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Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Improved Synthesis and Ground State Nuclear Magnetic Resonance Spectra of Tetrafluorophosphorane

A. H. Cowley* and R. W. Braun

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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.

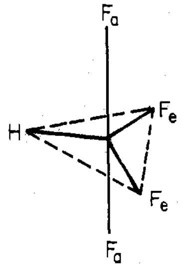
Results and Discussion

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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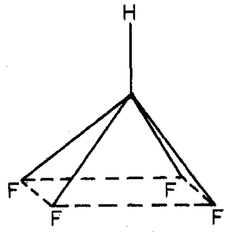

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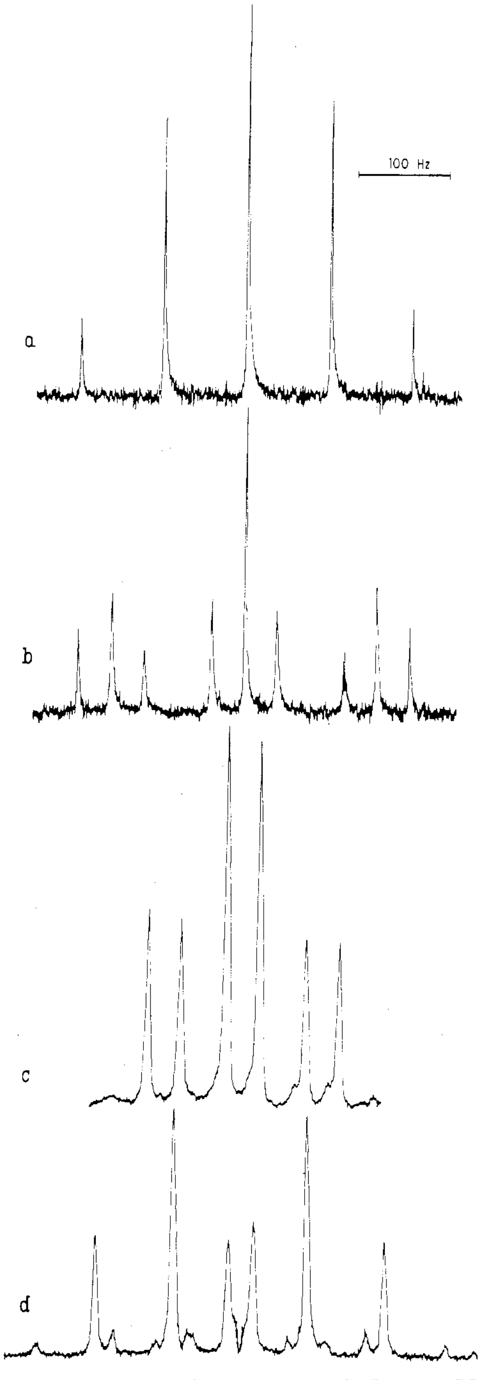

Figure 1. Nmr spectra of a 2.0 *M* solution of HPF_4 in $HCClF_2$: (a) downfield component of the 100-MHz ^1H spectrum at −80°; (b) downfield component of the 100-MHz ^1H spectrum at −140°; (c) downfield component of the 94.1-MHz ^{19}F(equatorial) resonance at −140°; (d) downfield component of the 94.1-MHz ^{19}F(axial) resonance at −140°.

spectroscopic equivalence of the fluorine atoms (see, *e.g.*, Figure 1a) could be due to structure **2**, it is more reasonably ascribed to the fluxional behavior of the trigonal-bipyramidal species, **1**. Accordingly it seemed appropriate to secure more extensive low-temperature nmr data in order to shed more light on this question.

When HPF_4 is dissolved in Freon-22 ($HCClF_2$) and cooled below −120°, two fluorine environments of equal abundance become detectable in both the ^1H and the ^{19}F spectra. This observation of the limiting spectrum establishes the trigonal-bipyramidal ground-state geometry (**1**) for HPF_4 and rules out structure **2**. The assignment of the +65.9- and +27.4-ppm ^{19}F resonances (relative to external CCl_3F) to the equatorial and axial fluorine sites, respectively, is based on the fact that the equatorial resonances appear at higher field.[7] Thus the large doublet splitting in Figure 1d is due to the H-P-F_a coupling and the small doublet splitting in Figure 1c is due to the H-P-F_e coupling; in both Figures 1c and 1d the triplet splitting is due to $J_{F_aPF_e}$. The low-temperature ^1H spectrum (Figure 1b) is likewise assignable on this basis. The following new coupling constant data are available from the limiting spectra: $J_{PF_a} = 941.0$ Hz; $J_{PF_e} = 1025$ Hz; $J_{HPF_a} = 147.5$ Hz; $J_{HPF_e} = 36.47$ Hz; $J_{F_aPF_e} = 87.89$ Hz.

Registry No. Tetrafluorophosphorane, 36994-84-0.

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Contribution from the Institute "Ruder Boskovic,"
Bijenicka 54, Zagreb, Croatia, Yugoslavia

Preparation and Kinetics of the Aquation of Pentaaquo(3-picoline)chromium(III) Ion

M. Orhanovic* and M. Avdagic

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Comparisons of kinetic and thermodynamic parameters for the aquation and anation reactions of the $Cr(H_2O)_5X^{2+}$ series of complex ions (X = uninegative ions) have given important information about the mechanisms of these reactions.[1] The chemistry of analogous chromium complexes[2] with a net charge other than 2+ was of interest to us and is reported here.

The reaction of diperoxychromium(IV) amines with acids has proved useful as a route to produce chromium(III) diamines and triamines.[3] Similar adducts of nitrogen bases with diperoxychromium(VI) species, $BCr(O)(O_2)_2$, are reported to decompose in acidic aqueous solution to hexaaquochromium(III) ion and chromate ion, the relative amounts of which vary with pH.[4] We find that the reaction of acidic ferrous perchlorate with some base adducts of diperoxychromium(VI) species produces monosubstituted chromium(III) ions, $(H_2O)_5CrB^{n+}$. This paper deals with the preparation of pentaaquo(3-picoline)chromium(III) ion and with the kinetics of its aquation. The aquation kinetics of

$$(H_2O)_5Cr(3\text{-pic})^{3+} + H^+ \rightarrow Cr(H_2O)_6^{3+} + H(3\text{-pic})^+ \qquad (1)$$

was studied as a function of acidity and temperature.[5]

Experimental Section

Preparation of Pentaaquo(3-picoline)chromium(III). To a cooled

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