

All of the above mentioned data indicate that the anion radical of the eight-member analog of benzyne has formed. The relative stability of II in comparison with benzyne is explained in part by the reduced ring strain caused by the triple bond in the eight-member system.

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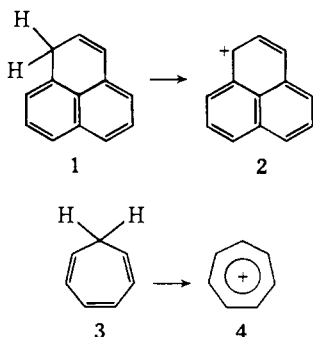
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### Carbonium Ion Formation by Oxidation of Hydrocarbons by Fluorosulfonic Acid Solutions

Sir:

The formation of carbonium ions from hydrocarbons in strong acids by a process which is formally a hydride abstraction is well known.<sup>1-3</sup> SbF<sub>5</sub> is known to be quite active<sup>4,5</sup> and both Olah and Hogeveen have presented evidence for hydride abstraction by a proton.<sup>6-9</sup> We wish to report that some hydrocarbons are oxidized to carbonium ions in fluorosulfonic acid with the concomitant production of sulfur dioxide. We also report the formation of carbonium ions by SO<sub>3</sub> oxidation in aprotic media. The formation of sulfur dioxide during the generation of carbonium ions from hydrocarbons in fluorosulfonic acid does not arise by reduction of SO<sub>3</sub> or fluorosulfonic acid by hydrogen. These observations, together with the report of facile hydride abstraction by SbF<sub>5</sub>,<sup>5</sup> indicate the existence of several mecha-



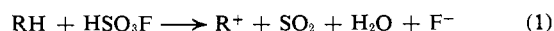
nisms for cation formation from hydrocarbons in superacids. Much work remains to be done in this area

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to unequivocally establish the mechanisms by which hydrocarbons form carbonium ions in superacids.

The compounds shown above give rise rapidly to the indicated carbonium ions when the hydrocarbons are dissolved in neat fluorosulfonic acid at 25°. In both cases the hydrocarbon was added slowly to a stirred solution of the acid. Carbonium ion structures were verified by nmr spectroscopy, the ions having been reported previously.<sup>10,11</sup> Gas samples were withdrawn into an evacuated bulb and analyzed by mass spectroscopy. Large peaks at *m/e* 64 and 48 were observed indicating the presence of SO<sub>2</sub> or SO<sub>3</sub>. No increase in the small background peak at *m/e* 2 was observed. To demonstrate that we would have detected hydrogen if it was present, we repeated the procedure using a small amount of zinc and sulfuric acid and observed a very large peak at *m/e* 2. Fluorosulfonic acid also was run in the mass spectrometer, and no peaks at *m/e* 64 and 48 were observed. To verify that these peaks were indeed due to SO<sub>2</sub>, classical qualitative analysis techniques were used since it proved impossible to distinguish between SO<sub>2</sub> and SO<sub>3</sub> using mass spectrometry.<sup>12</sup> Blank runs confirmed our ability to distinguish between SO<sub>2</sub> and SO<sub>3</sub>. No SO<sub>2</sub> could be detected in the vapors above pure fluorosulfonic acid, but a positive test for SO<sub>2</sub> was obtained following the generation of ions 2 and 4, confirming that the gas analyzed mass spectrometrically was SO<sub>2</sub>. Stirring fluorosulfonic acid with hydrogen gas produced no SO<sub>2</sub>, in agreement with earlier observations.<sup>13,14</sup>

The yields of carbonium ions vary with the precursor, the acid strength, and the mode of addition of the precursor to the acid. Using weighed amounts of tetramethylammonium bromide as an internal standard, the yield of ion from a precursor could be measured. Conversions ranging from 30% (cycloheptatriene in FSO<sub>3</sub>H at 25°) to 100% (cycloheptatriene oxidized with SO<sub>3</sub> in SO<sub>2</sub> at -28°) were observed. The other products were polymeric. The amount of SO<sub>2</sub> produced was determined by sweeping it out of the reaction mixture with a stream of dry N<sub>2</sub> into a standardized I<sub>2</sub> solution. The loss of I<sub>2</sub> was measured by titration with thiosulfate.<sup>15</sup> In all cases examined, SO<sub>2</sub> yields were within experimental error (±1%) of the cation yields determined by nmr. We cannot distinguish between oxidation by FSO<sub>3</sub>H or by SO<sub>3</sub> formed by the equilibrium dissociation of FSO<sub>3</sub>H. The overall stoichiometry is the same and is shown in eq 1.



In another experiment cycloheptatriene was treated with SO<sub>3</sub> in SO<sub>2</sub> solution at -78°. The tropylium ion was formed quantitatively and cleanly. In sulfuric acid, cycloheptatriene and phenalene also give the tropylium ion and phenalenium ion (2), respectively. Deno has observed that xanthene forms the xanthyl cation in aqueous sulfuric acid concentrations greater

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than 55%.<sup>16</sup> Both 4,4'-dimethoxydiphenylmethane and 4,4',4''-trimethoxytriphenylmethane also gave carbonium ions in concentrated sulfuric acid by a process that is formally a hydride abstraction.<sup>11</sup> The latter compound is cleaved in fluorosulfonic acid not oxidized.

