TABLE V

MASS SPECTRA OF HYDROPHOSPHORYL DIFLUORIDE AND HYDROTHIOPHOSPHORYL DIFLUORIDE

SPF_2H			OPF_2H		
m/e	Rel intensity[a]	Ion	m/e	Rel intensity[a,b]	Ion
102	52.9	SPF_2H^+	86	40.8	OPF_2H^+
101	6.9	SPF_2^+	85	10.6	OPF_2^+
83	1.6	$SPFH^+$	69	19.6	PF_2^+
82	3.2	SPF^+	67	8.6	$OPFH^+$
69	28.0	PF_2^+	66	10.2	OPF^+
63	4.2	SP^+	50	1.6	PF^+
50	3.2	PF^+	31	1.2	P^+

[a] Intensities are expressed as per cent total ionization, defined as ΣI_n where n refers to all ions with $m/e > 30$ whose intensity is $>2\%$ of the base peak. [b] A very weak peak at m/e 32 ($<0.5\%$) due to PH^+ was observed. No peaks at m/e 104 (*i.e.*, POF_3 or SIF_4) or m/e 88 (PF_3) were observed.

products. While we have not yet completely evaluated the effects of impurities and other conditions on the course of this complex decomposition, it is reasonable to suggest that the initial decomposition product, OPF_3, formed by some unknown route, reacts with the original hydrophosphoryl difluoride to form difluorophosphoric acid

$$OPF_3 + OPF_2H \longrightarrow PF_3 + F_2PO(OH)$$

and the difluorophosphoric acid in turn is consumed by reaction with the original hydrophosphoryl compound

$$2OPF_2H + F_2PO(OH) \longrightarrow PF_3 + OPF_3 + OPH(OH)_2$$

The sum of these two equations

$$3OPF_2H \longrightarrow 2PF_3 + OPH(OH)_2$$

gives an equation which is in fair agreement with the observed yield of phosphorus trifluoride. This scheme is consistent with the observations summarized in Table I and with the results of the decomposition study but is not proven. The reaction may involve rearrangement to the trivalent isomer, F_2POH, as the initial step.

Hydrophosphoryl difluoride yielded phosphorous acid and silicon tetrafluoride on hydrolysis; the latter is probably due to the reaction of hydrogen fluoride with glass

$$OPF_2H + 2H_2O \longrightarrow OPH(OH)_2 + 2HF$$

$$2HF + {}^1/_2SiO_2 \longrightarrow {}^1/_2SiF_4 + H_2O$$

The hydrolysis of SPF_2H also gave phosphorous acid and in addition hydrogen sulfide. Monothiophosphorous acid, $SPH(OH)_2$, is probably formed initially

$$SPF_2H + H_2O \longrightarrow SPH(OH)_2 + 2HF$$

and subsequently hydrolyzed to phosphorous acid and hydrogen sulfide

$$SPH(OH)_2 + H_2O \longrightarrow OPH(OH)_2 + H_2S$$

probably catalyzed by the hydrofluoric acid in the solution. In both cases the yield of silicon tetrafluoride was not quantitative. Hydrogen was not obtained in any of the hydrolysis reactions showing that the hydrogen atoms are not hydritic. The P–H bond probably maintains its integrity during hydrolysis as in the case of the hydrolysis[24] of PF_2H.

Both compounds have abnormal Trouton constants and notably higher boiling points than those of the parent fluorides, suggesting that they are associated, possibly through weak hydrogen bonding similar to that suggested for difluorophosphine.[1] More convincing support for association is provided by the concentration dependence of the hydrogen chemical shift and by shifts in the infrared frequencies with phase.[17] All of these effects are greatest for the phosphoryl compound where greater hydrogen-bonded association is reasonably expected. We hope to present more detailed evidence in a future publication.

Acknowledgment.—We thank Mr. G. Bigam for assistance with the nmr spectra and the National Research Council (Ottawa) for financial support.

