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Formation of Some Monopositive and Dipositive Carbonium Ions in Chlorosulphuric Acid. Part XV

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Tetraphenyl-p-xylene-glycol, tetraphenyl-phthalein and Dipheno(3–10′)thiazinyl are shown to form dipositive carbonium ions, but triphenyl acetic acid, 2-3-5-6 tetramethyl benzoic acid, 2-3-4-5-6 pentamethyl benzoic acid, tert-butyl alcohol, triphenyl carbinol, tri-p-tolyl carbinol, tri-o-tolyl carbinol, tri-p-chlorophenyl carbinol and tri-p-nitrophenyl carbinol form monopositive carbonium ions in chlorosulphuric acid, as revealed by conductometric and u.v. spectral studies. Oxalyl chloride decomposes while ethylene glycol is sulphonated in chlorosulphuric acid. Dichloroethane behaves as a non-electrolyte but dibromomethane disproportionates in this medium.

Introduction

Chlorosulphuric acid is weakly nucleophilic in character, therefore strongly electrophilic cations have been found to be quite stable in it. Some unusual cations of the types Se_8^{2+}, Se_4^{2+}, Te_4^{2+}, Te_2^{2+}, I_3^+ have already been reported [1–3] in chlorosulphuric acid; similarly the formation of some carbonium ions in this solvent has also been reported in the literature [4, 5]. The formation and the stabilization of such cations in this solvent have interested us in investigating the behaviour of various organic compounds in chlorosulphuric acid and the stabilization of any monopositive and dipositive carbonium ions.

Experimental

The design of the conductivity cells used and the method of conductance measurements have been described earlier [6].

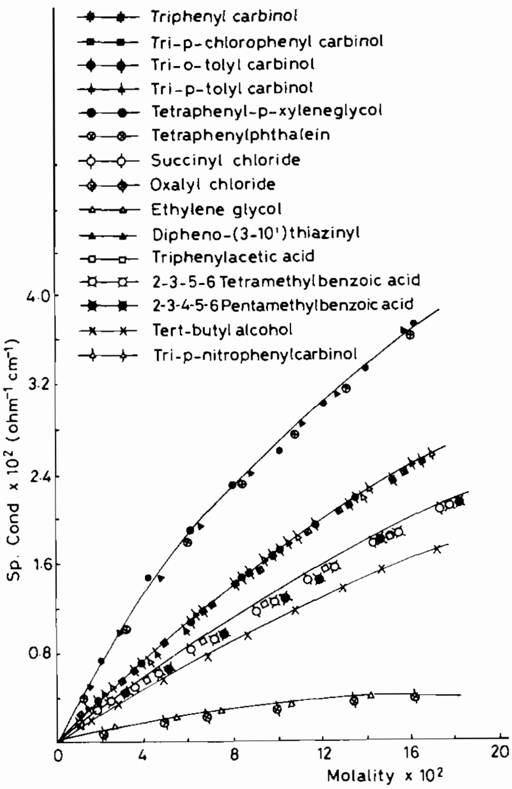

Fig. 1. Specific conductance of various solutes in HSO_3Cl at 25 °C.

Ultra-violet and visible absorption spectra of solutions of various solutes in chlorosulphuric acid were recorded in the range 200–800 nm on a Beckmann D.B. spectrophotometer. The instrument was run manually. Reference solutions were taken in quartz cells having path lengths of one cm or one mm. Chlorosulphuric acid (B.D.H.) technical grade was used as reported earlier [7].

All the compounds used during the experiment were either commercially available or were prepared and purified by published methods [8–10].

Results and Discussion

Interpolated values of specific conductance of various solutes at different concentrations in chloro-

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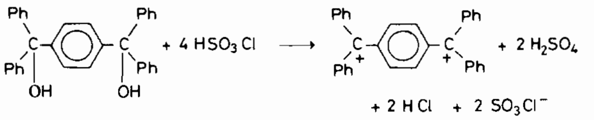
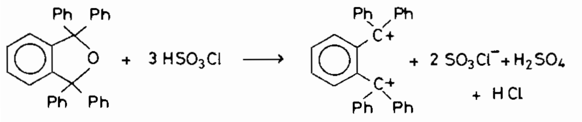
sulphuric acid are given in Fig. 1. The conductometric factor γ, the number of SO_3Cl^- ions produced per mol of solute for various solutes was determined as in [7].

