the ready dehydrogenation of ethylamine–borane at temperatures just above room temperature, and considering the inlet temperature of the mass spectrometer of *ca.* 170°, this observation cannot be taken as an indication for the formation of the aminoborane in the electrolysis procedure.

Tris(ethylamino)borane. In the course of this work tris(ethylamino)borane, $B(NHC_2H_5)_3$,[11] was isolated as a product of the thermal decomposition of ethylamine–borane in the presence of excess ethylamine.

The boron-11 chemical shift of tris(ethylamino)borane was observed on the neat liquid at δ −23.5 ppm which value is in agreement with data reported for other tris(amino)boranes. Solutions of the material in deuteriochloroform gave ^{1}H chemical shift values of δ 1.08 (triplet, CH_3-CH_2) and 2.90 ppm (quartet, CH_3-CH_2), in a 3:2 ratio (J_{HCCH} = 7 ± 0.5 Hz). No resonance signal could be identified for the nitrogen-bonded protons, probably due to quadrupole broadening. The infrared spectrum of the material compared with literature data.[12]

Registry No. $NaBH_4$, 16940-66-2; $C_2H_5NH_2 \cdot BH_3$, 15860-41-0; ethylamine, 75-04-7.

Acknowledgment. This work was supported by the Department of Defense under Project Themis Contract DAAB07-69-C-0366, administered by the U. S. Army Electronics Command, Fort Monmouth, N. J.

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Kinetics and Mechanism of Isomerization of α-Carbonato(triethylenetetramine)cobalt(III) Ion in Basic Aqueous Solution

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Received August 3, 1972

The tris-chelated complexes of cobalt(III) exhibit, almost without exception, unusual resistance to stereochemical rearrangement involving the cobalt(III) center. The racemization rates, for example, are exceedingly slow in aqueous solution except at elevated temperatures (usually well in excess of 50°) for such species as the tris(ethylenediamine),[1] bis(ethylenediamine)oxalato,[2] and bis(ethylenediamine)carbonato[3] complexes of cobalt(III). More recent studies[4,5] have demonstrated a similar stability for a number of β-diketone–cobalt(III) derivatives. The only apparent exception to this pattern is for the tris(oxalato) species,[6,7] the behavior of which, however, is complicated by the oxalate-cobalt(III) redox couple which, surprisingly enough, is not at all operative in the monooxalato system mentioned above.[2] With two of the bidentate species replaced by a tetradentate ligand such as triethylenediaminetetramine (trien) the same resistance to rearrangement at the cobalt(III) center is still observed[8] as expected, though loss of optical activity at other centers of asymmetry may occur rather readily even at room temperature.[9,10] The present study concerns the geometrical rearrangement of the "α" form of the tris-chelate complex ion $Co(trien)CO_3^+$ to the "β" analog, which occurs at a conveniently measurable rate in slightly basic aqueous solution at temperatures in excess of 50°. The pH dependence of the reaction, coupled with a knowledge of other kinetic and equilibrium properties of this complex ion,[11] enables some definite conclusions to be drawn concerning the mechanism of the isomerization.[12]

Experimental Section

α-Carbonato(triethylenetetramine)cobalt(III) perchlorate was prepared from *cis*-dichloro(triethylenetetramine)cobalt(III) following the method of Sargeson and Searle.[13] β-Carbonato(triethylenetetramine)cobalt(III) perchlorate was prepared as described in our earlier study.[11] The purity of the complexes was checked by analysis,[14] yielding the following data. *Anal.* Calcd for $[Co(trien)CO_3]ClO_4 \cdot H_2O$: Co, 15.40; C, 21.96; H, 5.23; N, 14.64. Found for α species: Co, 15.30; C, 21.85; H, 5.30; N, 14.50. Found for β species: Co, 15.35; C, 21.88; H, 5.30; N, 14.63.

The isomerization was studied at 55, 60, and 65° and $I = 0.5\ M$ ($NaClO_4$) on a Beckman DU spectrophotometer with a Gilford Model 220 digital readout attachment, utilizing the 503-nm peak at which the change in absorbance during the reaction is conveniently large.[15] The requisite amounts of sodium borate, perchloric acid (or sodium hydroxide, depending on the desired pH[16]), and sodium perchlorate solutions were placed in a 25-ml flask and thermostated long enough to achieve temperature equilibrium. A weighed amount of solid complex was then added and quickly dissolved, and the solution was made up to volume by addition of water at the experimental temperature. Aliquots of the borate-buffered reaction mixture were withdrawn at suitable intervals by means of an ice-jacketed pipet and the absorbances (A) were quickly determined, as were the pH's (utilizing a Beckman Expandomatic pH meter).

