

Chlorosulphuric Acid as a Non-aqueous Solvent: Part V—Acids & Bases of Chlorosulphuric Acid Solvent System

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Conductometric studies of various solutes in chlorosulphuric acid reveal that tetrahydrogensulphato boric acid [HB(HSO₄)₄] and tetrahydrogensulphato arsenic acid [HAs(HSO₄)₄] behave as acids, whereas solutes like H₂SeO₄, CH₃SO₃H and HPO₂F₂ behave as bases and CF₃COOH, CCl₃COOH and HSO₃F behave as non-electrolytes in this solvent system. Further, various nitrogen bases are found to behave as strong bases in chlorosulphuric acid.

FROM the extent of protonation of very weak bases in chlorosulphuric acid Robinson and Ciruna¹ concluded that chlorosulphuric acid is a stronger acid than sulphuric acid. Gillespie and coworkers² have shown that chlorosulphuric acid behaves as a very weak acid in 100% sulphuric acid. Waddington and Klanberg³ have reported that chlorosulphuric acid behaves as an acid in liquid hydrogen chloride.

The behaviour of various inorganic acids and bases in sulphuric², disulphuric⁴ and fluorosulphuric⁵ acids has been reported. However, similar studies in chlorosulphuric acid are lacking. Since chlorosulphuric acid is a stronger acid than sulphuric acid it was of interest to study the behaviour of various inorganic acids and bases in it to throw some light on their acidic or basic nature.

Materials and Methods

The design of the conductivity cells used and the method of conductance measurements have been described earlier⁶. Chlorosulphuric acid (BDH, technical grade) was purified by the method as reported previously⁷.

Pure samples of various acids were prepared by the literature methods^{2,8}. Tetrahydrogensulphato boric [HB(HSO₄)₄] and arsenic [HAs(HSO₄)₄] acids were prepared by dissolving the respective metal oxides in oleum⁹ (the compositions of which were known from their conductivity¹⁰ values).

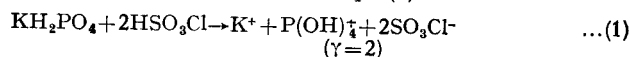
Various bases such as dimethylhydrazine, hydrazine, phenylhydrazine, hydrazine sulphate, dimethylaniline, *p*-nitroaniline, *o*-chloroaniline, *p*-chloroaniline, 2-chloro-4-nitroaniline, *p*-anisidine and piperidine were commercially available samples and were further purified by the well known methods^{11,12}.

Results and Discussion

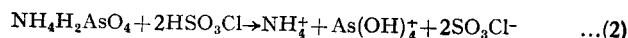
The interpolated values of specific conductance at different concentrations of various solutes in chlorosulphuric acid are given in Fig. 1. The conductometric factor, γ (the number of SO₃Cl⁻ ions produced per mole of the solute) for various solutes has been determined by comparing their conductance curves with that of potassium chloro-

sulphate (a strong base of chlorosulphuric acid solvent system) at similar concentrations.

It has already been reported by Arlman¹³ that phosphoric acid forms an ionic compound of composition P(OH)₄⁺ClO₄⁻ with perchloric acid. The presence of the cation P(OH)₄⁺ in sulphuric¹⁴, fluorosulphuric⁵ and disulphuric⁴ acids has also been reported. In an analogy potassium hydrogen phosphate, when dissolved in chlorosulphuric acid, forms a similar type of compound. From the conductance data it has been observed that diprotonation takes place in the case of this solute (Fig. 1). The possible mode of reaction may be represented as shown in Eq. (1)

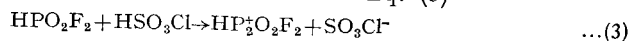


The presence of As(OH)₄⁺ ion has also been shown in fluorosulphuric⁵ and disulphuric⁴ acids. When ammonium salt of arsenic acid is dissolved in chlorosulphuric acid, highly conducting solutions are formed. The conductance data are suggestive of reaction (2) in this case



In order to determine the acidic or basic nature of these solutes, potassium chlorosulphate was added to their solutions in chlorosulphuric acid. In both the cases a continuous increase in conductance was observed indicating that phosphoric acid and KH₂PO₄ behave as bases in chlorosulphuric acid. From the γ values obtained, it is evident that they behave as strong bases.

