THE $TiCl_4$--TiF_4 SYSTEM
I. TITANIUM(IV) CHLORIDE FLUORIDES
II. FLUORINE-19 NMR STUDY IN TETRAHYDROFURAN

Thesis for the Degree of Ph. D.
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THESIS

This is to certify that the

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The $TiCl_4$--TiF_4 System
I. Titanium(IV) Chloride Fluorides
II. Fluorine-19 NMR Study in Tetrahydrofuran

presented by

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ABSTRACT

THE $TiCl_4$--TiF_4 SYSTEM
I. TITANIUM(IV) CHLORIDE FLUORIDES
II. FLUORINE-19 NMR STUDY IN TETRAHYDROFURAN

by Robert Scranton Borden

I. The $TiCl_4$--TiF_4 system was studied to determine if halogen exchange takes place and, if possible, to develop methods for the isolation of titanium(IV) chloride fluorides.

Halogen exchange and the existence of TiF_3Cl, TiF_2Cl_2, and $TiFCl_3$ were confirmed in the vapor phase by mass spectral studies.

$TiCl_4$ and TiF_4 react at $90^{\circ}C$ in the absence of solvent to give an apparent equilibrium mixture of starting compounds and mixed halides. Halogen exchange is postulated to proceed through a five-coordinate bridged intermediate. TiF_2Cl_2, a yellow solid, can be conveniently isolated in high yield but yellow solid TiF_3Cl was isolated only with difficulty and in low yield. $TiFCl_3$ was not isolated but is probably an unstable liquid which disproportionates at room temperature into TiF_2Cl_2 and $TiCl_4$. The thermal stabilities of the mixed halides are believed to be in the order $TiF_3Cl > TiF_2Cl_2 > TiFCl_3$. Neither TiF_3Cl nor TiF_2Cl_2 gave an X-ray diffraction pattern. A polymeric six-coordinate structure is suggested to account for the observed properties of these compounds.

II. The $TiCl_4$--TiF_4--tetrahydrofuran (THF) system was studied by ^{19}F magnetic resonance techniques to confirm that halogen exchange takes place, to identify the titanium(IV) chloride fluoride THF complexes, and to determine the stereochemistry of the isomers involved.

At room temperature spectral detail was lacking because of rapid THF and halide exchange, but at -60°C a well resolved spectrum was obtained which showed the presence of the titanium(IV) chloride fluoride THF complexes as well as the titanium tetrafluoride THF complex.

Approximate equilibrium constants were calculated for the formation of each mixed halide complex from the starting compounds. The difference in the free energy values calculated from experimental equilibrium constants and free energy values calculated from statistical equilibrium constants expected for random distribution were +220, +180, and -180 cal/mole for $TiF_3Cl\cdot 2THF$, $TiF_2Cl_2\cdot 2THF$, and $TiFCl_3\cdot 2THF$.

A detailed analysis of the low temperature ^{19}F magnetic resonance spectra gives the following information about each of the observed isomers.

<u>$TiF_4\cdot 2THF$</u>: The <u>cis</u> isomer strongly predominates with a <u>cis</u> to <u>trans</u> ratio of approximately 33 to 1. Two equal intensity triplets are observed for the <u>cis</u> isomer with δ_{FF} = 60 ppm and J_{FF} = 37.7 Hz. The <u>trans</u> isomer gives a singlet approximately 12 ppm upfield from the high field triplet of the <u>cis</u> isomer.

$TiF_3Cl \cdot 2THF$: Only one isomer is observed for this compound. The ^{19}F NMR data strongly suggest that this isomer contains THF groups cis to each other and two fluorine atoms trans to each other. This isomer gives rise to a low field triplet and a higher field doublet in 1 to 2 intensity ratio with δ_{FF} = 67 ppm and J_{FF} = 33.1 Hz.

$TiF_2Cl_2 \cdot 2THF$: Two isomers are observed for this compound. The presence of an enantiomorph isomer with similar ligands cis to each other is conclusively established by virtue of its unique splitting pattern. Two equal intensity doublets are observed for this isomer with δ_{FF} = 76 ppm and J_{FF} = 45 Hz. The second isomer, with an approximate ratio to the enantiomorph isomer of 5 to 1, appears as a singlet about 6 ppm downfield from the high field doublet of the enantiomorph isomer. The position of this peak suggests that it arises from an isomer with cis fluorine and either cis chlorine and trans THF or cis THF and trans chlorine. The former is somewhat more consistent with the observed data and, therefore, is slightly favored.

$TiFCl_3 \cdot 2THF$: A single ^{19}F resonance observed for this compound indicates the presence of only one isomer. Assignment of this resonance to a specific isomer is tenuous. The most consistent data are obtained by ascribing this resonance to the isomer containing _trans_ THF groups. A close second and third choice would be the isomer having _cis_ THF and _trans_ chlorine and the isomer having _cis_ THF and _cis_ chlorine.

THE $TiCl_4$--TiF_4 SYSTEM

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PART I

TITANIUM(IV) CHLORIDE FLUORIDES

INTRODUCTION

When this research began in February of 1965, only one mixed chloride fluoride of titanium had been reported. In 1903, Ruff and Ipsen (45) reported the isolation of a yellow solid intermediate from the reaction of $TiCl_4$ with HF or AgF. This material was found to contain a variable ratio of titanium, chlorine, and fluorine. Ruff and Ipsen were unable to obtain a product of constant composition. In 1953, Vorres (48,50) reported the preparation of yellow solid TiF_3Cl by the reaction of TiF_3 with elemental chlorine. Halogen analyses of the product differed from theory by several per cent. During the period between the studies of Ruff and those of Vorres, no additional work was done in this area.

In December of 1965, Dehnicke (10) reported the preparation of the yellow solid TiF_2Cl_2 by the reaction of chlorine monofluoride with $TiCl_4$. His note, however, was very brief and lacked substantiating evidence. Dehnicke (25) has also recently reported the preparation of the yellow-brown solid TiF_3Br by the reaction of bromine trifluoride with $TiBr_4$. Again experimental details and substantiating evidence are lacking.

The literature contains a number of references to mixed bromide chlorides, bromide iodides, and chloride iodides of titanium(IV). $TiCl_3Br$ and $TiCl_2Br_2$ were first prepared in 1876 by the action of bromine on $TiCl_3$ and $TiCl_2$, respectively (18,19). The $TiCl_4$--$TiBr_4$ system was studied in 1945 by Raman spectroscopy (11). The three mixed bromide chlorides were found to be in equilibrium with each other and with the pure halides, but separation of the pure components was not possible. The mixed halides of titanium(IV) are generally made by the oxidation of a lower valent titanium halide with a halogen of higher atomic weight than contained by the titanium halide. A number of patents cover the use of these compounds as polymerization catalysts (47).

Halogen exchange is well-known for a number of metal and nonmetal systems. The BF_3--BCl_3--BBr_3 system was examined in 1960 by nuclear magnetic resonance (NMR) spectroscopy (9). All the mixed halide compounds were observed but their isolation was not possible. Halogen exchange was established in 1964 for the AsF_3--$AsCl_3$ system by both ^{19}F NMR and mass spectroscopy (44). Isolation of the mixed halides was again not possible. Halogen exchange also has been confirmed for the PCl_3--PBr_3 system (17), however exchange in the PF_3Cl_2--PF_3Br_2 system apparently does not take place (29). The mixed halides of organo-silicon, -germanium, and -antimony also have been identified in mixtures of the pure halides (28,34,35).

Halogen exchange reactions between transition metal halides have not been studied extensively. The $CrCl_3$--$CrBr_3$ (22) and VCl_3--VBr_3 (30) systems have been examined and while solid solution formation was observed, halogen exchange was not conclusively established. The only case where halogen exchange between transition metal halides appears to be well-established is in the $TiCl_4$--$TiBr_4$ system (11).

A great deal of work on scrambling or redistribution exchange reactions has been done by J. R. Van Wazer, K. Moedritzer, and co-workers. They have published extensively in the Journal of the American Chemical Society and in Inorganic Chemistry from 1959 to the present time.

This dissertation reports an investigation of the $TiCl_4$--TiF_4 system. It was the intent to determine if halogen exchange takes place and, if so, the suitability of this system for the preparation of the titanium(IV) chloride fluorides.

EXPERIMENTAL

Purification of Reagents

A. Titanium Tetrachloride

Purified $TiCl_4$ was obtained from the J. T. Baker Chemical Company. For most reactions this material was used without further purification. When specified as distilled, the above material was distilled under nitrogen from decolorizing charcoal through a Vigreaux column into a flamed out receiver or directly into the reaction vessel; only the middle fraction was collected. Since $TiCl_4$ reacts with all stopcock greases tested, these were avoided by using Teflon stopcocks and Teflon sleeves for standard taper connections or by using specially constructed glass and Teflon systems containing no joints. Apiezon type W black wax was found satisfactory for making temporary standard taper glass to glass connections. The distilled material was a perfectly clear, colorless liquid.

B. Titanium Tetrafluoride

Titanium tetrafluoride as obtained from Alfa Inorganics was a gray-white powdery solid of an advertized minimum 97% purity. While the analysis of this material appeared in good agreement with theory, the physical properties of the sample indicated that further purification was necessary.

For example, on sublimation a substantial nonvolatile residue remained. The material was only partially soluble with slow reaction in water and the majority of the sample appeared to be insoluble in tetrahydrofuran. This commercial TiF_4 was purified by passing a stream of dry nitrogen over the sample in a flamed out Pyrex tube at 200-250°C. Several Teflon baffles were placed in the cold end of the tube to prevent the very finely divided TiF_4 from being swept from the system. A series of traps and a drying tower on the exit line prevented water vapor from diffusing back into the system. The pure white finely divided TiF_4 was removed from the tube in a dry box and stored in a tightly closed container. This material reacted vigorously with water or tetrahydrofuran[1] to give a clear solution. Attempts to vacuum sublime the commercial grade TiF_4 proved unsatisfactory. The sublimate formed a glassy solid that could not be conveniently removed from the cold finger.

Preparation of Titanium(IV) Chloride Fluorides

A. General Procedure

All reactions attempted were direct reactions between $TiCl_4$ and TiF_4 in the absence of solvent. Two basic techniques were employed. The first method involved a heterogeneous reaction where TiF_4 was suspended in $TiCl_4$, the

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[1] The tetrahydrofuran must be cooled to near its freezing point and the TiF_4 added slowly. If the addition takes place at room temperature a secondary reaction may take place to yield a red solution.

sample refluxed, and finally distilled. The second method involved passing a nitrogen stream saturated with $TiCl_4$ over a sample of TiF_4 in a heated tube. This gas phase method often produced materials of indefinite and variable composition.

In both methods great care was taken to work under an inert atmosphere and to avoid possible contact with stopcock grease, water, or other contaminants. Glassware was flamed out under vacuum and flushed with dry nitrogen prior to use. All glass and Teflon systems were employed.

B. Titanium Chloride Trifluoride

To a 100 ml distilling flask containing 11 grams (0.058 mole) of $TiCl_4$, 3.61 grams (0.029 mole) of TiF_4 was added. There was no initial reaction. Upon heating, the mixture turned yellow and began to boil at $\sim 90^{\circ}C$. The temperature of the heating mantle was raised to $160^{\circ}C$ and the sample allowed to reflux overnight. A bright yellow solid coated the upper walls of the reaction flask and the distillation column. The distillation column was then heated to permit refluxing liquid to begin distilling into the receiver flask. Yellow solid tended to plug the distillation take-off and made removal of liquid very difficult. The mantle temperature was raised to $200^{\circ}C$ and the sample distilled to dryness. The lower half of the distilling flask contained a dark gray solid whereas the upper half and the distilling column contained a bright yellow solid. This yellow solid was collected under an inert atmosphere and sublimed onto a cold finger in a short pathlength sublimator at 130°C and 0.1 mm Hg pressure. The sublimate was then resublimed at 100°C and 0.1 mm Hg pressure over a 48 hour period. A significant amount of residue remained after each sublimation. This indicates that part of the sublimate had decomposed under these conditions. Analysis of the bright yellow sublimate was as follows:

	Found	Average	Theory for TiF_3Cl
Titanium	33.85, 33.80	33.83	34.13
Chlorine	26.36, 26.40, 26.35	26.37	25.26
Fluorine	By Difference	39.80	40.61

Several samples having a composition approaching that of TiF_3Cl were obtained by passing a nitrogen stream saturated with $TiCl_4$ over a sample of TiF_4 in a heated tube. The material nearest the hot zone always had the lowest chlorine analysis, which usually ranged between 20 and 30% (theory for TiF_3Cl = 25.3% Cl). As the distance from the hot zone increased, the chlorine content of the sample also increased. Since only a small yield of material with variable composition was obtained by this method, no further efforts were made to develop it further for the preparation of TiF_3Cl.

C. Titanium Dichloride Difluoride

Titanium dichloride difluoride can be prepared in good yield by the direct reaction of solid TiF_4 and liquid $TiCl_4$

using a very large excess of the latter. The mixture is refluxed and then distilled. Excess $TiCl_4$ is removed from the distillate by vacuum evaporation, leaving TiF_2Cl_2 as a yellow solid. The apparatus (Figure 1) is thoroughly flamed out under vacuum and then flushed with dry nitrogen while the reactants are added to the reaction flask. The following procedure is typical for a run using commercial grade reactants.

TiF_4 (1.9 grams) and 40 ml (69 grams) of $TiCl_4$ were added to reaction flask A against an outward flow of nitrogen. The reaction flask was then heated to reflux for 15 minutes. The solution turned yellow and a small amount of bright yellow solid began to collect above the liquid level and in the distilling column. The vapor refluxed at 130°C whereas the boiling point for $TiCl_4$ is 136°C. The distilling column was heated to allow distillation to begin. The distillate which collected in flask B was a cloudy yellow color. The amount of solid contained in the distillate appeared to increase on standing as if it were precipitating from solution. The distillation was stopped with only a few milliliters of liquid remaining in the reaction flask. The distillation temperature had risen to 135°C and the material distilling over had become a much lighter clear yellow liquid. The distillate was frozen in a dry ice bath and then while the system was flushed with dry nitrogen the joint between flasks A and B was disconnected and closed with a glass cap.

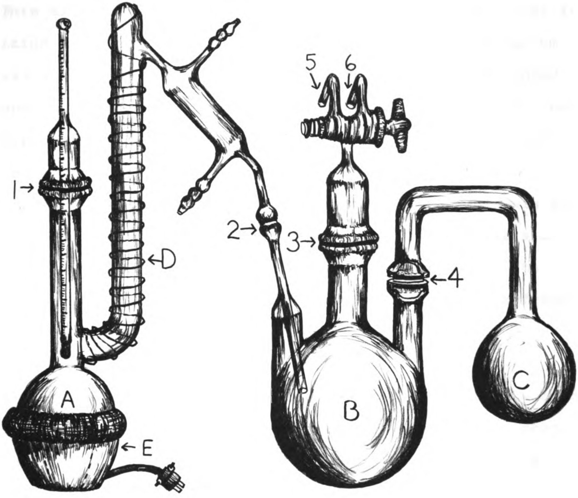


Figure 1. Apparatus for the preparation of TiF_2Cl_2.

(A) Reaction flask, 300 ml
(B) Product collection flask, 500 ml
(C) $TiCl_4$ collection flask, 300 ml
(D) Heated Vigreaux column, 8 inch
(E) Heating mantle
(1) Ring-seal joint for the introduction of reactants--30 mm
(2) "Solv-Seal" Teflon joint--5 mm
(3) Ring-Seal joint for product removal--30 mm
(4) "Solv-Seal" Teflon joint--15 mm
(5) Nitrogen inlet
(6) Vacuum connection

This allowed flasks B and C to be evacuated without volatilizing any liquid remaining in flask A. When a good vacuum was achieved, the connection to the vacuum pump was closed and the dry ice bath was moved from flask B to flask C. As flask B warmed to room temperature, $TiCl_4$ was volatilized and collected as a white solid in flask C. In order to achieve a reasonable transfer rate for the $TiCl_4$, it was sometimes necessary to refreeze the contents of both flasks B and C and re-evacuate the system. This provides for the removal of nitrogen that was trapped during the first freezing process.

Toward the end of the volatilization process, the material which collected in flask C was a light yellow color, indicating that some product or volatile impurity had been carried over. After all the liquid was removed from the bright yellow solid remaining in flask B, the system was swept with dry nitrogen as the joint between flasks B and C was disconnected and capped. Flask B (containing the sample) was then evacuated for 24 hours, after which the flask was moved into a dry box where the product was collected. Its analysis was as follows:

	Found	Average	Theory for TiF_2Cl_2
Titanium	30.36, 30.43	30.40	30.55
Chlorine	46.12, 46.04	46.08	45.22
Fluorine	By Difference	23.52	24.23

The analysis of the sample, which was slightly high in chlorine and low in fluorine, indicates slight contamination with $TiCl_4$ or $TiFCl_3$. Calculated on the basis that the impurity was $TiCl_4$, the sample would be 97% pure. The product weighed 2.6 grams for a yield of 53%. Using purified reactants a yield approaching 100% can be expected.

In some runs where a much larger excess of $TiCl_4$ was used, the distillate collected as a clear yellow solution. After standing for several minutes the clear solution turned cloudy and TiF_2Cl_2 precipitated as a fine yellow solid. When a much smaller excess of $TiCl_4$ was used, a great deal of solid formed in the distillation column and condenser; it tended to plug the apparatus.

Titanium dichloride difluoride also can be prepared by passing a nitrogen stream saturated with $TiCl_4$ over a sample of TiF_4 in a heated tube. The apparatus is shown in Figure 2. Dry nitrogen was bubbled through purified $TiCl_4$ at $80^{\circ}C$ at the rate of 80 ml/minute and then was passed over 5 grams of TiF_4 in a horizontal tube at $200^{\circ}C$ for 20 hours. Shortly after the process was started, a very finely divided light yellow solid collected along the length of the reaction tube extending from the furnace. Teflon baffles prevented this material from being carried out of the reaction tube. A great deal of care was required to maintain the proper concentration of $TiCl_4$ in the reaction tube. Too large an excess of $TiCl_4$ caused its condensation on the cold portion of the reaction tube. Too small an excess of $TiCl_4$ resulted in

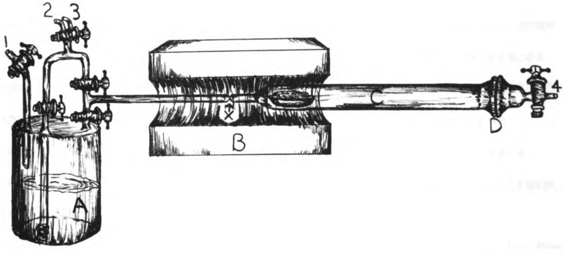


Figure 2. Gas phase reaction apparatus for the preparation of $TiF_{\underline{x}}Cl_{4-\underline{x}}$ compounds.

(A) Distilled $TiCl_4$ storage container
(B) Tube furnace
(C) Reaction tube, 30 mm
(D) Ring-seal joint, 30 mm
(X) Constriction at the point where the tube is to be sealed off
(1) Inlet from $TiCl_4$ distillation apparatus
(2) Nitrogen inlet
(3) Vacuum connection
(4) Connection to cold traps and drying tower

All stopcocks are Teflon

incomplete reaction and contamination of the product with higher fluorides (TiF_4 or TiF_3Cl). After the reaction period the TiF_4 was allowed to cool to room temperature and dry nitrogen was then passed over the sample for several minutes. Next, the reaction tube was evacuated for approximately 10 minutes before it was sealed off at point X with a torch and removed from the system. The sample was removed in two portions in the dry box. The portion nearest the hot zone was a heterogeneous mixture of small bright yellow pieces and a fine light yellow powder. Chlorine analyses of 21.09% and 33.88% confirmed the heterogeneous nature of this material. The portion farthest from the hot zone was a very fine light yellow solid which appeared fairly uniform. Its analysis was as follows:

	Found	Average	Theory for TiF_2Cl_2
Titanium	31.15, 31.10	31.13	30.55
Chlorine	45.64, 44.65, 45.23	45.17	45.22
Fluorine	By Difference	23.80	24.23

The spread in the chlorine analysis indicates that the sample was not completely homogeneous. During repeated runs the sample farthest from the hot zone always had the highest chlorine analysis, which usually approximated that required for TiF_2Cl_2. When a large excess of $TiCl_4$ was used such that the sample was actually wet, the chlorine analysis was quite high; this could be reduced to that required for TiF_2Cl_2 by vacuum drying.

The method just described for the preparation of TiF_2Cl_2 is neither as convenient nor is the quality and consistency of the product as good as with the first method described.

D. Titanium Trichloride Fluoride

Several unsuccessful attempts were made to isolate $TiFCl_3$. Observations made during these attempts tend to indicate that, at room temperature, $TiFCl_3$ is a liquid which undergoes disproportionation into TiF_2Cl_2 and $TiCl_4$. The method previously described for the preparation of TiF_2Cl_2, involving the direct reaction of solid TiF_4 with approximately a 30:1 molar excess of $TiCl_4$, was originally carried out in an attempt to prepare $TiFCl_3$. The extremely large excess of $TiCl_4$ would certainly be expected to favor the formation of $TiFCl_3$. The small amount of solid formed above the refluxing liquid in the reaction flask indicates that the formation of TiF_3Cl and TiF_2Cl_2 is not favored.

In another experiment a 4:1 ratio of TiF_4 to $TiCl_4$ was heated at 100°C for 24 hours. The contents of the flask were then filtered to yield a bright yellow liquid--presumably a solution of $TiFCl_3$ in $TiCl_4$. Analysis of this sample showed 74.2% chlorine, indicating that only 4% could be $TiFCl_3$. A portion of this sample was distilled at atmospheric pressure. At 134°C a clear, dark yellow distillate was collected. Upon standing, the clear distillate became cloudy and a yellow solid (subsequently shown to be TiF_2Cl_2) slowly formed. As the distillation was continued, the temperature rose to the boiling point of $TiCl_4$ and the material distilling over became colorless.

Distillation of samples at reduced pressure and temperature simply gave distillates that were more dilute solutions of the yellow liquid. At 30 mm Hg pressure and 47°C the distillate was still dark yellow. At 5 mm Hg and 35°C the distillate was light yellow. At lower pressure and at temperatures below 30°C, the distillate was nearly colorless.

Every attempt to separate the yellow solution into its components failed. Each time the solution was concentrated, a yellow solid (TiF_2Cl_2) formed.

