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(17) Additionally, μ-$Me_3MC_2B_4H_7$ (M = Sn, Pb) fail to undergo isomerization[13e] as do μ transition-metal derivatives of $C_2B_4H_8$.
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(21) Ruthenium-catalyzed exchange of deuterium with hydrogen bound to boron in 1,2- or 1,7-$C_2B_{10}H_{12}$ also occurs preferentially at the sites regarded as most prone to nucleophilic attack.[4]

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Electron Spin Resonance Evidence for the Formation of the NF_3^+ Radical Cation as an Intermediate in the Syntheses of NF_4^+ Salts by Low-Temperature Ultraviolet Photolysis

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Received July 18, 1977

The mechanism of the formation of NF_4^+ salts is of significant practical and theoretical interest. From a practical point of view, a better understanding of this mechanism would permit optimization of the reaction conditions for the direct syntheses of NF_4^+ salts, such as NF_4BF_4, NF_4PF_6, or NF_4GeF_5.[1] From a theoretical point of view, the formation of the NF_4^+ cation is intriguing[2] because its parent molecule NF_5 does not exist as a stable species. Since under the conditions used for most of the syntheses of NF_4^+ salts an F^+ cation should be extremely difficult, if not impossible, to prepare by chemical means, the following mechanism has previously been proposed[2] for the formation of NF_4AsF_6:

$$F_2 \xrightarrow{\Delta E} 2F\cdot \tag{1}$$

$$F\cdot + AsF_5 \rightarrow AsF_6\cdot \tag{2}$$

$$AsF_6\cdot + NF_3 \rightarrow \dot{N}F_3{}^+AsF_6{}^- \tag{3}$$

$$\dot{N}F_3{}^+AsF_6{}^- + F_2 \rightarrow NF_4{}^+AsF_6{}^- + F\cdot \tag{4}$$

In good agreement with the known experimental facts,[2] this mechanism requires only a moderate activation energy ($D°(F_2) = 36.8$ kcal mol^{-1}).[3] The two critical intermediates are the $AsF_6\cdot$ radical and the $\dot{N}F_3^+$ radical cation. Whereas the $AsF_6\cdot$ radical is unknown, the $\dot{N}F_3^+$ radical cation was shown[4] to form during γ irradiation of NF_4^+ salts at −196 °C. Although this observation of the $\dot{N}F_3^+$ cation demonstrated its possible existence at low temperature, it remained to be shown that the $\dot{N}F_3^+$ radical cation is indeed formed as an intermediate in the syntheses of NF_4^+ salts. We have now succeeded in observing experimentally the $\dot{N}F_3^+$ radical cation by ESR spectroscopy as an intermediate in the low-temperature UV photolyses of both the NF_3–F_2–AsF_5 and the NF_3–F_2–BF_3 systems. The results and implications derived from the observations are given in this paper.

Experimental Section

Binary and ternary mixtures of the starting materials were prepared for both the NF_3–F_2–BF_3 and the NF_3–F_2–AsF_5 systems in a stainless-steel Teflon FEP vacuum system. The sample tubes consisted of flamed-out quartz tubes of 4-mm o.d., 30-cm long, with a ballast volume of about 150 mL attached at the top. The starting materials were condensed into these tubes at −210 °C and the tubes were flame sealed. The NF_3 (Rocketdyne) was used without further purification, F_2 (Rocketdyne) was passed through a NaF scrubber for HF removal, and BF_3 (Matheson) and AsF_5 (Ozark Mahoning) were purified by fractional condensation prior to use. About 300 cm^3 of gas mixture was used for each sample tube in the following mole ratios: $NF_3{:}F_2 = 1{:}10$; $BF_3{:}F_2 = 1{:}10$; $AsF_5{:}F_2 = 1{:}10$; $NF_3{:}BF_3 = 1{:}1$; $NF_3{:}AsF_5 = 1{:}1$; $NF_3{:}F_2{:}BF_3 = 1{:}4{:}1$ and $1{:}2{:}1$; $NF_3{:}F_2{:}AsF_5 = 1{:}4{:}1$.

The ESR spectra were recorded as previously described.[5,6] Variable-temperature control over the temperature range 4–300 K was achieved with an Air Products liquid-helium-transfer refrigerator, Model LTD110. For the photolyses, an Oriel Model 6240 arc lamp with a 200-W Hg lamp was used. In some of the experiments, the starting materials were condensed at −196 °C into the tip of the ESR tube and were irradiated for 10–30 min while inserted in a liquid-nitrogen-filled unsilvered Dewar. The ESR tube was then quickly transferred to the precooled ESR spectrometer. In other experiments, the sample tubes were irradiated at various temperatures inside the ESR cavity.