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Hydrolysis of Titanium Tetrafluoride

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The hydrolysis of titanium tetrafluoride in various solutions is described. In a 40% TiF_4 aqueous solution evidence is presented for the polynuclear species $[TiF_4 \cdot Ti(OH)_4(H_2O)_2]$. An F^{19} study of the supernatant liquid from the hydrolysis of the adduct $TiF_4 \cdot 2HC(O)N(CH_3)_2$ showed the presence of $TiF_5 \cdot HC(O)N(CH_3)_2^-$, $TiF_5 \cdot H_2O^-$, and TiF_6^{2-}. The *cis*-$TiF_4 \cdot 2H_2O$ adduct was found as a product in dilute hydrogen fluoride solutions of TiF_4 in water. The hexafluorotitanate ion is stable in water but hydrolyzes in acidic solutions.

Introduction

The species $TiOF_4^{2-}$, $TiOF^+$, $TiOF_2$, and $TiOF_3^-$ were reported to be present in hydrogen fluoride solutions of Ti(IV).[2] It was also noted that the hexafluorotitanate ion was not stable in aqueous solutions but was rapidly hydrolyzed to $TiOF_4^{2-}$ and more slowly to

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(1) Soviet scientist from the N. S. Kurnakov Institute, Moscow, on a Scientific Exchange Program between the National Academy of Sciences of the U.S.A. and the U.S.S.R.

(2) V. Caglioti, L. Ciavatta, and A. Libereti, *J. Inorg. Nucl. Chem.*, **15**, 115 (1960).