E. Other Possible Compounds

Throughout the development of the syntheses of TiF_3Cl and TiF_2Cl_2, numerous samples were obtained which had compositions intermediate between these two. Several examples follow:

Commercial grade TiF_4 was ground to a fine powder and 48.2 grams of this was added to 172 ml of commercial grade $TiCl_4$ in a 500 ml flask. The $TiCl_4$ and TiF_4 were in a 4:1 molar ratio. The flask was heated to 100°C in an oil bath and stirred with a magnetic stirrer for 24 hours. A heavy yellow coating covered the upper walls of the flask. This sample was collected and found to contain 34% chlorine. Excess liquid was removed from the dirty yellow solid remaining in the bottom of the flask. After drying, the sample contained 24.85% chlorine. Sublimation of this material gave a bright yellow solid containing 38.5% chlorine and 31.5% titanium. This corresponds to $Ti_3F_7Cl_5$ or $2TiF_2Cl_2 \cdot TiF_3Cl$ which requires 38.57% chlorine and 31.74% titanium.

Another solid sample was obtained by distilling the liquid removed from the original reaction mixture. In the first fraction distilled from this liquid, a solid formed. This solid was separated by filtration and then dried by passing dry nitrogen over it for five minutes, after which the solid was placed under vacuum for five minutes. The resulting material contained 53.7% chlorine, which corresponds to $Ti_2F_3Cl_5$ (possibly $TiF_3Cl \cdot TiCl_4$ or $TiF_2Cl_2 \cdot TiFCl_3$) which requires 53.7% chlorine. However, the correspondence between the analytical results and a fixed stoichiometry is probably fortuitous. It is most likely that this sample was TiF_2Cl_2 wet with incompletely removed $TiCl_4$.

The occurrence of nonstoichiometric samples and the possibility of addition compounds will be discussed in more detail in the discussion section. At this point, suffice it to say that mass spectral data which presently will be discussed do not show the presence of any mixed chloride fluoride species other than TiF_3Cl, TiF_2Cl_2, and $TiFCl_3$. Therefore more complex species apparently do not exist in the vapor phase and their existence in distinct molecular form, other than as possible addition compounds, in the solid state is doubtful.

F. Physical Properties

Both titanium chloride trifluoride and titanium dichloride difluoride are bright yellow solids which are not easily distinguished by physical appearance. They are both insoluble in common nondonor solvents such as benzene, toluene, hexane, and carbon tetrachloride. In donor solvents such as tetrahydrofuran, fluorine-19 NMR studies have shown that disproportionation takes place to give a solution containing, in equilibrium, all the titanium(IV) chloride fluoride addition complexes of tetrahydrofuran. The results of these studies will be more fully discussed in Part II of this thesis.

Both TiF_3Cl and TiF_2Cl_2 react with donor substances having an active hydrogen such as water, alcohols, and silanols. The reaction with silanols is discussed in more detail in Appendix I. Exposure to the atmosphere causes the samples to hydrolyze to a white powder which is believed to be either $TiO(OH)F$ or $TiOF_2$. The X-ray diffraction pattern corresponds to that reported by Vorres and Donohue (49) for $TiOF_2$ (Table 1). Dehnicke (10), however, reports that the material thought to be $TiOF_2$ by Vorres is actually $TiO(OH)F$. No additional effort has been made to resolve this variance. Both TiF_3Cl and TiF_2Cl_2 give no X-ray diffraction pattern and appear to be amorphous. Titanium chloride trifluoride appears to be somewhat more thermally stable than titanium dichloride difluoride. In a sealed melting point tube TiF_3Cl showed the first visible sign of decomposition at 215°C whereas TiF_2Cl_2

Table 1. X-ray powder diffraction data for the hydrolysis product of TiF_3Cl and TiF_2Cl_2.

Observed Data	Reported by Vorres (49) for $TiOF_2$	
d	d	Plane
3.80	3.76	100
2.69	2.67	110
2.20	2.18	111
1.90	1.89	200
1.70	1.69	210
1.56	1.54	211
1.35	1.34	220
1.27	1.26	221,300

began to decompose at 140°C. At higher temperatures a yellow liquid distilled from the samples leaving a gray residue. The gray residue, which was probably TiF_4, sublimes away in an open flame.

Mass Spectroscopy

A. Instrumentation

All mass spectra were obtained with a Bendix time of flight mass spectrometer. Sample introduction was accomplished either externally through about one foot of quarter-inch copper tubing which lead to the ionizing beam or internally by adding the sample to a Knudsen effusion cell which was placed inside the mass spectrometer and directly below the ionizing beam. The system was originally designed for high temperature effusion studies and it was not possible to measure the relatively low temperatures at which the effusion cell was operated. The effusion cell was heated very slowly until a pressure rise was observed in the system indicating that the sample was volatilizing.

B. Titanium Tetrachloride

Figures 3a and 3b show the mass spectrum obtained for a sample of distilled titanium tetrachloride that was externally introduced into the mass spectrometer. At an ionizing potential of 25 electron volts the following species were observed: $TiCl_4^+$, $TiCl_3^+$, $TiCl_2^+$, $TiCl^+$, HCl^+, and Cl^+.

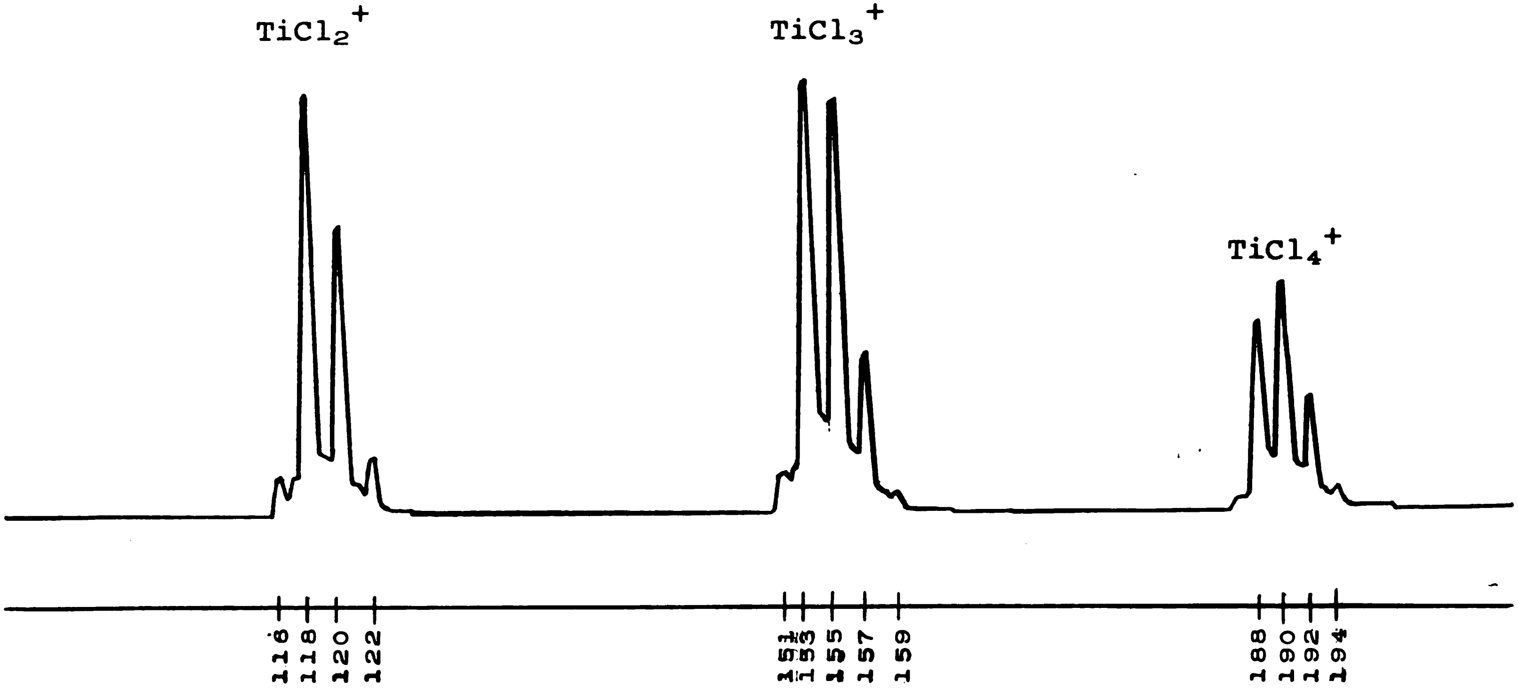


Figure 3a. Mass spectrum of $TiCl_4$ at 25 ev ionizing potential. High mass region.

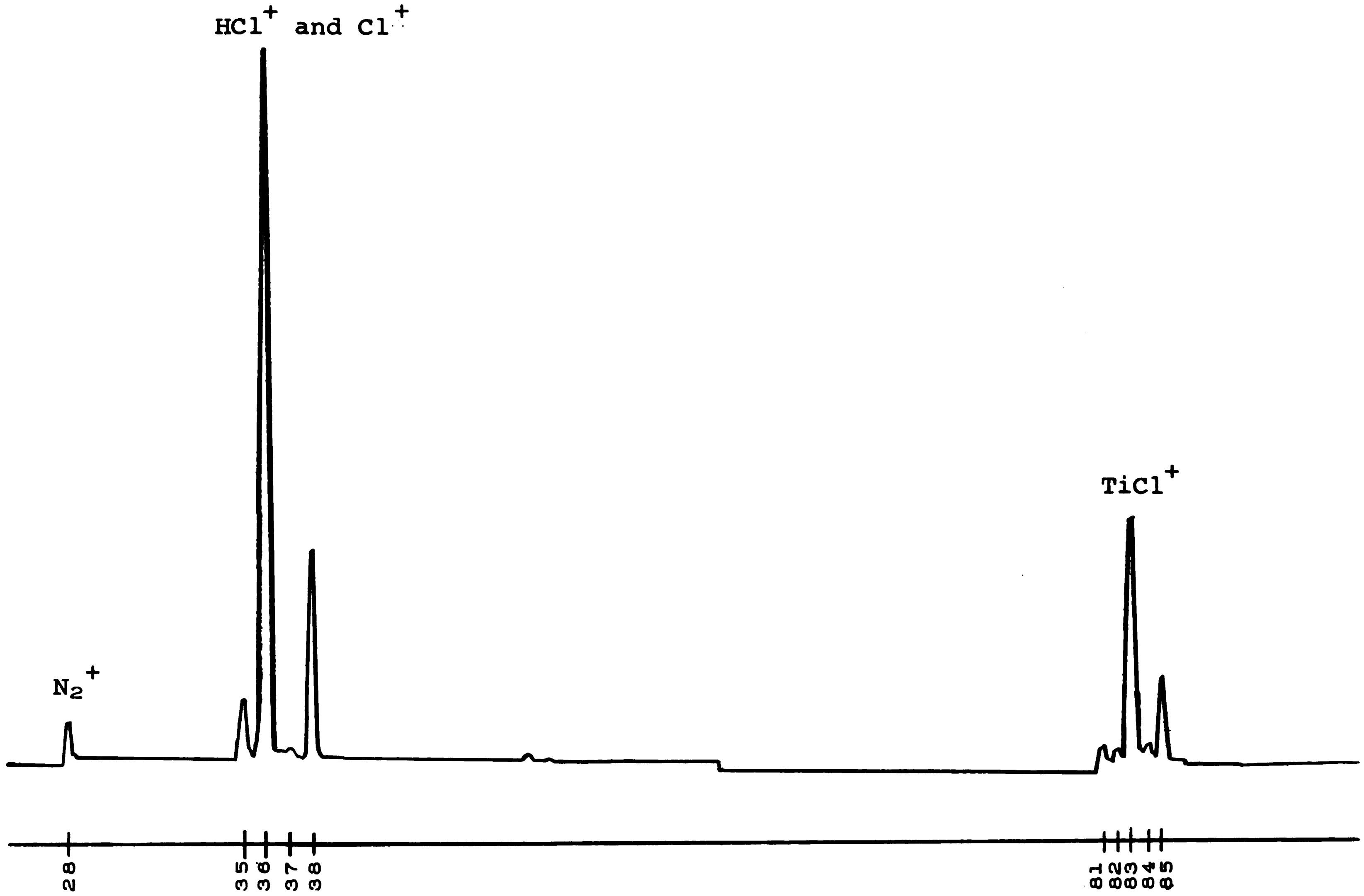


Figure 3b. Mass spectrum of $TiCl_4$ at 25 ev ionizing potential. Low mass region.

Table 2. Mass spectral data. $TiCl_4$ at 25 ev ionizing potential.

Species	Mass-to-charge Ratio	Mass Abundance Ratio		Species Abundance Ratio
		Calculated	Observed	
$TiCl_4^+$	194	12	11	54
	192	51	51	
	190	100	100	
	188	80	83	
	186	7.6	6.2	
$TiCl_3^+$	159	5.1	4.4	100
	157	35	37	
	155	98	96	
	153	100	100	
	151	9.7	8.9	
$TiCl_2^+$	122	14	14	75
	120	67	68	
	118	100	100	
	116	10	9.0	
$TiCl^+$	85	38	37	42
	84	10	7.9	
	83	100	100	
	82	9.7	7.9	
	81	10	10	
HCl^+	38	32	29	92
	36	100	100	
Cl^+	37	32	20	7.6
	35	100	100	
N_2^+	28	--	--	3.8

Table 2 includes the calculated and observed mass-to-charge ratio, mass intensity ratios, and the relative abundance of each species. The rather intense mass peaks observed for HCl may be due to slight hydrolysis of the sample as it passed through the external inlet system or perhaps to HCl as an impurity in the sample. No mass peaks were observed for any oxygen-containing species.

C. Titanium(IV) Chloride Fluorides

A sample of TiF_2Cl_2 was placed in a glass container and connected through the external inlet to the mass spectrometer. At an ionizing potential of 25 electron volts and with the sample at room temperature only the cracking pattern of $TiCl_4$ was observed. The $TiCl_4$ background disappeared after pumping on the sample for a short period. The sample was then slowly heated and at 55°C both $TiCl_4$ and $TiFCl_3$ were observed in the spectrum. The species present were $TiCl_4^+$, $TiCl_3^+$, $TiCl_2^+$, $TiCl^+$, $TiFCl_3^+$, $TiFCl_2^+$, and $TiFCl^+$. Figures 4a and 4b show this spectrum and Table 3 contains the enumerated data. By increasing the sample temperature and the ionizing potential, more intense mass peaks were observed. These data are shown in Figure 5 and Table 4. In both these spectra, the sample pressure was fairly unstable. The relative abundance of the species present is therefore of doubtful significance except to show that $TiCl_4$ was present in much higher concentration than $TiFCl_3$.

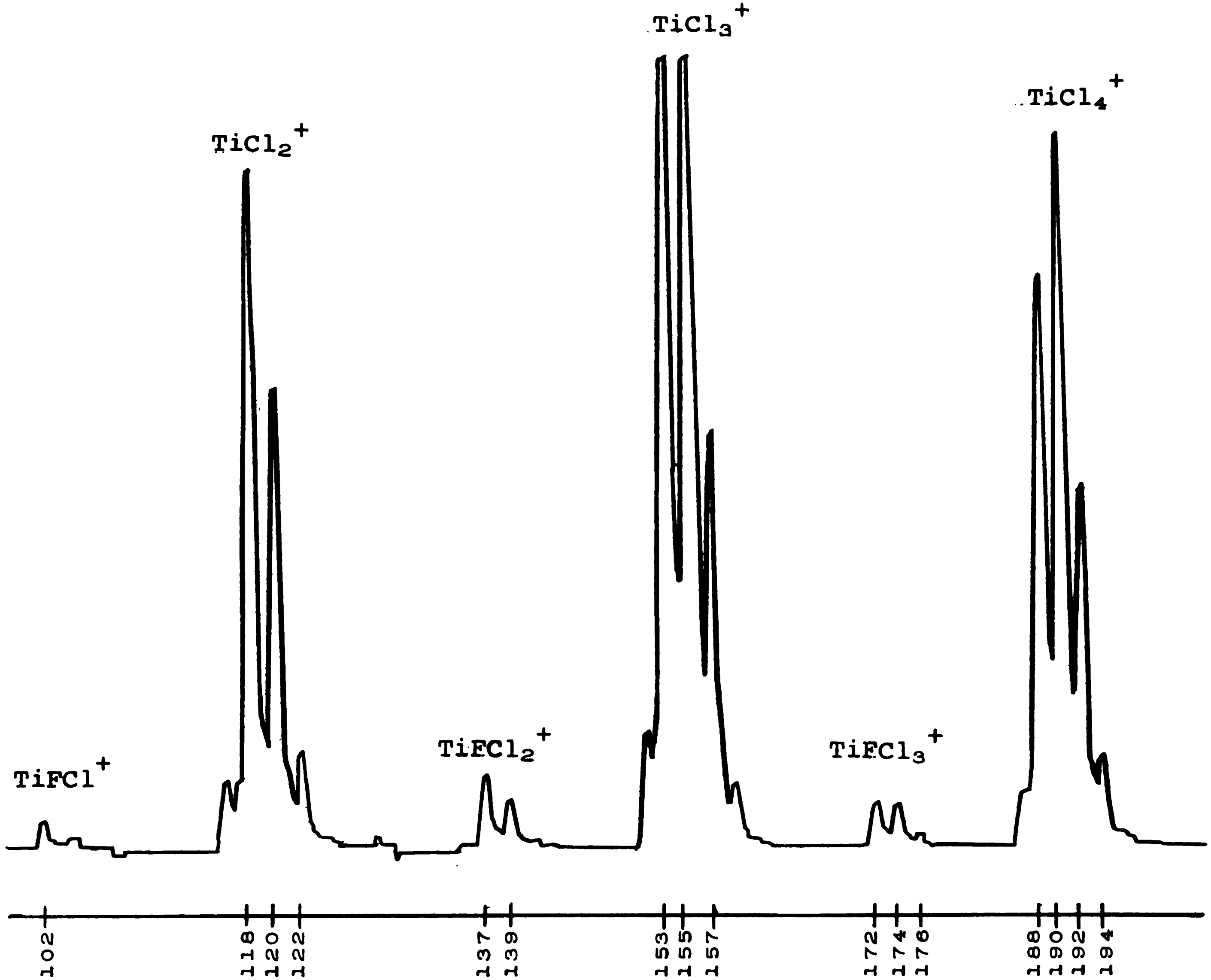


Figure 4a. Mass spectra of $TiCl_4$ and $TiFCl_3$ at 25 ev ionizing potential. High mass region.

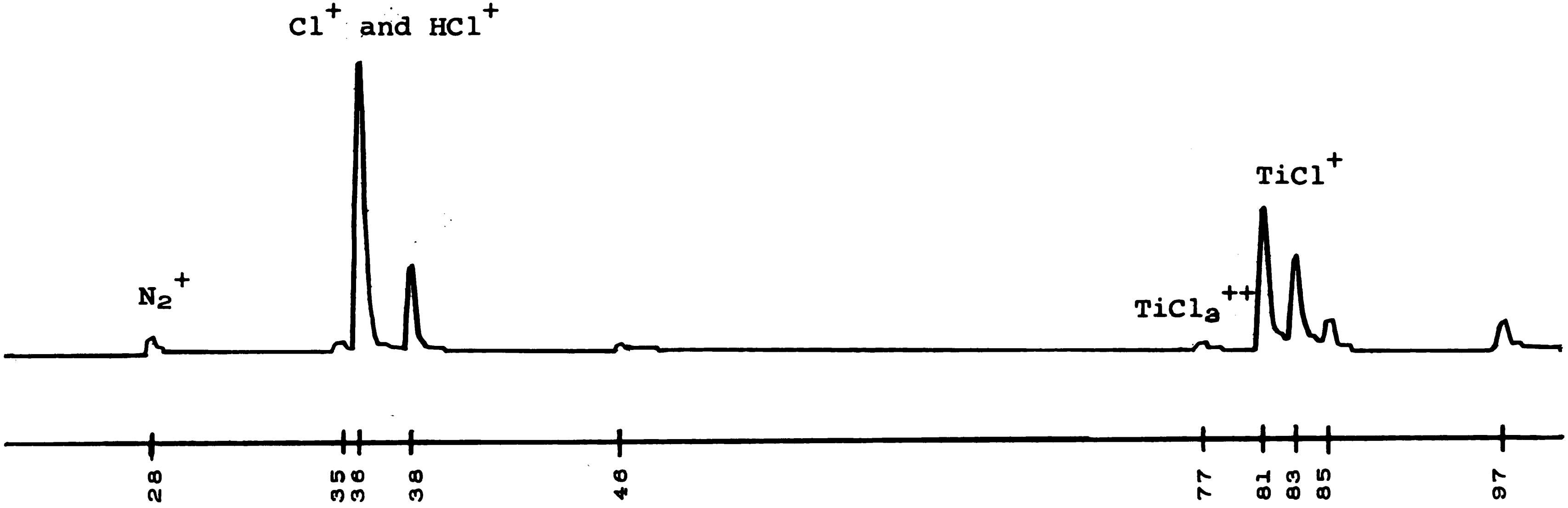


Figure 4b. Mass spectrum of $TiCl_4$ and $TiFCl_3$ at 25 ev ionizing potential. Low mass region.

Table 3. Mass spectral data. $TiCl_4$ and $TiFCl_3$ at 25 ev ionizing potential. Externally introduced sample at 55°C.

