

that Hart and Fish were actually observing ArCOOH_2^+ .³

Before resolving this confusing situation, it is well to explain some of the problems in the n.m.r. studies. Concentrations of ArCOOH_2^+ and ArCO^+ are equal in 97% H_2SO_4 .^{2,4} Thus minor changes in the acidity in this region produce major changes in the n.m.r. spectrum. Furthermore, addition of the 5–10% of ArCCl_3 (or ArCOOH) required for the n.m.r. measurements produces a large decrease in the effective acidity, the exact amount being difficult to estimate. With these difficulties in mind, the results were as follows.

96% H_2SO_4 .—Addition of 5% ArCCl_3 to 96% H_2SO_4 produces an n.m.r. spectrum that is identical with that of ArCOOH_2^+ at the first observation, 2 min. after mixing at 25°. The identity can be unequivocally demonstrated by addition of ArCOOH to the ArCCl_3 solution and showing that the bands of ArCOOH_2^+ at 2.34, 2.43, and 7.08 are exactly reproduced.

Addition of 10% ArCCl_3 to 99% H_2SO_4 produces an identical spectrum and it is presumed that the reaction of ArCCl_3 with H_2SO_4 has effectively lowered the acidity to the neighborhood of 96% H_2SO_4 . We believe that this is what happened in Hart and Fish's experiment.

99% H_2SO_4 .—An equimolar mixture of ArCCl_3 and ArCOOH can be added to 5% SO_3 –95% H_2SO_4 to produce immediately the n.m.r. spectrum of ArCO^+ . There is no hint of any second species so that the ArCCl_3 must be immediately solvolysing to ArCO^+ and the effective acidity must be in the neighborhood of 99% H_2SO_4 . The rate of conversion of ArCCl_3 to ArCO^+ is orders of magnitude faster than the rates of formation of ArCO^+ reported by Hart and Roobal⁵ based on studies of the change in visible and ultraviolet absorption spectra with time. Although there would appear to be a direct conflict of results, it is possible that the large amounts of ClSO_3H and HCl may catalyze the solvolysis. Clarification of this matter will require further study.

30% SO_3 –70% H_2SO_4 .—Addition of 5% ArCCl_3 to 30% SO_3 –70% H_2SO_4 produces a new species that is neither ArCOOH_2^+ nor ArCO^+ . The n.m.r. bands of the new species are at 2.60, 2.94, and 7.47 p.p.m. with areas of 3:6:2. The band positions of ArCO^+ are at 2.60, 2.73, and 7.41 p.p.m.² so that the two species are clearly distinct although the band position of the *p*-methyl group is identical in each spectrum.

It does not seem likely that a structure such as ArC^2+Cl could produce a spectrum so close to that of ArCO^+ . The positive charge on carbonium ions always causes large downfield shifts in the n.m.r. band positions⁶ and a second positive charge should produce a comparable further shift. In any event, the n.m.r. spectrum is in accord with expectations for a monopositive cation and Gillespie and Robinson's ArC^+Cl_2 is a likely candidate. The new species is thus provisionally assigned the ArC^+Cl_2 structure.

100% H_2SO_4 .—The most revealing of the n.m.r. experiments are those in which 5–10% ArCCl_3 is added to 5% SO_3 –95% H_2SO_4 . It is possible to achieve systems

(3) A uniform displacement of 0.13 p.p.m. is explained by the fact that Hart and Fish used benzene as an external standard whereas we have used $(\text{CH}_3)_4\text{N}^+$ as an internal standard.

(4) W. S. Schubert, J. Donohue, and J. D. Gardner, *J. Am. Chem. Soc.*, **76**, 9 (1954).

(5) H. Hart and N. R. Roobal, *ibid.*, **86**, 1373 (1964).

(6) N. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

in which the n.m.r. spectrum of ArC^+Cl_2 is immediately formed, but which shifts to the spectrum of ArCO^+ with a half-time of 30 min. for conversion at 25°. Throughout this shift, the n.m.r. bands of ArC^+Cl_2 and ArCO^+ remain completely distinct with no change other than the diminution of the ArC^+Cl_2 bands and the rise of those of ArCO^+ . After several hours, the spectrum of ArCO^+ is obtained without hint of any extraneous bands.

It is important to recognize that the n.m.r. spectrum of this new species, provisionally ArC^+Cl_2 , was not reported in any of the papers of Hart and Fish. Thus the report that the n.m.r. spectrum of stable salts of ArC^2+Cl in SO_2 is the same as that of the ArC^2+Cl ion in H_2SO_4 ⁷ raises serious questions regarding their work on the stable salts.

