carried out. Robinson[8] has reported that antimony pentachloride behaves as strong Lewis acid in chlorosulphuric acid. When antimony pentachloride is added to the solutions of these anhydrides in chlorosulphuric acid there is a decrease in conductance (Fig. 2) and this decrease in conductance is due to the reaction (9)
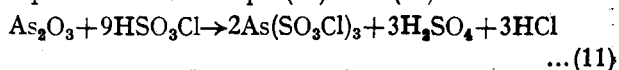
$$H_2^+SO_3Cl + SO_3Cl^- \rightleftharpoons 2HSO_3Cl \quad \dots(9)$$
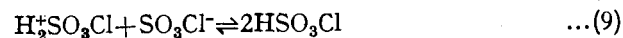
After complete removal of the (SO_3Cl^-) ions from the solution, further addition of antimony pentachloride causes an increase in the conductance which is probably due to the formation of an acid of the type $H[SbCl_2(SO_3Cl)_3SO_3Cl]$ similar to $H[SbF_2(SO_3F)_3SO_3F]$ already known in the case of fluorosulphuric acid system. From the positions of minima in the conductance composition curves it is evident that all these solutes produce two moles of SO_3Cl^- and behave in a similar manner.

Engelbrecht and Stoll[9] have reported that P_2O_5 forms phosphoryl fluoride when dissolved in fluoro-

sulphuric acid. Paul and coworkers[10-12] have reported that fluorosulphuric acid is dehydrated by phosphorous pentoxide to form disulphuryl difluoride and trisulphuryl fluoride whereas disulphuric acid is dehydrated to form free sulphur trioxide which further gives trisulphuric acid. Phosphorous pentoxide gives solutions of low conductance in chlorosulphuric acid, accompanied probably with the formation of sulphur oxychlorides which are known to behave as non-electrolytes[4]. The possible mode of solvolytic reaction can be represented as shown in Eq. (10).

$$P_2O_5+9HSO_3Cl \rightarrow 2H_3PO_4+4S_2O_5Cl_2+H_2SO_4+HCl$$
$$\dots(10)$$
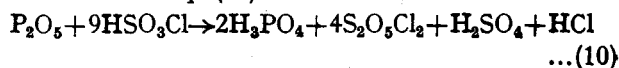
Arsenic pentoxide is extensively soluble in chlorosulphuric acid on warming to give conducting solutions. It may be assumed that when this solute is added to chlorosulphuric acid solvolysis takes place and the solvolysed product is slightly ionized to produce a significant change in conductance. Arsenic trioxide has a very limited solubility in chlorosulphuric acid yielding solutions of low conductance (Fig. 1). The possible modes of reactions occurring in these solutions may be represented as in Eqs. (11) and (12).

$$As_2O_3+9HSO_3Cl \rightarrow 2As(SO_3Cl)_3+3H_2SO_4+3HCl$$
$$\dots(11)$$

or

$$As_2O_3+3HSO_3Cl \rightarrow 2AsOSO_3Cl+H_2SO_4+HCl \quad \dots(12)$$

One can expect the possibility of the formation of the species $As(SO_3Cl)_3$, analogous to $As(SO_3F)_3$ in fluorosulphuric acid. If $As(SO_3Cl)_3$ is formed it may further show amphoteric behaviour in chlorosulphuric acid according to the reaction (13)
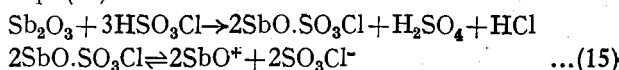
$$As(SO_3Cl)_3 \rightarrow As(SO_3Cl)_2^+ + SO_3Cl^- \quad \dots(13)$$
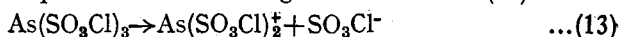
and should give higher value of Υ. $As(SO_3Cl)_3$ may further react with another SO_3Cl^- ion from chlorosulphuric acid to form the species of the type $As(SO_3Cl)_4^-$ (Eq. 14)

$$As(SO_3Cl)_3+SO_3Cl^- \rightleftharpoons As(SO_3Cl)_4^- \quad \dots(14)$$
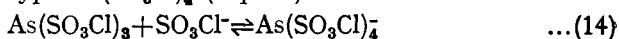
which will further lower the Υ value to a greater extent. But as there was no change of conductance during these investigations, the possibility of the Eq. (11) representing the mode of reaction must be ruled out. The low conductance values of the solutions are either due to the weak electrolytic behaviour of sulphuric and hydrochloric acids or due to the slight ionization of $AsOSO_3Cl$ which further supports the mode of reaction represented by Eq. (12).