Unlike phosphoric acid, difluorophosphoric acid gives solutions of very low conductance in chlorosulphuric acid indicating it to be a weak acid or a weak base. A continuous increase in conductance in the presence of KSO₃Cl in this case also suggests weakly basic nature of difluorophosphoric acid in chlorosulphuric acid. This observation is quite reasonable since in the formation of difluorophosphoric acid the basicity of P=O group is considerably reduced. The partial ionization of difluorophosphoric acid in chlorosulphuric acid may be represented as shown in Eq. (3)



It is known that both selenic and methanesulphonic acids behave as non-electrolytes in

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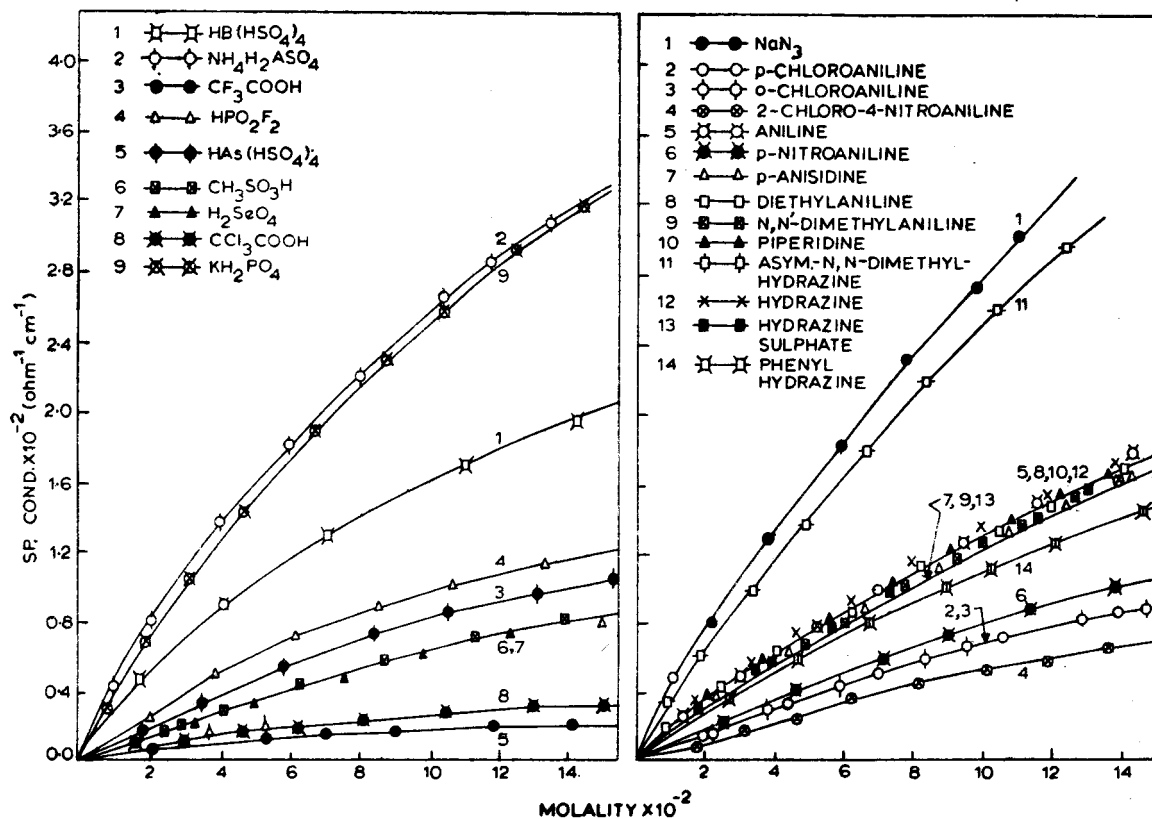


Fig. 1 — Specific conductance of various solutes in chlorosulphuric acid at 25°

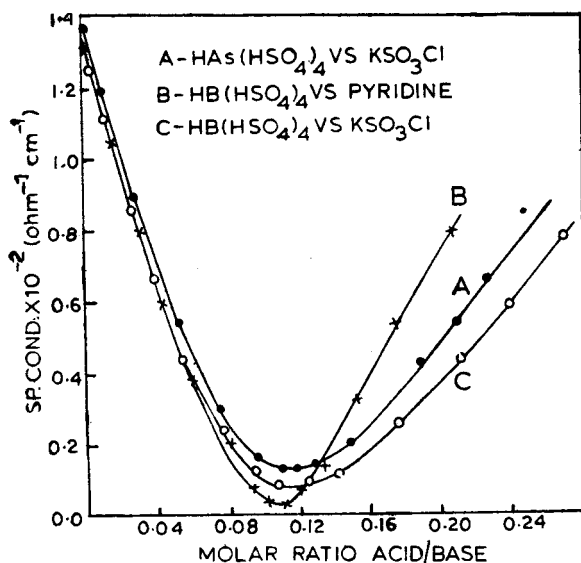


Fig. 2 — Acid/base titration of some acids in chlorosulphuric acid at 25°

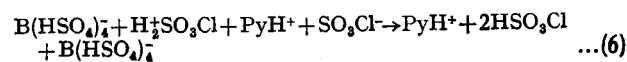
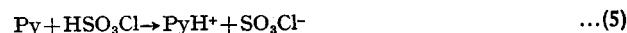
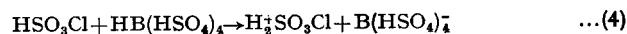
sulphuric² acid whereas they behave as weak bases in fluorosulphuric⁵ and disulphuric⁴ acids. Both selenic and methanesulphonic acids give fairly conducting solutions when dissolved in chlorosulphuric acid. However, from the conductance data it has been observed that they behave as weak bases in this solvent system. The solutions of fluorosulphuric acid in chlorosulphuric acid are non-conducting