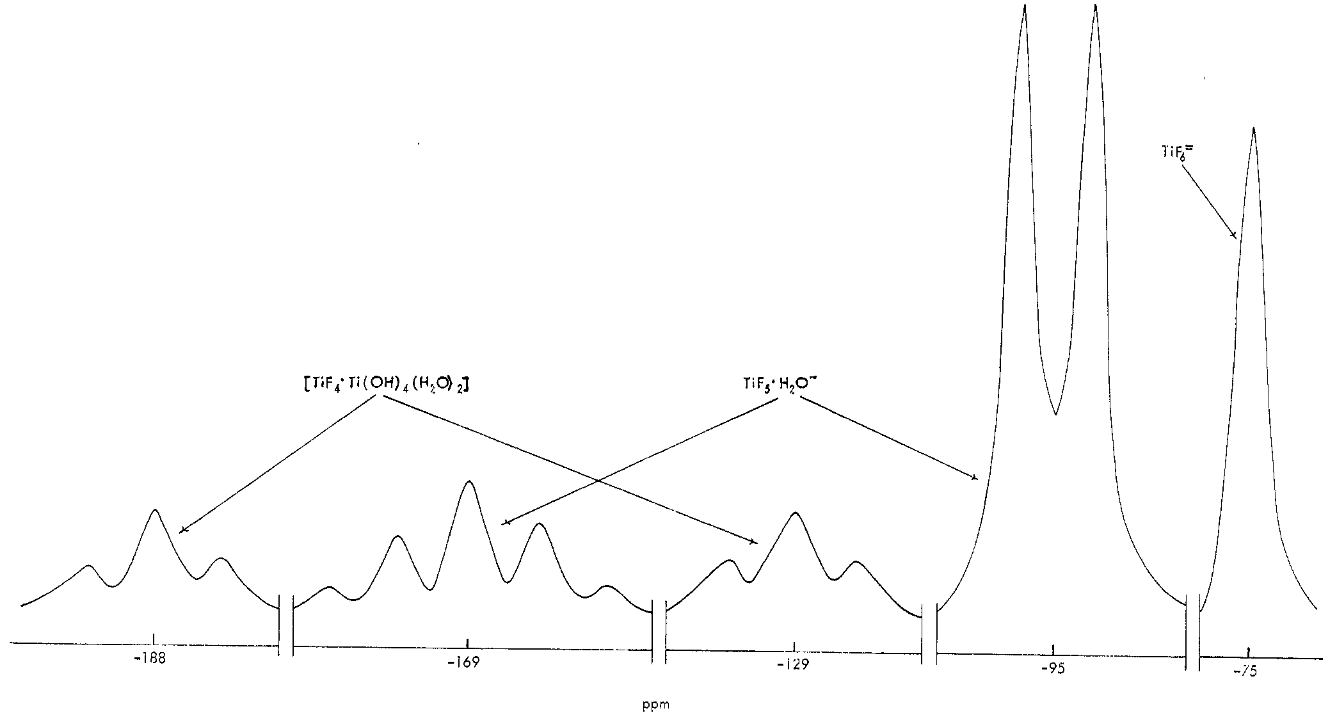

Figure 1.—F^{19} high-resolution spectrum of a 40% TiF_4 aqueous solution at −40°. Chemical shifts with respect to external $CFCl_3$.

other less fluorinated species. However, another study[3] indicated that the extent of hydrolysis of TiF_6^{2-} in aqueous solution is very limited. Equivalent conductance and pH measurements suggested that in the following equilibrium n was much less than 1

$$TiF_6^{2-} + nH_2O \rightleftharpoons TiF_{6-n}(OH)_n^{2-} + nHF$$

Buslaev and co-workers[4] studied the three-component system consisting of water, hydrogen fluoride, and titanium dioxide. A compound corresponding to the stoichiometry $TiOF_2 \cdot H_2O$ was isolated from the solid phase. From conductivity studies of aqueous solutions of hydrofluoric acid and TiO_2, the following species were reported to be present: $H[TiF_4(OH)(H_2O)]$, $H[TiF_5 \cdot H_2O]$, and $H_2[TiF_6]$. Owing to the uncertainty concerning the species present in the titanium(IV)–hydrogen fluoride–water system, we have studied the hydrolysis of titanium tetrafluoride using fluorine-19 nuclear magnetic resonance spectroscopy. In this paper the fluorine resonance spectra of various titanium tetrafluoride solutions are described.

Experimental Section

Materials.—Titanium tetrafluoride obtained from Allied Chemical Corp. was used without further purification. $TiF_4 \cdot 2$-$HC(O)N(CH_3)_2$ and $TiF_4 \cdot 2(4\text{-}CH_3C_5H_4NO)$ were prepared by the method of Muetterties.[5] The hexafluorotitanate ion was prepared in aqueous solution by addition of NH_4F to TiF_4. The excess NH_4F was removed by washing with a CH_3OH–H_2O mixture.

Analyses.—Analysis of the solutions was determined by a previously described procedure.[6]

Instrumental Data.—The fluorine nmr spectra were obtained with a Varian A 56/60A high-resolution spectrometer equipped with a V-6057 variable-temperature accessory. The spectra were calibrated in ppm displacements from external $CFCl_3$.

Results and Discussion

The results of an nmr study of a 40% TIF_4 aqueous solution at −40° are summarized in Table I. The spectrum consists of five resonances as shown in Figure 1. The singlet resonance at −75 ppm (relative to external $CFCl_3$) was assigned to the hexafluorotitanate ion since the chemical shift corresponds to that obtained for an aqueous solution of $(NH_4)_2TiF_6$.

TABLE I

F^{19} CHEMICAL SHIFTS, COUPLING CONSTANTS, AND RELATIVE INTENSITIES FOR CONCENTRATED AQUEOUS TITANIUM TETRAFLUORIDE SOLUTIONS AT −40°

Multiplet	Rel integ intensities, %	Comparison of multiplet intensities	Chem shift, ppm (external $CFCl_3$ ref)	Coupling constant, cps (for F–F)
Triplet	7	(triplet:triplet)	−188[a]	36[b]
Triplet	7	1:1	−129	36
Doublet	52	(doublet:quintet)	−95	36
Quintet	13	4:1	−169	36
Singlet	22		−75	. . .

[a] ±1 ppm. [b] ±1 cps.

The quintet and doublet resonances (Figure 1) are assigned to the complex anion $TiF_5 \cdot H_2O^-$. The relative intensities of the doublet to quintet (4:1) and coupling constant are similar to the spectra obtained for the $TiF_5 \cdot ROH^-$ complex ions.[7] Previously, Buslaev and Tcherbakov[8] reported the presence of the $TiF_5 \cdot H_2O^-$ ion and TiF_6^{2-} as major products in the

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[3] R. H. Schmitt, E. L. Grove, and R. D. Brown, *J. Am. Chem. Soc.*, **82**, 5292 (1960).