Bismuth trioxide and antimony trioxide dissolve in chlorosulphuric acid to give milky, stable solutions. The possible mode of reactions is shown in Eq. (15).

$$Sb_2O_3+3HSO_3Cl \rightarrow 2SbO.SO_3Cl+H_2SO_4+HCl$$
$$2SbO.SO_3Cl \rightleftharpoons 2SbO^+ + 2SO_3Cl^- \quad \dots(15)$$

Eq. (15) requires a value of two for the conductivity factor (Υ) but the low conductance and milky appearance show that $SbO.SO_3Cl$ species formed are insoluble in chlorosulphuric acid possibly because of extensive polymerization. Similar observations have already been made in the case

of fluorosulphuric and disulphuric acids. The possibility of the reaction (16)

$$Sb_2O_3 + 3HSO_3Cl \rightarrow 2SbO^+ + H_3^+O + 3SO_3Cl^- \quad \ldots(16)$$
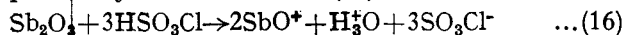
may be ruled out as it requires higher value of Υ.

In the case of the solutions of bismuth trioxide in chlorosulphuric acid also similar types of arguments can be put forward.
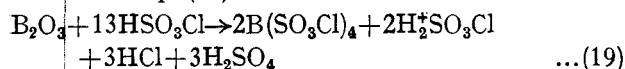
Boric anhydride (B_2O_3) is readily soluble in sulphuric and disulphuric acids to give the species of the type $B(HSO_4)_4^-$ ions. But it dissolves very slowly in chlorosulphuric acid. However, the solubility can be increased just by warming. The solutions are found to be quite stable and conducting. It is possible that it might get solvolysed when dissolved in chlorosulphuric acid to form $B(SO_3Cl)_3$ (Eq. 17)

$$B_2O_3 + 9HSO_3Cl \rightarrow 2B(SO_3Cl)_3 + 3H_2SO_4 + 3HCl \ldots(17)$$
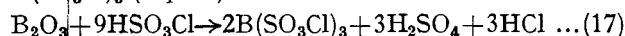
But when a strong base KSO_3Cl or benzoic acid is added to the solution there is always a decrease in conductance which suggests that boron trichlorosulphate behaves as an acid of this solvent system and combines with SO_3Cl^- ions to form $HB(SO_3Cl)_4^-$ according to the Eq. (18)

$$B(SO_3Cl)_3 + SO_3Cl^- \rightarrow B(SO_3Cl^-)_4 \quad \ldots(18)$$
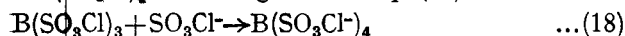
So the overall reaction may be represented as shown in Eq. (19)

$$B_2O_3 + 13HSO_3Cl \rightarrow 2B(SO_3Cl)_4 + 2H_2^+SO_3Cl$$
$$+ 3HCl + 3H_2SO_4 \quad \ldots(19)$$

At higher concentration $B(SO_3Cl)_4$ ion has a tendency to polymerize. A similar type of polymerization with B—O—B bond has already been reported by Gillespie and coworkers[13,14] from the Raman spectroscopy of concentrated solutions of B_2O_3 in sulphuric acid.

In order to confirm further the nature of B_2O_3 in chlorosulphuric acid, some acid-base conductometric titrations have also been carried out between the solutions of B_2O_3 in chlorosulphuric acid and the strong base KSO_3Cl or benzoic acid (Fig. 2). From the shape of the conductance curves which have sharp end points, it has been inferred that the acid $HB(SO_3Cl)_4$ thus formed behaves as a strong acid in this solvent.

The behaviour of various organic acid anhydrides has already been reported in other strong acids where they are shown to behave as weak bases. Acetic anhydride undergoes self-dissociation as $Ac_2O \rightleftharpoons Ac^+ + OAc^-$.

Although it contains three basic oxygen atoms, yet it is monoprotonated in sulphuric and fluorosulphuric acids whereas it forms acyl ions in disulphuric acid. But the solution of acetic anhydride in chlorosulphuric acid are highly conducting and quite stable. When its conductance is compared with that of KSO_3Cl, it is found that it behaves as a strong monoacid base in chlorosulphuric acid. Similarly benzoic anhydride, isobutyric

Compound	$K_b \times 10^2$			
	HSO_3Cl	H_2SO_4	$H_2S_2O_7$	HSO_3F
Phthalic anhydride	19·87	15·86	Fully ionized	24·56
Monochloroacetic anhydride	23·65	20·56	do	32·88
Maleic anhydride	43·96	38·96	79·86	54·92
Succinic anhydride	44·45	36·72	88·08	54·92

anhydride and propionic anhydride form clear and highly conducting solutions when dissolved in chlorosulphuric acid. From the Υ values obtained in the case of all these solutes it has been observed that all of them behave as strong monoacid bases in it. But the solutions of succinic anhydride, maleic anhydride, phthalic anhydride and monochloroacetic anhydride in chlorosulphuric acid have lower conductance values which indicate that all these anhydrides behave as weak bases in this solvent.

The dissociation constants of these acid anhydrides have also been determined in chlorosulphuric acid and when these values are compared with those obtained in the case of sulphuric, fluorosulphuric and disulphuric acids (Table 1), it has been inferred that chlorosulphuric acid is a weaker proton donor as compared to fluorosulphuric and disulphuric acids, but stronger than sulphuric acid.

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