Species	Mass-to-charge Ratio	Mass Abundance Ratio		Species Abundance Ratio
		Calculated	Observed	
$TiCl_4^+$	194	12	12	62
	192	52	51	
	190	100	100	
	188	80	81	
	186	7.6	7.3	
$TiFCl_3^+$	176	35	32	3.6
	174	98	98	
	172	100	100	
$TiCl_3^+$	159	5.1	5.1	100
	157	35	35	
	155	98	97	
	153	100	100	
	151	9.7	9.5	
$TiFCl_2^+$	139	67	66	4.6
	137	100	100	
$TiCl_2^+$	122	14	14	44
	120	67	68	
	118	100	100	
	116	10	9.5	
$TiFCl^+$	102	--	--	1.3
$TiCl^+$	85	38	33	4.5
	83	100	100	
	81	10.4	152 ?	
HCl^+	38	32	29	11
	36	100	100	
Cl^+	35	--	--	--
N_2^+	28	--	--	--

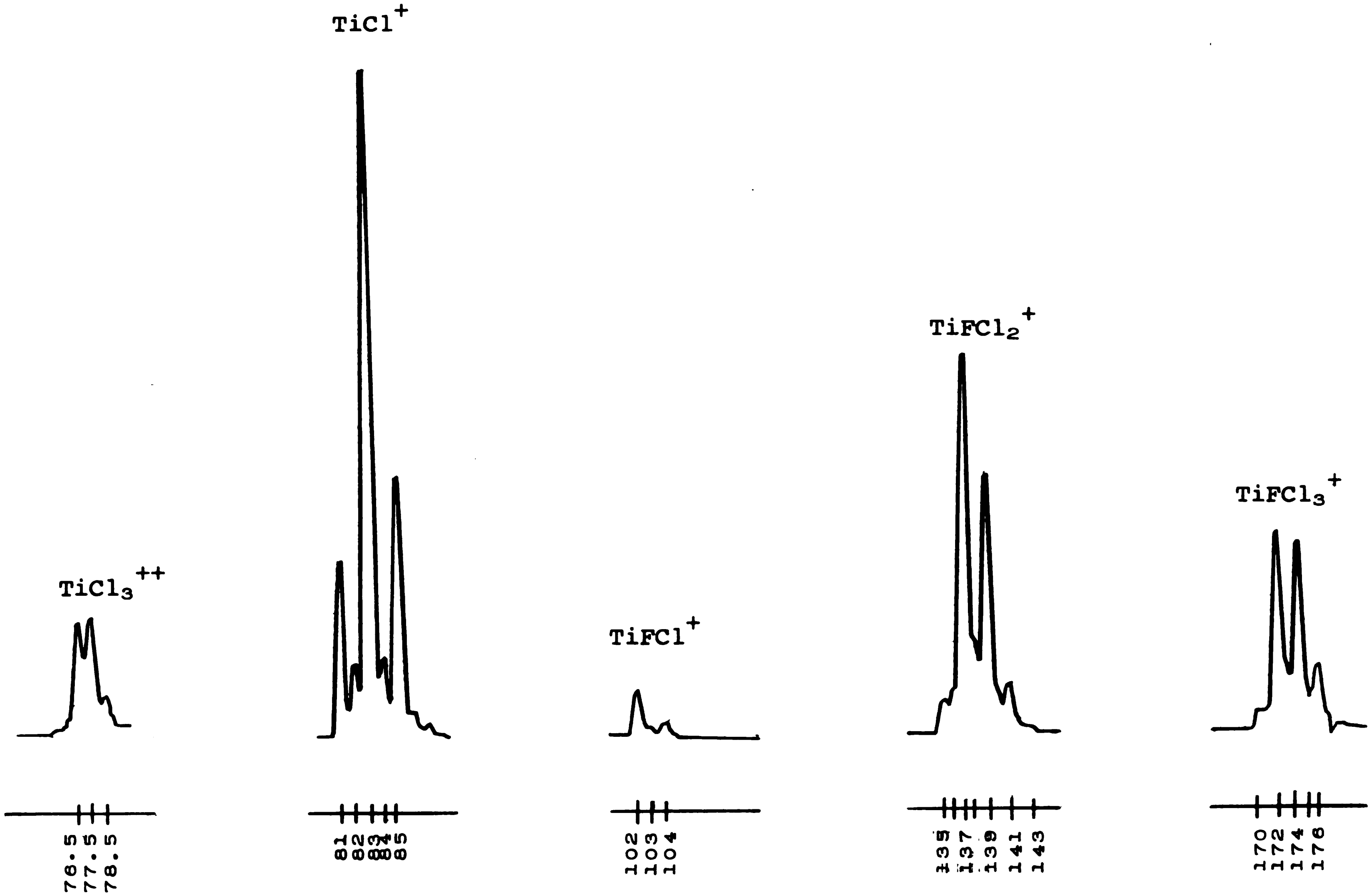


Figure 5. Mass spectra of $TiCl_4$ and $TiFCl_3$. Selected species at 25 and 70 ev ionizing potentials.

Table 4. Mass spectral data. $TiCl_4$ and $TiFCl_3$, selected peaks. Externally introduced sample.

Species	Mass-to-charge Ratio	Mass Abundance Ratio		Sample Temperature	Ionizing Potential
		Calculated	Observed		
$TiFCl_3^+$	176	35	33	70°C	25 ev
	174	98	96		
	172	100	100		
	170	9.7	10		
$TiFCl_2^+$	143	--	--	70°C	70 ev
	141	14	13		
	139	67	68		
	137	100	100		
	135	10	8.1		
$TiFCl^+$	104	38	35	80°C	25 ev
	103	10	17		
	102	100	100		
$TiCl_3^{++}$	78.5	35	33	80°C	70 ev
	77.5	98	100		
	76.5	100	97		
$TiCl^+$	85	38	39	80°C	70 ev
	84	10	12		
	83	100	100		
	82	9.7	11		
	81	10	27		

A sample of mixed titanium(IV) chloride fluoride having a composition corresponding to $2TiF_2Cl_2 \cdot TiF_3Cl$ was placed in a high nickel content stainless steel effusion cell and placed directly below the ionizing beam in the mass spectrometer. At room temperature no mass peaks were observed. The sample was slowly heated until enough sample was volatilized to give a usable spectrum. The spectrum which appears in Figure 6 clearly shows the existence in the vapor phase of $TiCl_4$, $TiFCl_3$, TiF_2Cl_2, and TiF_3Cl. The data calculated from this spectrum are given in Table 5.

Analytical Methods

A. Titanium Analysis

Determination of titanium was accomplished in one of three ways:

i. Gravimetric determination. Samples were hydrolyzed and ignited to TiO_2. A 0.3 gram sample was accurately weighed into a platinum crucible under nitrogen. The sample was then exposed to the atmosphere and allowed to hydrolyze. Three to four milliliters of six molar sulfuric acid were added and the sample was carefully heated to dryness. The sulfuric acid treatment was repeated and the sample was then ignited to constant weight. From the weight of the titanium dioxide thus obtained the per cent titanium in the sample was calculated. The ignited TiO_2 was not pure white but salmon in color. In a number of cases low results were obtained and

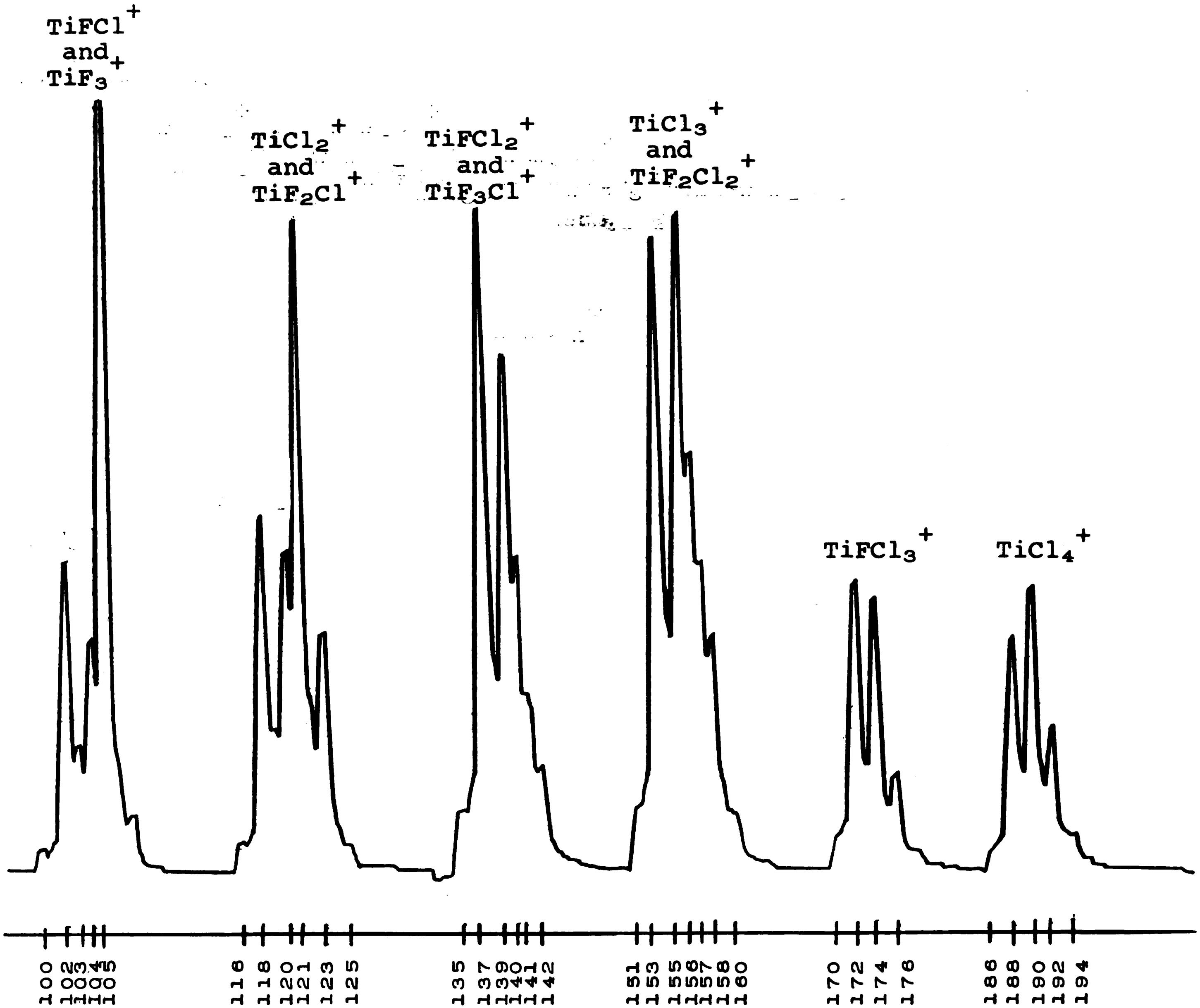


Figure 6a. Mass spectra of $TiF_{\underline{x}}Cl_{4-\underline{x}}$ compounds at 50 ev ionizing potential. High mass region.

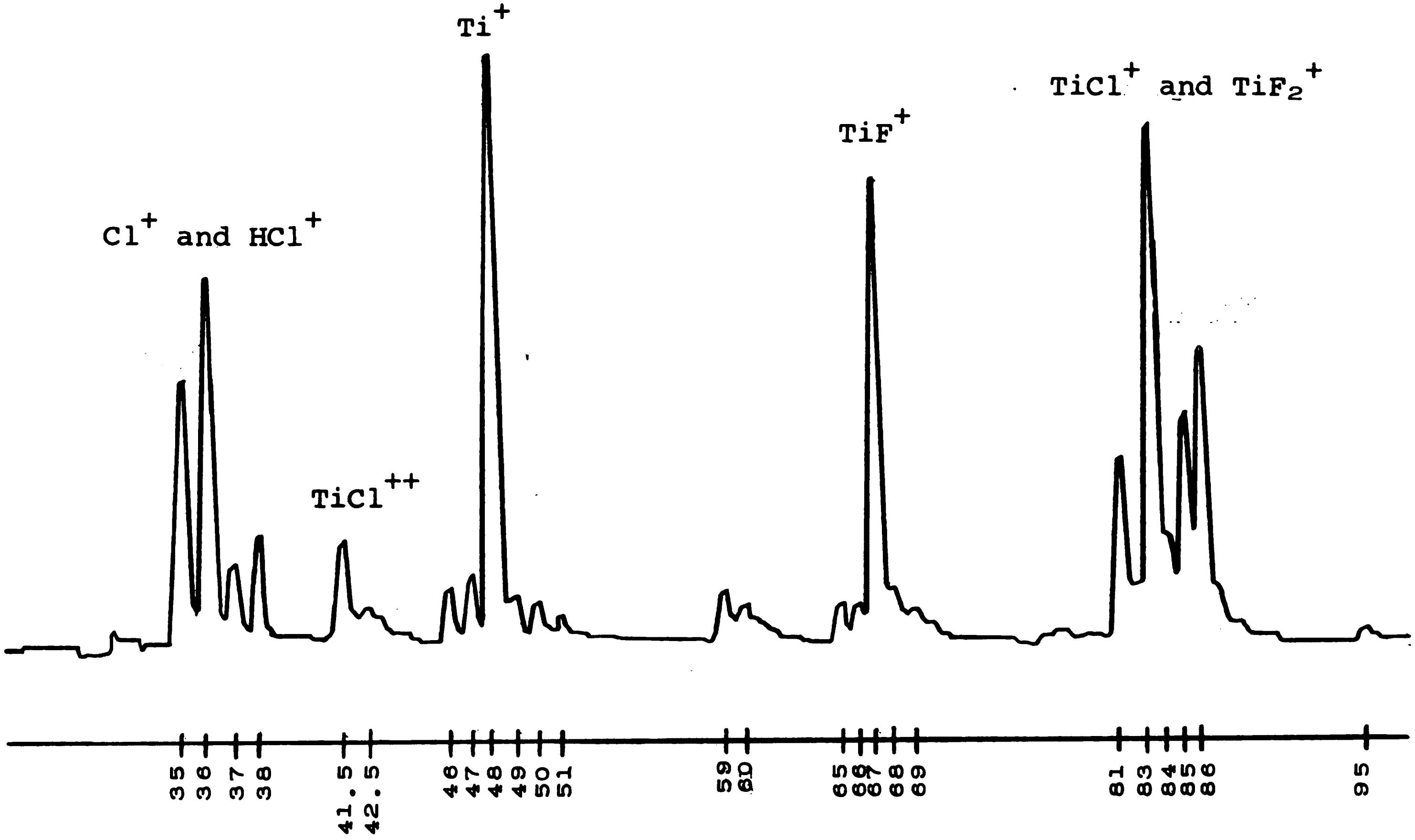


Figure 6b. Mass spectra of $TiF_{\underline{x}}Cl_{4-\underline{x}}$ compounds at 50 ev ionizing potential. Low mass region.

Table 5. Mass spectral data TiF_xCl_{4-x} compounds at 50 ev ionizing potential.

Table 5. Mass spectral data. TiF_xCl_{4-x} compounds at 50 ev ionizing potential. Knudsen effusion method.

Species	Mass-to-charge Ratio	Mass Abundance Ratio Theory	Mass Abundance Ratio Observed
$TiCl_4^+$	194	12	13
	192	52	50
	190	100	100
	188	80	83
	186	7.6	8.7
$TiFCl_3^+$	176	35	34
	174	98	95
	172	100	100
	170	9.7	13

- -

The following species have some overlapping mass peaks.

Species	Mass-to-charge Ratio	Mass Abundance Ratio Theory		Mass Abundance Ratio Calculated*		Calculated Sum	Measured Intensity
		$TiF_2Cl_2^+$	$TiCl_3^+$	$TiF_2Cl_2^+$	$TiCl_3^+$		
$TiF_2Cl_2^+$ and $TiCl_3^+$	160	14	--	7.9	--	7.9	9.5
	158	67	--	38	--	38	38
	157	13	35	7.2	36	43	49
	156	100	9.4	57	10	67	67
	155	7.5	98	4.3	100	104	106
	153	--	100	--	102	102	102
	151	--	9.7	--	10	10	10

continued

Table 5. Continued

Species	Mass-to-charge Ratio	Mass Abundance Ratio				Calculated Sum	Measured Intensity
		Theory		Calculated			
		TiF_3Cl^+	$TiFCl_2^+$	TiF_3Cl^+	$TiFCl_2^+$		
TiF_3Cl^+ and $TiFCl_2^+$	142	38	--	16.5	--	16.5	16.5
	141	10	14	4.4	15	19	28
	140	100	4.3	43	4.6	48	50
	139	10	67	4.2	72	76	83
	137	--	100	--	107	107	107
	135	--	10	--	11	11	11
		TiF_2Cl^+	$TiCl_2^+$	TiF_2Cl^+	$TiCl_2^+$		
TiF_2Cl^+ and $TiCl_2^+$	125	2.3	--	2.3	--	2.3	4
	123	38	--	38	--	38	38
	121	100	4.3	100	2.5	103	105
	120	10	67	10	38	48	51
	119	10	13	10	7.2	17	23
	118	--	100	--	57	57	57
	116	--	10	--	5.7	5.7	4.5
		TiF_3^+	$TiFCl^+$	TiF_3^+	$TiFCl^+$		
TiF_3^+ and $TiFCl^+$	107	7.2	--	9.0	--	9.0	9.0
	105	100	2.3	139	1	140	>125
	104	10	38	14	19	33	37
	103	11	10	15	5.0	20	20
	102	--	100	--	50	50	50
	100	--	10	--	5.0	5.0	4.0
$TiCl_4^{++}$?	95	Very small peak observed					

continued

Table 5. Continued

Species	Mass-to-charge Ratio	Mass Abundance Ratio				Calculated Sum	Measured Intensity
		Theory		Calculated			
		TiF_2^+	TiF_2^+	TiF_2^+	$TiCl^+$		
TiF_2^+ and $TiCl^+$	86	100	2.3	39	1.5	40	40
	85	10	38	3.9	27	31	31
	84	11	10	4.2	7.2	11	14
	83	--	100	--	72	72	72
	81	--	10	--	7.2	7.2	25

- -

Species	Mass-to-charge Ratio	Mass Abundance Ratio	
		Theory	Observed
TiF^+	69	7.2	7.6
	68	7.4	8.1
	67	100	100
	66	10	9.2
	65	11	11
$TiCl_2^{++}$?	60	67	69
	59	100	100
?	51	Very small unknown peak	
Ti^+	50	7.2	6.7
	49	7.4	7.8
	48	100	100
	47	10	12
	46	11	10
$TiCl^{++}$	42.5	38	33
	41.5	100	100

continued

Table 5. Continued

Species	Mass-to-charge Ratio	Mass Abundance Ratio	
		Theory	Observed
HCl^+	38	32	30
	36	100	100
Cl^+	37	32	30
	35	100	100

[*] Calculated values were obtained by taking the measured intensity of the largest nonoverlapping mass peak for each species as a standard and then calculating the expected intensity for the other isotopic mass peaks so as to maintain the proper theoretical mass abundance ratio. The sum of these calculated values should agree with the measured intensities.

in some cases there was evidence that the sample reacted with the platinum crucible. The method was also very time consuming.

ii. Neutron activation analysis. Several samples were sealed in polyethylene containers and sent to the Dow Chemical Company for neutron activation analysis. By this method it was possible to determine chlorine, fluorine, and oxygen in addition to titanium. A very large sample (three to ten grams) was required. The error expected by this method was on the order of two per cent, which is relatively high. Due to the large samples required, this method received little use. Its main advantage was to establish the absence of oxygen in the samples submitted.

iii. Titration of titanium(III) with standard iron(III) solution. This method was developed by Rahm (43) and modified by Scheffer (46) for the determination of titanium in titanium dioxide and in ore samples. With only slight further modification this method has been conveniently applied to the determination of titanium in the titanium(IV) chloride fluorides.

A 0.1 to 0.2 gram sample was accurately weighed under nitrogen and then added to a 500 ml Erlenmeyer flask containing 20 mls of concentrated sulfuric acid, 10 mls of H_2O, and 8 grams of ammonium sulfate. The sample dissolved on heating. When fumes of SO_3 were observed, heating was discontinued and the sample was allowed to cool to room temperature. One hundred twenty grams of water and 20 mls of concentrated hydrochloric acid were then added and the solution brought to a boil. Reduction of titanium(IV) to titanium(III) was then accomplished by adding one gram of high purity aluminum foil. The apparatus was designed so that as the reduction reaction subsided and the solution cooled, saturated sodium bicarbonate solution was pulled back into the reaction flask to provide a non-oxidizing atmosphere of carbon dioxide. The titration with standardized iron(III) solution was carried out under nitrogen after the sample had cooled to room temperature. The iron(III) solution was prepared so that one milliliter was equivalent to approximately three milligrams of titanium. Ammonium thiocyanate was used to determine the equivalence point by indicating the first excess of iron(III). This method was precise and proved to be very convenient for a large number of samples.

B. Chlorine Analysis

In addition to the neutron activation method previously mentioned, chlorine was determined by a modified Volhard procedure.

A 0.1 to 0.2 gram sample was accurately weighed under nitrogen in a one dram glass vial tightly sealed with a polyethylene cap. The vial was then cooled to dry ice temperature to retard the hydrolysis reaction. With the cap removed, the vial was carefully dropped into a 125 ml iodine flask containing a known excess of silver nitrate solution and ten milliliters of 6 <u>N</u> HNO_3. The iodine flask was quickly stoppered and tilted so that the vial would fall over and allow the sample to react with the silver nitrate solution. After digesting the sample for several minutes, it was filtered to remove the AgCl precipitate. The standard Volhard method (31) was then followed.

C. Fluorine Analysis

Several methods in addition to neutron activation analysis were attempted in order to determine fluorine, but these met without success. Attempts to precipitate the fluoride as lead chloride fluoride failed when it was found that titanium coprecipitated. The complete removal of titanium prior to the lead chloride fluoride precipitation proved to be extremely difficult. In another attempt to determine fluorine, the sample was allowed to hydrolyze in the atmosphere to remove the chloride as hydrogen chloride. Steam was then passed over the sample to remove the fluoride as hydrofluoric acid. The acid thus obtained was titrated with standard base, but inconsistent results were obtained.

Since neutron activation analysis had shown oxygen contamination not to be a problem and since the only other elements present (chlorine and titanium) could be accurately determined, fluorine was determined by difference.

D. X-ray Diffraction Data

The crystallographic *d*-spacings for the hydrolysis product of TiF_2Cl_2 and TiF_3Cl were calculated from film data obtained with a North American Philips powder diffraction unit using copper k_α radiation. A Debye--Scherrer powder diffraction camera of 114.6 mm diameter was used.

DISCUSSION

Mass Spectroscopy

Observation of the three titanium(IV) chloride fluorides by mass spectroscopy conclusively establishes that halogen exchange has taken place and that these compounds have independent existence.

Species assignments were made by correlating the observed mass-to-charge ratios and their intensity ratios with those calculated from probability theory for the isotopic masses of each compound. The isotopes of titanium, chlorine, and fluorine are listed in Table 6 along with their relative abundances (26).

Table 6. Isotopic abundance.

Titanium	Chlorine	Fluorine
^{46}Ti - 8.0%	^{35}Cl - 75.5%	^{19}F - 100%
^{47}Ti - 7.4%	^{37}Cl - 24.5%	
^{48}Ti - 73.8%		
^{49}Ti - 5.5%		
^{50}Ti - 5.3%		

For any given titanium isotope, the probability of forming any of the five possible species $\mathrm{Ti^{35}Cl_{\underline{n}}{}^{37}Cl_{(4-\underline{n})}}$, where $\underline{n}$ = 0, 1, 2, 3, or 4, is given by the expression

$$P_{4,\underline{n}} = \frac{4!}{(\underline{n}!)\ (4-\underline{n})!}\ (75.5)^{\underline{n}}(24.5)^{(4-\underline{n})}$$

These values, when multiplied by the isotopic abundance of each titanium isotope, give the relative isotopic abundances for all the possible $TiCl_4$ masses. Summing all the values for the same mass number gives the calculated relative intensities of all the mass-to-charge peaks for this species. Similar calculations were carried out for each species expected.

