

A Stable Dipositive Chlorocarbonium Ion

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$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -Hexachloro-*p*-xylene dissolves slowly in 100% H_2SO_4 and rapidly in HSO_3Cl , forming light orange and dark red solutions respectively. Conductance, NMR and UV studies indicate that it forms the stable dipositive carbonium ion $Cl_2\overset{+}{C}C_6H_4\overset{+}{C}Cl_2$, in the former medium and the monopositive carbonium ion $Cl_3CC_6H_4\overset{+}{C}Cl_2$, in the latter.

MULTICHARGED aryl carbonium ions, where the positive centres are stabilized by the delocalization of the positive charge over more than one benzene nucleus, are well known both in solution¹ and in the form of their crystalline salts². Salts of di- and tri-positive carbonium ions derived from a single benzene nucleus and stabilised by tropylium³ or oxolenium rings⁴ directly attached to the ionizing centre, have also been reported. However, attempts at preparing dipositive chloro- or fluoro-carbonium ions stabilized by only one benzene ring have, so far, involved obtaining 'extraordinary' dipositive carbonium ions requiring a double ionization at the same centre for their formation^{5,6}. It was thought that a carbonium ion of this type might be obtainable if ionization occurred at different centres attached to the same benzene nucleus. With this end in view, the behaviour of $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexachloro-*p*-xylene, $CCl_3C_6H_4CCl_3$ (I) was studied in sulphuric and chlorosulphonic acids.

Materials and Methods

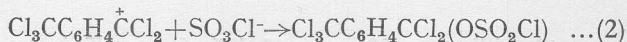
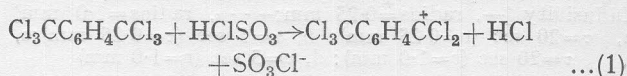
$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -Hexachloro-*p*-xylene (Eastman-Kodak practical grade) was used after recrystallization from acetone. Chlorosulphonic acid (BDH, reagent grade) was used as such. Sulphuric acid of minimum conductance (corresponding to 100% sulphuric acid) was prepared by mixing the requisite amounts of 20% oleum (Swastik Chemicals) and 98% sulphuric acid (BDH). The conductivity cell was similar to that used by Ciruna *et al.*⁷. Conductance measurements were carried out at $35 \pm 0.1^\circ$ 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

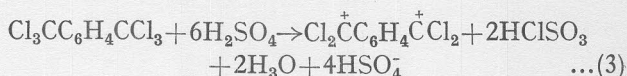
$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -Hexachloro-*p*-xylene (I) dissolves readily in chlorosulphonic acid with evolution of HCl to form a red coloured solution. Conductance measurements made in the concentration range up to 0.1*m* showed it to be fully ionized and behaving as a 1:1 electrolyte, giving a conductance curve which

closely followed that of KCl⁷. The following reactions may be taking place in this medium:



The conductance decreases with time, that of 0.1*m* solution decreasing to roughly one-third of its original value after a week, indicating that perhaps the carbonium ion was slowly converting into its chlorosulphate (Eq. 2).

In 100% sulphuric acid (I) dissolves slowly, over a period of 7-8 hr to give a light orange solution and a conductivity γ value (in the concentration range up to 0.1*m*) between 2 and 3 (ref. 8). Acid-base titrations with 0.1*m* oleum⁹ gave a conductance minimum at a *nb/na* value between 0.24 and 0.19. Keeping in view the possibility of some loss of HCl in these experiments, these results were interpreted to indicate the formation of a dipositive carbonium ion according to the reaction represented by Eq. 3.



The formation of 4 moles of bisulphate per mole of carbonium ion gives rise to theoretical γ and *nb/na* values of 4 and 0.18 respectively. The conductance of a solution of (I) in 100% sulphuric acid was found to remain unchanged up to one week, indicating the indication to be quite stable in this medium.

Hydrolysis of the solution of (I), in both $HClSO_3$ and 100% H_2SO_4 , resulted in the formation of terephthalic acid.

No interaction between $SbCl_5$ and (I) was noted in CCl_4 solution although a large number of carbonium ion hexachloroantimonates have been prepared in this way^{2a-c,10}.

The NMR spectrum of (I) in 100% sulphuric acid gave a singlet at 8.68 δ . A solution of (I) in 20% oleum aged for 44 days gave a similar spectrum, confirming the formation of a dipositive carbonium ion in these media. The peak position is at a higher δ value than that of a solution of (I) in CCl_4 (8.2 δ). However, the extent of deshielding is less than that

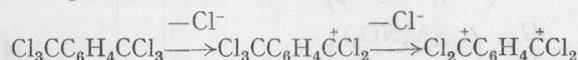
observer in the case of monovalent carbonium ion obtained in chlorosulphonic acid. The spectrum in sulphuric acid was unchanged after a week confirming the high stability of the dication in this medium.

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 monovalent carbonium ion in this medium. The spectrum was found to change slowly with time, converting almost completely into an unidentified species ($\sim 8.5\delta$), presumably the chlorosulphate, after five days.

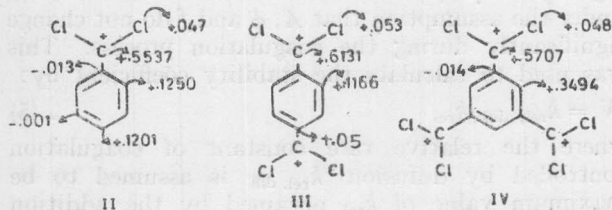
The electronic spectrum of (I) in 100% sulphuric acid showed bands at 265 and 320 nm while in CHCl_3 solution, three bands at 250, 274 and 281 nm are obtained. In chlorosulphonic acid, a strong band at 390 nm was observed. The marked bathochromic shift observed in proceeding from chloroform to the strongly acidic media was a further indication of carbonium ion formation.

Simple HMO calculations using an IBM 1120 computer, were carried out on the monovalent (II), divalent (III) and trivalent (IV) species and delocalization energies and charge densities were computed for them. Approximate values for the heteroatom parameters, as recommended by Streitwieser¹¹ were used. II, III and IV were found to have delocalization energies of 2.94 β , 3.77 β and 4.79 β 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 chlorosulphonic acid⁶ and in the form of its hexachloroantimonate salt^{10a}.

The differences in the behaviour of (I) in 100% H_2SO_4 and HClSO_3 are probably related to the large dielectric constant of the former medium ($\epsilon = 100$) as compared to that of the latter ($\epsilon = 60$) (ref. 7). If dicarbonium ion formation takes place by a two-step mechanism as shown below:



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.

Acknowledgement

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