[4] Yu. A. Buslaev, V. A. Bochkayeva, and N. S. Nikolaev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 388 (1962).

[5] E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

[6] N. S. Nikolaev and Yu. A. Buslaev, *Zh. Neorgan. Khim.*, **4**, 205 (1959).

[7] R. O. Ragsdale and B. B. Stewart, *Inorg. Chem.*, **2**, 1002 (1963).

[8] Yu. A. Buslaev and V. A. Tcherbakov, *Dokl. Akad. Nauk SSSR*, **170**, 845 (1966).

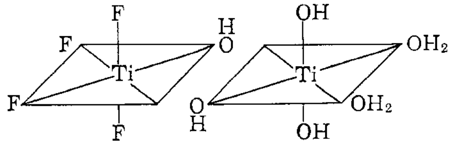
hydrolysis of TiF_4 in water. The assignment of the $TiF_5 \cdot H_2O^-$ was based on analogy to the $TiF_5 \cdot ROH^-$ complexes[7] since only the doublet was resolved in the fluorine-19 nmr spectrum.

The two triplet resonances (Figure 1) are of equal intensity and the coupling constants are similar to those found for octahedral *cis*-$TiF_4 \cdot 2B$ adducts.[5,9,10] At first it was thought that these resonances were due to unhydrolyzed $TiF_4 \cdot 2H_2O$. However, $TiF_5 \cdot H_2O^-$ and TiF_6^{2-} are major products of the hydrolysis reaction, and there must be a species present which has less than four fluorines per titanium (a low form). Since essentially no precipitate was observed, the formation of the low-form TiO_2 is ruled out. The two triplets were assigned to a low form because no other F^{19} resonances which could be attributed to such a species were observed. Because of the similarity of the two triplets to the F^{19} spectra of the *cis*-$TiF_4 \cdot 2B$ complexes, it is reasonable to suggest that the structure of the low form is similar to that of *cis*-$TiF_4 \cdot 2B$. One would not expect much difference in the chemical shifts of species similar to *cis*-$TiF_4 \cdot 2B$.

Taking into consideration the relative intensities of the fluorine-19 resonances shown in Table I, an equation is obtained with the stoichiometry

$$7TiF_4 + 14H_2O \longrightarrow [TiF_4 \cdot Ti(OH)_4(H_2O)_2] + 5H_3O^+ + 3.5TiF_5 \cdot H_2O^- + TiF_6^{2-} \quad (1)$$

This equation is not rigorously balanced since nmr spectroscopy is not sensitive enough to detect 100% of the fluorine in the system. As a result we cannot rule out the presence of species such as $TiF_3^+(aq)$ particularly if they are involved in fairly rapid exchange processes. Although based upon concentration of the low form and upon the fact that exchange was not too rapid to detect the other fluorotitanate species, it does not seem that other low forms could be present in high enough concentrations to account for the fluorine ion which is required for the formation of $TiF_5 \cdot H_2O^-$ and TiF_6^{2-}. The proposed low form, $[TiF_4 \cdot Ti(OH)_4(H_2O)_2]$, has an empirical formula which is similar to $TiOF_2 \cdot H_2O$, which has been shown to exist in the solid state.[4] We suggest that in solution this fluorine complex is a polynuclear species with one part of the molecule having the four fluorines in a *cis* arrangement



This structure is consistent with the two 1:2:1 triplets of equal intensity, with a coupling constant which is similar to that of other octahedral $TiF_4 \cdot 2B$ complexes, and with the chemical shifts which are approximately 10 ppm upfield to that reported for the *cis*-$TiF_4 \cdot 2ROH$ adducts.[7] This new complex is consistent with the chemistry of Ti(IV) which usually forms octahedral complexes with a *cis* configuration.[5,7,9,11] The proposed dimeric species is isomeric with a number of other possible species. The nmr data require a symmetrical arrangement of the ligands coordinated to Ti^{4+} in $Ti(OH)_4(H_2O)_2$ in order to observe two 1:2:1 triplets for TiF_4. There is another hydroxy-bridged symmetrical structure which can be drawn and there are some unsymmetrical structures which can be ruled out. Before commenting further on the dimeric species we need to consider other experimental results.