The above evidence pertains exclusively to the case where Ar is the 2,4,6-trimethylphenyl group. The other two cases of supposed ArC^2+Cl ions are under study.

Acknowledgment.—We are grateful to the Petroleum Research Fund of the American Chemical Society for support of this work and to the National Science Foundation for funds to purchase the Varian A-60 n.m.r. spectrometer.

(7) H. Hart and J. S. Fleming, *Tetrahedron Letters*, 983 (1962).

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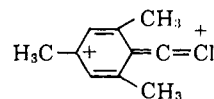
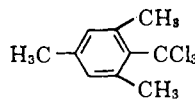
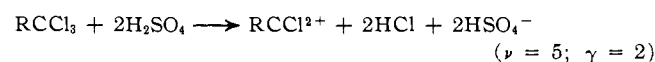
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On Carbonium Ions in Chlorosulfuric Acid

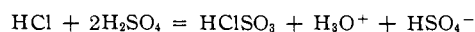
Sir:

It has been claimed previously¹ that polymethyltrichloromethylbenzenes, such as trichloromethylmesitylene (I), dissolve in strong sulfuric acid to give stable dipositive carbonium ions, e.g., II, according to the equation

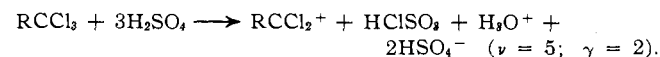


This conclusion was based mainly on a study of freezing point depressions, which showed that each molecule of RCCl_3 reacts with sulfuric acid to give five particles ($\nu = 5$), and electrical conductivity measurements which showed that two of the particles are hydrogen sulfate ions ($\gamma = 2$).

It has been shown recently² that HCl reacts almost quantitatively with sulfuric acid to form chlorosulfuric acid and it was claimed that the reaction of



RCCl_3 with sulfuric acid is in fact



(1) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **80**, 5894 (1958); **82**, 5419 (1960); **83**, 4460, (1961).

(2) R. J. Gillespie and E. A. Robinson, *ibid.*, **86**, 5676 (1964).

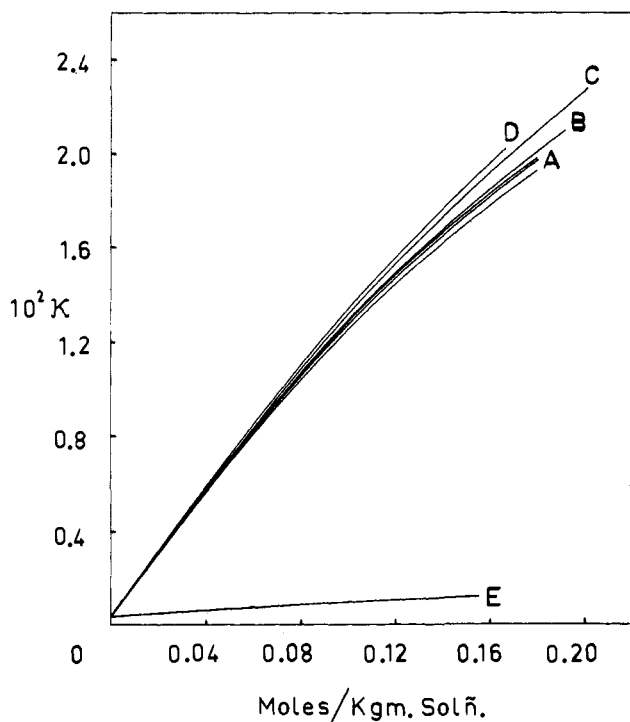


Fig. 1.—Electrical conductivities of solutions of: A, alkali metal chlorosulfates; B, benzoic acid; C, acetic acid; D, mesitoyl chloride; E, hydrogen chloride; in chlorosulfuric acid.

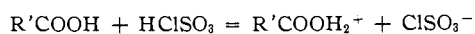
to give a *monopositive* carbonium ion rather than a *dipositive* species.

We have confirmed the ionization to form a monopositive carbonium ion by studying the electrical conductivities of solutions in chlorosulfuric acid.

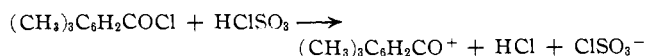
Pure chlorosulfuric acid has a small electrical conductivity ($\kappa = 4 \times 10^{-4}$ ohm $^{-1}$ cm. $^{-1}$ at 25°). However, alkali metal chlorosulfates dissolve in HClSO₃ to give highly conducting solutions (Fig. 1). Solutions of LiSO₃Cl, NaSO₃Cl, and KSO₃Cl have very similar molar conductances and it seems reasonable to conclude that these salts are fully dissociated in HClSO₃ and that a large proportion of the current is carried by the ClSO₃⁻ ion.