The following species were observed and confirmed to have the expected charge-to-mass and intensity ratios.

Parent Compound	Observed Identifying Species
$TiCl_4$	$TiCl_4^+$, $TiCl_3^+$, $TiCl_2^+$, $TiCl^+$
$TiFCl_3$	$TiFCl_3^+$, $TiFCl_2^+$, $TiFCl^+$, TiF^+
TiF_2Cl_2	$TiF_2Cl_2^+$, TiF_2Cl^+, TiF_2^+
TiF_3Cl	TiF_3Cl^+, TiF_3^+
TiF_4	Not observed

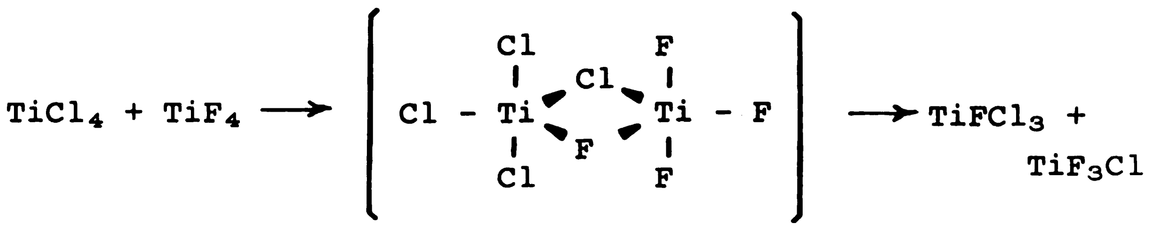
There can be little doubt as to the identification of these species and therefore little doubt about the existence of the parent compounds in the vapor state. This conclusively establishes that halogen exchange has taken place to give all the titanium(IV) chloride fluorides.

The Knudsen effusion method (3) was employed to overcome the difficulties encountered in the external introduction of the sample into the mass spectrometer. It was particularly expected to reduce the chance of intermolecular gas phase collisions and thereby give more explicit information regarding the nature of the solid sample. The presence of $TiCl_4$ as well as the titanium(IV) chloride fluorides in the vapor above these samples indicates either that the samples are mixtures of all these species or--more likely--that the sample undergoes incongruous vaporization, disproportionating to give the observed species.

The failure to observe any species more complex than those listed tends to eliminate $Ti_2F_3Cl_5$, $Ti_3F_7Cl_5$ and other bridging type complexes as existing in distinct molecular form.

Theoretical Considerations

In considering an idealized reaction between gaseous tetrahedral molecules, the reaction might be expected to proceed through an intermediate addition type "activation complex" as the following reaction suggests:



The existence of numerous five-coordinate addition complexes of titanium gives some credence to the postulation of this intermediate (8,27,36).

As this reaction continues, the concentrations of $TiFCl_3$ and TiF_3Cl increase and they begin to react with the starting material and themselves. Van Wazer (33) pointed out in a study of scrambling reactions of tetrahedral silicon compounds that at equilibrium there are twelve ways for two pairs of five components (two reactants and three mixed products) to react to form the other components. The twelve reactions for the idealized exchange between $TiCl_4$ and TiF_4 follow:

(1) $TiCl_4 + TiF_4 \rightarrow TiF_3Cl + TiFCl_3$

(2) $TiCl_4 + TiF_3Cl \rightarrow TiF_2Cl_2 + TiFCl_3$

(3) $TiF_4 + TiFCl_3 \rightarrow TiF_2Cl_2 + TiF_3Cl$

(4) $TiCl_4 + TiF_2Cl_2 \rightarrow 2TiFCl_3$

(5) $TiF_4 + TiF_2Cl_2 \rightarrow 2TiF_3Cl$

(6) $TiF_3Cl + TiFCl_3 \rightarrow 2TiF_2Cl_2$

(7) $TiF_3Cl + TiFCl_3 \rightarrow TiCl_4 + TiF_4$

(8) $TiF_2Cl_2 + TiFCl_3 \rightarrow TiCl_4 + TiF_3Cl$

(9) $TiF_2Cl_2 + TiF_3Cl \rightarrow TiF_4 + TiFCl_3$

(10) $2TiFCl_3 \rightarrow TiCl_4 + TiF_2Cl_2$

(11) $2TiF_3Cl \rightarrow TiF_4 + TiF_2Cl_2$

(12) $2TiF_2Cl_2 \rightarrow TiF_3Cl + TiFCl_3$

Equations seven through twelve are simply the reverse reactions of the first six.

The ideal case for gaseous tetrahedral molecules is far from the actual case. The greatest factor contributing to the nonideality of the system is that TiF_4, TiF_3Cl, and TiF_2Cl_2 are solids and probably are octahedrally coordinated. $TiFCl_3$ was not isolated, but it is believed to be a liquid at room temperature. $TiCl_4$ is a liquid and known to have tetrahedral coordination. TiF_4 is an amorphous solid and structural details are unknown. Its structure is perhaps best described as containing a disordered array of polymeric six-coordinate titanium chains which have fluorine bridge bonding. Titanium could be eight-coordinate as is ZrF_4, however if this were the case, one would expect a more ordered crystalline structure and insolubility in donor solvents. The low sublimation temperature of TiF_4 (284°C) indicates that the structure is not ionic as has been suggested by some authors.

The effect of solid structures with greater than four coordination for titanium would be to increase the stabilities of these components due to increased molecular bond energies. These energies might be expected to increase with increasing fluorine. The observed decomposition temperatures of TiF_3Cl and TiF_2Cl_2 of 215°C and 140°C, respectively, tend to support this contention. The net effect of these deviations from ideality would be to give a larger equilibrium concentration of TiF_4, TiF_3Cl, and perhaps TiF_2Cl_2 than would be predicted for random ordering.

Interpretation of Experimental Results

A. Heterogeneous Reaction

The key to interpreting the experimental data probably rests with the only mixed halide not isolated, $TiFCl_3$. It is postulated that this compound is an unstable yellow liquid at room temperature and that it undergoes spontaneous disproportionation to TiF_2Cl_2 and $TiCl_4$.

In an isolated system under fixed conditions of temperature and pressure, TiF_3Cl, TiF_2Cl_2, and $TiFCl_3$ are undoubtedly in equilibrium with each other and with $TiCl_4$ and TiF_4. However, under the actual experimental conditions, the most volatile components $TiFCl_3$ and $TiCl_4$ would volatilize and condense on the walls of the reaction container. In this concentrated form, $TiFCl_3$ is believed to disproportionate to give the yellow solid TiF_2Cl_2. TiF_2Cl_2 could then undergo further reaction according to equation 8 or equation 12 to produce TiF_3Cl. The yellow solid observed on the wall of the reaction container probably was a mixture of TiF_2Cl_2 and TiF_3Cl.

TiF_3Cl was isolated from a reaction in which the temperatures employed were approximately 80°C higher than for the other reactions. This would certainly hasten conversion of TiF_2Cl_2 to TiF_3Cl by equation 12. Some TiF_4 could also have been formed according to equation 11. Since the sample isolated from this reaction was sublimed twice in a short path sublimator, it is reasonable to expect the isolation of relatively pure TiF_3Cl. In many other reactions where lower temperatures were maintained, the yellow solid isolated had an analysis between TiF_3Cl and TiF_2Cl_2.

Titanium dichloride difluoride was isolated from a yellow liquid distilled from a reaction mixture containing $TiCl_4$ and TiF_4 in a 30:1 molar ratio (p. 9). The large excess of $TiCl_4$ should favor the formation of $TiFCl_3$, which probably was distilled along with $TiCl_4$ into the receiver flask. Upon standing, TiF_2Cl_2 forms as a yellow solid and the excess $TiCl_4$ was then pulled off under vacuum. Isolation of solid TiF_2Cl_2 from the yellow liquid strongly indicates that some sort of molecular rearrangement takes place. Since TiF_2Cl_2 is known from mass spectroscopy studies to exist in the vapor state at elevated temperatures, it is conceivable for some TiF_2Cl_2 to have been distilled directly; however, considering the large excess of $TiCl_4$, it is expected that any gaseous TiF_2Cl_2 would have been converted to $TiFCl_3$ according to equation 4.

Perhaps the best evidence for the formation of $TiFCl_3$ as an intermediate in the preparation of TiF_2Cl_2 comes from the mass spectral results. When a sample of TiF_2Cl_2 was connected externally to the mass spectrometer through a one foot length of quarter-inch copper tubing and the sample heated, the only compounds observed were $TiCl_4$ and $TiFCl_3$. This conclusively establishes $TiFCl_3$ as a substance of finite stability and high volatility. TiF_2Cl_2 was probably condensed on the cool walls of the copper tube. Considering the relatively high concentration of $TiCl_4$ in the gas phase it is also possible that any gaseous TiF_2Cl_2 was converted to $TiFCl_3$ according to equation 4 before reaching the mass spectrometer.

B. Gas Phase Reaction

In considering the results from the gas phase reaction, where $TiCl_4$ vapor was passed over TiF_4 in a heated tube (p. 12), the twelve reactions previously discussed can again be considered. The predominant reactions in this case probably would be 1 and 2. TiF_3Cl initially produced in reaction 1 could undergo further collision with $TiCl_4$ which is in excess in the gas phase to produce TiF_2Cl_2 by equation 2.

Material closest to the hot zone always had the highest fluorine analysis and probably was a mixture of TiF_4, TiF_3Cl, and TiF_2Cl_2 whereas the sample farthest from the hot zone always had an analysis close to TiF_2Cl_2. Under the conditions of this reaction, it is believed that TiF_2Cl_2 is the major product and that TiF_3Cl and $TiFCl_3$ are produced in smaller amounts. The material that deposits near the hot zone probably undergoes decomposition according to equations 11 and 12 to produce increased amounts of TiF_3Cl and TiF_4. No solid sample was ever isolated with a chlorine analysis higher than that expected for TiF_2Cl_2.

A significant amount of yellow liquid and solid always collected in the cold traps positioned after the reaction tube. Some of the solid was probably carried by the nitrogen stream past the baffles to the traps. It is also possible that some $TiFCl_3$ which had been formed initially in the reaction later underwent disproportionation according to equation 10 to yield solid TiF_2Cl_2 and $TiCl_4$. The yellow liquid was probably a solution of $TiFCl_3$ in $TiCl_4$. Failure to obtain any solid with a chlorine concentration higher than expected for TiF_2Cl_2 and the observation of the yellow solution in the cold traps further supports the contention that $TiFCl_3$ is a liquid.

Solid State Structure

The solid state structures of TiF_4, TiF_3Cl, and TiF_2Cl_2 are unknown. In a brief note, Dehnicke (10) claimed to have prepared TiF_2Cl_2 and reported an X-ray diffraction pattern as well as infrared data for the solid sample. From the infrared spectrum he concluded that TiF_2Cl_2 has $\underline{C_{2v}}$ symmetry with tetrahedral halide arrangement around the titanium. He also concluded that the metal-chlorine bond is strengthened and the metal-fluorine bond is weakened in comparison with TiF_4 and $TiCl_4$. The reaction employed is represented by the following equation:

$$TiCl_4 + 2ClF \xrightarrow{0^\circ C} TiF_2Cl_2 + 2Cl_2$$

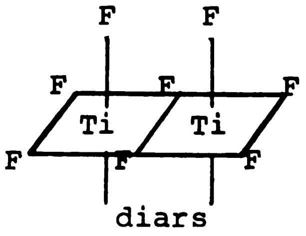
Unfortunately no analysis or further details are given.

If a large excess of $TiCl_4$ were employed, formation of $TiFCl_3$ followed by disproportionation to TiF_2Cl_2 might be expected. A more nearly stoichiometric ratio of reactants should give mixtures of products as in the case of $TiCl_4$-TiF_4 exchange.

None of the samples prepared by the $TiCl_4$-TiF_4 exchange reaction, including TiF_2Cl_2, has shown an X-ray diffraction pattern. TiF_3Cl prepared by chlorination of TiF_3 by Vorres (48) also did not give a diffraction pattern.

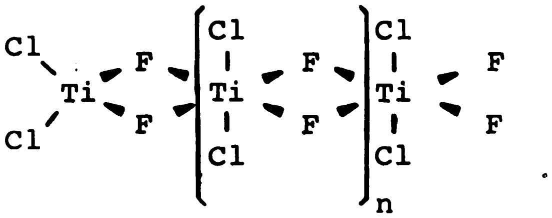
The existence of an ordered solid state structure for TiF_2Cl_2 is doubtful in view of the amorphous nature of TiF_4 and TiF_3Cl; however under appropriate conditions an ordered structure may well be possible. The existence of a solid state structure for TiF_2Cl_2 with $\underline{C_{2v}}$ symmetry and tetrahedral halide coordination, either ordered or disordered, is extremely doubtful.

Samples of TiF_2Cl_2 subjected to pressures as low as 1×10^{-7} mm Hg in the mass spectrometer showed no significant vapor pressure at room temperature. At elevated temperature $TiCl_4$ was first given off, followed by $TiFCl_3$, then TiF_2Cl_2, and finally TiF_3Cl. This behavior suggests extremely strong intermolecular interactions which would not be expected for the tetrahedral structure. It seems far more reasonable to suspect sixfold octahedral coordination, most probably with fluorine bridge bonding. Fluorine bridge bonding is well-established (36). The example closest to the present case occurs in the complex formed between TiF_4 and o-phenylenebis(dimethylarsine) (diars) which has the formula $(TiF_4)_2$diars. On the basis of infrared evidence this complex is believed to have the structure indicated below (7).



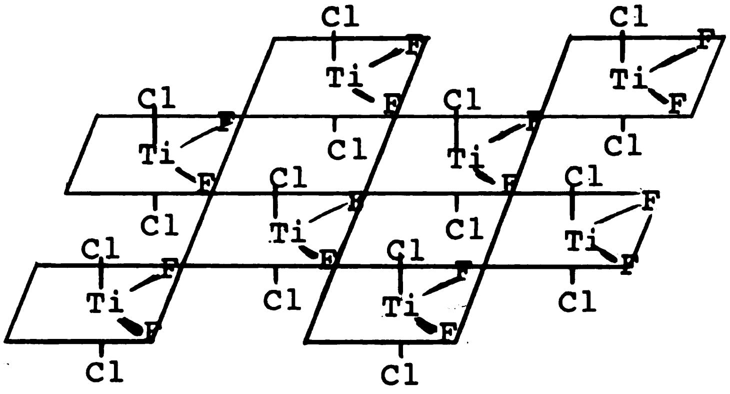
Chlorine bridge bonding also has been well-established in such complexes as $(TiCl_4\text{-}POCl_3)_2$ (4) and $(TiCl_4\text{-}AcOEt)_2$ (5). Where a choice exists between fluorine and chlorine, it would seem more reasonable to predict fluorine bridge bonding on the basis of its greater ionic character. $TiFCl_3$ is incapable of forming a six-coordinate solid state structure employing only fluorine bridging. $TiFCl_3$ is also the only titanium(IV) chloride fluoride not isolated in the solid state. There are numerous six-coordinate structures that can be drawn for TiF_3Cl and TiF_2Cl_2. Some of the possible types for TiF_2Cl_2 are listed below.

(A) Chain polymer:

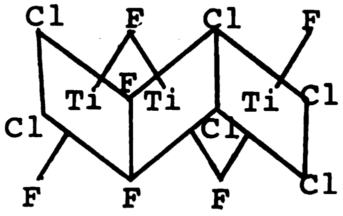


(B) Helix polymer: This type is not easily drawn but may be visualized by considering cis coordination of the chlorine atoms on each titanium atom. This causes the chain to wind around in the form of a helix.

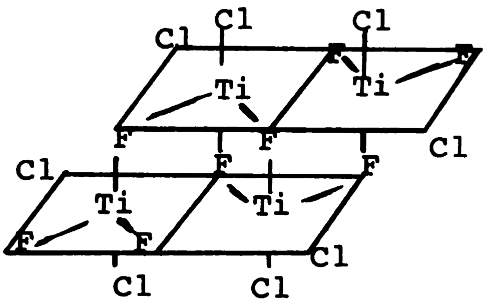
(C) Sheet structure



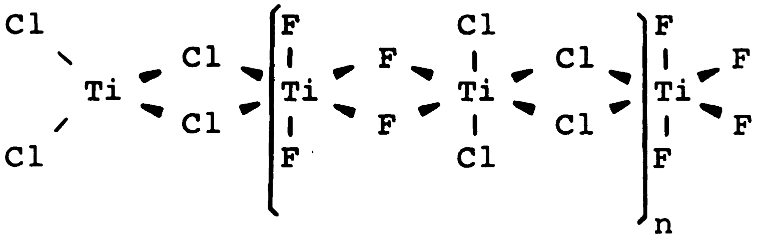
(D) Trimer



(E) Tetramer



(F) Polyadduct



Of the structures shown, A and B would seem to be the most consistent with the observed properties of this compound. Long range disorder is common for polymeric substances and would account for its amorphous nature. A polymeric sample would be expected to have a very low vapor pressure. Heating the sample in a vacuum could cause a rupture anywhere in the chain, resulting in extensive molecular rearrangement and loss of the more volatile species. This is consistent with the mass spectroscopy data. It is interesting to note that the monomeric units composing structure B have $\underline{C_{2v}}$ symmetry. In addition the Ti-F bonds would be weakened due to bridge bonding. This structure, therefore, correlates nicely with the infrared data presented by Dehnicke (10). Structures C and E are judged less likely than A and B since they would be expected to contribute to long range order resulting in a sharp diffraction pattern. Structures D and F are considered less likely than A and B since they involve chlorine bridge bonding.

CONCLUSION

Titanium tetrachloride and titanium tetrafluoride have been found to undergo halogen exchange to produce the titanium(IV) chloride fluorides. Under appropriate conditions TiF_2Cl_2 can conveniently be isolated in good yield as a yellow solid. TiF_3Cl was also isolated as a yellow solid but only in low yield. $TiFCl_3$ was not isolated but is believed to be an unstable yellow liquid at room temperature which undergoes disproportionation to TiF_2Cl_2 and $TiCl_4$.

The thermal stabilities of the titanium(IV) chloride fluorides appear to be in the order $TiF_3Cl > TiF_2Cl_2 > TiFCl_3$. Titanium chloride trifluoride and titanium dichloride difluoride give no X-ray diffraction pattern. A polymeric six-coordinate structure involving fluorine bridge bonding is suggested to account for the observed properties of these compounds. TiF_3Cl, TiF_2Cl_2, and $TiFCl_3$ also have been conclusively identified in the gas phase by mass spectrometric techniques.

SIGNIFICANCE

Previous difficulties encountered in attempts to prepare titanium(IV) chloride fluorides can now be understood in terms of the halogen exchange equilibrium process established for the $TiCl_4$--TiF_4 system. The observation of a yellow solid containing titanium, chlorine, and fluorine in a variable nonstoichiometric ratio by Ruff and Ipsen (45) and the isolation of TiF_3Cl which had an analysis 2.3% higher than theory in chlorine and 5.2% lower than theory in fluorine by Vorres (48) can now be attributed to this halogen exchange equilibrium process.

The isolation of TiF_3Cl and TiF_2Cl_2 indicates that under certain conditions halogen exchange processes are useful for preparing mixed halide compounds. It is possible that the methods developed for the isolation of TiF_3Cl and TiF_2Cl_2 could be applied to the TiF_4--$TiBr_4$ system and the TiF_4--TiI_4 system to allow for the isolation of titanium(IV) bromide fluorides and titanium(IV) fluoride iodides.

The method developed for the convenient and economical production of TiF_2Cl_2 will allow this compound to be examined for catalytic activity and as a potentially useful synthetic intermediate. $TiCl_4$, $TiBr_4$, TiI_4 and the mixed halides of these compounds have been patented as polymerization catalysts.

TiF_2Cl_2 is therefore a potentially useful catalyst. As a synthetic intermediate, TiF_2Cl_2 might be valuable in the preparation of a variety of compounds containing a TiF_2-group.

RECOMMENDATIONS FOR FUTURE WORK

1. The $TiCl_4$--TiF_4 system should be examined in non-donor solvents such as chloroform, benzene, and trifluoroacetic acid.

2. Attempts should be made to isolate $TiFCl_3$ by low temperature vacuum line techniques.

3. Solutions of titanium(IV) chloride fluorides in $TiCl_4$ or in trifluoroacetic acid should be examined by ^{19}F magnetic resonance.

4. Attempts should be made to obtain crystalline samples of TiF_4, TiF_3Cl, and TiF_2Cl_2, perhaps by recrystallization from trifluoroacetic acid.

5. A more detailed study should be made of the hydrolytic and thermal stability of TiF_3Cl and TiF_2Cl_2. The composition of the hydrolysis product should be determined.

6. Methods for preparing the mixed halides by the reaction of $TiCl_4$ with other metal and nonmetal fluorides should be investigated.

7. The use of TiF_2Cl_2 as a synthetic intermediate should be studied.

8. The TiF_4--$TiBr_4$ system and similar systems should be examined by employing the methods and techniques developed for the $TiCl_4$--TiF_4 system.

PART II

FLUORINE-19 NMR STUDY IN TETRAHYDROFURAN

INTRODUCTION

Fluorine-19 magnetic resonance studies were originally undertaken in an attempt to characterize more fully the titanium(IV) chloride fluoride compounds previously discussed. Titanium tetrachloride and titanium tetrafluoride as well as the mixed halide compounds should form addition complexes with tetrahydrofuran (THF) and other fairly small monodentate coordinating agents, where two donor molecules are bonded to the titanium(IV) halide. It should be possible to distinguish between these complexes by differences in their ^{19}F nuclear magnetic resonance (NMR) spectra.

These studies show that the mixed halide compounds undergo disproportionation in THF solution to give an equilibrium mixture of $TiF_4 \cdot 2THF$, $TiF_3Cl \cdot 2THF$, $TiF_2Cl_2 \cdot 2THF$, $TiFCl_3 \cdot 2THF$, and $TiCl_4 \cdot 2THF$. The nature of the $TiCl_4 \cdot 2THF$--$TiF_4 \cdot 2THF$ system is the subject of the following investigation.

EXPERIMENTAL

Instrumentation

Fluorine-19 magnetic resonance spectra were obtained with a Varian Associates HA-100 high-resolution spectrometer operating at 94.1 mc/sec. The Michigan State University spectrometer was used for recording some spectra, but most were obtained with the instrument at the Dow Chemical Company. Their spectrometer had been modified to permit an unlimited sweep frequency offset (51) and a means for conveniently positioning or eliminating side bands.