Results and Discussion

The pseudo-first-order rate constants for the α to β conversion were evaluated from conventional log $(A_\infty - A_t)$ *vs.* time plots, which were linear during several half-times of reaction. The final spectra indicated that the product was entirely the β form of the complex. Data were obtained at three temperatures within the acidity range $7 < pH < 10$ and are recorded in Table I. Plots of these data are sigmoid in form with a clearly apparent tangential approach to minima in the observed rate constant, k_{obsd}, below pH 8. There also appears to be an approach to maxima above pH 10 but it was

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Table I. Effect of Hydrogen Ion Concentration on the Rate of the $\alpha \rightarrow \beta$ Isomerization of the Co(trien)CO_3^+ Ion[a]

55°		60°		65°	
pH	$10^4 k_{obsd}$, sec^{-1}	pH	$10^4 k_{obsd}$, sec^{-1}	pH	$10^4 k_{obsd}$, sec^{-1}
7.2	1.0	7.1	2.1	7.5	4.0
7.8	1.0	7.2	2.2	7.8	4.1
8.2	1.2	7.6	2.0	8.0	4.3
8.3	1.1	7.8	2.1	8.25	4.6
8.35	1.1	8.0	2.0	8.5	5.5
8.55	1.3	8.1	2.0	8.55	6.0
8.65	1.3	8.2	2.55[b]	8.65	6.6
8.8	1.6	8.4	2.6	8.7	6.9
8.9	1.75	8.5	2.8	8.8	7.3[c]
9.1	2.1	8.6	3.3	9.0	8.1
9.4	2.6	8.65	3.35	9.2	9.0
9.8	3.4	8.75	3.2	9.35	9.4
10.0	3.55	8.8	3.35[b]	9.6	9.8
10.3	3.65	8.9	3.4	9.95	10.2
		9.0	3.8[b]	10.2	10.5
		9.2	4.7		
		9.3	4.8		
		9.65	5.45[b]		
		10.0	5.65		
		10.3	5.5		

[a] [Co(trien)CO_3^+] = 0.005 *M*; ionic strength 0.5 *M*. [b] Mean of two runs. [c] Mean of three runs.

impossible to establish this fact unequivocally due to the parallel base hydrolysis of the complex which becomes competitive above pH 10. The nature of the k_{obsd} *vs.* pH relationship is typical of a system involving an acid-base equilibrium with different rate constants governing the reactions of the acidic and basic forms. A simple mechanism which is in keeping with this concept and is consistent with much of the known chemistry[11,17] of tetraminecobalt(III)-carbonato complexes is presented in Figure 1. This involves as its first step the rapid water-promoted ring-opening equilibration of the α species, governed by the equilibrium constant K^{α}_1, the product of which is in equilibrium with its conjugate base form as determined by the acid dissociation constant K^{α}_2. The rate constants for isomerization of the acidic and basic forms of the ring-opened α complex are k_1 and k_2, respectively, with equilibrium constants for the product β complex K^{β}_1 and K^{β}_2. The latter are the analogs of the constants already defined for the α species. The rate law which corresponds to this mechanism takes the form

$$k_{obsd} = \frac{k_1 K^{\alpha}_1 (H^+) + k_2 K^{\alpha}_1 K^{\alpha}_2}{(H^+) + K^{\alpha}_1 (H^+) + K^{\alpha}_1 K^{\alpha}_2} \quad (1)$$

Since K^{α}_1 is known to be much less than unity[17] and pK^{α}_2 must be[18] close to 9, it is obvious from eq 1 that k_{obsd} approaches $k_1 K^{\alpha}_1/(1 + K^{\alpha}_1)$ as a limit at the low-pH end of the experimental data, enabling determination of the latter composite constant quite accurately from the flat portion of the sigmoid curve below pH 8. However, as was stated earlier, the high-pH limit of the curve is not attainable experimentally, though k_{obsd} approaches k_2 as a limit at very high pH. We are well below this limit but have found it possible to evaluate k_2 by means of a linear approximation procedure. At the low-pH end it is seen that eq 1 reduces to

$$k_{obsd} = \frac{k_1 K^{\alpha}_1}{1 + K^{\alpha}_1} + \frac{k_2 K^{\alpha}_1 K^{\alpha}_2}{(1 + K^{\alpha}_1)(H^+)} \quad (2)$$

