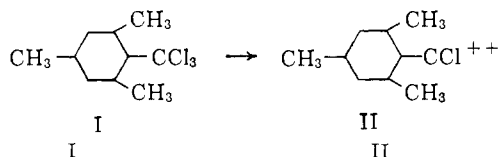
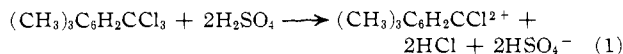


## COMMUNICATIONS TO THE EDITOR

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

Sir:

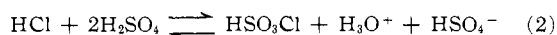
Hart and Fish<sup>1-3</sup> have presented evidence that trichloromethylmesitylene (I) ionizes in sulfuric acid with the formation of the dicarbonium ion II, according to eq. 1, and that pentamethyltrichloromethylbenzene



and trichloromethylprehnitene 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 trichloromethylmesitylene we do not agree with Hart and Fish's interpretation of these results.

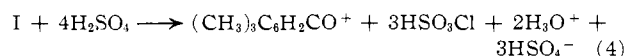
We find from conductometric and cryoscopic studies of solutions of HCl in 100%  $\text{H}_2\text{SO}_4$  that it is not a non-electrolyte as required by eq. 1 but that per mole it produces almost 1 mole of hydrogen sulfate ion and almost 3 moles of particles. We conclude that it is almost quantitatively ionized in dilute solution according to the equation



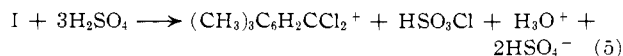
The freezing point depression and electrical conductivities of sulfuric acid solutions of I are almost identical with those of mesityl chloride; *i.e.*, the latter compound also gives  $\nu = 5$  and  $\gamma = 2$ . The formation of the mesityl ion ( $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CO}^+$ ) from mesityl chloride was shown by the ultraviolet absorption spectrum ( $\lambda_{\text{max}} 2820 \text{ \AA.}$ , ( $\epsilon_{\text{max}} 20,900$ )). The only reasonable interpretation of these results is that mesityl chloride ionizes according to eq. 3. Again we note that



HCl reacts with sulfuric acid as in (2). However I does not give the mesityl ion as claimed recently by Deno, Friedman, and Mockus<sup>4</sup> as this would require  $\nu = 9$  and  $\gamma = 3$ .



We suggest that I ionizes to give the mesityldichlorocarbonium ion (eq. 5). In support of this suggestion



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  $\text{HSO}_3\text{Cl}$ , 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  $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CCl}_2^+$  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.

DEPARTMENT OF CHEMISTRY  
MCMMASTER UNIVERSITY  
HAMILTON, ONTARIO  
DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF TORONTO  
TORONTO, ONTARIO

R. J. GILLESPIE

E. A. ROBINSON

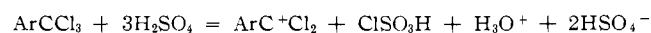
RECEIVED OCTOBER 3, 1964

The Supposed  $\text{ArC}^2+\text{Cl}$  Ions

Sir:

Hart and Fish<sup>1</sup> reported that three different  $\alpha, \alpha, \alpha$ -trichloropolymethylbenzenes ionized to dipositive cations of the formula  $(\text{aryl})\text{C}^2+\text{Cl}$  in 100%  $\text{H}_2\text{SO}_4$ . 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%  $\text{H}_2\text{SO}_4$ . Gillespie and Robinson now report in the immediately preceding communication that HCl establishes an equilibrium with  $\text{ClSO}_3\text{H}$  that is largely in favor of  $\text{ClSO}_3\text{H}$ . This one fact invalidates the first three lines of evidence and leads Gillespie and Robinson to propose that the product is actually  $\text{ArC}^+\text{Cl}_2$  formed according to the equation



We have investigated the n.m.r. spectra of solutions of  $\text{ArCCl}_3$  in acids ranging from 90%  $\text{H}_2\text{SO}_4$  to 30%  $\text{SO}_3$ -70%  $\text{H}_2\text{SO}_4$  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  $\text{ArCOOH}_2^+$  and  $\text{ArCO}^+$ , which were available from a similar set of studies on  $\text{ArCOOH}$  solutions.<sup>2</sup> The most surprising fact is that the n.m.r. spectrum reported for  $\text{ArC}^2+\text{Cl}$  is identical with that of  $\text{ArCOOH}_2^+$ , 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).