Trifluoroacetic acid (TFA) and trichlorofluoromethane, $CFCl_3$, were employed both as internal and external reference standards. The fluorine-19 magnetic resonance region from -430 ppm to +360 ppm from $CFCl_3$ was investigated. All observed ^{19}F magnetic resonances were downfield from $CFCl_3$ in the region between -305 ppm and -163 ppm. The conversion factor (14) relating the two standards employed is given by the expression $\delta_{TFA} = \delta_{CFCl_3} - 76.54$.

Preparation of the ^{19}F NMR Samples

A. Purification of Reagents

All reagents were carefully purified for use in the preparation of the NMR samples. Purification of $TiCl_4$ and

TiF_4 has been previously discussed in Part I (p. 5). Reagent grade THF was distilled from lithium aluminum hydride into a flamed out glass ampoule which was sealed by means of a Teflon stopcock. The ampoule was then moved into a dry box where NMR samples were prepared.

B. Preparation of THF Solutions

Solutions for NMR study were prepared in a dry box under dry nitrogen. Titanium tetrachloride could be handled in this atmosphere without any observable hydrolysis. Solutions were prepared both from titanium(IV) chloride fluorides and from mixtures of $TiCl_4$ and TiF_4. When THF complexes were formed by direct addition at room temperature, a vigorous reaction took place producing a great deal of heat. To prevent decomposition of the samples (see footnote page 6) or loss of volatile material, it was necessary to cool the reagents to the freezing point of THF (-65°C) and then mix the reagents slowly. Cooling was accomplished by circulating liquid nitrogen between the walls of a double-walled beaker which contained sample vials holding the reagents.

Titanium(IV) chloride fluoride solutions were prepared by adding a known volume of THF at -65°C to a known weight of mixed halide. Thus for the preparation of 1.0 <u>M</u> TiF_2Cl_2 solution, 1.45 ml of THF at -65°C was added by means of a hypodermic syringe to 0.23 gram of TiF_2Cl_2. A yellow liquid and solid were instantly formed with the evolution THF vapor as a white fog. As the mixture warmed to room temperature the yellow solid dissolved to give a clear yellow solution.

Some solutions were prepared directly from $TiCl_4$ and TiF_4. Separate THF solutions of $TiCl_4$ and TiF_4 of known concentration were prepared by the same procedure used for mixed halides. These were then mixed to give solutions of the desired $TiCl_4$ to TiF_4 ratio. Low solubility of the $TiCl_4 \cdot 2THF$ complex in excess THF necessitated such dilute final solutions that the ^{19}F resonance for some components could not be observed for large $TiCl_4:TiF_4$ ratios. Solutions of sufficient concentration were prepared by first isolating the $TiCl_4 \cdot 2THF$ complex and then adding it directly to solutions of $TiF_4 \cdot 2THF$. The various difficulties encountered in preparing solutions directly from $TiCl_4$ and TiF_4 resulted in concentration values that were only approximate. Solutions of more accurately known concentrations could probably have been prepared from $TiCl_4 \cdot 2THF$ and $TiF_4 \cdot 2THF$ had these complexes both been isolated.

C. Preparation of NMR Samples

After the preparation of a solution, it was carefully added through a glass dropper with a long narrow tip to a flamed out 5 mm thin walled NMR sample tube. The upper neck of the NMR tube was inserted through a one-hole rubber stopper which was then inserted into the neck of an inverted 50 ml filter flask which had a stopcock side arm. This arrangement allowed the sample to be removed from the dry box while an inert atmosphere was maintained over the sample. The sample tube was then immersed in liquid nitrogen to freeze the sample. After evacuation through the side arm on the 50 ml flask, the tube was sealed off with a hand torch.

D. Decomposition

Samples prepared under less than rigorously anhydrous conditions decomposed slowly to produce a brown-black solid residue, whereas those obtained under absolutely anhydrous conditions appeared to be indefinitely stable at room temperature. The NMR samples were stored at -78°C to retard possible decomposition. Identical samples stored at room temperature, however, showed no difference in their ^{19}F magnetic resonance spectra.

E. Complex Formation

Addition of bright yellow $TiCl_4 \cdot 2THF$ solution to an excess of colorless $TiF_4 \cdot 2THF$ solution produced a colorless solution. A noticeable yellow color was not observed until nearly equivalent amounts of the two solutions had been mixed. This indicates that $TiF_3Cl \cdot 2THF$, probably $TiF_2Cl_2 \cdot 2THF$, and possibly $TiFCl_3 \cdot 2THF$ are colorless in THF solution.

^{19}F Magnetic Resonance of $TiF_4 \cdot 2THF$

A 0.5 M sample of TiF_4 in THF was prepared as previously described. At room temperature a single broad ^{19}F magnetic resonance peak was observed at about -18600 Hz (-197 ppm) downfield from the external reference $CFCl_3$. As the sample temperature was reduced, the peak first broadened and then separated into two singlets at -40°C. At -50°C the singlets began to split into triplets and at -60°C these were well resolved. A very small singlet was also observed upfield from these two triplets. The spectra obtained for this sample are shown in Figures 7a-c. Table 7 summarizes the data obtained from these spectra at -60°C.

The equal intensity triplets t_4^- and t_4^+ arise from the cis-$TiF_4 \cdot 2THF$ isomer. It is likely that the singlet S_4 arises from the trans isomer. The intensity of S_4 indicated that the species producing this resonance was present in very low concentration.

Assuming that S_4 represents the trans isomer of $TiF_4 \cdot 2THF$, the equilibrium constant for the following reaction can be determined.

$$\underline{\text{trans}}\text{-TiF}_4\cdot 2\text{THF} \rightleftharpoons \underline{\text{cis}}\text{-TiF}_4\cdot 2\text{THF}$$

$$K = \frac{[\underline{\text{cis}}\text{-TiF}_4\cdot 2\text{THF}]}{[\underline{\text{trans}}\text{-TiF}_4\cdot 2\text{THF}]} = \frac{196}{6} = 33 \text{ at } -60^\circ\text{C}$$

Since these are the only data available and since S_4 was so small that accurate determination of the intensity ratio was not possible, the value of K is only approximate.

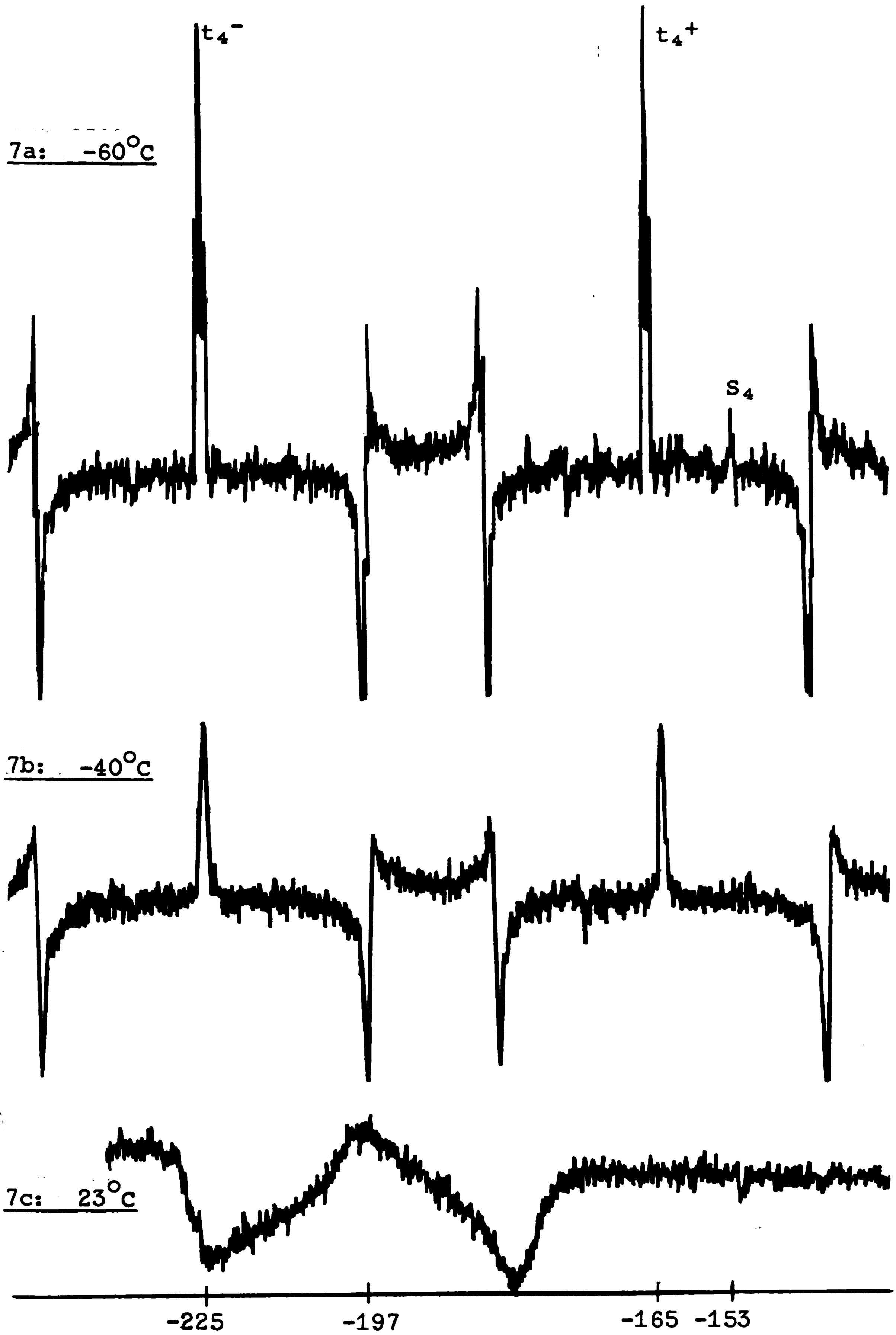


Figure 7. ^{19}F magnetic resonance of 0.5 M $TiF_4 \cdot 2THF$ at -60 (a), -40 (b) and 23°C (c). (External reference: $CFCl_3$)

Table 7. ^{19}F chemical shift* and coupling constants for $TiF_4 \cdot 2THF$ at -60°C.

Peak Designation	δ_{CFCl_3} Hz	δ_{CFCl_3} ppm	J_{FF} Hz	Intensity Ratio
t_4^-	-21200	-225	37	96
t_4^+	-15500	-165	37	100
S_4	-14400	-153	--	6
$t_4^- - t_4^+$	-5730	-60.9	--	--

*^{19}F chemical shifts measured from $CFCl_3$ external reference.

^{19}F Magnetic Resonance of $TiF_xCl_{4-x}\cdot 2THF$ Solutions

Fluorine-19 magnetic resonance spectra were obtained for the following samples.

Sample	Description
1.	1.0 M TiF_2Cl_2 in THF at -70°C
2.	0.5 M TiF_2Cl_2 in THF at -60°C
3.	0.32 M TiF_2Cl_2 and 0.17 M TiF_3Cl in THF at -60°C
4.	0.35 M TiF_3Cl in THF at -60°C

At room temperature these samples showed only a rough base line. At -60°C all samples showed a nicely resolved spectrum which indicated the presence of the titanium(IV) chloride fluoride THF complexes as well as $TiF_4\cdot 2THF$.

The spectrum obtained for 1.0 M TiF_2Cl_2 (sample 1) is shown in Figure 8. It is typical of the other samples except for the intensity of the various resonance peaks. Tables 8 and 9 summarize the ^{19}F chemical shift and coupling constant data for these samples. Assignment of the specific ^{19}F magnetic resonances to the species from which they arise is also indicated in Table 9. The justification for these assignments is given in detail in the discussion section. Table 10 lists the measured intensities for the observed resonance peaks and the relative intensities for each compound or isomer.

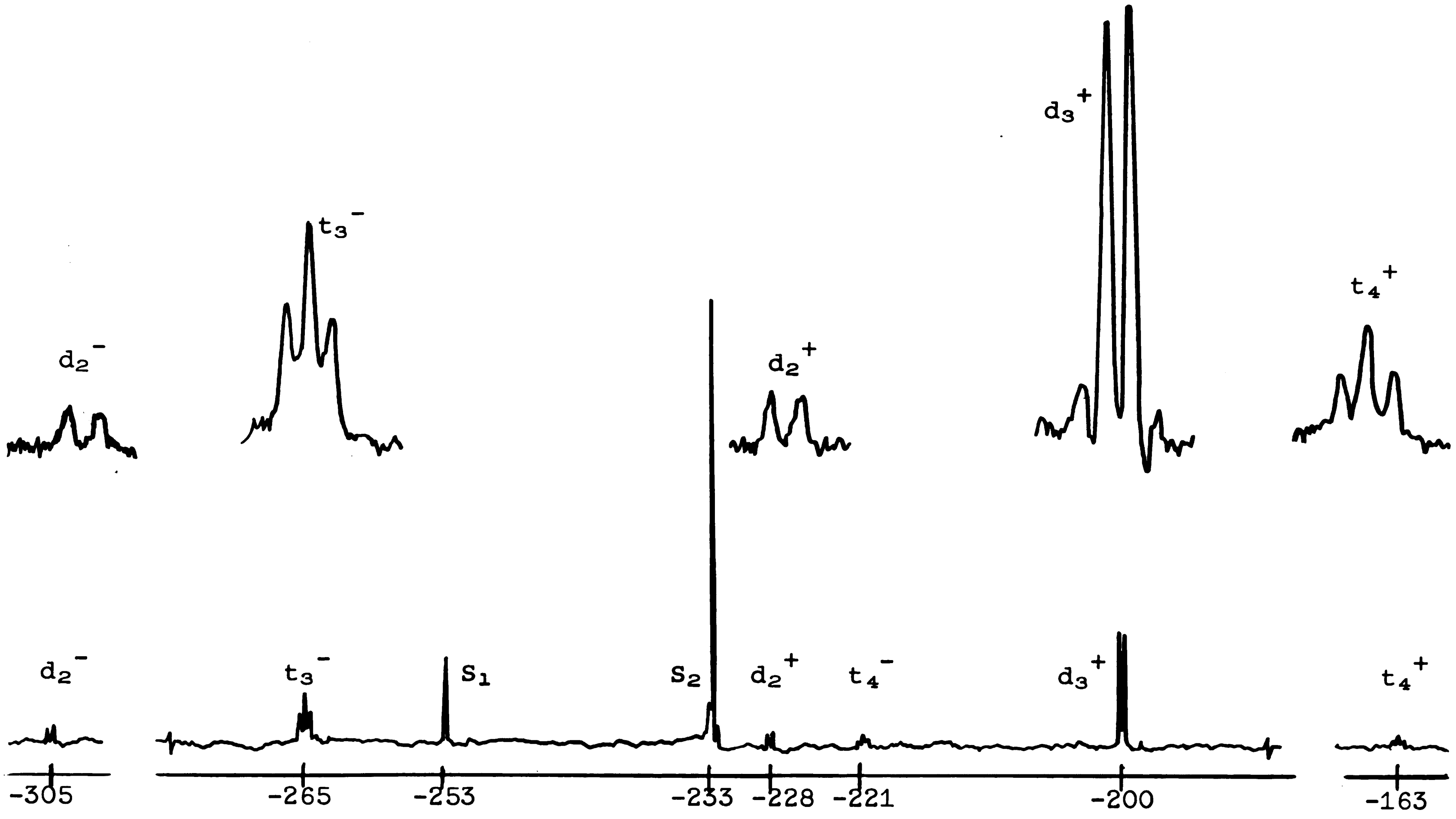


Figure 8. ^{19}F magnetic resonance of 1.0 M TiF_2Cl_2/THF at -70°C. (External reference: $CFCl_3$)

Table 8. ^{19}F chemical shifts* for $TiF_{\underline{x}}Cl_{4-\underline{x}}\cdot 2THF$ samples at -60°C.

Peak Designation	Sample 1**		Sample 2		Sample 3		Sample 4	
	1.0 $\underline{M}$ TiF_2Cl_2/THF		0.5 $\underline{M}$ TiF_2Cl_2/THF		0.32 $\underline{M}$ TiF_2Cl_2/THF 0.17 $\underline{M}$ TiF_3Cl/THF		0.35 $\underline{M}$ TiF_3Cl/THF	
	Hz	ppm	Hz	ppm	Hz	ppm	Hz	ppm
d_2^-	-28700	-305	--	--	--	--	--	--
t_3^-	-24900	-265	-25000	-266	-25000	-266	-25100	-267
S_1	-23800	-253	-23800	-253	-23700	-252	-23800	-253
S_2	-21900	-233	-21800	-232	-21800	-232	-21800	-232
d_2^+	-21500	-228	-21400	-227	-21300	-226	-21300	-226
t_4^-	-20800	-221	-20800	-221	-20900	-222	-20900	-222
d_3^+	-18800	-200	-18800	-200	-18800	-200	-18800	-200
t_4^+	-15300	-163	-15300	-163	-15300	-163	-15300	-163

*^{19}F chemical shifts measured from $CFCl_3$ external reference

**Measurements made at -70°C.

Table 9. Peak assignment and ^{19}F coupling constants for $TiF_{\underline{x}}Cl_{4-\underline{x}}$ samples.

Compound	Peak Designation	Relative Intensity	F-F Coupling Constants*				J_{FF}*	δ_{FF}
			Sample 1	Sample 2	Sample 3	Sample 4	Average	
$TiF_4 \cdot 2THF$	t_4^-	1	36-37	37.8	37.5	36.3	37+	5600 Hz
	t_4^+	1	----	37.3	----	37	37+	59 ppm
$TiF_3Cl \cdot 2THF$	t_3^-	1	33-34	33.5	34	32.7	33+	6200 Hz
	d_3^+	2	33-34	34	34	33	33+	66 ppm
$TiF_2Cl_2 \cdot 2THF$	S_2	----	----	----	----	----	----	----
$TiF_2Cl_2 \cdot 2THF$	d_2^-	1	45	----	----	----	45	7200 Hz
	d_2^+	1	45.5	45	45	47	45+	77 ppm
$TiFCl_3 \cdot 2THF$	S_1	----	----	----	----	----	----	----

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[*] F-F coupling constants are given in Hertz (cycles per seconds).

Table 10. Intensity data for $\mathrm{TiF}_{\underline{x}}\mathrm{Cl}_{4-\underline{x}}\cdot 2\mathrm{THF}$ samples.

Compound	Peak Designation	Sample 1 1.0 M TiF_2Cl_2/THF		Sample 2 0.5 M TiF_2Cl_2/THF		Sample 3 0.32 M TiF_2Cl_2/THF 0.17 M TiF_3Cl/THF		Sample 4 0.35 M TiF_3Cl/THF	
$TiF_4\cdot 2THF$	t_4^- t_4^+	4 4	8	5 5	10	24 26	50	10 10	20
$TiF_3Cl\cdot 2THF$	t_3^- d_3^+	17 34	51	28 57	85	56 104	160	24 48	72
$TiF_2Cl_2\cdot 2THF$	S_2	70		64		71		40	
$TiF_2Cl_2\cdot 2THF$	d_2^- d_2^+	6 6	12	8 8	16	10 10	20	6 6	12
$TiFCl_3\cdot 2THF$	S_1	14		15		11		4	

^{19}F Magnetic Resonance of $TiCl_4$--TiF_4/THF Solutions

The following samples involving mixtures of $TiCl_4$ and TiF_4 in THF were prepared as previously described.

Sample	Description
5.	0.29 M TiF_4 + 0.097 M $TiCl_4$ in THF/TFA*
6.	0.24 M TiF_4 + 0.20 M $TiCl_4$ in THF/TFA*
7.	0.16 M TiF_4 + 0.16 M $TiCl_4$ in THF/$CFCl_3$**
8.	0.36 M TiF_4 + 0.72 M $TiCl_4$ in THF/TFA*
9.	0.067 M TiF_4 + 0.20 M $TiCl_4$ in THF/TFA*

*Trifluoroacetic acid (TFA) as internal reference

**Trichlorofluoromethane ($CFCl_3$) as internal reference

These samples were used to establish that an equilibrium exists between $TiF_4\cdot 2THF$ and $TiCl_4\cdot 2THF$ involving all the titanium(IV) chloride fluoride THF complexes. It was also expected that ^{19}F magnetic resonance intensity data would confirm the assignment of the two singlets, S_1 to $TiFCl_3\cdot 2THF$ and S_2 to $TiF_2Cl_2\cdot 2THF$.

The spectra obtained for these samples showed the same ^{19}F magnetic resonance peaks observed for the samples prepared from the titanium(IV) chloride fluorides. The samples containing a high ratio of TiF_4 to $TiCl_4$ showed very strong ^{19}F magnetic resonance peaks for $TiF_4 \cdot 2THF$ (t_4^- and t_4^+) and $TiF_3Cl \cdot 2THF$ (t_3^- and d_3^+) and progressively weaker peaks for $TiF_2Cl_2 \cdot 2THF$ (S_2) and $TiFCl_3 \cdot 2THF$ (S_1). In sample 5 where the ratio of TiF_4 to $TiCl_4$ was 3:1 the S_1 resonance for $TiFCl_3 \cdot 2THF$ was not observed. As the ratio of $TiCl_4$ to TiF_4 increased, the ^{19}F resonance peaks for $TiF_4 \cdot 2THF$ disappeared and the S_1 ^{19}F resonance for $TiFCl_3 \cdot 2THF$ became the most predominant.

To establish that TFA was not catalyzing the halogen exchange reaction between $TiF_4 \cdot 2THF$ and $TiCl_4 \cdot 2THF$, sample 7 was prepared with $CFCl_3$ as the internal reference. Every effort was made to prevent hydrolysis or contamination with HCl. Since this sample gave essentially the same spectrum as the other samples in this series, it appears that TFA is not responsible for the exchange process. Because of the extreme sensitivity of the $TiCl_4$ toward hydrolysis and the resulting formation of HCl, acid catalysis of the reaction cannot, however, be ruled out. The fact that no ^{19}F resonance was observed for HF indicates only that this substance was not present in sufficient concentration to be observed.