Results and Discussion

UV photolysis of both the NF_3–F_2–AsF_5 and the NF_3–F_2–BF_3 systems produced an intensely violet species which exhibited the ESR signal shown in Figure 1, traces A and B. Comparison with the previously published[4] anisotropic spectrum of the $\dot{N}F_3^+$ cation (trace C, Figure 1) establishes beyond doubt the presence of $\dot{N}F_3^+$ in our samples. The spectra are assigned on the basis of anisotropic hyperfine coupling to three fluorine atoms ($I = {}^1/_2$) and approximately isotropic hyperfine coupling to one nitrogen atom ($I = 1$). The **g** matrix is isotropic to within the line width. The spectra thus appear as a quartet of triplets as shown in Figure 1. The broader line widths observed in the spectra of UV-irradiated NF_3–F_2–AsF_5 and NF_3–F_2–BF_3 mixtures than in γ-irradiated NF_4SbF_6 may be the result of exchange or of dipolar interactions of materials on the surfaces of the solid components of the mixtures.

The observation of identical signals for both the BF_3- and the AsF_5-containing system proves that the signal must be due to a species not containing boron or arsenic. By carrying out irradiation experiments of the sample within the ESR cavity at −196 °C, it was shown that the signal strength increased during irradiation but did not decrease when the lamp was turned off. The thermal stability of the signal in the absence of UV radiation depended on the strength of the Lewis acid used. For the stronger Lewis acid AsF_5, the signal did not change significantly up to about −105 °C, whereas for BF_3 decomposition started at about −155 °C. When the sample tubes were warmed to ambient temperature, they contained white stable solids which were identified by Raman spectroscopy as NF_4AsF_6 and NF_4BF_4, respectively.[1,7,8] Irradiation of all possible binary mixtures, i.e., NF_3–F_2, Lewis acid–F_2, and NF_3–Lewis acid, under comparable conditions did not produce any ESR signal attributable to $\dot{N}F_3^+$.

A positive identification of the proposed $AsF_6\cdot$ or $BF_4\cdot$ radical intermediates was not possible in the above experi-

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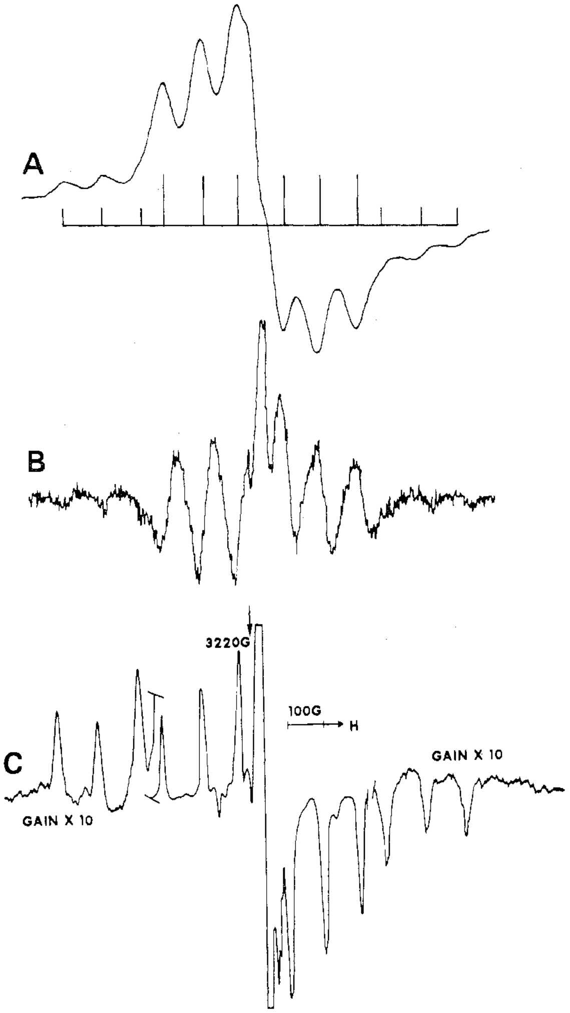