Since no $TiF_4 \cdot 2H_2O$ was detected in aqueous TiF_4 solutions, the hydrolysis of TiF_4 in ethanol was investigated. Various amounts of water were added to concentrated TiF_4–C_2H_5OH solutions. The resulting solutions were examined by fluorine-19 nmr spectroscopy. In a solution which consisted of 15% H_2O, 38% TiF_4, and 47% C_2H_5OH several hydrolysis products were detected, but they are of low concentration, and only $TiF_5 \cdot H_2O^-$ and $TiF_5 \cdot C_2H_5OH^-$ were positively identified. In all of the solutions which contained less water, $TiF_4 \cdot 2C_2H_5OH$ complexes were detected. When a 36% H_2O, 28% TiF_4, and 36% C_2H_5OH solution is obtained, the nmr spectra are similar to those recorded for the TiF_4–H_2O solutions. In this mixture the major fluorotitanate ions are $TiF_5 \cdot H_2O^-$, $TiF_5 \cdot C_2H_5OH^-$, $[TiF_4 \cdot Ti(OH)_4(H_2O)_2]$, and TiF_6^{2-}. No evidence was found for the $TiF_4 \cdot 2H_2O$ complex in the ethanol solutions.

The hydrolysis of the N,N-dimethylformamide adduct $TiF_4 \cdot 2HC(O)N(CH_3)_2$ was studied. Upon addition of $TiF_4 \cdot 2HC(O)N(CH_3)_2$ to water, precipitation occurred immediately. The nmr spectra of the supernatant liquid showed the presence of $TiF_5 \cdot HC(O)N(CH_3)_2^-$, $TiF_5 \cdot H_2O^-$, and TiF_6^{2-}. A spectrum of this solution is shown in Figure 2. No low form was detected in solution and analysis of the residue indicated that the low form(s) was precipitated since a Ti:F ratio ~1:2–3 was found.

Addition of N,N-dimethylformamide to aqueous TiF_4 solutions gave similar results (*i.e.*, precipitation and formation of $TiF_5 \cdot HC(O)N(CH_3)_2^-$, $TiF_5 \cdot H_2O^-$, and TiF_6^{2-}). As can be seen from eq 1, aqueous TiF_4 solutions are acidic, and the presence of a base such as N,N-dimethylformamide would decrease the acidity of the solution. As the acidity of the solution is decreased, precipitation of the low form(s) occurs. Similar results were obtained for an aqueous solution of $TiF_4 \cdot 2(4\text{-}CH_3C_5H_4NO)$. The low form(s) precipitated and the species $TiF_5 \cdot H_2O^-$, $TiF_5 \cdot (4\text{-}CH_3C_5H_4NO)^-$, and TiF_6^{2-} were detected in the solution by F^{19} nmr spectroscopy. The concentration of $TiF_5 \cdot (4\text{-}CH_3C_5H_4NO)^-$ was low, and only the doublet in the nmr spectrum could be resolved.

Hydrogen fluoride–titanium tetrafluoride–water solutions were studied in an effort to elucidate the hydrolysis scheme. These data are summarized in Table II. A solution which has a HF:TiF_4 ratio of 1:1 gives the following equation based upon the relative integrated intensities of the F^{19} signals (eq 2).

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(10) D. S. Dyer and R. O. Ragsdale, *J. Phys. Chem.*, **71**, 2309 (1967).

(11) D. S. Dyer and R. O. Ragsdale, *Chem. Commun.*, 601 (1966).

