# COMMUNICATIONS TO THE EDITOR

On the Supposed Formation of Extraordinary Dipositive Carbonium Ions in Sulfuric Acid

Sir:

Hart and Fish[1-3] have presented evidence that trichloromethylmesitylene (I) ionizes in sulfuric acid with the formation of the dicarbonium ion II, according to eq. 1, and that pentamethyltrichlormethylbenzene

$$(CH_3)_3C_6H_2CCl_3 + 2H_2SO_4 \longrightarrow (CH_3)_3C_6H_2CCl^{2+} + 2HCl + 2HSO_4^- \quad (1)$$
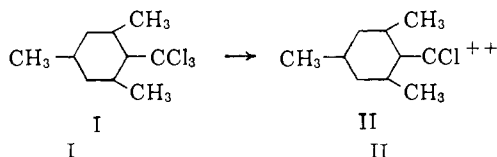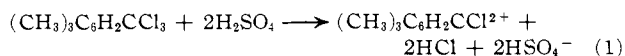
and trichlormethylprehnitene behave in a similar manner. They claim that all three compounds give a fivefold depression of the freezing point of sulfuric acid ($\nu = 5$), that conductance measurements show the formation of two hydrogen sulfate ions ($\gamma = 2$) from each molecule of solute, and that 2 moles of hydrogen chloride are swept from the sulfuric acid solutions by a current of dry nitrogen.

Although we have confirmed the cryoscopic and conductometric measurements on trichlormethylmesitylene we do not agree with Hart and Fish's interpretation of these results.

We find from conductometric and cryoscopic studies of solutions of HCl in 100% H_2SO_4 that it is not a nonelectrolyte as required by eq. 1 but that per mole it produces almost 1 mole of hydrogen sulfate ion and almost 3 moles of particles. We conclude that it is almost quantitatively ionized in dilute solution according to the equation

$$HCl + 2H_2SO_4 \rightleftharpoons HSO_3Cl + H_3O^+ + HSO_4^- \quad (2)$$
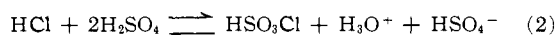
The freezing point depression and electrical conductivities of sulfuric acid solutions of I are almost identical with those of mesitoyl chloride; *i.e.*, the latter compound also gives $\nu = 5$ and $\gamma = 2$. The formation of the mesitoyl ion ($(CH_3)_3C_6H_2CO^+$) from mesitoyl chloride was shown by the ultraviolet absorption spectrum (λ_{max} 2820 Å., (ϵ_{max} 20,900)). The only reasonable interpretation of these results is that mesitoyl chloride ionizes according to eq. 3. Again we note that

$$(CH_3)_3C_6H_2COCl + 3H_2SO_4 \longrightarrow (CH_3)_3C_6H_2CO^+ + HSO_3Cl + H_3O^+ + 2HSO_4^- \quad (3)$$
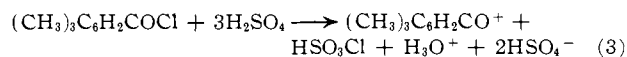
HCl reacts with sulfuric acid as in (2). However I does not give the mesitoyl ion as claimed recently by Deno, Friedman, and Mockus[4] as this would require $\nu = 9$ and $\gamma = 3$.

$$I + 4H_2SO_4 \longrightarrow (CH_3)_3C_6H_2CO^+ + 3HSO_3Cl + 2H_3O^+ + 3HSO_4^- \quad (4)$$
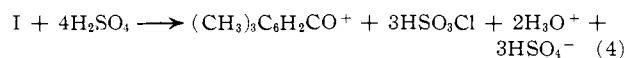
We suggest that I ionizes to give the mesityldichlorocarbonium ion (eq. 5). In support of this suggestion

$$I + 3H_2SO_4 \longrightarrow (CH_3)_3C_6H_2CCl_2^+ + HSO_3Cl + H_3O^+ + 2HSO_4^- \quad (5)$$
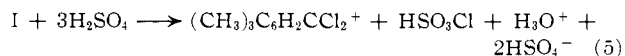
we find that only 1 mole of HCl can be swept out of the solution rapidly (*i.e.*, in about 0.5 hr.) by dry nitrogen although further HCl, in fact even more than 1 additional mole, can be swept out by continued passage of dry nitrogen for several hours. Although we believe that the HCl is present in sulfuric acid very largely in the form of HSO_3Cl, it is nevertheless removed as HCl by dry nitrogen as a consequence of the reversal of equilibrium (2) which lies largely but not completely on the right-hand side. The removal of more than 1 mole of HCl means that the cation $(CH_3)_3C_6H_2CCl_2^+$ reacts further and this is substantiated by the fact that during the sweeping out of HCl the color of the solution changes from red to yellow. The sweeping out experiments are complicated, however, by the fact that the rate at which HCl is removed is markedly increased by the presence of very small amounts of water in the sulfuric acid, and further studies of this reaction are needed.