Figure 1. ESR spectra of the $\dot{N}F_3{}^+$ radical cation obtained by UV photolysis of NF_3–F_2–BF_3 at −196 °C: trace A, first derivative; trace B, second derivative. For comparison, the known[4] first-derivative spectrum of $\dot{N}F_3{}^+$ obtained by γ irradiation of polycrystalline NF_4SbF_6 at −196 °C is given as trace C.

ments. The observation of hyperfine splittings for the free $AsF_6\cdot$ or $BF_4\cdot$ radical at temperatures above several Kelvins is not likely because they would be in orbitally degenerate states which could cause rapid spin relaxation resulting in a strongly temperature-dependent line width. Furthermore, if we assume the existence of an $AsF_6\cdot$ or $BF_4\cdot$ radical in an ionic lattice, rapid electron exchange between the radicals and the corresponding anions is possible which would destroy hyperfine structure. The line width of the resulting signal would depend on the rate of exchange. Finally, in our experiments we were dealing with polymeric solid AsF_5 or BF_3 phases which on combination with a fluorine radical are not likely to result in an isolated $AsF_6\cdot$ or $BF_4\cdot$ radical. In our experiments, several ESR signals were observed in addition to $\dot{N}F_3{}^+$. However, in the absence of observable hyperfine structure we prefer not to make any assignments.

On the basis of our results, the following conclusions can be reached concerning the formation mechanism of $NF_4{}^+$ salts. (i) The $\dot{N}F_3{}^+$ radical cation is indeed an important intermediate. (ii) The requirement of UV activation and of both F_2 and a Lewis acid for the synthesis of $\dot{N}F_3{}^+$ is in agreement with steps 1 and 2 of the given mechanism. (iii) The strength of the Lewis acid determines the thermal stability and lifetime of the intermediate $\dot{N}F_3{}^+$ salt formed. This can account for the low-temperature conditions required for the synthesis of the $NF_4{}^+$ salts of weaker Lewis acids. (iv) In the absence of UV irradiation, the $\dot{N}F_3{}^+$ salts do not spontaneously react with the large excess of liquid F_2 present. This indicates that in the absence of an activation energy source the thermodynamically feasible[2] chain-propagation step $\dot{N}F_3{}^+AsF_6{}^- + F_2 \rightarrow NF_4{}^+AsF_6{}^- + F\cdot$ does not play an important role. Possibly, the conversion of $\dot{N}F_3{}^+AsF_6{}^-$ to $NF_4{}^+AsF_6{}^-$ may require $F\cdot$ atoms according to

$$\dot{N}F_3{}^+AsF_6{}^- + F\cdot \rightarrow NF_4{}^+AsF_6{}^- \qquad (5)$$

Since the intermediate $\dot{N}F_3{}^+$ salt is an ionic solid, its reaction with a fluorine atom might well be a heterogeneous diffusion-controlled reaction and step 5 might be the rate-determining step in the mechanism. It was shown that at temperatures above −196 °C, where a given $\dot{N}F_3{}^+$ salt is still stable in the absence of light, UV irradiation causes a rapid decay of the $\dot{N}F_3{}^+$ ESR signal. However, it was not possible to distinguish whether this decay was caused by photodecomposition of the intermediate $\dot{N}F_3{}^+$ salt or by the reaction of the latter with the generated F atoms according to step 5.

Acknowledgment. We are grateful to Mr. R. D. Wilson for experimental help and to Drs. L. R. Grant, C. J. Schack, and W. Wilson for helpful discussions. This work was financially supported by the Power and Chemistry Programs of the Office of Naval Research and by the U.S. Army Research Office.

Registry No. $\dot{N}F_3{}^+$, 54384-83-7; NF_4AsF_6, 16871-75-3; NF_4BF_4, 15640-93-4.

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Attachment of 1,2-Dicarbadodecaborane(12) to Polystyrene. Catalysis by a Polymer-Bound Rhodium Complex

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Received June 7, 1977

Paxon and Hawthorne[1] reported the preparation of hydridorhodium carboranes and their use as homogeneous hydrogenation and isomerization catalysts. We obtained similar results for a hydridorhodium thiaborane.[2] The attachment of homogeneous rhodium catalysts to polystyrene, their reactions, and their advantages have been studied by Grubbs[3] Collman,[4] and Pittman[5] and their co-workers. Although we have been unable to devise a convenient means to attach a thiaborane to polystyrene, we report here a scheme for the attachment of carborane to polystyrene and its conversion to a polymer-bound rhodium complex which functions as a hydrogenation catalyst.[1]