The spectra obtained for these samples are presented in Figures 9 through 13. The use of an internal reference permitted more accurate measurement of chemical shifts and coupling constants than had previously been achieved. These data are presented in Table 11. Intensity data have been

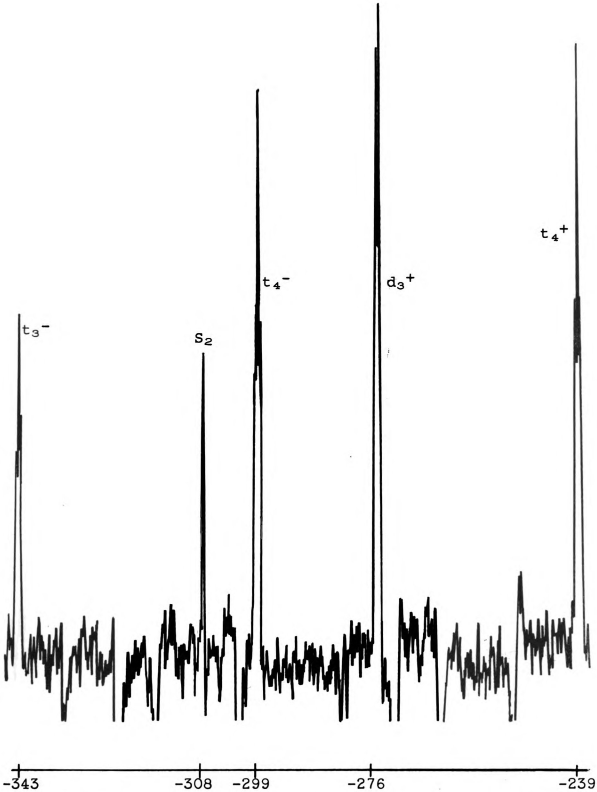


Figure 9a. ^{19}F magnetic resonance of 0.29 $\underline{M}$ TiF_4 + 0.097 $\underline{M}$ $TiCl_4$/THF at -60°C. (Internal reference: TFA)

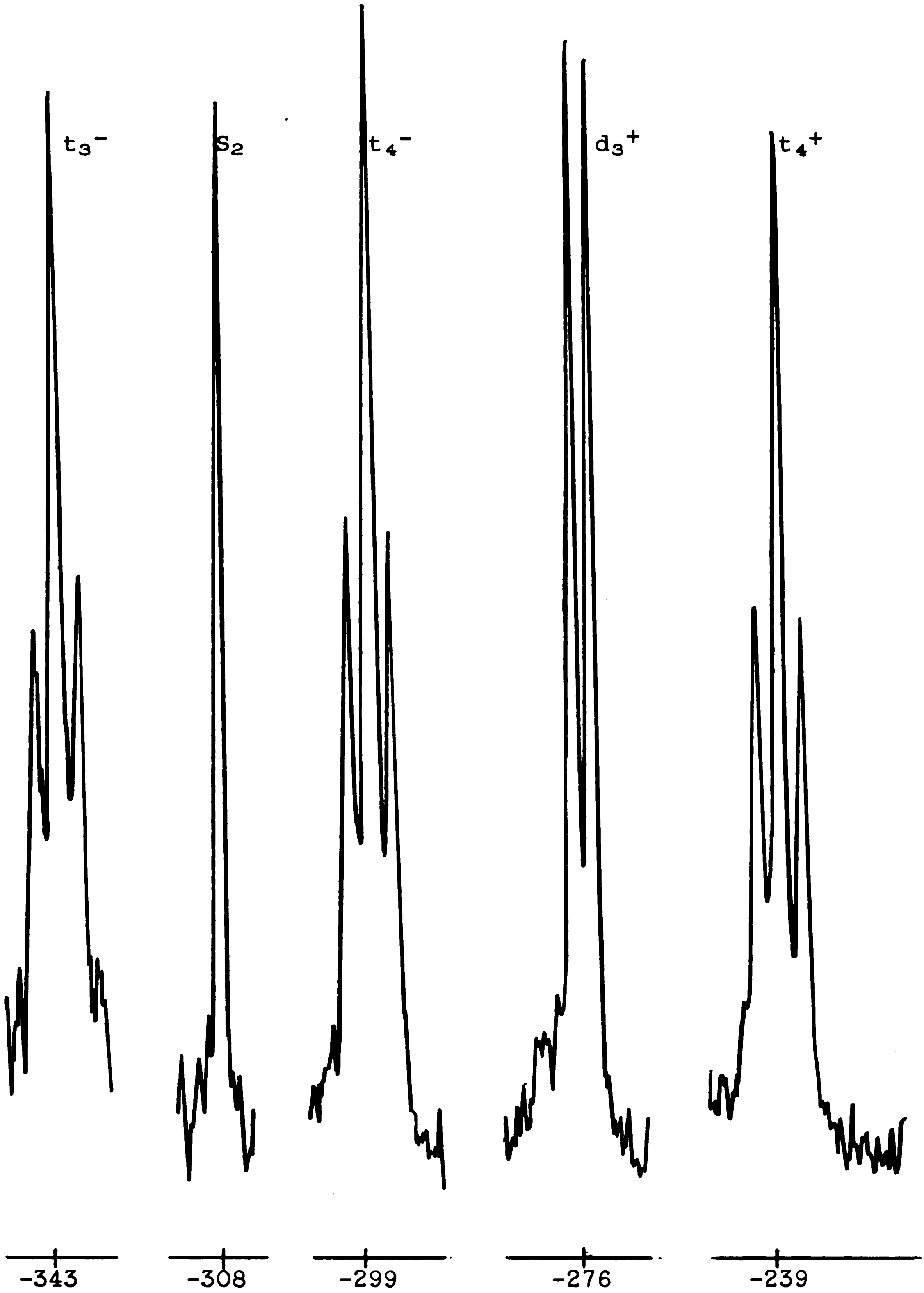


Figure 9b. Expanded view of ^{19}F resonances in Figure 9a. (Internal reference: TFA)

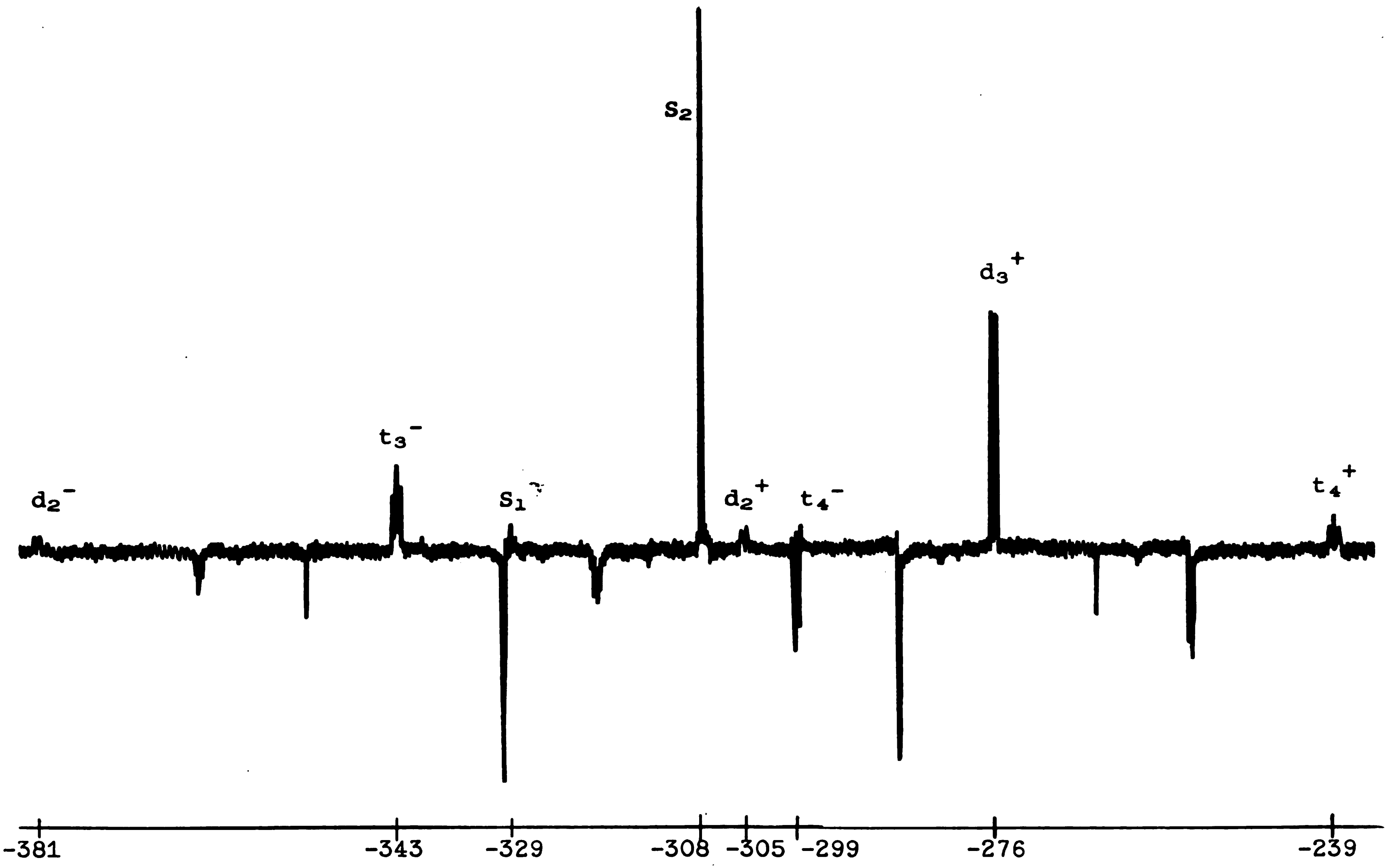


Figure.10. ^{19}F magnetic resonance of 0.24 M TiF_4 + 0.20 M $TiCl_4$/THF at -60°C. (Internal reference: TFA)

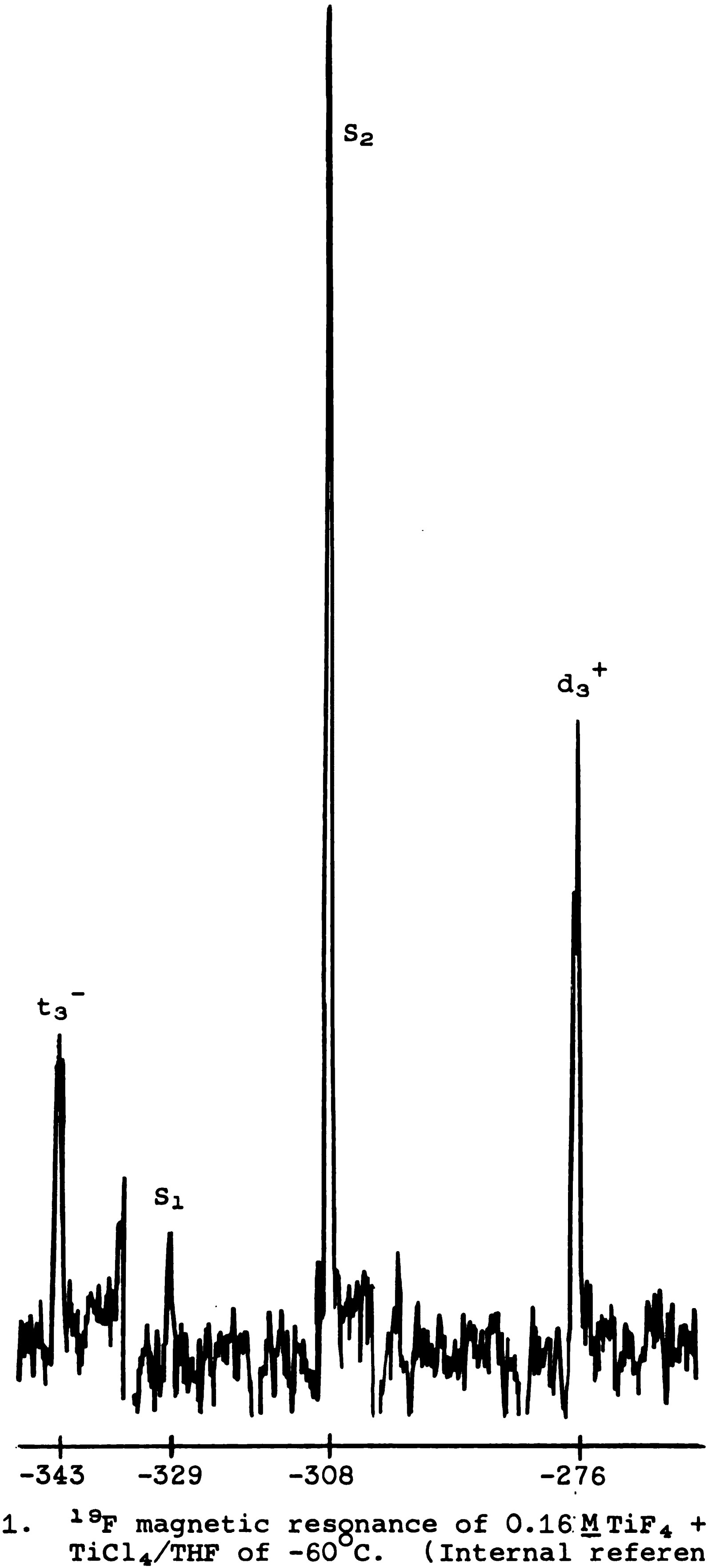


Figure 11. ^{19}F magnetic resonance of 0.16 M TiF_4 + 0.16 M $TiCl_4$/THF of -60°C. (Internal reference: $CFCl_3$, values converted to TFA scale)

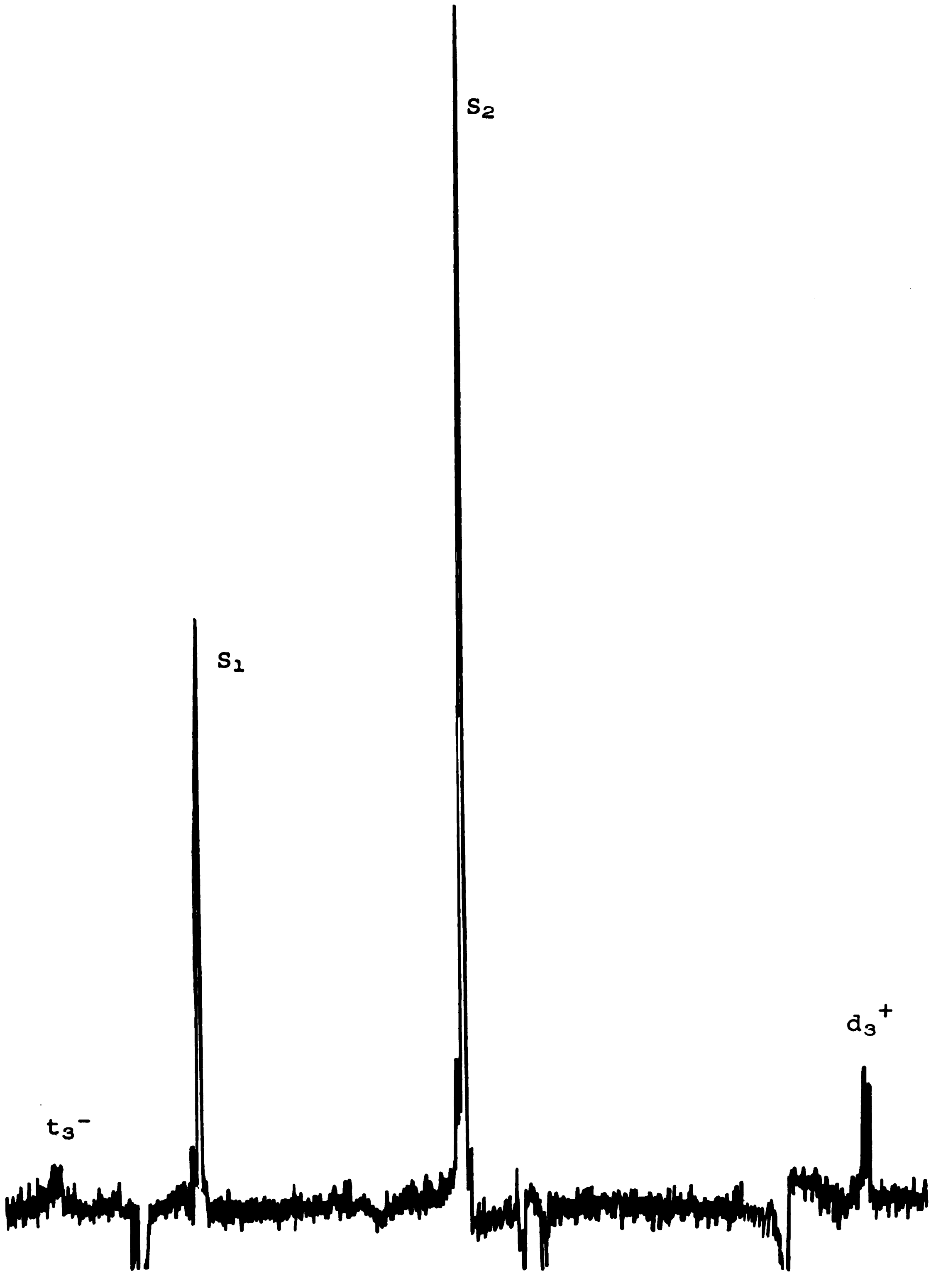


Figure 12. ^{19}F magnetic resonance of 0.36 M TiF$_4$ + 0.72 M TiCl$_4$/THF at -60°C. (Internal reference: TFA)

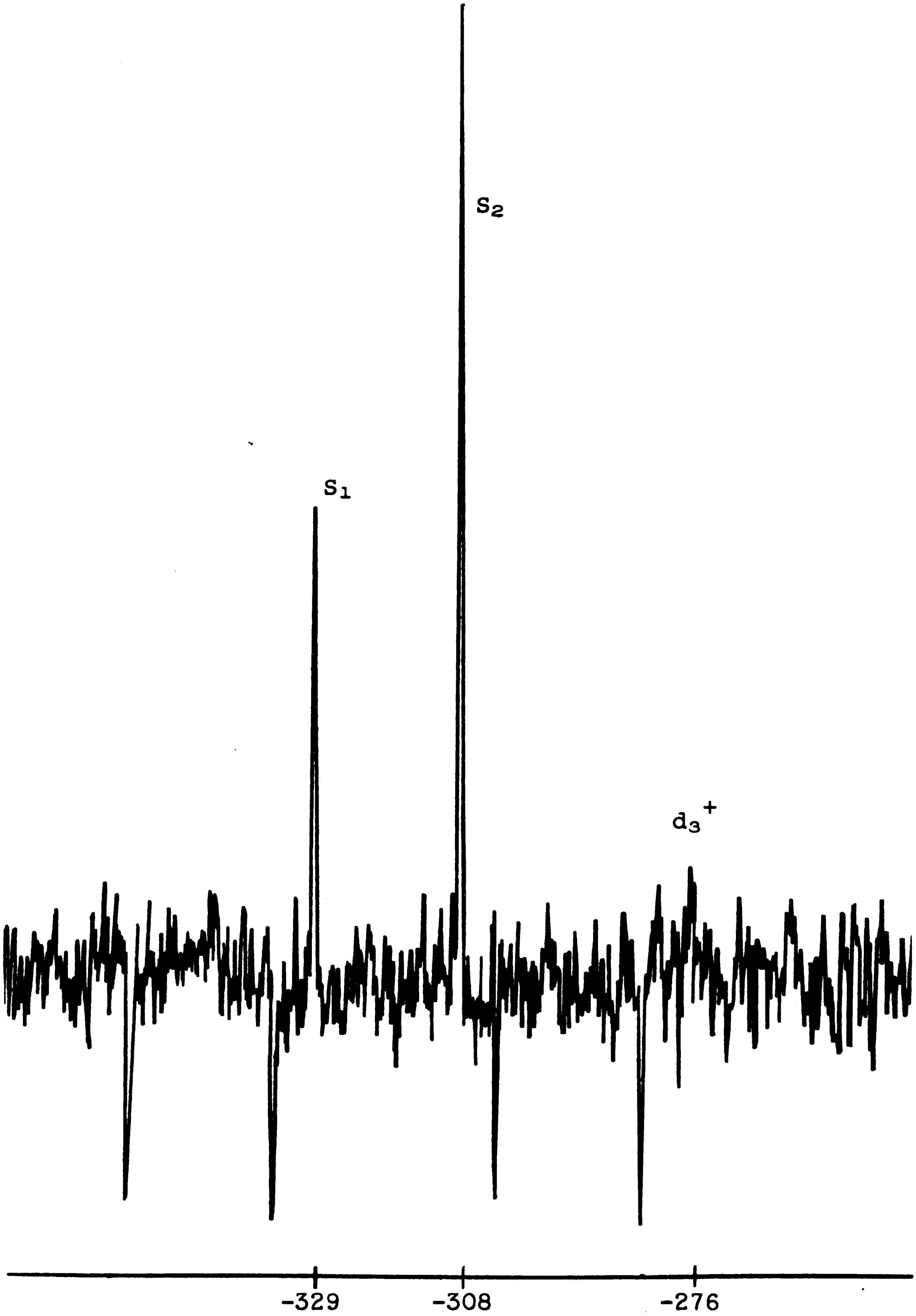


Figure 13. ^{19}F magnetic resonance of 0.067 M TiF$_4$ + 0.20 M TiCl$_4$/THF at -60°C. (Internal reference: TFA)

Table 11. ^{19}F chemical shifts** and coupling constants for $TiCl_4$–TiF_4/THF samples at -60°C.