Tetraphenyl-*p*-xylene glycol forms red solutions in chlorosulphuric acid. These solutions are found to be quite stable and conducting. Ultra-violet and visible spectra of the solutions show a strong absorption band at 450 nm, analogous to that reported in sulphuric acid [11]. This suggests the formation of dipositive carbonium ions. Moreover, it has been observed that on pouring these solutions onto crushed ice, the original compound separates out suggesting that no sulphonation/oxidation took place. However, the conductance data (Fig. 1) when compared with that of KSO_3Cl (a strong base of the system, ref. 7) suggests the possible mode of reaction as;



Both H_2SO_4 and HCl produced during the above reactions behave as weak bases in chlorosulphuric acid.

Tetraphenyl phthalein gives highly conducting, stable solutions in chlorosulphuric acid. These solutions in chlorosulphuric acid give the original compound when poured onto crushed ice, indicating that there is no sulphonation/oxidation of the above compound in this solvent. From the experimental γ value, Fig. 1, it is concluded that dipositive carbonium ions are formed according to the reaction:



The multicharged cations are quite stable towards sulphonation because of the presence of various resonating structures [12].

Oxalyl chloride decomposes in chlorosulphuric acid to give carbon monoxide and carbonyl chloride. Succinyl chloride however, is protonated when dissolved in HSO_3Cl and the conductance of the solution is comparable to that of KSO_3Cl, which further rules out the possibility of the formation of any carbonium or oxocarbonium ions. Ethylene glycol is sulphonated in HSO_3Cl and the products behave as very weak bases:

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2HSO_3Cl \longrightarrow \begin{array}{l} CH_2HSO_4 \\ | \\ CH_2HSO_4 \end{array} + 2HCl$$

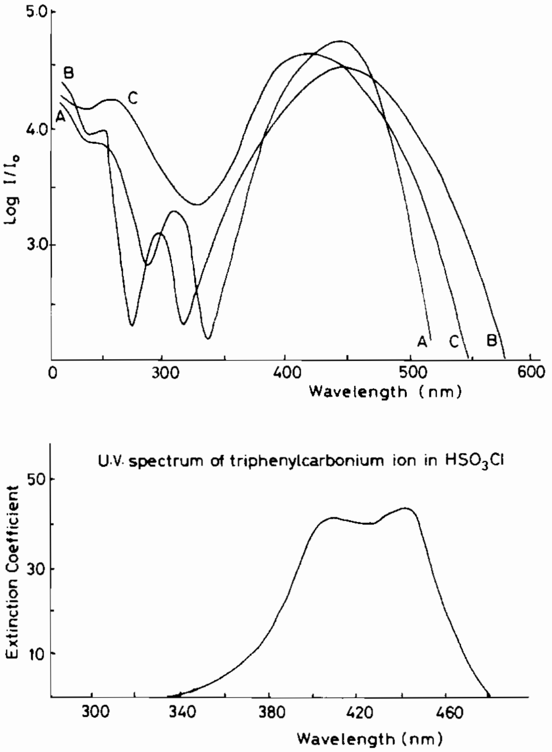


Fig. 2a. Absorption spectra of phenols in HSO_3Cl. A = tri-*p*-tolyl carbinol; B = tri-*o*-tolyl carbinol; C = tri-*p*-nitrophenyl carbinol.