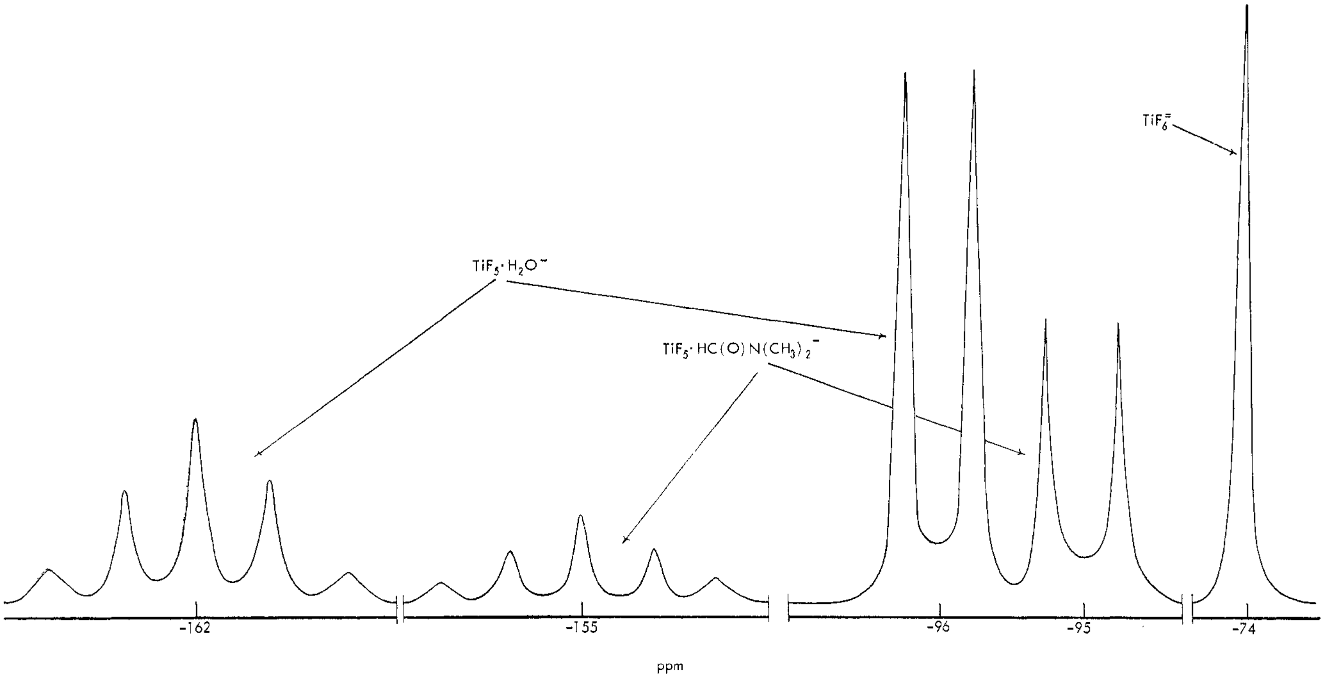

Figure 2.—F^{19} high-resolution spectrum of the supernatant liquid of a $TiF_4 \cdot 2HC(O)N(CH_3)_2$–$H_2O$ solution at −30°. Chemical shifts with respect to external $CFCl_3$.

TABLE II

F^{19} CHEMICAL SHIFTS (PPM) AND RELATIVE INTENSITIES FOR SOME HYDROGEN FLUORIDE SOLUTIONS OF TiF_4 IN WATER

	"Low form"			$TiF_5 \cdot H_2O^-$			TiF_6^{2-}		
HF:TiF₄	Multiplet	Chem shift	Relative per cent	Multiplet	Chem shift	Relative per cent	Multiplet	Chem shift	Relative per cent
0.5	Triplet	−129	10	Doublet	−94	47	Singlet	−72	22
	Triplet	−193	10	Quintet	−173	11			
1	Triplet	−126	8	Doublet	−93	51	Singlet	−73	22
	Triplet	−198	8	Quintet	−182	11			
2				Doublet	−95	13	Singlet	−72	84
				Quintet	*a*	3			
4							Singlet	−71	>95

[a] Concentration was low, the quintet was not detected, and the relative per cent was based on the doublet.

