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MULTICHARGED CARBONIUM IONS - IV

STABLE CRYSTALLINE SALTS

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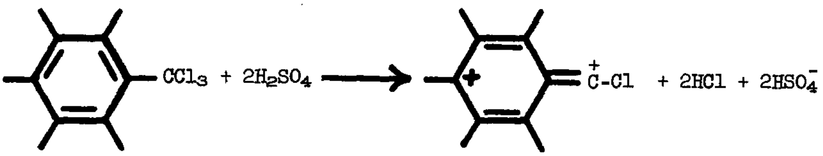
IN previous papers[1a-c] evidence was presented that trichloromethylpentamethylbenzene (I) and related compounds ionize in sulfuric acid as shown.



I II

Support for formation of dicarbonium ion II came from cryoscopic, stoichiometric and conductivity measurements on the acid solutions, and also from their visible, ultraviolet and N.M.R. spectra. It was pointed out[1a,b] that Lewis acids such as aluminum chloride or boron fluoride may also bring about the ionization of I to II. We now wish to report the isolation of pure crystalline salts of II.

In an apparatus protected at all times from atmospheric moisture, a slurry of 4.30 g of I in 20 ml of anhydrous liquid sulfur dioxide was treated with an SO_2 solution of HBF_4 (prepared by adding 5 g of anhydrous HF to a solution of 50 ml of SO_2 containing about 20 g of BF_3). The red-

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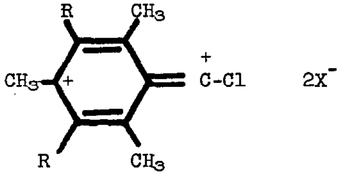
[1a] H. Hart and R.W. Fish, J. Amer. Chem. Soc. 80, 5894 (1958); [b] 82, 5419 (1960); [c] 83, 4460 (1961).

purple solution was stirred for 2 hr, then allowed to warm to room temperature and evacuated to dryness. Recrystallization of the dark red residue from liquid SO_2 gave a nearly quantitative yield of the bis-tetrafluoroborate (III), m.p. 147-148° (the crystals darkened above 130°). Because of sensitivity to moisture, the salt was not subjected to elemental analysis, but three analytical criteria were consistent with the assigned structure. Samples were hydrolyzed in 33 per cent aqueous acetone at room temperature for 15 min, then analyzed for BF_4^- (gravimetrically with nitron[2]), Cl^- (gravimetrically with silver ion) and titrated with standard sodium hydroxide for total acid (hydrolysis should give four equivalents of acid). [Found: BF_4, 46.6, 46.4; Cl, 9.42, 9.45; N.E., 90.5, 90.8. Calc. for $C_{12}H_{15}Cl(BF_4)_2$: BF_4, 47.1; Cl, 9.64; N.E., 92.1]. Hydrolysis gave a quantitative yield of pentamethylbenzoic acid. The N.M.R. spectrum of III in liquid SO_2 showed peaks at 7.40, 7.63 and 7.90 τ with relative areas 2:1:2 and the visible spectrum in the same solvent showed bands at 542 mμ (ε 2502), 393 mμ (ε 26,050) and 382 mμ (ε 25,390). These spectra differ only slightly from those of sulfuric acid solutions of I.[1b] The infrared spectrum of III (KBr pellet) showed an intense broad band at 8.9-9.7 μ characteristic of the tetrafluoroborate anion.[3]



III R = CH_3, X = BF_4
IV R = H, X = BF_4
V R = CH_3, X = BCl_4

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[2] W. Lange, *Ber. Dtsch. Chem. Ges.* 59, 2107 (1926).

[3] M.A. Battiste, *J. Amer. Chem. Soc.* 83, 4101 (1961); D.W.A. Sharp and N. Sheppard, *J. Chem. Soc.* 674 (1957).

In an entirely analogous manner IV was prepared from trichloromethylmesitylene.[1c] It was dark red, m.p. 127-128°. [Found: BF_4, 50.0, 49.9; Cl, 10.6, 10.7; N.E., 86.5, 86.6. Calc. for $C_{10}H_{11}Cl(BF_4)_2$: BF_4, 51.0; Cl, 10.4; N.E., 85.1]. Its N.M.R. spectrum in liquid SO_2 showed peaks at 3.04, 7.70 and 7.78 τ (relative areas 2:6:3) which agrees with the previous[1c] sulfuric acid spectrum.

The corresponding tetrachloroborates were prepared by reaction of the trichloromethyl compounds with boron trichloride in liquid SO_2 (attempts to use BCl_3 alone as reactant and solvent were unsuccessful). For example, to 0.89 g of I in 20 ml of liquid SO_2 there was added 1.57 g of boron trichloride. After stirring the red solution for 1 hr, the solvent and excess BCl_3 were removed and the dark residue was recrystallized from liquid SO_2, giving a nearly quantitative yield of V, m.p. 152-153°. The N.M.R. visible and ultraviolet spectra were nearly identical to those of III. Hydrolyzed samples were analyzed for chloride gravimetrically. [Found: Cl, 61.12. Calc. for $C_{12}H_{15}Cl(BCl_4)_2$: Cl, 63.82]. The infrared spectrum in liquid SO_2 (the region between 6.0 and 9.5 μ is obscured by the solvent) showed bands at 3.36, 3.45, 9.76, 10.35, 10.60, 11.52, 12.11, 12.46, 13.1-13.55 (broad), 14.06 and 14.40 μ. The broad band at 13.1-13.55 μ is due to the tetrachloroborate ion.[4]

Similar procedures have also been used to make aromatic acylium salts. For example, pentamethylbenzoylium tetrafluoroborate, prepared from the acid chloride, is a colorless crystalline salt, m.p. 120°, with N.M.R. bands at 7.64, 7.71 and 7.74 τ (relative areas 2:1:2) in liquid SO_2. [Found: BF_4, 32.6, 32.7; N.E., 132.1, 130.6. Calc. for $C_{12}H_{15}OBF_4$: BF_4, 33.1; N.E., 131.0].

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[4] W. Kynaston, B.E. Larcombe and H.S. Turner, J. Chem. Soc. 1772 (1960).

The salts described in this communication are virtually insoluble in carbon tetrachloride, chloroform, benzene and hexane, but soluble in ether, acetonitrile, trifluoracetic acid and liquid SO_2.

The study of preparation of other examples, and of their chemistry, is being continued[5].

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[5] Since this work was submitted, a detailed study of acylium (oxocarbonium) salts appeared [G.A. Olah, S.J. Kuhn, W.S. Tolgyesi and E.B. Baker, J. Amer. Chem. Soc. **84**, 2733 (1962)]. Also related to the present work is the reported isolation by H.H. Freedman and A.M. Frantz, Jr., J. Amer. Chem. Soc., in press, of a crystalline salt of the tetraphenylcyclobutene dication.