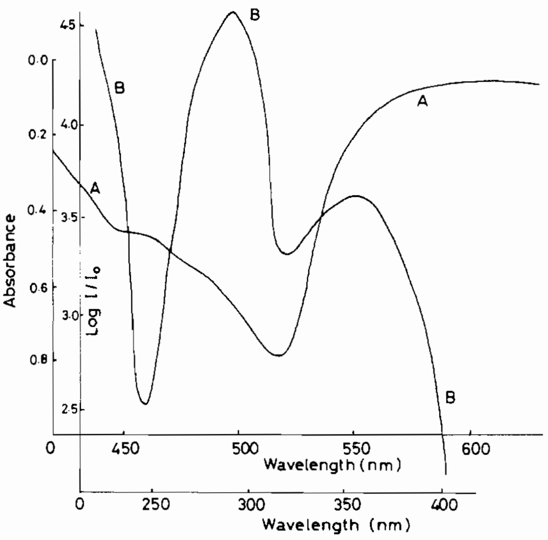
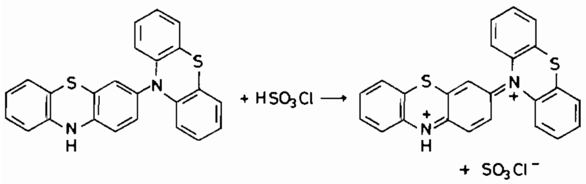


Fig. 2. A = Absorption spectrum of dipheno-(3–10′)thiazinyl in HSO_3Cl. B = U.V. spectrum of 2-3-4-5-6-pentamethyl benzoic acid in HSO_3Cl.

Dichloroethane behaves as a non-electrolyte in HSO_3Cl but dibromomethane disproportionates to form elemental bromine, which behaves as a non-electrolyte in HSO_3Cl.

Dipheno-(3–10′)thiazinyl in chlorosulphuric acid gives dark red solutions. The intensity of the colour does not change with time. The solutions are found to be highly conducting and stable. It has also been observed that during the reaction there is no smell of SO_2, which further indicates that there is no rupture of the ring, ruling out the possibility of any sulphonation of the compound. Ultraviolet and visible spectra of the red solutions show distinct absorption bands at 446 and 524 nm, which are the characteristic peaks of the dipositive carbonium ions (Fig. 2b). The calculated values of the molar extinction coefficient are indentical to those reported in sulphuric acid [8]. Further support of the formation of dipositive carbonium ions has been obtained from the conductance data of these solutions when compared with that of a strong base of the system, and hence the mode of reaction may be predicted as:



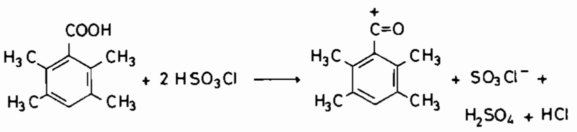
Triphenylacetic acid forms conducting stable solutions in HSO_3Cl. During the reaction carbon monoxide is evolved. Conductance data (Fig. 1) indicate the possible mode of reaction as:

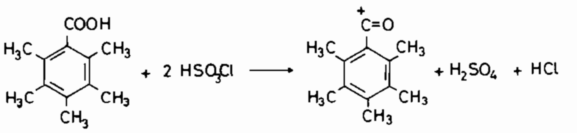
$$(C_6H_5)_3CCOOH + 2HSO_3Cl \longrightarrow$$

$$(C_6H_5)_3C^+ + CO + SO_3Cl^- + H_2SO_4 + HCl$$

Both H_2SO_4 and HCl produced during the above reaction behave as weak bases in HSO_3Cl [7]. The formation of carbonium ions in the above reaction is further confirmed by taking the u.v. spectra of those solutions which gave absorption bands at 408 and 440 nm (Fig. 2a) with molar extinction coefficients of 36400 and 37350 respectively, the characteristic bands of $(C_6H_5)_3C^+$, and which are identical to those reported in other strong acids [12].

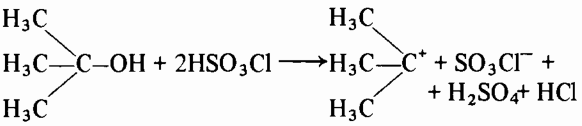
The compounds 2-3-5-6 tetramethyl and 2-3-4-5-6 pentamethyl benzoic acids form highly conducting solutions in chlorosulphuric acid according to the possible modes of reactions as:





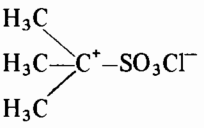
Both H_2SO_4 and HCl produced during the above reactions behave as weak bases in this solvent. The formation of monopositive carbonium ions is further confirmed by taking the u.v. spectra of the above solutions, and was found to be analogous to that already reported in other strong acid [13].