The results described above can be rationalized by the oxidation of hydrocarbons to carbonium ions by FSO<sub>3</sub>H (or SO<sub>3</sub>). The oxidative generation of carbonium ions is not new; for example, they can be generated by oxidation with Br<sub>2</sub>,<sup>17,18</sup> and the preparation of the tropylium ion by oxidation with NO<sub>2</sub><sup>+</sup> has been reported.<sup>19</sup> Fluorsulfonic acid, if purified by distillation in glass, invariably contains some excess SO<sub>3</sub> due to the reaction of HF with the glass. SO<sub>3</sub> is known to be a strong oxidizing agent and is known to oxidize hydrocarbons to complex mixtures of products.<sup>20</sup>

In mixtures of fluorosulfonic acid and antimony pentafluoride, isobutane is converted smoothly to the *tert*-butyl carbonium ion.<sup>2</sup> This reaction has been presented both as a hydride abstraction by a proton<sup>3,21,22</sup> and as an oxidation by antimony pentafluoride.<sup>5</sup> We observed neither hydrogen nor sulfur dioxide when carrying out this reaction in SbF<sub>5</sub>-FSO<sub>3</sub>H mixtures. However, cycloheptatriene does yield SO<sub>2</sub> during the formation of the tropylium ion in these media. Thus it is clear that the cation formation from alkanes is proceeding by a mechanism different than that reported here. This suggests that the mechanism described here is limited to the formation of rather stable cations and that the stability of the cation plays a role in determining the process by which it is formed.

Apparently there are three processes by which carbonium ions can be generated from hydrocarbons in magic acid solutions: (1) oxidation by FSO<sub>3</sub>H (or SO<sub>3</sub>); (2) oxidation by SbF<sub>5</sub>; and (3) hydride abstraction by a proton. The sensitivity of these processes to the nature of the medium and the structure of the hydrocarbon has not yet been explored sufficiently.

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## Reaction of Plutonium Triiodide with Sodium in Liquid Anhydrous Ammonia

Sir:

Reduction of metal halides by an alkali metal in liquid anhydrous ammonia has been shown to produce the

elemental metal in the case of iron,<sup>1</sup> cobalt,<sup>2</sup> nickel,<sup>3,4</sup> titanium,<sup>5</sup> ruthenium,<sup>6</sup> rhodium,<sup>6</sup> palladium,<sup>6</sup> iridium,<sup>7</sup> osmium,<sup>8</sup> and bismuth,<sup>9</sup> although in most cases the product also contains metal amide and/or nitride. In the case of the more electropositive lanthanide and actinide elements, the metal is not produced to a significant degree; reaction of a solution of potassium in liquid anhydrous ammonia with samarium trifluoroacetate,<sup>10</sup> thorium tetrabromide,<sup>11</sup> and uranium(III) and -(IV) chloride and bromide<sup>12</sup> failed to produce the metal, the simple amide, or the nitride. There are no published reports of plutonium reactions in this system. We report in this communication our results from the reduction of plutonium(III) iodide with alkali metal-ammonia solutions to form the nitride in relatively high purity.

In a typical experiment, 100 ml of a 0.065 *M* solution of sodium in liquid anhydrous ammonia was added rapidly to 400 ml of a 0.01 *M* solution of PuI<sub>3</sub> in the same solvent at -45°. (The liquid anhydrous ammonia (Air Products "ultra high purity") was further purified by distillation before use.) A black, finely divided precipitate was obtained, which was separated by filtration, washed three times with 50-ml portions of liquid anhydrous ammonia, and dried overnight in a vacuum desiccator. Nitrogen content of the product (as determined by alkaline fusion followed by Kjeldahl distillation<sup>13</sup>) in a series of runs averaged 5.1 ± 0.5% (calculated for PuN, 5.5%) suggesting that the product contained approximately 10% impurity. This suspicion was supported by plutonium analyses of the product (by coulometric titration), which gave values in the 80-87% range (calculated for PuN, 94.5%). Infrared spectra of the product in the range 400-4000 cm<sup>-1</sup> failed to detect N-H bonds, indicating the absence of amides, imides, and ammoniates, the only other plausible nitrogen-containing species, and showed only a broad diffuse absorption of the type to be expected for a metal nitride. Residual sodium in the product, as determined by atomic absorption analysis, averaged about 0.5%. Qualitative tests for iodide were negative.

The conclusion based on elemental and infrared analyses that the as-precipitated material was plutonium nitride could not be verified by X-ray powder diffraction analysis, because of the lack of crystals large enough to permit a pattern to be obtained. However, samples of the product that were annealed under vacuum at 700° for 48 hr resulted in larger crystallites whose X-ray data,

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