A plot of k_{obsd} *vs.* $1/(H^+)$ should be linear up to pH ~8.5 and will yield an intercept (I_1) of $k_1 K^{\alpha}_1/(1 + K^{\alpha}_1)$ and a slope (S_1) of $k_2 K^{\alpha}_1 K^{\alpha}_2/(1 + K^{\alpha}_1)$. At the moderately high-pH end (pH >8.5), one can use the full eq 1 in the form

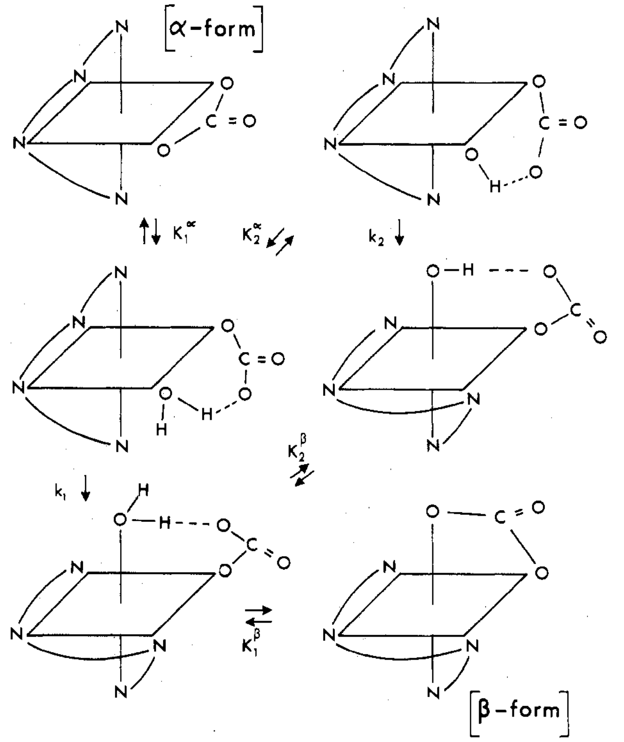

Figure 1. Mechanism of $\alpha \rightarrow \beta$ isomerization of the Co(trien)CO_3^+ ion.

$$\frac{I_1(H^+) + S_1}{k_{obsd}} = (H^+) + \frac{K^{\alpha}_1 K^{\alpha}_2}{1 + K^{\alpha}_1} \quad (3)$$

When the left-hand side of eq 3 is plotted against (H^+), a straight line should be obtained of intercept $K^{\alpha}_1 K^{\alpha}_2/(1 + K^{\alpha}_1)$ which when divided into S_1 yields k_2. This plotting procedure for the 60° data is illustrated in Figure 2.

The results of the graphic analysis of the three sets of experimental data are presented in Table II, along with the derived temperature variation parameters. The internal consistency of the figures is confirmed by the following test. One can readily derive from eq 1 that $pK^{\alpha}_1 K^{\alpha}_2/(1 + K^{\alpha}_1)$ is equivalent to the pH at which $k_{obsd} = {}^1/_2[k_1 K^{\alpha}_1/(1 + K^{\alpha}_1) + k_2]$, *i.e.*, the halfway point between the low-pH minimum and the high-pH maximum. Inspection of the data of Table I in these terms shows that, for example, the expected value of $pK^{\alpha}_1 K^{\alpha}_2/(1 + K^{\alpha}_1)$ is about 9.1, in good agreement with the 9.3 value indicated by the I_2 figure of Table II.

Unfortunately, it is not possible to isolate values for k_1 and K^{α}_1 specifically from these experiments, but some reasonable estimates may be made. It is known[18] that for the closely related complex ion Co(tren)CO_3^+ (tren = tris(β-aminoethylamine)) pK^{α}_2 = 8.66 at 20° and I = 0.1 *M*. Assuming the same kind of temperature dependence for this constant as for bicarbonate ion[19] one might expect a decrease of about 0.4 log unit over the 40° temperature range, suggesting a value for pK^{α}_2 at 60° of about 8.3. This puts K^{α}_1 at this temperature at about 0.1, a quite acceptable value in view of the known data at lower temperatures.[17] This figure leads to a value for k_1 at 60° of about 2×10^{-3}, 3 times as great as k_2 under the same conditions. The enthalpy of activation for k_1 cannot be unequivocally separated from ΔH^{α}_1, since the temperature-dependence data for I_2 (Table II) are not very