and hence it acts as a non-electrolyte in this solvent. Solutions of trifluoroacetic and trichloroacetic acids in chlorosulphuric acid show slight enhancement in conductance and hence these may also be considered to behave as non-electrolytes. The slight increase in conductance may be due to the fact that these solutes just sufficiently ionize to compensate for the decrease in conductance caused by their unionized portions.

Tetrahydrogensulphato boric acid gives highly conducting solutions when dissolved in chlorosulphuric acid. When a fully ionized base such as pyridine or KSO_3Cl is added to the solution the conductance value decreases and then increases again. From the position of the minimum (Fig. 2) which has the conductance value almost equal to that of the pure solvent, following conclusions may be drawn:

(i) $\text{HB}(\text{HSO}_4)_4$ is a highly ionized acid in chlorosulphuric acid.

(ii) Since the neutralization reaction involves the substitution of $\text{H}_2^+\text{SO}_3\text{Cl}$ ion by PyH^+ ion, the sharp fall in conductance of the solution, on addition of pyridine indicates that $\text{H}_2^+\text{SO}_3\text{Cl}$ ion has very high mobility as compared to PyH^+ ion. The neutralization reaction may be represented as shown in Eqs. 4-6:



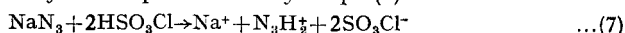
(iii) At the end of the neutralization reaction the solution is left with the species PyH^+ and $\text{B}(\text{HSO}_4)_4^-$. Should the cations other than $\text{H}_2\text{SO}_3\text{Cl}$ contribute significantly towards conductance, the position of the minimum in the conductance curve would have indicated much higher conductance than that of the pure solvent.

Similarly tetrahydrogensulphato arsenic acid behaves as an acid in chlorosulphuric acid. But from a comparison of its conductance-composition curve (Fig. 1) with that of tetrahydrogensulphato boric acid, it is evident that it is a much weaker acid than tetrahydrogensulphato boric acid. This finds further confirmation from the work of Barr and coworkers² in sulphuric acid solvent system.

The behaviour of various nitrogen bases has already been reported in different protonic acids^{4,5}. Chlorosulphuric acid being a stronger acid than sulphuric acid, a study on the behaviour of these bases in it may be of some help to throw some light on the relative strengths of these protonic acids. Earlier workers¹⁵ have reported that α -picoline and pyridine behave as strong bases in chlorosulphuric acid. It has also been shown that both the nitrogen atoms of *p*-phenyldiamine get protonated when dissolved in this acid. Solutions of hydrazine in chlorosulphuric acid are highly conducting. From the conductance data it has been observed that it behaves as a strong base in this acid. But from the conductance data alone it is unreasonable to suggest which one of the two nitrogen atoms gets protonated. Unlike hydrazine, dimethylhydrazine gives solutions which are highly conducting. The higher value of conductance as compared to that of hydrazine may be due to the substitution of methyl groups in the hydrazine molecule which further increases the basicity of the nitrogen atoms. However, from the γ value obtained, it has been observed that in dimethylhydrazine both the nitrogen atoms are protonated. Solutions of hydrazine sulphate in chlorosulphuric acid are found to be highly conducting and stable. Conductance data show that it behaves as a mono-protonated base in this solvent. Phenylhydrazine dissolves in chlorosulphuric acid to give conducting solutions. It has further been observed that some sulphonation takes place in the case of this solute. However, from the γ value obtained, it has been concluded that phenylhydrazine also behaves as

a mono-protonated base in chlorosulphuric acid. The γ value was found to be slightly lower than one. This is possibly due to the presence of sulphonation products which are non-electrolytes in this solvent.

When sodium azide is dissolved in chlorosulphuric acid, highly conducting and stable solutions are obtained. From the conductance data it has been concluded that it behaves as a doubly protonated base in this solvent. The possible mode of reaction may be represented by Eq. (7):



From the conductance measurements of the solutions of aniline, dimethylaniline, diethylaniline, piperidine and *p*-anisidine in chlorosulphuric acid, it is observed that all these solutes behave as strong bases in it. *p*-Chloroaniline, *o*-chloroaniline, *p*-nitroaniline and 2-chloro-4-nitroaniline give solutions having low conductances when dissolved in chlorosulphuric acid. From the conductance data it has been concluded that they behave as weak bases in this solvent system.

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