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The Supposed ArC²⁺Cl Ions

Sir:

Hart and Fish[1] reported that three different α,α,α-trichloropolymethylbenzenes ionized to dipositive cations of the formula (aryl)$C^{2+}Cl$ in 100% H_2SO_4. The evidence was based on cryoscopic studies, conductometric studies, HCl evolution, and n.m.r. spectra.

The interpretation of the first three lines of evidence was based on the untested assumption that HCl was inert in 100% H_2SO_4. Gillespie and Robinson now report in the immediately preceding communication that HCl establishes an equilibrium with $ClSO_3H$ that is largely in favor of $ClSO_3H$. This one fact invalidates the first three lines of evidence and leads Gillespie and Robinson to propose that the product is actually ArC^+Cl_2 formed according to the equation

$$ArCCl_3 + 3H_2SO_4 = ArC^+Cl_2 + ClSO_3H + H_3O^+ + 2HSO_4^-$$
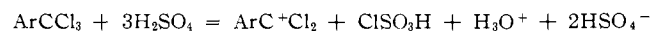
We have investigated the n.m.r. spectra of solutions of $ArCCl_3$ in acids ranging from 90% H_2SO_4 to 30% SO_3–70% H_2SO_4 for the case in which Ar is the 2,4,6-trimethylphenyl group. The results have been compared with the n.m.r. spectra of $ArCOOH_2^+$ and $ArCO^+$, which were available from a similar set of studies on ArCOOH solutions.[2] The most surprising fact is that the n.m.r. spectrum reported for $ArC^{2+}Cl$ is identical with that of $ArCOOH_2^+$, and it is concluded

(1) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **80**, 5894 (1958).
(2) H. Hart and R. W. Fish, *ibid.*, **82**, 5419 (1960).
(3) H. Hart and R. W. Fish, *ibid.*, **83**, 4460 (1961).
(4) N. C. Deno, N. Friedman, and J. Mockus, private communication.

(1) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **80**, 5894 (1958); **82**, 5419 (1960); **83**, 4460 (1961).
(2) N. Deno, C. U. Pittman, Jr., and M. J. Wisotsky. *ibid.*, **86**, 4370 (1964).

that Hart and Fish were actually observing Ar-COOH$_2$+.[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$_2$SO$_4$.[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$_2$SO$_4$.—Addition of 5% ArCCl$_3$ to 96% H$_2$SO$_4$ 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$_2$SO$_4$ produces an identical spectrum and it is presumed that the reaction of ArCCl$_3$ with H$_2$SO$_4$ has effectively lowered the acidity to the neighborhood of 96% H$_2$SO$_4$. We believe that this is what happened in Hart and Fish's experiment.

99% H$_2$SO$_4$.—An equimolar mixture of ArCCl$_3$ and ArCOOH can be added to 5% SO$_3$-95% H$_2$SO$_4$ to produce immediately the n.m.r. spectrum of ArCO+. There is no hint of any second species so that the Ar-CCl$_3$ must be immediately solvolyzing to ArCO+ and the effective acidity must be in the neighborhood of 99% H$_2$SO$_4$. 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 Roobal[5] 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$_3$H and HCl may catalyze the solvolysis. Clarification of this matter will require further study.

30% SO$_3$-70% H$_2$SO$_4$.—Addition of 5% ArCCl$_3$ to 30% SO$_3$-70% H$_2$SO$_4$ 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 Ar-C^{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 positions[6] 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$_2$SO$_4$.—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$_2$SO$_4$. It is possible to achieve systems

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$_2$SO$_4$[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.

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

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On Carbonium Ions in Chlorosulfuric Acid

Sir:

It has been claimed previously[1] that polymethyl-trichloromethylbenzenes, such as trichloromethyl-mesitylene (I), dissolve in strong sulfuric acid to give stable dipositive carbonium ions, e.g., II, according to the equation
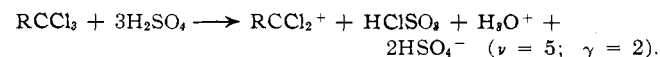
$$RCCl_3 + 2H_2SO_4 \longrightarrow RCCl^{2+} + 2HCl + 2HSO_4^-$$
$$(\nu = 5; \; \gamma = 2)$$

I   II
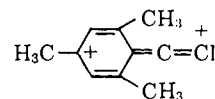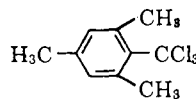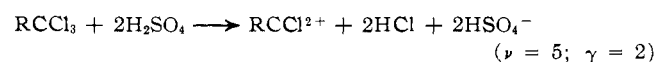
This conclusion was based mainly on a study of freezing point depressions, which showed that each molecule of RCCl$_3$ reacts with sulfuric acid to give five particles ($\nu = 5$), and electrical conductivity measurements which showed that two of the particles are hydrogen sulfate ions ($\gamma = 2$).

It has been shown recently[2] that HCl reacts almost quantitatively with sulfuric acid to form chlorosulfuric acid and it was claimed that the reaction of

$$HCl + 2H_2SO_4 = HClSO_3 + H_3O^+ + HSO_4^-$$

RCCl$_3$ with sulfuric acid is in fact

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

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(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 (CH$_3$)$_4$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).

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(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).