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Table II. Rate Parameters for the α → β Isomerization of the $Co(trien)CO_3^+$ Ion[a]

	55°	60°	65°
$I_1 = \dfrac{10^4 k_1 K^\alpha{}_1}{1 + K^\alpha{}_1}$ (sec^{-1})[b]	0.95 ± 0.05	1.91 ± 0.03	3.68 ± 0.09
$S_1 = \dfrac{10^{13} k_2 K^\alpha{}_1 K^\alpha{}_2}{1 + K^\alpha{}_1}$ $(M^{-1}\ sec^{-1})$	1.0 ± 0.1	3.1 ± 0.2	6.2 ± 0.3
$I_2 = \dfrac{10^{10} K^\alpha{}_1 K^\alpha{}_2}{1 + K^\alpha{}_1}$ (M^{-1})	2.3 ± 0.2	4.6 ± 0.5	5.5 ± 0.1
$S_1/I_2 = 10^4 k_2$ (sec^{-1})[c]	4.3 ± 0.6	6.7 ± 1.0	11.3 ± 0.7

[a] Error limits quoted are the standard deviations derived from least-squares analyses of the various linear plots. [b] $\Delta H^\ddagger{}_1 + \Delta H^\alpha{}_1 = 29 \pm 1$ kcal/mol; $\Delta S^\ddagger{}_1 + \Delta S^\alpha{}_1 = 12 \pm 2$ eu. [c] $\Delta H^\ddagger{}_2 = 21 \pm 1$ kcal/mol; $\Delta S^\ddagger{}_2 = -11 \pm 2$ eu.

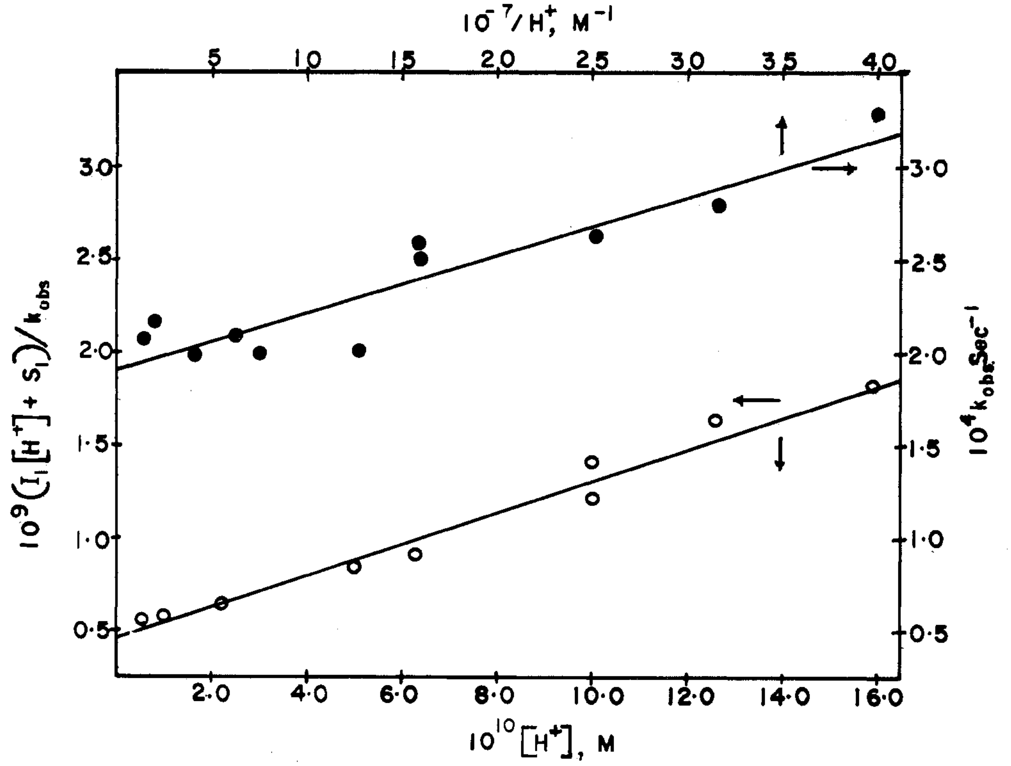

Figure 2. Linear plot of data at 60°: closed circles, k_{obsd} *vs.* $1/(H^+)$ for pH ≤8.5, to yield intercept I_1 and slope S_1; open circles, $(I_1(H^+) + S_1)/k_{obsd}$ *vs.* (H^+) for pH ≥8.5, to yield I_2 and S_2.

