A Stable Dipositive Chlorocarbonium Ion

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\[ \text{a,a,a',a',a'-Hexachloro-p-xylene dissolves slowly in } 100\% \text{ H}_2\text{SO}_4 \text{ and rapidly in } \text{HSO}_3\text{Cl}, \]

forming light orange and dark red solutions respectively. Conductance, NMR and UV studies indicate that it forms the stable dipositive carbonium ion \( \text{Cl}_2\text{CC}_6\text{H}_4\text{Cl}_2+ \) in the former medium and the monopositive carbonium ion \( \text{Cl}_2\text{CC}_6\text{H}_4\text{Cl}_2^- \) in the latter.

**Materials and Methods**

\( \text{a,a,a',a',a'-Hexachloro-p-xylene (Eastman-Kodak practical grade) was used after recrystallization from acetone. Chlorosulphonic acid (BDH, reagent grade) was used as such. Sulphuric acid of minimum conductance (corresponding to } 100\% \text{ sulphuric acid) was prepared by mixing the requisite amounts of } 20\% \text{ oleum (Swastik Chemicals) and } 98\% \text{ sulphuric acid (BDH). The conductivity cell was similar to that used by Ciruna et al.} \)

Conductance measurements were carried out at } 35 \pm 0.1^\circ \text{C using a Systronics conductivity bridge, model 321.}

The NMR spectra were recorded on a Varian A-60 spectrometer, at room temperature using hexamethyl disilazane as an external standard.

**Results and Discussion**

\( \text{a,a,a',a',a'-Hexachloro-p-xylene (I) dissolves readily in chlorosulphonic acid with evolution of HCl to form a red coloured solution. Conductance measurements made in the concentration range up to } 0-1m \text{ showed it to be fully ionized and behaving as a 1:1 electrolyte, giving a conductance curve which closely followed that of KCl.} \)

The following reactions may be taking place in this medium:

\[
\begin{align*}
\text{Cl}_2\text{CC}_6\text{H}_4\text{Cl}_2+6\text{H}_2\text{SO}_4 & \rightarrow \text{Cl}_2\text{CC}_6\text{H}_4\text{Cl}_2 \picture{155.png}
observer in the case of monopositive carbonium ion obtained in chlorosulphonic acid. The spectrum in sulphuric acid was unchanged after a week confirming the high stability of the dication in this medium.

In chlorosulphonic acid, the NMR spectrum of (I) consisted of doublets centred at 9.15 δ and 8.58 δ (J = 8.9 Hz) indicating the formation of a monopositive carbonium ion in this medium. The spectrum was found to change slowly with time, converting almost completely into an unidentified species (~δ38), presumably the chlorosulphate, after five days.

The electronic spectrum of (I) in 100% sulphuric acid showed bands at 265 and 320 nm while in CHCl₃ solution, three bands at 250, 274 and 281 nm are obtained. In chlorosulphonic acid, a strong band at 390 nm was observed. The marked bathochromic shift observed in proceeding from chloroform to the strongly acidic media was a further indication of carbonium ion formation.

Simple HMO calculations using an IBM 1120 computer, were carried out on the monopositive (II), dipositive (III) and tripositive (IV) species and delocalization energies and charge densities were computed for them. Approximate values for the heteroatom parameters, as recommended by Streitwieser, were used. II, III and IV were found to have delocalization energies of 2.94, 3.77 and 4.79 respectively, showing that inherent instability was not a barrier to the formation of III and IV and indicating them to be stable relative to II. II has already been reported as a fairly stable species in hexachloroantimonate salt

The differences in the behaviour of (I) in 100% H₂SO₄ and HClSO₄ are probably related to the large dielectric constant of the former medium (ε = 100) as compared to that of the latter (ε = 60). If dicarbonium ion formation takes place by a two-step mechanism as shown below:

\[ \text{Cl}_3\text{CC}_4\text{H}_3\text{CCl}_3 \rightarrow \text{Cl}_2\text{CC}_4\text{H}_2\text{CCl}_2 \rightarrow \text{Cl}_2\text{CC}_4\text{H}_2\text{CCl}_2 \]

the chlorine atoms of the trichloromethyl group will be bound more firmly to carbon at the intermediate stage than at the initial stage, (on account of the inductive effect of the positive charge which is delocalized onto the carbon atom adjacent to the ionizing centre) and require a medium of higher dielectric constant than chlorosulphonic acid for their ionization. However, the possibility that the difference in the behaviour of (I) in the two solvents is due to some inherent difference in their properties, cannot be ruled out.

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