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MONOPOSITIVE CHLOROCARBONIUM IONS

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Deno and co-workers (1) have recently reported the n.m.r. spectra of solutions of trichloromethylmesitylene, $ArCCl_3$, in sulphuric acid and oleum. They conclude that in 96% aqueous acid the mesitoic acidium ion, $ArCOOH_2^+$, is formed, in 99% H_2SO_4 the mesitoyl cation, $ArCO^+$, is formed, and in 30% oleum a new species is produced which has three peaks in the n.m.r. spectrum of relative areas 2:6:3, (δ = 2.60, 2.94, 7.47)[*] and which is, therefore, neither $ArCO^+$ nor $ArCOOH_2^+$. This spectrum they tentatively ascribe to the $Ar\overset{+}{C}Cl_2$ ion, which we have shown (2) to be formed quantitatively in dilute solution in 100% acid. In 100% H_2SO_4 Deno and co-workers (1) found that the spectrum ascribed to $Ar\overset{+}{C}Cl_2$ is formed initially but changes to the spectrum of $Ar\overset{+}{C}O$ with a half-life of about thirty minutes at 25°C. Throughout the change the n.m.r. peaks of $Ar\overset{+}{C}Cl_2$ remained distinctly resolved with no change other than a decrease in intensity

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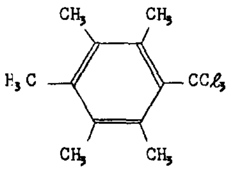
[*] These chemical shifts are quoted in p.p.m. from tetramethylsilane but they were obtained indirectly using $(CH_3)_4N^+$ as an intermediate standard.

while the peaks of $Ar\overset{+}{C}O$ increased in intensity.

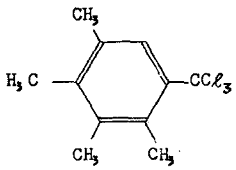
During the course of the work reported recently (2) we also observed that the n.m.r. spectrum of $Ar\overset{+}{C}Cl_2$ in H_2SO_4 changes with time to give a spectrum that is identical with that of $ArCO_2H$ in H_2SO_4, i.e., the acyl ion $ArCO^+$ (Table I). Our observations were made in 100% H_2SO_4 but the change in the n.m.r. spectrum with time was similar to that reported by Deno and co-workers and was accompanied by a change in the colour of the solution from red to yellow. Hart and Roobal (3) have studied the rate of decomposition of the red species formed from $ArCCl_3$ in sulphuric acid, which they believed to be the $ArCCl^{2+}$ ion, and which we have shown to be the $ArCCl_2{}^+$ ion. The mesitoyl cation is colourless and thus the change from a red to a <u>yellow</u> solution is unexplained. However the colour could be due to very small traces of some impurity. On pouring either the red or the yellow solution onto ice mesitoic acid was recovered.

We have also studied solutions of trichloromethylmesitylene in chlorosulphuric acid and fluorosulphuric acid. Conductimetric studies (4) have shown that a monopositive dichlorocarbonium ion is formed in chlorosulphuric acid, and the n.m.r. spectra are identical to that attributed to $Ar.\overset{+}{C}Cl_2$ in sulphuric acid. These solutions were found to be more stable than those in sulphuric acid.

Cryoscopic and conductimetric measurements on dilute solutions of trichloromethylpentamethyl benzene I, and trichloromethylprehnitene II, in



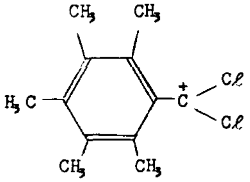
I

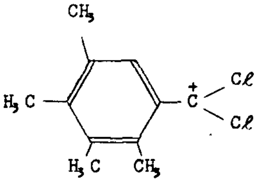


II

100% H_2SO_4 are consistent with the formation of five particles from each molecule of solute ($\nu = 5$), two of which are hydrogen-sulphate ions ($\gamma = 2$), and conductimetric acid-base titrations with dilute oleum show that of the cations formed one is an H_3O^+ ion and the other a monopositive carbonium ion, (Ia, IIa). i.e., the reactions are

$$RCCl_3 + 3H_2SO_4 = RCCl_2 + HClSO_3 + H_3O^+ + 2HSO_4^-, \quad (\nu = 5, \ \gamma = 2).$$


Ia


IIa

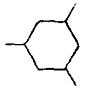
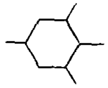
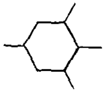
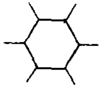
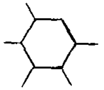
Solutions of I and II in chlorosulphuric acid or fluorosulphuric acid gave spectra identical to those observed initially in sulphuric acid. These spectra, (Table I), we assign to the monopositive chlorocarbonium ions Ia and IIa. In both cases the n.m.r. spectra of solutions in sulphuric acid change in a similar way to that described above for solutions of trichloromethylmesitylene in this solvent, the spectrum ascribed to the monocarbonium ion being gradually replaced by that of the corresponding acylium ion.

REFERENCES

1. N. C. Deno, N. Friedman, and J. Mockus, J. Amer. Chem. Soc., **86**, 5676 (1964).
2. R. J. Gillespie and E. A. Robinson, ibid., **86**, 5676 (1964).
3. H. Hart and N. R. Roobal, ibid., **86**, 1373 (1964).
4. E. A. Robinson and J. A. Ciruna, ibid., **86**, 5677 (1964).

TABLE I

N.M.R. Spectra[a,b]

Solute		Solvent			
		CCl_4	100% H_2SO_4	HSO_3Cl	HSO_3F
	COOH	6.81 2.41 2.27 (2) (6) (3)	7.22 2.52 2.37[c] (2) (6) (3)	-	-
	$COCl$	6.77 2.30 2.23 (2) (6) (3)	7.22 2.52 2.37[c] (2) (6) (3)	7.24 7.52 2.38[c] (2) (6) (3)	-
	CCl_3	6.88 2.78 2.27 (2) (6) (3)	7.29 2.73 2.39[d] (2) (6) (3) 7.23 2.53 2.39[e] (2) (6) (3)	7.32 2.75 2.40[d] (2) (6) (3)	7.32 2.73 2.38[d] (2) (6) (3)
	CCl_3	2.61 2.28 (9) (6)	2.62 2.39 2.12[d] (6) (3) (6) 2.47 2.34 2.14[e] (6) (3) (6)	2.66 2.42 2.16[d] (6) (3) (6)	2.60 2.36 2.09[d] (6) (3) (6)
	CCl_3	7.84 2.69 2.41 2.32 (1) (3) (3) (6)	- 2.70 2.46 2.24[d] (3) (3) (6) 7.60 2.52 2.34 2.19[e] (1) (3) (3) (6)	8.12 2.69 2.42 2.26[d] (1) (3) (3) (6)	8.18 2.65 2.40 2.21[d] (1) (3) (3) (6)

a. Chemical shifts in p.p.m. from an external standard consisting of a dilute solution of $(CH_3)_4Si$ in $CDCl_3$. The shifts have been corrected for the difference in susceptibility of $CDCl_3$ and the solvent; they were obtained by exchanging the sample and reference tubes while running the spectra.

b. relative areas in parentheses

c. RCO^+ ion

d. $RCCl_2^+$ ion (initial spectrum)

e. RCO^+ ion (final spectrum)