

than 55%.¹⁶ 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.¹¹ 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 FSO₃H (or SO₃). The oxidative generation of carbonium ions is not new; for example, they can be generated by oxidation with Br₂,^{17,18} and the preparation of the tropylium ion by oxidation with NO₂⁺ has been reported.¹⁹ Fluorosulfonic acid, if purified by distillation in glass, invariably contains some excess SO₃ due to the reaction of HF with the glass. SO₃ is known to be a strong oxidizing agent and is known to oxidize hydrocarbons to complex mixtures of products.²⁰

In mixtures of fluorosulfonic acid and antimony pentafluoride, isobutane is converted smoothly to the *tert*-butyl carbonium ion.² This reaction has been presented both as a hydride abstraction by a proton^{3,21,22} and as an oxidation by antimony pentafluoride.⁵ We observed neither hydrogen nor sulfur dioxide when carrying out this reaction in SbF₅-FSO₃H mixtures. However, cycloheptatriene does yield SO₂ 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 FSO₃H (or SO₃); (2) oxidation by SbF₅; 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,¹ cobalt,² nickel,^{3,4} titanium,⁵ ruthenium,⁶ rhodium,⁶ palladium,⁶ iridium,⁷ osmium,⁸ and bismuth,⁹ 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,¹⁰ thorium tetrabromide,¹¹ and uranium(III) and -(IV) chloride and bromide¹² 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 PuI₃ 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 distillation¹³) 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⁻¹ 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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Table I. X-Ray Powder Diffraction Data for PuN

| Lattice planes (<i>hkl</i>) | PuN ^a <i>d</i> (Å) | Annealed reaction product ^b <i>d</i> (Å) |
|----------------------------------|----------------------------------|--|
| (111) | 2.83 | 2.83 |
| (200) | 2.45 | 2.45 |
| (220) | 1.73 | 1.73 |
| (311) | 1.48 | 1.48 |
| (222) | 1.42 | 1.42 |
| (400) | 1.23 | 1.23 |
| (331) | 1.12 | 1.13 |
| (420) | 1.10 | 1.10 |
| (422) | 1.00 | 1.00 |
| (511) | 0.943 | 0.944 |
| (440) | 0.867 | 0.868 |
| (531) | 0.829 | 0.830 |
| (600) | 0.818 | 0.818 |

Calculated lattice parameters: ^a PuN sample (prepared by conventional techniques at Oak Ridge National Laboratory), $a_0 = 4.905 \pm 0.001$ Å. ^b Annealed reaction product: $a_0 = 4.909 \pm 0.001$ Å; PuN $a_0 = 4.903$ – 4.908 Å (J. M. Cleveland, "The Chemistry of Plutonium," Gordon and Breach, New York, N. Y., 1970, p 413).

shown in Table I, was that of PuN and thus confirmed the identity of the product and the absence of an appreciable amount of metallic plutonium. Since the samples were heated *in vacuo* and since their nitrogen content did not increase during heating, the possibility that the nitride was formed during annealing must be ruled out.

The relatively complete reaction to form plutonium nitride contrasts with the behavior of the transition metals cited above, which generally form mixtures of the metal, the amide, and the nitride. We believe that this difference is caused primarily by the greater reactivity of plutonium. A possible mechanism involves reduction of plutonium(III) to plutonium(0), which then reacts with ammonia to form the nitride. Although metallic plutonium and plutonium hydride do not react with ammonia at an appreciable rate at low temperatures, the reaction is rapid at 600° and in fact is a common method for the preparation of PuN. In the present case, individual atoms of plutonium could react with ammonia as soon as they are formed, before they have an opportunity to aggregate into larger—and hence less reactive—particles. Under these conditions, it is reasonable to expect that reaction with ammonia could occur at low temperatures. Support for this postulated mechanism was also obtained from an experiment in which an ammonia solution of PuI₃ was electrolyzed to produce a cathode deposit containing 3.4% nitrogen, suggesting partial conversion of the metal deposit to the nitride. (This experiment was not repeated because of the formation of explosive NI₃ on the anode.) The reaction would not occur as readily with transition metals, however, because of their lower reactivity.

Another possible mechanism involves the formation of small quantities of plutonium(0), which catalyzes the reaction of sodium with ammonia to form amide; the latter reacts with plutonium(III) to produce plutonium amide which is then deammoniated to form the nitride. This possibility was investigated by treating a NaNH₂ solution in ammonia with a solution of PuI₃ in the same solvent; a red-brown gelatinous precipitate was obtained which, after washing and vacuum drying, was found to contain less than 2% nitrogen—far too low for either PuN or Pu(NH₂)₃. (Also, the infrared spectrum of the product indicated the absence of N–H bonds.)

Hence, the mechanism involving formation of plutonium amide appears unlikely.

In addition, the potassium solutions used in the earlier work are known to have a greater tendency than sodium toward ammonolysis to form the amide,¹⁴ and this can react competitively with metal ions to precipitate the respective amide, thus yielding a mixed product. Use of sodium in the present experiments would therefore lead to a purer precipitate.

Reactions of uranium and thorium have also been investigated. Results of these experiments, as well as a more complete description of the plutonium studies and their possible practical significance will be published elsewhere.

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Synthesis and Characterization of Di- μ -thiocyanato-bis[hydrogen bis(diphenylphosphinato)]dipalladium(II). A Complex Containing a Novel Symmetrically Hydrogen-Bonded Anion

Sir:

The reactions of coordinated ligands have provided synthetic routes to many novel compounds, such as metal carbene complexes or macrocyclic chelates. The reactivity of coordinated phosphorus ligands,¹ however, has not been studied extensively in spite of the importance of phosphines in coordination chemistry. The tertiary alkyl- or arylphosphine complexes were reported to be resistant to attack by water although the chlorophosphine complexes of Pt(II) and Pd(II) can be readily hydrolyzed.² In contrast, we have found that the acetylenic phosphine complexes MCl₂(Ph₂PC-CCF₃)₂, M = Pd or Pt and Ph is phenyl, undergo hydrolysis with cleavage of the alkynyl groups and the formation of chloro-bridged dimers. The analogous bromo and thiocyanato complexes were prepared by metathetical reactions. The unusual nature of these complexes prompted an X-ray crystal structure study of the thiocyanato-bridged species Pd₂(SCN)₂[(Ph₂PO)₂H]₂ which has revealed the existence of the unusual hydrogen bis-(diphenylphosphinate) anion. This anion contains a rare symmetrical hydrogen bond between the Ph₂PO moieties. Furthermore, our results may be of more

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