Peak Designation	Sample 5 Hz	Sample 6 Hz	Sample 7 Hz	Sample 8 Hz	Sample 9 Hz	δ_{TFA} ppm	J_{FF} Hz
d_2^-	θ	-35,900*	θ	θ	θ	-381*	45*
t_3^-	-32,200	✓	✓	✓	θ	-343	33.1
S_1	θ	✓	✓	-31,000	✓	-329	----
S_2	-29,000	✓	✓	✓	✓	-308	----
d_2^+	θ	-28,700*	θ	θ	θ	-305*	45*
t_4^-	-28,100	✓	θ	θ	θ	-299	----
d_3^+	-26,000	✓	✓	✓	✓	-276	33.1
t_4^+	-22,500	✓	θ	θ	θ	-239	37.7

Compound	Peak Designation	Relative Intensity	J_{FF} Hz	δ_{FF}
$TiF_4 \cdot 2THF$	t_4^-	1	---	5600 Hz
	t_4^+	1	37.7	60 ppm
$TiF_3Cl \cdot 2THF$	t_3^-	1	33.1	6200 Hz
	d_3^+	2	33.1	67 ppm
$TiF_2Cl_2 \cdot 2THF$	S_2	----	----	----
$TiF_2Cl_2 \cdot 2THF$	d_2^-	1	45*	7200 Hz
	d_2^+	1	45*	76 ppm
$TiFCl_3 \cdot 2THF$	S_1	----	----	----

**^{19}F chemical shifts measured from TFA internal reference; *These values are less reliable due to the inability to lock on the internal standard; θ ^{19}F magnetic resonance peaks were too weak to be observed; ✓ ^{19}F magnetic resonance peaks were observed at essentially the same value given for one of the other samples.

treated quantitatively and the equilibrium mole per cent values for each component are given in Table 12. These values are not precise because of uncertainty in the initial concentrations of these samples. It is entirely possible that the concentrations of $TiCl_4$ in samples 5, 7, and 9 were significantly less than that indicated. This error could have arisen from the lower than expected solubility of $TiCl_4 \cdot 2THF$ in excess THF. Samples 6 and 8 were prepared by a different method and are probably more accurate. Table 12 is presented only to indicate the relative change in the equilibrium concentrations of the species present as the initial concentration ratio of TiF_4 to $TiCl_4$ changes. This table clearly shows that the maximum concentration of $TiF_2Cl_2 \cdot 2THF$ is observed for a 1:1 ratio. The concentration of $TiFCl_3 \cdot 2THF$ is insignificant with a large ratio of TiF_4 to $TiCl_4$ but it becomes the predominant species as the ratio of TiF_4 to $TiCl_4$ becomes small. These equilibrium mole per cent values were calculated from the intensity of the ^{19}F magnetic resonance peaks as previously assigned (see Table 9) for each component. The relative concentration trend agrees very well with that expected for such an equilibrium system and, therefore, adds justification for the fluorine-19 magnetic resonance peak assignments previously made. The method of calculating mole per cent values from ^{19}F magnetic resonance intensity data will be presented in the section dealing with equilibrium constants (p. 105).

Table 12. Equilibrium mole per cent values for $TiCl_4$--TiF_4/THF samples.

Compound	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	^{19}F Magnetic resonance peak
$TiF_4 \cdot 2THF$	38.5	6.3	----	----	----	t_4^-, t_4^+
$TiF_3Cl \cdot 2THF$	42.4	35.7	33.9	7.7	6.6	t_3^-, d_3^+
$TiF_2Cl_2 \cdot 2THF$	9.9	48.5	47.2	36.7	26.7	S_2, d_2^-, d_2^+
$TiFCl_3 \cdot 2THF$	9.2	3.7	8.4	36.5	26.7	S_1
$TiCl_4 \cdot 2THF$		5.8	10.4	19.1	40.0	----

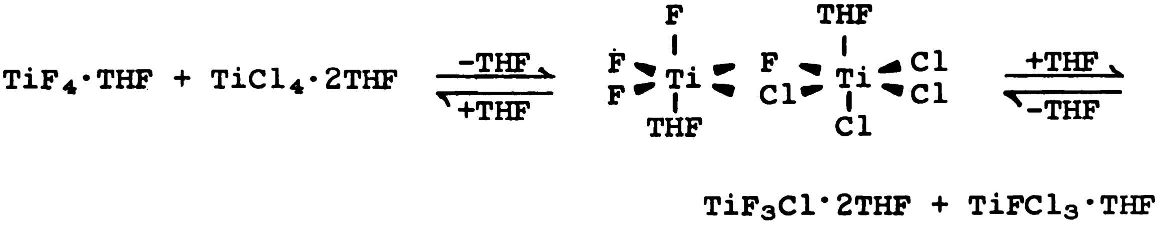
Sample	Description
5	0.29 <u>M</u> TiF_4, 0.097 <u>M</u> $TiCl_4$/THF
6	0.24 <u>M</u> TiF_4, 0.20 <u>M</u> $TiCl_4$/THF
7	0.16 <u>M</u> TiF_4, 0.16 <u>M</u> $TiCl_4$/THF
8	0.36 <u>M</u> TiF_4, 0.72 <u>M</u> $TiCl_4$/THF
9	0.067 <u>M</u> TiF_4, 0.20 <u>M</u> $TiCl_4$/THF

DISCUSSION

Halogen Exchange

There are a number of possible mechanisms by which halogen exchange can take place in octahedral titanium(IV) chloride fluoride tetrahydrofuran complexes. Muetterties (36) has found rapid ($K \geq 10^3$ sec^{-1}) donor molecule exchange for TiF_4 complexes dissolved in excess complexing agent at -25 to +25°C. This suggests the possibility of the following bridging mechanism.

$$TiF_4 \cdot 2THF \underset{+THF}{\overset{-THF}{\rightleftharpoons}} TiF_4 \cdot THF$$



$$TiFCl_3 \cdot THF \underset{-THF}{\overset{+THF}{\rightleftharpoons}} TiFCl_3 \cdot 2THF$$

Six equilibrium equations describe all the ways that two components can react by the above mechanism to produce new components. These reactions are analogous to those previously presented to describe the halogen exchange between TiF_4 and $TiCl_4$.

(1) $1/2(TiCl_4 \cdot 2THF) + 1/2(TiF_4 \cdot 2THF) \rightleftharpoons 1/2(TiF_3Cl \cdot 2THF) + 1/2(TiFCl_3 \cdot 2THF)$

(2) $1/2(TiCl_4 \cdot 2THF) + 1/2(TiF_3Cl \cdot 2THF) \rightleftharpoons 1/2(TiF_2Cl_2 \cdot 2THF) + 1/2(TiFCl_3 \cdot 2THF)$

(3) $1/2(TiF_4 \cdot 2THF) + 1/2(TiFCl_3 \cdot 2THF) \rightleftharpoons 1/2(TiF_2Cl_2 \cdot 2THF) + 1/2(TiF_3Cl \cdot 2THF)$

(4) $1/2(TiCl_4 \cdot 2THF) + 1/2(TiF_2Cl_2 \cdot 2THF) \rightleftharpoons TiFCl_3 \cdot 2THF$

(5) $1/2(TiF_4 \cdot 2THF) + 1/2(TiF_2Cl_2 \cdot 2THF) \rightleftharpoons TiF_3Cl \cdot 2THF$

(6) $1/2(TiF_3Cl \cdot 2THF) + 1/2(TiFCl_3 \cdot 2THF) \rightleftharpoons TiF_2Cl_2 \cdot 2THF$

A second plausible mechanism involves acid catalyzed halide exchange. Attempts were made to exclude this possibility, but because of the nature of the reactants, elimination of catalytic amounts of acid would be nearly impossible. The presence of HF was not observed by ^{19}F magnetic resonance for any of the samples investigated, but the observation of very small amounts would not be expected. Muetterties (37) has suggested that acid catalyzed fluoride exchange may be responsible for the line broadening of the ^{19}F resonance observed for some fluoroanions.

^{19}F Magnetic Resonance--Stereochemical Considerations

$TiF_3Cl \cdot 2THF$ and $TiFCl_3 \cdot 2THF$ each have three possible geometrical isomers whereas $TiF_2Cl_2 \cdot 2THF$ has six stereoisomers (five geometrical isomers and one pair of enantiomorphs) (24).

$TiF_4 \cdot 2THF$ and $TiCl_4 \cdot 2THF$ each have two possible isomers. Table 13 lists each compound and its possible isomers.

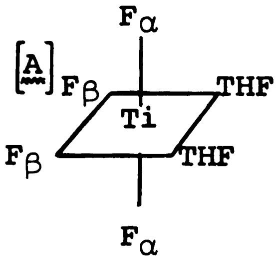
A fluorine atom is designated by F_α if it is *trans* to another fluorine, F_β if *trans* to a THF group, and F_γ if *trans* to a chlorine atom. These three types of fluorine atoms constitute those in any given isomer that can be distinguished from each other by ^{19}F magnetic resonance. Fluorine atoms having the same designation in a given isomer (either α, β, or γ) cannot be distinguished by ^{19}F NMR.

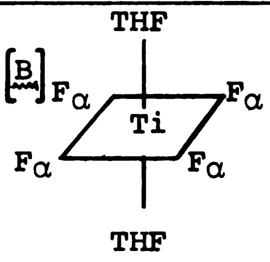
The *cis* isomer of $TiF_4 \cdot 2THF$ (**A**) contains two groups of equivalent fluorine, F_α and F_β. The first order ^{19}F magnetic resonance spectrum for this isomer would consist of two equal intensity triplets typical for an A_2X_2 system. Since all fluorines are equivalent for *trans*-$TiF_4 \cdot 2THF$ (**B**), only a single ^{19}F resonance would be expected .

The first order ^{19}F magnetic resonance spectrum for each $TiF_3Cl \cdot 2THF$ isomer would consist of a doublet and a triplet of 2:1 intensity ratio typical for an A_2X system inasmuch as each isomer contains two equivalent fluorine atoms. Since both fluorines are equivalent in isomers **F**, **G**, **H**, and **I** of $TiF_2Cl_2 \cdot 2THF$, they would give rise to a single ^{19}F resonance. The enantiomorphs **Ja** and **Jb** have two dissimilar fluorine atoms. As an AX system, the ^{19}F magnetic resonance would consist of two doublets.

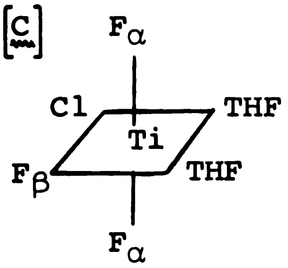
Table 13. Isomers of titanium(IV) chloride fluoride THF compounds.

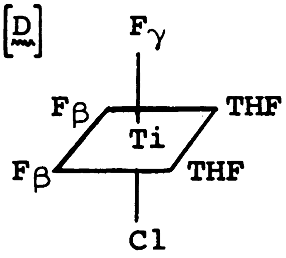
$TiF_4 \cdot 2THF$

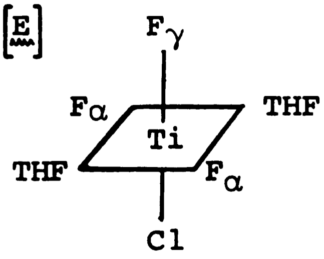
A


B


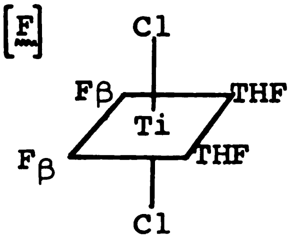
$TiF_3Cl \cdot 2THF$

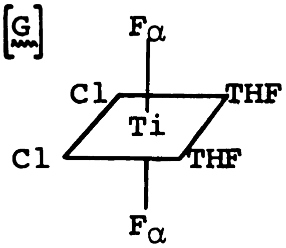
C


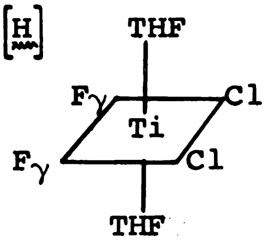
D


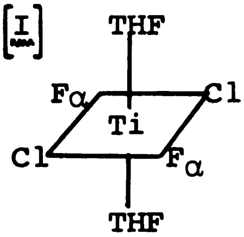
E


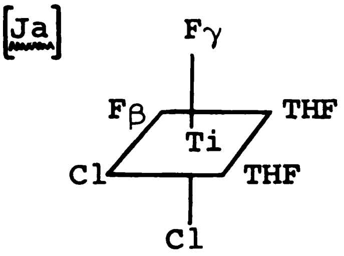
$TiF_2Cl_2 \cdot 2THF$

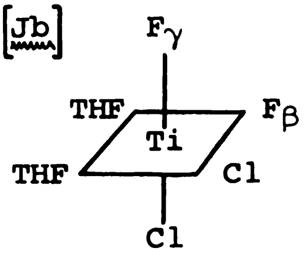
F


G


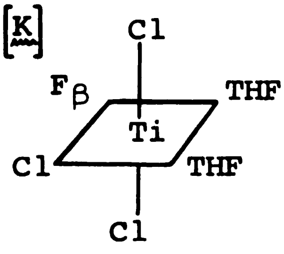
H


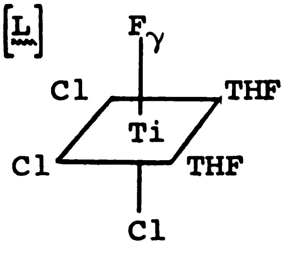
I


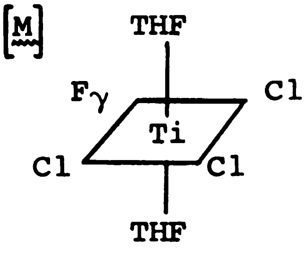
Ja


Jb


$TiFCl_3 \cdot 2THF$

K


L


M


The three isomers of $TiFCl_3 \cdot 2THF$, each having only one fluorine, would give rise to a single ^{19}F resonance.

^{19}F Magnetic Resonance--$TiF_4 \cdot 2THF$

A. Prior Studies

Muetterties (36) has examined the ^{19}F magnetic resonance of a number of $TiF_4 \cdot 2L$ complexes, where L is a monodentate ligand, including the $TiF_4 \cdot 2THF$ complex. In all cases, at low temperature, two equal intensity triplets were observed, indicating the existence of only the *cis*-$TiF_4 \cdot 2THF$ (A) isomer.

Ragsdale and Dyer (12) studied *cis*-*trans* isomerism for $TiF_4 \cdot 2L$ complexes where L was a substituted pyridine 1-oxide ligand. When L was pyridine 1-oxide, only the *cis* isomer was observed. When L was 2-methylpyridine 1-oxide, the spectrum showed, in addition to the two triplets, a small singlet just upfield from the highest field triplet. This singlet accounted for approximately 10% of the spectral intensity and was assigned to the *trans* structure. The 2,6-dimethylpyridine 1-oxide complex of TiF_4 gave only a single ^{19}F magnetic resonance in a position just above the high field triplet for the pyridine 1-oxide complex and just below the high field triplet for the 2,6-dimethylpyridine 1-oxide complex. This singlet was also assigned to the *trans* structure. From this study it was concluded that the fluorines *trans* to the ligands (F_β) are shifted to lower field than the fluorines *trans* to each other (F_α).

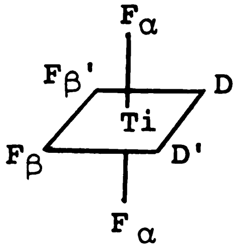
Ragsdale and Stewart (40) prepared a number of $[TiF_5 \cdot ROH]^-$ complexes for which ^{19}F NMR showed a low field quintuplet and a high field doublet in a 1:4 intensity ratio. The low field quintuplet must arise from the fluorine trans to the ligand, in agreement with the above conclusion.

B. Theoretical Interpretation

The chemical shift appears to be dependent upon the degree of fluorine to titanium $p\pi \longrightarrow d\pi$ bonding. Titanium(IV) has a $3d^0$ configuration. In octahedral complexes, the d_{xy}, d_{yz}, and d_{xz} orbitals are available for π bonding along the x, y, and z axes, respectively. Weak π bonding groups trans to a fluorine would allow for strong $p\pi \longrightarrow d\pi$ bonding from fluorine to titanium. This should decrease the fluorine shielding constant and cause a downfield shift in the ^{19}F magnetic resonance. Fluorines trans to a strong π bonding donor such as another fluorine should appear at higher field strength.

C. Supporting Evidence

Ragsdale and Dyer (13) support this reasoning in a study of mixed ligand complexes of titanium tetrafluoride. A series of cis-$TiF_4 \cdot DD'$ complexes were studied where D was N,N-dimethylacetamide and D' was a para substituted pyridine 1-oxide.



This complex contains two equivalent (F_α) and two non-equivalent (F_β and F_β') fluorine atoms and gave rise to a spectrum typical of an A_2MX system. The lowest field resonance was a triplet due to F_β which was *trans* to the weakest π bond donor D. A second triplet due to F_β' (*trans* to D') was slightly further upfield. A doublet of doublets was found at significantly higher fields due to the F_α fluorines which were *trans* to each other. As the *para* substituents of D' were varied to weaken the π bonding between the oxygen and the titanium, the triplet due to F_β' moved downfield. The observed coupling constants also seem to indicate the degree of fluorine to titanium π bonding. The coupling constants measured by Ragsdale and Dyer (13) were: $J_{\alpha\beta}' = 34\text{-}35$ Hz, $J_{\alpha\beta} = 39$ Hz, $J_{\beta\beta'} = 48$ Hz. This order $J_{\beta\beta'} >> J_{\alpha\beta} > J_{\alpha\beta'}$ is also the order expected on the basis of greater coupling for the more strongly π bonded groups. The expected order of π bonding strength is $F_\beta > F_{\beta'} >> F_\alpha$. This reasoning is consistent with the belief that F-F coupling for geminal groups is transmitted both through the bond and through space (16). Increased $p\pi \longrightarrow d\pi$ bonding would be expected both to increase the bond strength and to reduce the bond length, thereby reducing the distance between fluorine atoms.

D. Interpretation of Spectra

The observed ^{19}F magnetic resonance spectra for $TiF_4 \cdot 2THF$ are shown on page 66. For *cis*-$TiF_4 \cdot 2THF$ (isomer *A*), $\delta_{F_\alpha F_\beta} = 60.9$ ppm and $J_{F_\alpha F_\beta} = 37+$ Hz. A small singlet S_4 is observed 12 ppm upfield from the upfield triplet t_4^+. The low field triplet t_4^- is ascribed to F_β and the high field triplet t_4^+ to F_α. The S_4 singlet most probably arises from the trans-$TiF_4 \cdot 2THF$ complex (isomer B). This complex contains only F_α fluorine and its ^{19}F resonance should be very near the F_α resonance exihibited for the cis isomer. As Ragsdale and Dyer (12) have shown for the $TiF_4 \cdot 2(2\text{-}CH_3C_5H_4NO)$ complex, the trans isomer gives a single F_α resonance at slightly higher field than the F_α triplet for the cis isomer. There is, therefore, little doubt that S_4 is due to the trans isomer. The equilibrium constant calculated for the conversion of the trans to the cis isomer (p. 65) is equal to 33 at -60°C. Only 3% of the $TiF_4 \cdot 2THF$ isomer exists in the trans form. The enhanced stability of the cis isomer can be attributed mainly to the increased bond strength of the F_β fluorines due to $p\pi \longrightarrow d\pi$ interactions. On the basis of random ordering, the cis compound also should be preferred over the trans compound by a 4:1 ratio. The trans form would only be preferred if ligands having large steric repulsion were employed. It is interesting to note that both the cis- and trans-$SnF_4 \cdot 2C_2H_5OH$ isomers are observed in roughly equal proportions at -50°C by ^{19}F NMR (41,42). Tin has a $4d^{10}$ configuration which prevents $p\pi \longrightarrow d\pi$ interaction. The chemical shift difference $\delta_{F_\alpha F_\beta}$ for the cis-$SnF_4 \cdot 2C_2H_5OH$ isomer was very small, giving rise to a complex multiplet characteristic of an A_2B_2 system. The difference in the chemical shift for the cis multiplet and the trans singlet was approximately 5 ppm.

^{19}F Magnetic Resonance--$TiF_2Cl_2 \cdot 2THF$, Isomer J

A. Interpretation of Spectra

Of all the possible $TiF_xCl_{4-x} \cdot 2THF$ isomers only $TiF_4 \cdot 2THF$ isomer A and $TiF_2Cl_2 \cdot 2THF$ isomer J give unique splitting patterns. The presence of two equal intensity doublets having the same coupling constants in the ^{19}F magnetic resonance spectrum for an equilibrium mixture of these complexes confirms the presence of $TiF_2Cl_2 \cdot 2THF$ isomer J. The chemical shift difference and the coupling constant for this isomer are $\delta_{F_\beta F_\gamma} = 76$ ppm and $J_{F_\beta F_\gamma} = 45$ Hz, respectively.

B. Theoretical Considerations for a π Bonding Order F > THF > Cl

The expected $p\pi \rightarrow d\pi$ donation ability of the groups bonded to titanium is F > THF > Cl. The low field doublet d_2^- would then arise from the group trans to the chlorine, F_γ, and the higher field doublet d_2^+ would arise from the F_β group trans to the THF. The relatively large F-F coupling constant indicates that considerable $p\pi \rightarrow d\pi$ fluorine to titanium bonding is involved, as would be expected from the above assignments. The fairly large $\delta_{F_\beta F_\gamma}$ value indicates that chlorine is a considerably weaker π bond donor than THF. The observed $\delta_{F_\alpha F_\beta}$ value of 60.9 ppm for $TiF_4 \cdot 2THF$ isomer A and a $\delta_{F_\beta F_\gamma}$ value of 76 ppm for $TiF_2Cl_2 \cdot 2THF$ isomer J indicate that

THF is slightly closer to fluorine than chlorine in its ability to form π bonds.

C. Theoretical Considerations for a π Bonding Order F > Cl > THF

It is more difficult to account for these observations if the relative π bonding ability of THF and Cl are inverted from that previously suggested. For a π bonding order of F > Cl > THF, the expected $\delta_{F_\beta F_\gamma}$ value would be less than $\delta_{F_\alpha F_\beta}$ or < 60 ppm. The value of $\delta_{F_\beta F_\gamma}$ would only approach 60 ppm as the π bonding strength of fluorine and chlorine converge. The belief that $\delta_{F_\alpha F_\beta}$ should remain fairly constant for the entire series $TiF_{\underline{x}}Cl_{4-\underline{x}} \cdot 2THF$ may, however, be an assumption that grossly oversimplifies the actual situation. As chlorine atoms replace fluorine in this series, steric effects may come into play which could cause a change in the relative π bonding ability of the groups involved. Replacement of two fluorine atoms on $TiF_4 \cdot 2THF$ with chlorine atoms might be expected to increase the THF--Ti bond distance; this would decrease the THF $\rightarrow$ Ti $p\pi \longrightarrow d\pi$ bonding and allow for greater $F_\beta \rightarrow$ Ti $p\pi \longrightarrow d\pi$ bonding. Replacing strong π bonding groups with weaker groups may also allow those remaining fluorines to increase their degree of π bonding. The net effect would be a much larger value of $\delta_{F_\beta F_\gamma}$ than expected on the basis of $\delta_{F_\alpha F_\beta}$ for $TiF_4 \cdot 2THF$ isomer $\underline{A}$ and a π bonding order F > Cl > THF. If the π bonding order for this isomer is in fact F > Cl > THF, then the low field doublet d_2^- would arise from F_β and the high field doublet d_2^+ from F_γ.

Since both π bonding orders can be justified by the experimental results, both will be used in the spectral interpretation. The more intuitively obvious π bonding order F > THF > Cl will be discussed first.