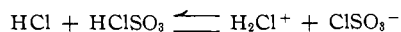
Benzoic and acetic acids, which behave as fully ionized bases in sulfuric acid,³ and therefore assuredly are also fully protonated in the stronger chlorosulfuric acid, give solutions with very similar conductances to those of the alkali metal salts (Fig. 1).



Mesitoyl chloride dissolves in chlorosulfuric acid to give the well-known mesitoyl cation



This ion was readily identified from its n.m.r. and ultraviolet absorption spectra (Table I). The electrical conductivities of the solutions are slightly greater than those of simple bases. The difference is attributed to the behavior of HCl in chlorosulfuric acid as a weak



base and is confirmed by the moderate conductivities of solutions of HCl in HClSO₃ (Fig. 1).

(3) R. J. Gillespie and J. A. Leisten, *Quart. Rev. (London)*, **8**, 40 (1954).

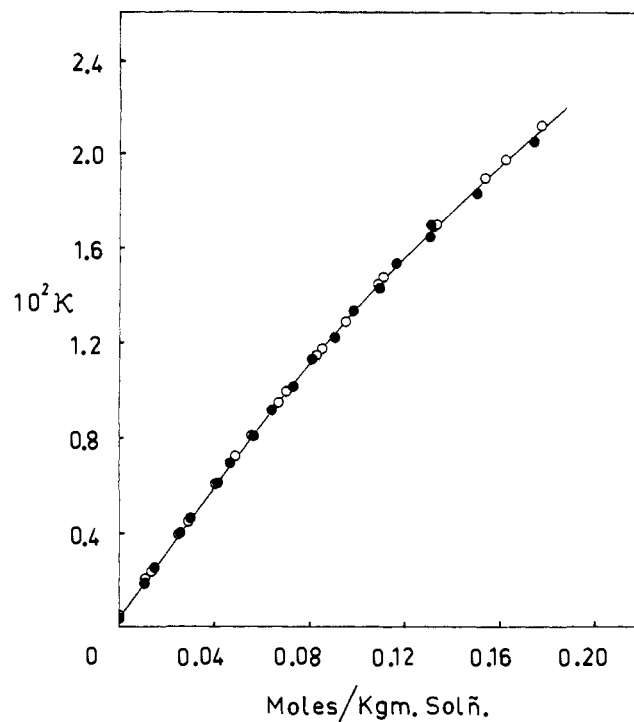


Fig. 2.—Comparison of the electrical conductivities of solutions of trichloromethylmesitylene O, and mesitoyl chloride ●, in chlorosulfuric acid.

Solutions of trichloromethylmesitylene in HClSO₃ are rather more stable than those in H₂SO₄ and have conductances which are very similar to those of solu-

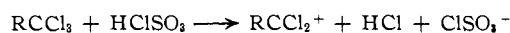
TABLE I
N.M.R. AND ULTRAVIOLET-VISIBLE SPECTRA OF SOLUTIONS OF MESITOYL CHLORIDE AND TRICHLOROMETHYLMESITYLENE IN HClSO₃^a AND H₂SO₄^b

	HClSO ₃			H ₂ SO ₄		
	τ_1	τ_2	τ_3	τ_1	τ_2	τ_3
RCOCl	2.64(2)	7.36(6)	7.50(3)	2.63(2)	7.33(6)	7.48(3)
RCCl ₃	2.56(2)	7.13(6)	7.48(3)	2.56(2)	7.12(6)	7.46(3)

	HClSO ₃		H ₂ SO ₄		
	λ_{max} , m μ		λ_{max} , m μ		
RCOCl	282(s)	339(s)	282(s)	339(w)	
RCCl ₃	283(w)	376(s)	486(w)	281(w)	373(s) 486(w)

^a Solutions were quite stable with time. ^b Solutions changed with time. ^c τ -values in p.p.m.; relative areas in parenthesis. ^d s = strong band; w = weak band; spectra not recorded below 260 m μ .

tions of mesitoyl chloride (Fig. 2), consistent with the reaction



together with partial protonation of the HCl formed. The n.m.r. and ultraviolet absorption spectra of solutions of trichloromethylmesitylene in chlorosulfuric acid are similar to those observed for this compound in 100% sulfuric acid (Table I), and thus we conclude that the same species RCCl_2^+ is formed in both solvents.

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