$$5.5TiF_4 + 5.5HF + 5.5H_2O \longrightarrow TiF_4 \cdot 2H_2O + 3.5TiF_5 \cdot H_2O^- + TiF_6^{2-} + 5.5H_3O^+ \quad (2)$$

These results suggest that in hydrogen fluoride solutions of the appropriate concentrations, it is possible for $TiF_4 \cdot 2H_2O$ to exist. Fairly rapid exchange was occurring, and the spectra were obtained at −50° to help slow down the exchange. One suggested exchange process is the dissociation of $TiF_4 \cdot 2H_2O$

$$TiF_4 \cdot 2H_2O + H_2O \rightleftarrows TiF_4OH \cdot H_2O^- + H_3O^+ \quad (3)$$

In an $HF:TiF_4$ ratio of 3:1, both $TiF_5 \cdot H_2O^-$ (the quintet could not be resolved) and TiF_6^{2-} were detected. The hexafluorotitanate ion was the major species, and the $TiF_5 \cdot H_2O^-$ doublet was very broad at −50°, indicating rapid exchange. In a titanium tetrafluoride: hydrogen fluoride ratio of 1:4, only TiF_6^{2-} was observed.

It is interesting that the $TiF_4 \cdot 2H_2O$ complex can be detected in hydrogen fluoride–water solutions of TiF_4 but not in aqueous solutions of TiF_4. This is probably due to the availability of fluoride ions from the dissociation of HF. That is, fluoride ion for the formation of $TiF_5 \cdot H_2O^-$ and TiF_6^{2-} could come from HF rather than $TiF_4 \cdot 2H_2O$. Addition of HF would also cause a shift in the equilibrium shown in eq 3.

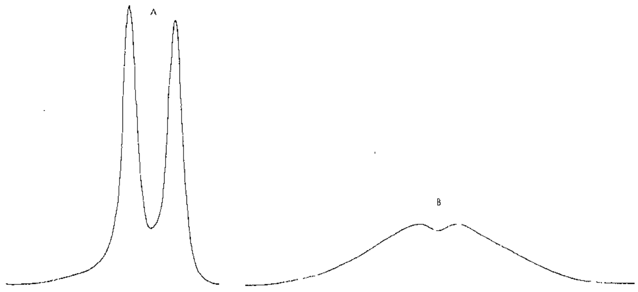

Figure 3.—A comparison of the $TiF_5 \cdot H_2O^-$ F^{19} doublets where A represents the spectrum for an initial $HF:TiF_4$ ratio of 1:1 and B represents the spectrum for a $HF:TiF_4$ ratio of 2:1 at −50°.

It should be noted that the chemical shifts for $TiF_4 \cdot 2H_2O$ and $[TiF_4 \cdot Ti(OH)_4(H_2O)_2]$ are quite similar. The evidence for $[TiF_4 \cdot Ti(OH)_4(H_2O)_2]$ is not based upon the difference in chemical shifts as the shifts change some with concentration, but our conclusion comes from a consideration of the above results and experiments with TiO_2. Instead of adding TiF_4 to water, one adds hydrofluoric acid to TiO_2; results similar to eq 1 or 2 are obtained depending upon the respective concentrations of TiO_2 and HF(aq). The excess TiO_2 was filtered from the solution before making the nmr measurements.

In contrast to the report of Caglioti and co-workers[2] and in agreement with Schmitt, *et al.*,[3] we find that the TiF_6^{2-} ion is very stable in water. Over long periods of time only a sharp singlet is seen in the F^{19} nmr spectrum of the solution at room temperature. $(NH_4)_2TiF_6$ in a 10% HCl solution was prepared and examined by nmr spectroscopy. The spectrum showed the presence of $TiF_5 \cdot H_2O^-$ and TiF_6^{2-}. These species were in a 2:3 ratio. The formation of $TiF_5 \cdot H_2O^-$ is suggested to occur by the mechanism

$$TiF_6^{2-} + H_3O^+ \overset{\text{fast}}{\rightleftharpoons} F_5TiFH^- + H_2O$$

$$F_5TiFH^- + H_2O \xrightarrow{\text{slow}} F_5TiH_2O^- + HF$$

For TiF_6^{2-} to hydrolyze in water, an acid solution is required, because the formation of a hydrogen bond and subsequent formation of HF helps to break the Ti–F bond.