conclusive and one must use an assumed value of $\Delta H^\alpha{}_2$ in any case. However, a reasonable guess for $\Delta H^\alpha{}_1$ is about 10 kcal/mol so that $\Delta H^\ddagger{}_1$ and $\Delta H^\ddagger{}_2$ are almost identical at close to 20 kcal/mol, a value somewhat lower than is found for isomerizations of cobalt(III) diaquobis(ethylenediamine) chelates, for which the activation enthalpies are between 25 and 30 kcal/mol.[20]

The minor difference in the isomerization rate constants for the acidic and basic forms of the ring-opened complex supports an "intramolecular twist" mechanism for the process rather than a "five-coordinate intermediate" mechanism. For the former, the transition states for the k_1 and k_2 reactions (see Figure 1) will be almost identical, while for the latter one must visualize dissociation of water and hydroxyl groups, respectively, to form either square-pyrimidal or trigonal-bipyrimidal intermediates which retain the carbonate group. In general, there are fairly large differences in the rates of dissociation of water and hydroxyl from a cobalt(III) center,[20] though in the present instance the dissociation of either or both groups may well be promoted by the presence of the cis carbonate ligand. However, inspection of models of the $Co(trien)CO_3^+$ stereoisomers does not indicate that either type of five-coordinate intermediate can do much to facilitate rearrangement of the nitrogen-carbon atom skeleton of trien from α to β geometries, since the interchange of nitrogen ligands is necessary to achieve isomerization no matter what happens to the ligands in the fifth and sixth positions. It is of interest that the inversion rate[3] of d-$Co(en)_2CO_3^+$ at pH 9 and 60° is 10^{-4} sec^{-1} as compared to the 4×10^{-4} sec^{-1} value for the α to β trien complex reaction. Since the enthalpies of activation are also of similar magnitude, it seems very likely that the two reactions are closely related. It is known that carbonate ion dissociation is of no significance to the former process, since it was established[3] that carbonate exchange is much more rapid than racemization and obeys different rate laws, adding further credence to the "twist" concept of the isomerization mechanism.

Registry No. α-Carbonato(triethylenetetramine)cobalt(III) perchlorate, 36994-86-2; β-carbonato(triethylenetetramine)cobalt(III) perchlorate, 35322-62-4.

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Acknowledgment. Support of this research by the National Science Foundation under the terms of Grant No. GP-10641 to the State University of New York at Buffalo is gratefully acknowledged.

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Improved Synthesis and Ground State Nuclear Magnetic Resonance Spectra of Tetrafluorophosphorane

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Received August 22, 1972

The synthesis of tetrafluorophosphorane, HPF_4, was first accomplished by the reaction of hydrogen fluoride with phosphorous acid.[1,2] However, only small yields (~20%) of HPF_4 are realized in this synthesis; moreover the method requires the use of Kel-F and Monel vacuum line equipment for handling the hydrogen fluoride. More recently Treichel, Goodrich, and Pierce[3] reported that slightly improved yields (~30%) of HPF_4 can be obtained from the gas-phase reaction of $(CH_3)_3SnH$ with PF_5. This synthesis has the advantage that it does not require special vacuum line equipment; however it has the disadvantage that the HPF_4 is difficult to separate from the concomitantly formed H_2PF_3. It was, therefore, desirable to develop a more facile, higher yield synthesis of HPF_4.

Previous nmr studies[2,3] of HPF_4 have demonstrated that the fluorine nuclei remain equivalent down to −114°. Microwave spectroscopic data[4] for HPF_4 and DPF_4 could be satisfactorily accommodated in terms of a C_{2v} structure in which the hydride ligand occupies an equatorial site of a trigonal bipyramid; however, a less likely rectangular-pyramidal C_{2v} model with four fluorine atoms in a single set of equivalent positions could not be eliminated from consideration. In this article we report more extensive low-temperature ^1H and ^{31}F nmr data which are pertinent to the ground-state structure of HPF_4.

