

THE SYNTHESIS OF FLUORAMMONIUM SALTS<sup>1</sup>

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Of the four possible fluorine-substituted ammonium ions, only the tetrafluoro derivative has been reported as a stable salt.<sup>2,3</sup> Difluoramine and trifluoramine have been reported to form reversible complexes with Lewis acids at low temperatures. Fluoramine was claimed to be a by-product of the electrolysis of ammonium bifluoride<sup>5,6</sup> but the results have been shown to be in error.<sup>7</sup> Dimethylfluoramine was synthesized by the fluorination of unsymmetrical dimethylsulfamide and the compound was sufficiently basic to form a stable hydrochloride.<sup>8</sup> Fluorimonium salts prepared by the rearrangement of alkyl difluoramines<sup>9</sup> can also be considered as alkylidene derivatives of substituted fluoramines.

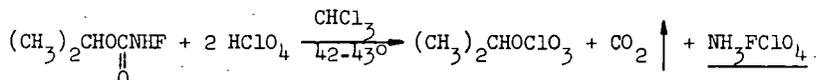
Simple salts of fluoramine have now been prepared by the reaction of alkyl N-fluorocarbamates with strong acids. The starting materials are synthesized readily by the fluorination of alkyl carbamates.<sup>10</sup>

Fluoramonium Bisulfate. Fluorimonium salts have been prepared and characterized in sulfuric acid. Under these conditions, the hydrolysis of N-fluorocarbamates in sulfuric acid would be expected to give the fluoramonium ion, which also should be stable.

When a solution of ethyl N-fluorocarbamate in concentrated sulfuric acid was heated at 85 to 90°, carbon dioxide and ethylene were evolved. The F<sup>19</sup> nmr spectrum of the sulfuric acid solution consisted of a quartet at 36.8 ppm relative to external trifluoroacetic acid, with a coupling constant of 38 cps. Thus, the fluorine was coupled to three equivalent hydrogens, and it is noteworthy that the hydrogens did not exchange rapidly with the solvent. By contrast, the F<sup>19</sup> spectrum of an unheated solution of ethyl N-fluorocarbamate in sulfuric acid consisted of a single broadened signal at 27.5 ppm; the NH protons of the starting material thus exchanged with the solvent rapidly by the nmr time scale.



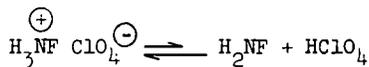
It is well-recognized that the maximum acid strength of a solution is limited by the acidity of the conjugate acid of the solvent. For this reason, perchloric acid is a stronger acid in acetic acid than in aqueous solution.<sup>13</sup> Perchloric acid is soluble in chloroform<sup>14</sup>; therefore, this solvent, which has very low basicity, should enhance the acidity. Indeed, isopropyl N-fluorocarbamate reacted more rapidly with a 10% solution of anhydrous perchloric acid in chloroform, than with the 70% commercial reagent. An additional advantage was that fluorammonium perchlorate was insoluble in chloroform. Analytically pure product was isolated directly in quantitative yield. The fate of the isopropyl group was not determined, but inasmuch as carbon dioxide free of propylene was liberated, it appears likely that isopropyl perchlorate was formed; if it was formed, it would remain in solution.<sup>15</sup>



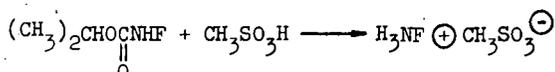
Fluorammonium perchlorate was a white solid which melted with decomposition at 104 to 105°. Differential thermal analysis showed a sharp exotherm at this temperature. The impact sensitivity was the same as that of RDX. The salt was hygroscopic and decomposed rapidly in the presence of atmospheric moisture. Although the synthesis and isolation was carried out in glass equipment under an atmosphere of dry nitrogen, some etching of the glass was visible after several hours of contact with the salt. However, samples have been stored at room temperature for several months, without decomposition, in fluorocarbon or passivated-nickel containers.

Fluorammonium perchlorate was insoluble in hydrocarbons and halocarbons; it was soluble in simple esters, nitriles, nitroalkanes, and in such ethers as monoglyme and tetrahydrofuran. It formed a 1:1 complex with dioxane. Concentrated solutions (e.g., 30 to 50%) in any solvents were unstable, and in several instances, fumed off shortly after they were prepared. Addition of chloroform to the ethyl acetate solution precipitated unchanged fluorammonium perchlorate.

The fluorine nmr spectrum of fluorammonium perchlorate in sulfuric acid consisted of a quartet ( $J = 44.1$  cps) at 34.3 ppm from trifluoroacetic acid ( $\phi = 110.8$ ), while the proton spectrum showed a doublet ( $J = 44$  cps) at 10.28  $\delta$ .<sup>16</sup> However, when acetonitrile was used as the nmr solvent, the proton spectrum gave a broadened singlet at 10.7  $\delta$ , while the fluorine spectrum gave a slightly unsymmetrical singlet at 122.4  $\phi$ . In ethyl acetate, the proton signal was a sharp singlet at 11.5  $\delta$ , and the fluorine signal was a sharp singlet at 122.8  $\phi$ . Thus, rapid hydrogen exchange took place in the organic solvents but not in sulfuric acid. If the mechanism of exchange were direct displacement of protons, a higher rate could be expected in sulfuric acid than in the organic solvents. The more basic solvents apparently allow dissociation of fluorammonium perchlorate, to a small extent, to fluoramine and perchloric acid. The high volatility of fluorammonium perchlorate, compared to that of ammonium perchlorate might also be the result of dissociation.

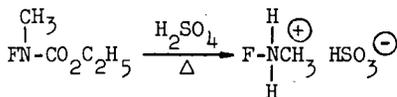


Fluorammonium Methanesulfonate - Fluorammonium methanesulfonate was synthesized by heating ethyl N-fluorocarbamate and methanesulfonic acid at 90°. The salt was precipitated by the addition of ether. The melting point and dta exotherm were essentially the same as those of the perchlorate, and of the perchlorate-dioxane complex; this temperature range appears to be the stability limit of the fluorammonium ion.

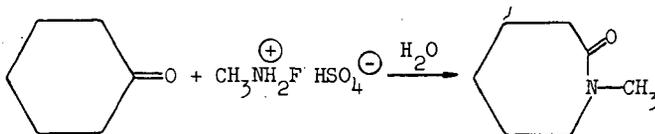


The infrared spectrum is described in the Experimental Section.

Methylfluorammonium Bisulfate - To determine whether substituted fluorammonium salts could be prepared by these methods, the reaction of ethyl N-fluoro-N-methylcarbamate with sulfuric acid was studied. Gas was evolved at 85 to 95°. The  $F^{19}$  nmr spectrum of the sulfuric acid solution consisted of an incompletely resolved triplet of quartets at -29.5 ppm (external trifluoroacetic acid reference), with coupling constants of 42 cps to the  $NH_2$  and 28 cps to the methyl.



A sulfuric acid solution prepared in this manner reacted with cyclohexanone and water to give N-methylcaprolactam.



These reactions are analogous to those of the unsubstituted fluorocarbamates and indicate broad applicability of the synthesis methods.

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16. One member of the doublet was obscured by the solvent signal in concentrated sulfuric acid, but was visible using 101% sulfuric acid.