This result is consistent with the reported acid-catalyzed fluorine exchange between SiF_6^{2-} species.[12] These results are also in agreement with the proposed mechanism for the acid-catalyzed hydrolysis of *trans*-$Co(en)_2F_2^+$ where the formation of a hydrogen bond to fluorine weakens the Co–F bond.[13]

In Figure 3 the $TiF_5 \cdot H_2O^-$ doublet for an initial HF:TiF_4 ratio of 1:1 is compared to the doublet for an initial HF:TiF_4 ratio of 2:1. Exchange is much faster in the more acidic solution. We suggest that the exchange is due to exchange of both water and fluoride ion. The fluoride ion exchange is facilitated in more acidic solutions by the initial formation of a hydrogen bond, thus lending additional support for the mechanism proposed above.

Acknowledgment.—Support of this work by the Air Force, Materials Laboratory, Research and Technology Division, Wright-Patterson AFB, Ohio, is gratefully acknowledged.

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(13) F. Basolo, W. R. Matoush, and R. G. Pearson, *ibid.*, **78**, 4883 (1956)

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Vibrational Frequencies and Force Constants of Some Group IVa and Group Va Hexafluoride Ions[1]

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Infrared and Raman spectral data are reported for crystalline salts containing the ions PF_6^-, AsF_6^-, SbF_6^-, SiF_6^{2-}, GeF_6^{2-}, and SnF_6^{2-}. Five of the six fundamental vibrational frequencies of each ion were assigned on the basis of an O_h structure, and simple valence force constants were calculated.

Introduction

Incomplete infrared and Raman spectral data are available in the literature on a number of crystalline hexafluoride ions of group IVa and group Va metals. Since spectral data on solid substances are harder to obtain and more likely to be ambiguous than similar data for liquids and gases, this field has been largely neglected. However, by careful design of the sample cells, we obtained rather good Raman spectra of the hexafluoride ions of P, As, Sb, Si, Ge, and Sn. Infrared spectra of these compounds were also secured.

Experimental Section

Baker and Adamson reagent grade Na_2SiF_6 was further purified by recrystallization from aqueous HF solution. To prepare K_2GeF_6, GeO_2 (Fischer Scientific Co.) was heated with 48% HF for several days. The filtrate was diluted to 500 ml and the pH was adjusted to 1.5 with KOH. The crystals of K_2GeF_6, which formed after evaporation at room temperature, were filtered and dried in a stream of nitrogen. Na_2SnF_6 was prepared by adding 48% aqueous HF to an aqueous solution of $Na_2SnO_3 \cdot 3H_2O$ (Baker and Adamson) until all of the initially precipitated SnO_2 redissolved. The solution was allowed to evaporate slowly and the crystals were dried with a stream of nitrogen. The KPF_6 was Matheson Coleman and Bell material, 98–100% pure. $CsAsF_6$ was obtained by dissolving CsF in 48% aqueous HF. AsF_5 gas (Ozark Mahoning Co.), diluted with nitrogen, was passed through the solution until no further precipitate was formed. The solid $CsAsF_6$ precipitate was washed with 48% HF and vacuum dried. $LiSbF_6$ was formed from dry LiF in a Kel-F reactor attached to a metal vacuum system. Anhydrous HF was added to the LiF with stirring, and purified SbF_5 was then slowly condensed into the reactor. The products were removed from the vacuum line and dissolved in anhydrous HF from which $LiSbF_6$ was obtained by fractional crystallization. Inert polyethylene and Kel-F containers were used for all preparations.

The Raman spectra of the solid powders were observed by means of a Cary Model 81 Raman spectrophotometer. Samples were contained in conical quartz tubes. Tapered conical sample tubes for solids are described by Brandmüller and Moser.[2] Our tubes were similar to that pictured by Busey and Keller.[3]

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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