Simple aliphatic alcohols behave as bases in chlorosulphuric acid [15], but the higher aliphatic alcohols, such as butyl and tert-butyl alcohols when dissolved in chlorosulphuric acid, initially form light-yellow solutions which immediately change to brown. It has also been observed that the conductance of the solution changes with time with the increase in intensity of the colour, which finally changes to dark brown after 3–4 hours (depending upon the concentration of the solute) when the solutions are quite stable. These observations indicate that during the reactions some rearrangement takes place and some hydrocarbon may be formed which behaves as a non-electrolyte in this solvent. However, the experimental γ values indicate the possible mode of reaction as:



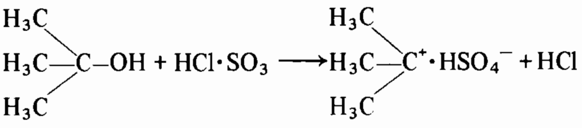
$$(H_3C)_3C\text{–}OH + 2HSO_3Cl \longrightarrow (H_3C)_3C^+ + SO_3Cl^- + H_2SO_4 + HCl$$

The experimentally lower than required value of γ by the above equation may be due to the possibility that the species



$$(H_3C)_3C^+\text{–}SO_3Cl^-$$

is not completely ionized. It is also possible that even tert-butyl hydrogen sulphate may be formed as a result of the reaction:



$$(H_3C)_3C\text{–}OH + HCl\cdot SO_3 \longrightarrow (H_3C)_3C^+\cdot HSO_4^- + HCl$$

and it behaves as a fairly strong base which may be protonated. With the limited data of conductance alone, we cannot suggest any mechanism for the rearrangement.

Triphenyl carbinol forms triphenyl carbonium ions in sulphuric [12], methanesulphuric [15] and disulphuric [13] acids. Chlorosulphuric acid is a stronger acid than sulphuric and methane-sulphuric acids but weaker than disulphuric acid and is a poor dehydrating agent. Therefore the carbonium ions which are stable in H_2SO_4 and CH_3SO_3H should be expected to be more stable in chlorosulphuric acid. It is interesting therefore to investigate the behaviour of these carbinols in chlorosulphuric acid, which will help in differentiating their basicities in comparison to other strong protonic acids.

Triphenyl carbinol forms yellow solutions in chlorosulphuric acid. These solutions are conducting and stable. However, the conductance data when compared with a reference solute (*i.e.*; KSO_3Cl, a strong base of this system) indicate the possible mode of reaction as:

$$(C_6H_5)_3COH + 2HSO_3Cl \longrightarrow (C_6H_5)_3C^+ + SO_3Cl^- + HCl + H_2SO_4$$

The formation of triphenyl carbonium ion in the above reaction is further confirmed by taking the solution spectra. The u.v. spectra show two absorption bands at 410 and 438 nm which are found identical to those reported in other strong acids. The molar extinction coefficient for the 410 nm band further supports the complete ionization of triphenyl carbinol.

Tri-*p*-tolyl carbinol, tri-*o*-tolyl carbinol, tri-*p*-chlorophenyl carbinol and tri-*p*-nitrophenyl carbinol give stable, highly-conducting orange solutions in chlorosulphuric acid. It has also been observed that during the above reactions there is no evolution of SO_2. Moreover when these coloured solutions are poured onto crushed ice, the colour of the solution changes and the original compounds are obtained quantitatively. These observations further suggest that there is no sulphonation of the ring during these reactions. However, from the conductance values in chlorosulphuric acid, it has been observed that the compounds all behave in a manner analogous to that of triphenyl carbinol. The reaction in general for all these solutes may be suggested as:

$$(X{-}C_6H_4)_3COH + 2HSO_3Cl \longrightarrow (X{-}C_6H_4)_3C^+ + SO_3Cl^- + HCl + H_2SO_4$$

(where X = *o*-tolyl, *p*-tolyl, *p*-chlorophenyl and *p*-nitrophenyl). Whereas H_2SO_4 and HCl behave as weak bases in this solvent.

Ultra-violet and visible absorption spectra of these solutions of carbinols in HSO_3Cl (Fig. 2a) are found to be identical to those already reported in other acids [10, 13], which further supports the formation of the above carbonium ions in chlorosulphuric acid.

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