Experimental Section

Materials. Trimethylchlorosilane and $NaBH_4$ were procured commercially and used without subsequent purification. Diglyme[bis(2-methoxyethyl) ether] was purified by treatment with, vacuum distillation from, and storage over $LiAlH_4$. Prior to use the diglyme was vacuum distilled from $LiAlH_4$. Phosphorus pentafluoride (Matheson Gas Products) was purified by trap to trap distillation until it assumed tensimetric homogeneity.[5]

Trimethylsilane was prepared by the reaction of $(CH_3)_3SiCl$ with $NaBH_4$ in diglyme solution essentially following the procedure described by Birnbaum and Javora.[6] At the conclusion of the reaction the system was evacuated and all volatiles were transferred into a −196° trap. The volatile products were separated by trap to trap distillation on a vacuum system with U traps maintained at −84, −117, and −196°. The $(CH_3)_3SiH$ condensed in the −117° trap.

Tetrafluorophosphorane. The gas-phase reaction of $(CH_3)_3SiH$ with PF_5 was conducted in a two-bulb reactor which is very similar to the one described by Treichel, Goodrich, and Pierce.[3] Prior to use the reactor was connected to the vacuum line and flamed out several times over a 24-hr period. In a typical reaction 27.0 mmol of $(CH_3)_3SiH$ was condensed into the smaller (500-ml) bulb and allowed to volatilize completely after closing the interconnecting stopcock. Phosphorus pentafluoride (28.0 mmol) was then condensed into the larger (2000-ml) bulb and allowed to assume ambient temperature after closing the stopcock leading to the vacuum system. The interconnecting stopcock was then opened carefully so that a controlled gas-phase reaction ensued in the larger bulb. As soon as the reaction was complete, the volatiles were transferred to the vacuum line and distilled through a series of U traps held at −112, −126, and −196°. A 69% yield (18.6 mmol) of HPF_4 condensed in the −126° trap. The vapor tensions and ir spectra of HPF_4 were in conformity with the literature values.[2,3]

Nmr Spectra. All spectra were measured on a Varian Associates HA-100 spectrometer equipped with a variable-temperature accessory. The probe temperatures were calibrated against the freezing points of pure cyclopropane (−126°) and fluorodichloromethane (−135°). Samples were prepared by condensing the appropriate quantities of HPF_4 and Freon-22 ($HCClF_2$) into a calibrated 5-mm nmr tube. The tubes were sealed off *in vacuo* at −196°. The spectra which are presented in Figure 1 were obtained with and without NaF in the nmr tubes.

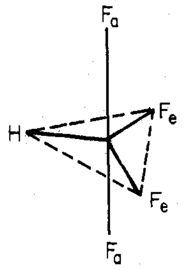
Results and Discussion

Tetrafluorophosphorane can be synthesized conveniently and rapidly in approximately 70% yield by the gas-phase reaction of $(CH_3)_3SiH$ with PF_5 according to the equation

$$(CH_3)_3SiH + PF_5 \rightarrow PF_4H + (CH_3)_3SiF$$

It is apparent that the yield of HPF_4 is more than doubled when the hydride source is changed from $(CH_3)_3SnH$ to $(CH_3)_3SiH$. This is ascribable to the higher volatility of $(CH_3)_3SiH$ which permits the silane to be added to the PF_5, thereby ensuring that reaction takes place in the presence of an excess of the latter. Reverse addition was obligatory in the case of the less volatile $(CH_3)_3SnH$,[3] thus biasing the reaction conditions in favor of the production of H_2PF_3. Only traces of H_2PF_3 are detectable in the $(CH_3)_3SiH$ synthesis providing a slight excess of PF_5 is employed, thus obviating the problem of separating H_2PF_3 from HPF_4. An additional advantage of the greater volatility of $(CH_3)_3SiH$ is that it permits the reaction to be conducted on a larger scale for a given size of apparatus.

In a microwave spectroscopic study of HPF_4 it was demonstrated that the most plausible geometry corresponds to the C_{2v} structure 1 in which the hydride ligand occupies an equatorial site of a trigonal bipyramid. However, it was not possible to exclude a less likely C_{2v} model (2) in which the four fluorine atoms are located in the basal plane of a rectangular pyramid. This structural question was not resolvable on the basis of previously published nmr spectral data in the range +32 to −114°. Although the observed



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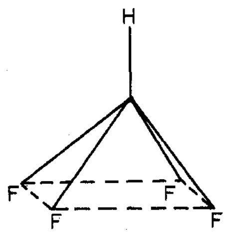

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