Interpretation of Spectra

A. Temperature Effects

The effect of temperature on the ^{19}F spectra of addition complexes of TiF_4 has been discussed by Muetterties (36) and Ragsdale (12,13,40). Loss of the fine structure and coalescence of the low temperature peaks into a broad singlet at room temperature was attributed to donor molecule exchange. Ligand exchange has also been established for $Ti(acac)_4$ and $Ti(tfac)_4$ (1,2,38). The formation of the mixed halide complexes from $TiCl_4 \cdot 2THF$ and $TiF_4 \cdot 2THF$ clearly establishes that halide exchange also takes place. The loss of fine structure at temperatures above -50°C and collapse of all ^{19}F resonance peaks at room temperature for the $TiF_{\underline{x}}Cl_{4-\underline{x}} \cdot 2THF$ compounds is therefore attributed to both donor molecule exchange and halide exchange.

B. Observed ^{19}F Resonances

The low temperature ^{19}F magnetic resonance spectrum for the titanium(IV) chloride fluoride THF equilibrium mixture shows, in addition to the peaks t_4^- and t_4^+ for $TiF_4 \cdot 2THF$

isomer **A** and d_2^- and d_2^+ for $TiF_2Cl_2\cdot 2THF$ isomer **J**, a triplet t_3^- and doublet d_3^+ in 2:1 ratio--which must arise from an isomer of $TiF_3Cl\cdot 2THF$--and two singlets with S_1 at lower field than S_2. A study of the intensity of these singlets with regard to the initial ratio of $TiCl_4$ to TiF_4 has conclusively established that S_2 arises from $TiF_2Cl_2\cdot 2THF$ and S_1 arises from $TiFCl_3\cdot 2THF$.

C. π Bonding Order F > THF > Cl

i. $TiF_3Cl\cdot 2THF$. Assuming the π bonding strength of ligands to be F > THF > Cl, the three isomers of $TiF_3Cl\cdot 2THF$ should each give a low field triplet and a higher field doublet. $TiF_3Cl\cdot 2THF$ isomer **C** would be expected to have $\delta_{F_\alpha F_\beta}$ and $J_{F_\alpha F_\beta}$ values on the order of those observed for $TiF_4\cdot 2THF$ isomer **A** ($\delta_{F_\alpha F_\beta} = 60$ ppm, $J_{F_\alpha F_\beta} = 37.7$ Hz). $TiF_3Cl\cdot 2THF$ isomer **D** with β- and γ-fluorine should give chemical shift and coupling constant values close to those observed for $TiF_2Cl_2\cdot 2THF$ isomer **J** ($\delta_{F_\beta F_\gamma} = 76$ ppm, $J_{F_\beta F_\gamma} = 45$ Hz). The third isomer $TiF_3Cl\cdot 2THF$ isomer **E** with α- and γ-fluorine should have a chemical shift approximately equal to the sum of $\delta_{F_\alpha F_\beta}$ and $\delta_{F_\beta F_\gamma}$ or a $\delta_{F_\alpha F_\gamma}$ value of ~135 ppm. Its coupling constant should be larger than $J_{F_\alpha F_\beta}$ and probably smaller than $J_{F_\beta F_\gamma}$ or $37.7\text{ Hz} < J_{F_\alpha F_\gamma} < 45\text{ Hz}$.

The observed chemical shift difference of $\delta_{FF} = 67$ ppm and coupling constant $J_{FF} = 33.1$ can only be accounted for by α- and β-fluorine which leads to the selection of $TiF_3Cl\cdot 2THF$

isomer **C**. The low field triplet t_3^- and the high field doublet d_3^+ are therefore ascribed respectively to F_β and F_α of $TiF_3Cl \cdot 2THF$ isomer **C**.

ii. $TiF_2Cl_2 \cdot 2THF$. The singlet S_2 arises from isomer **F**, **G**, **H**, or **I** or $TiF_2Cl_2 \cdot 2THF$. This resonance appears about 6 ppm downfield from the higher field d_2^+ (F_β) doublet of $TiF_2Cl_2 \cdot 2THF$ isomer **J**. The low field doublet d_2^- (F_γ) is ~70 ppm downfield from S_2. If the singlet S_2 arose from an α-fluorine it would be expected ~60 ppm upfield from d_2^+. For a β-fluorine, the resonance should be near d_2^+ and a γ-fluorine should be observed near d_2^-. The observation of S_2 very near d_2^+ indicates that the resonance arises from a β-fluorine. The only isomer having two equivalent β-fluorines is $TiF_2Cl_2 \cdot 2THF$ isomer **F**. The S_2 peak is assigned to the F_β resonance of this isomer.

iii. $TiFCl_3 \cdot 2THF$. Isomers of $TiFCl_3 \cdot 2THF$ give only a single ^{19}F resonance peak. Any specific isomer assignment must therefore be somewhat tenuous. As fluorine atoms are replaced with chlorine atoms in the series $TiF_{\underline{x}}Cl_{4-\underline{x}} \cdot 2THF$, the chemical shift from the reference moves to lower field strengths. This is contrary to the chemical shift expected on the basis of inductive effects but is justified on the bases of the expected increase in $p\pi \longrightarrow d\pi$ bonding. Inductive effects in covalent fluorine compounds are considered to be weak in comparison with the paramagnetic shielding due to $p\pi \longrightarrow d\pi$ interactions (15,39). In systems where

π bonding is possible, ^{19}F resonances generally shift to low field as fluorine atoms are replaced with less electronegative atoms. Table 14 clearly illustrates this point for the boron fluoride halides and several other examples. The J_{BF} coupling constants also show the effect of increased π bonding. Table 15 lists the various chemical shifts observed for $TiF_{\underline{x}}Cl_{4-\underline{x}}\cdot 2THF$ compounds. The three isomers of $TiFCl_3\cdot 2THF$ contain only β- and γ-fluorine. Assuming the β-fluorine of isomer **K** to be responsible for the observed ^{19}F resonance S_1, a reasonable decrease of 24 ppm is observed for the chemical shift difference between $TiF_2Cl_2\cdot 2THF$ and $TiFCl_3\cdot 2THF$. If S_1 resulted from a γ-fluorine of isomers **L** or **M**, a net increase in the chemical shift of 50 ppm would be observed. It seems more reasonable to select $TiFCl_3\cdot 2THF$ isomer **K** as the isomer responsible for S_1.

A disturbing feature of Table 15 is the discontinuity in the decreasing chemical shift with decreasing fluorine at $TiF_2Cl_2\cdot 2THF$. The change in δ_{FF} for each step in the series $TiF_{\underline{x}}Cl_{4-\underline{x}}\cdot 2THF$ with decreasing fluorine is -35, +38, and -24 ppm. It might be possible to justify a small increase in δ_{FF} because of inductive effects or perhaps steric interactions but an increase of 38 ppm is very difficult to rationalize.

D. π Bonding Order F > Cl > THF

Reinterpreting the spectra with an assumed π bonding order F > Cl > THF leads to the following conclusions.

Table 14. ^{19}F chemical shifts for selected compounds where π bonding is postulated.

Boron Fluoride Halide System (9)

Compound	δ_{BF_3} ppm	J_{BF} Hz
BF_3	0	15
BF_2Cl	-51.5	34
BF_2Br	-68.4	56
$BFCl_2$	-99.0	74
$BFClBr$	-114.8	92
$BFBr_2$	-130.4	108

Carbon Chloride Fluoride System (32)

Compound	δ_{CF_4} ppm
CF_4	0
CF_3Cl	-36.8
CF_2Cl_2	-60.4
$CFCl_3$	-76.7

Phosphorus(V) Chloride Fluoride System (6,23)

Compound	δ_{FF}* (ppm) ^{F}(axial)	δ_{FF}* (ppm) ^{F}(equitorial)
PF_5	+66.5	--
PF_4Cl	+23.5	--
PF_3Cl_2	-67.4	+41.5
PF_2Cl_3	-123.0	--
$PFCl_4$	-132	--

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*$CFCl_3$ used as internal reference.

Table 15. ^{19}F chemical shifts and coupling constants for the $TiF_{\underline{x}}Cl_{4-\underline{x}}\cdot 2THF$ isomers proposed from a π bonding order F > THF > Cl.

Isomer	δ_{F_α}* ppm	δ_{F_β}* ppm	δ_{F_γ}* ppm	$J_{F_\alpha F_\beta}$ Hz	$J_{F_\beta F_\gamma}$ Hz	$\Delta\delta$ ppm
$TiF_4\cdot 2THF$ **A**	$-239\ t_4^{+}$	$-299\ t_4^{-}$	---	37.7	---	---
$TiF_4\cdot 2THF$ **B**	$-227\ S_4$	---	---	---	---	---
$TiF_3Cl\cdot 2THF$ **C**	$-276\ d_3^{+}$	$-343\ t_3^{-}$	---	33.1	---	-35
$TiF_2Cl_2\cdot 2THF$ **J**	---	$-305\ d_2^{+}$	$-381\ d_2^{-}$	---	45	+38
$TiF_2Cl_2\cdot 2THF$ **F**	---	$-308\ S_2$	---	---	---	
$TiFCl_3\cdot 2THF$ **K**	---	$-329\ S_1$	---	---	---	-24

* ^{19}F chemical shifts measured from TFA as internal reference.

i. $TiF_3Cl\cdot 2THF$. Isomers C and E would both give a low field triplet and a high field doublet but because isomer D would give an inverted splitting pattern, it can be eliminated from consideration. The $\delta_{F_\alpha F_\beta}$ expected for isomer C should be larger than that expected for $\delta_{F_\alpha F_\beta}$ of $TiF_4\cdot 2THF$ isomer A whereas $J_{F_\alpha F_\beta}$ should be about the same for both compounds. Isomer E should have $\delta_{F_\alpha F_\gamma}$ and $J_{F_\alpha F_\gamma}$ values much smaller than the corresponding values predicted for isomer C and presumably smaller than those observed for $TiF_4\cdot 2THF$ isomer A. The chemical shift and coupling constant values observed for $TiF_3Cl\cdot 2THF$ appear to be more consistent with isomer C, but isomer E is not conclusively ruled out.

ii. $TiF_2Cl_2\cdot 2THF$. The low field doublet d_2^- would arise from the β-fluorine and the high field doublet d_2^+ from the γ-fluorine of isomer J. The strong singlet S_2 which is very near d_2^+ is therefore expected to arise from a F_γ resonance of isomer H.

iii. $TiFCl_3\cdot 2THF$. A decrease in the chemical shift with decreasing fluorine for the series $TiF_{x}Cl_{4-x}\cdot 2THF$ can only be maintained if the S_1 peak arises from a F_γ resonance. Both isomers L and M contain γ-fluorine, but isomer M is slightly favored on the basis of its structural consistency with $TiF_2Cl_2\cdot 2THF$ isomer H.

E. Summary

Table 16 lists the expected $TiF_{x}Cl_{4-x}\cdot 2THF$ isomers, assuming a π bonding order of F > Cl > THF. The assignments

Table 16. ^{19}F chemical shift and coupling constants for the $TiF_{x}Cl_{4-x}\cdot 2THF$ isomers proposed from a π bonding order F > Cl > THF.

Isomer	δ_{F_α}* ppm	δ_{F_γ}* ppm	δ_{F_β}* ppm	$J_{F_\alpha F_\beta}$ Hz	$J_{F_\beta F_\gamma}$ Hz	$\Delta\delta$ ppm
$TiF_4\cdot 2THF$ A	$-239\ t_4^+$	---	$-299\ t_4^-$	37.7	---	---
$TiF_4\cdot 2THF$ B	$-227\ S_4$	---	---	---	---	---
$TiF_3Cl\cdot 2THF$ C	$-276\ d_3^+$	---	$-343\ t_3^-$	33.1	---	-40
$TiF_2Cl_2\cdot 2THF$ J	---	$-305\ d_2^+$	$-381\ d_2^-$	---	45	-35
$TiF_2Cl_2\cdot 2THF$ H	---	$-308\ S_2$	---	---	---	---
$TiFCl_3\cdot 2THF$ M	---	$-329\ S_1$	---	---	---	-20

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* ^{19}F chemical shifts measured from TFA as internal reference.

indicated in this table are preferred over those given in Table 15 because of their greater consistency in the downfield ^{19}F chemical shift with decreasing fluorine. Most of the isomers listed are the same in both tables. The only difference rests in the selection of isomer H over isomer F for $TiF_2Cl_2 \cdot 2THF$ and isomer M over isomer K for $TiFCl_3 \cdot 2THF$.

Stereochemistry

A. Influencing Factors

This system is too complex to allow accurate stereochemical predictions by Gillespie's Valence-Shell Electron-Pair Repulsion (VSEPR) theory (20,21). The major factor complicating stereochemical predictions is the effect of $p\pi \longrightarrow d\pi$ bonding on the bond energy of the molecule and the degree to which this multiple bonding enhances electronic repulsions.

B. $TiF_4 \cdot 2THF$

On the basis of VSEPR, isomer B ought to be the preferred structure. That isomer A is observed to be the most stable is indicative of increased Ti-F bond energy resulting from enhanced $p\pi \longrightarrow d\pi$ interaction. In this case it appears that the enhanced stability due to π bonding outweighs the VSEPR effects.

C. $TiF_3Cl\cdot 2THF$

The most stable structure by virtue of enhanced π bonding should be isomer **D**, whereas VSEPR theory predicts this isomer to be the least stable. Isomer **D** is observed to be the least consistent with the observed NMR data. In this case, it appears that π bonding stabilization is not the controlling factor. Choosing between isomers **C** and **E** is difficult on the basis of VSEPR theory. If Cl-Cl repulsion is greater than THF-THF repulsion, then isomer **C** would be slightly favored. The NMR data suggest that the observed isomer is **C**, but it does not eliminate the possible existence of isomer **E**.

D. $TiF_2Cl_2\cdot 2THF$

Isomer **F** would be the energetically most stable for a π bonding order Cl > THF. The inverted π bonding order would indicate that isomer **H** is the most energetically favored. In either case isomer **J** would be the second most energetically favored. VSEPR theory suggests isomers **G** and **I** as the most stable. The NMR data indicate as the most stable either isomer **F** for the π bonding order THF > Cl or isomer **H** for the inverted π bonding order. The presence of isomer **J** in low concentration is also confirmed. There appears to be no agreement among these observations.

E. $TiFCl_3\cdot 2THF$

If the π bonding order is Cl > THF, then consideration of π bonding stabilization makes **K** the isomer of choice, but the inverted π bonding order suggests that isomers **L** and **M** are more stable than **K**. VSEPR theory predicts that isomer **M** is the most stable. The NMR data fit with the spectrum anticipated for isomer **K** if the π bonding order is THF > Cl; for the inverted π bonding order the data fit the pattern expected for either isomer **L** or **M**.

EQUILIBRIUM CONSTANTS

Experimental Data

Equilibrium concentrations were calculated from fluorine-19 magnetic resonance intensity data obtained for samples 1, 2, and 3 (Table 10). The spectra were recorded without side bands and with a sweep width such that the ^{19}F magnetic resonances appeared as lines (Figure 8). The height of these lines was taken as proportional to the intensity of the ^{19}F magnetic resonance. The spectrum for sample 1 was obtained at -70°C. The spectra for samples 2 and 3 were obtained at -60°C.

Equilibrium Considerations

In addition to the six equilibrium equations listed in the discussion section (p. 85), several additional equilibrium expressions can be considered.

The following equations represent the formation equilibria of the mixed chloride fluoride complexes from their parent compounds.

(7) $1/4(TiCl_4 \cdot 2THF) + 3/4(TiF_4 \cdot 2THF) \rightleftharpoons TiF_3Cl \cdot 2THF$

(8) $1/2(TiCl_4 \cdot 2THF) + 1/2(TiF_4 \cdot 2THF) \rightleftharpoons TiF_2Cl_2 \cdot 2THF$

(9) $3/4(TiCl_4 \cdot 2THF) + 1/4(TiF_4 \cdot 2THF) \rightleftharpoons TiFCl_3 \cdot 2THF$

Equation 10 represents the equilibrium between the two observed isomers of $TiF_2Cl_2 \cdot 2THF$.

$$(10)\quad TiF_2Cl_2 \cdot 2THF\ (\underset{\sim}{J}) \rightleftharpoons TiF_2Cl_2 \cdot 2THF\ (\underset{\sim}{F} \text{ or } \underset{\sim}{H})$$

The isomers represented in this equation are presumed to be correct on the basis of the observed ^{19}F NMR data (see pp. 96-102).

Since $TiCl_4 \cdot 2THF$ cannot be observed directly by ^{19}F NMR, its concentration must be determined by difference. Equilibrium calculations requiring a knowledge of the concentration of $TiCl_4 \cdot 2THF$ are therefore subject to large error. A number of equilibria exist in solution which do not directly depend upon $TiCl_4 \cdot 2THF$. These are represented by equations 3, 5, and 6. The calculated equilibrium constants for equations 3, 5, and 6 should be significantly more accurate than those calculated for equations 1, 2, 4, 7, 8, and 9. Since equilibrium constants calculated for equations 1, 2, and 4 are expected to be of very low accuracy and since they would add little useful knowledge, they will no longer be considered.

Method of Calculation

Calculation of equilibrium concentrations from intensity data is complicated by the fact that $TiCl_4 \cdot 2THF$ cannot be observed by ^{19}F NMR. The total peak intensity observed for each of the other compounds is proportional to the relative amount of fluorine contained in each compound. For all the species but $TiCl_4 \cdot 2THF$, the relative amount of chlorine contained in each was determined by multiplying the relative amount of fluorine by the stoichiometric ratio of chlorine to fluorine for that species. The overall ratio of chlorine to fluorine is determined by the known stoichiometry of the initial sample. The relative amount of chlorine contained in $TiCl_4 \cdot 2THF$ was therefore determined by difference. The relative molar ratio of each species was then obtained by dividing the relative amount of fluorine by the number of fluorine atoms per molecule or by dividing the relative amount of chlorine by the number of chlorine atoms per molecule. Initial molar concentrations were finally arrived at by converting the relative scale to a mole per cent scale and then multiplying by the initial concentration. Since the stoichiometry for the equilibrium equations does not change in going from reactants to products, the total molar concentration at equilibrium equals the initial molar concentration. Concentration values therefore are not actually necessary since the mole ratio or mole per cent values could be used in their place in determining the equilibrium constant.

Equilibrium Concentrations

Sample 1 had an initial concentration of 1.0 M TiF_2Cl_2 in THF. Table 17 gives the measured intensity values obtained from the spectrum of this sample at -70°C (Figure 8) as well as the calculated values leading to the equilibrium concentrations.

Table 17. Equilibrium calculations for 1.0 M $TiF_2Cl_2 \cdot 2THF$ at -70°C.

Compound	Measured Intensity	Relative Amount Fluorine	Relative Amount Chlorine	Molar Ratio	Mole Per cent	Equilibrium Concn. (M)
$TiF_4 \cdot 2THF$	8	5.2	0	1.3	2.6	0.026
$TiF_3Cl \cdot 2THF$	51	32.9	11.0	11.0	22.0	0.220
$TiF_2Cl_2 \cdot 2THF$ (F or H)	70	45.2	45.2	22.6	45.2	0.452
$TiF_2Cl_2 \cdot 2THF$ (J)	12	7.7	7.7	3.8	7.7	0.077
$TiFCl_3 \cdot 2THF$	14	9.0	27.0	9.0	18.0	0.180
$TiCl_4 \cdot 2THF$	0	0	9.1	2.3	4.6	0.046

Explanation of Table

1. Measured intensity values were obtained from the ^{19}F magnetic resonance spectrum.

2. Relative amount of fluorine values are proportional to the measured intensity values on the basis of 100.

3. Relative amount of chlorine values for all the compounds other than $TiCl_4 \cdot 2THF$ were obtained by multiplying the relative amount of fluorine values by the atomic ratio of chlorine to fluorine for each compound. The relative amount of chlorine for $TiCl_4 \cdot 2THF$ was determined by subtracting the sum of the relative amount of chlorine values from 100. The 100 was arrived at since the stoichiometric ratio of chlorine to fluorine was 1:1 for the initial sample, $TiF_2Cl_2 \cdot 2THF$, and since the relative amount of fluorine values were based on 100.

4. Molar ratio values equal the relative amount of fluorine divided by the number of fluorines per molecule or the relative amount of chlorine divided by the number of chlorines per molecule.

5. Mole percent values are proportional to the molar ratio values.

6. Equilibrium concentrations were obtained by taking the indicated mole per cent of the initial molar concentration (1.0 M).

Sample 2 had an initial concentration of 0.5 M $TiF_2Cl_2 \cdot 2THF$. The data calculated for this sample at $-60^{\circ}C$ are presented in Table 18.

Sample 3 was initially 0.32 M $TiF_2Cl_2 \cdot 2THF$ and 0.17 M $TiF_3Cl \cdot 2THF$. The stoichiometric ratio of chlorine to fluorine in this sample was 0.81 to 1.15. The total relative amount of chlorine on the basis of 100 for the relative amount of fluorine must be $\frac{0.81}{1.15}$ x 100 or 70. The data calculated for this sample at $-60^{\circ}C$ are presented in Table 19.

Equilibrium Constants

A. Experimental Equilibrium Constants

Equilibrium constants are calculated from the following mass action expressions obtained for each of the seven equations previously discussed (p. 105).

$$K_3 = \frac{[TiF_2Cl_2 \cdot 2THF]^{\frac{1}{2}}[TiF_3Cl \cdot 2THF]^{\frac{1}{2}}}{[TiF_4 \cdot 2THF]^{\frac{1}{2}}[TiFCl_3 \cdot 2THF]^{\frac{1}{2}}}$$

$$K_5 = \frac{[TiF_3Cl \cdot 2THF]}{[TiF_4 \cdot 2THF]^{\frac{1}{2}}[TiF_2Cl_2 \cdot 2THF]^{\frac{1}{2}}}$$

$$K_6 = \frac{[TiF_2Cl_2 \cdot 2THF]}{[TiF_3Cl \cdot 2THF]^{\frac{1}{2}}[TiFCl_3 \cdot 2THF]^{\frac{1}{2}}}$$

$$K_7 = \frac{[TiF_3Cl \cdot 2THF]}{[TiCl_4 \cdot 2THF]^{\frac{1}{4}}[TiF_4 \cdot 2THF]^{\frac{3}{4}}}$$

$$K_8 = \frac{[TiF_2Cl_2 \cdot 2THF]}{[TiCl_4 \cdot 2THF]^{\frac{1}{2}}[TiF_4 \cdot 2THF]^{\frac{1}{2}}}$$

Table 18. Equilibrium calculations for 0.5 M $TiF_2Cl_2 \cdot 2THF$ at -60°C.

Compound	Measured Intensity	Relative Amount Fluorine	Relative Amount Chlorine	Molar Ratio	Mole Per cent	Equilibrium Concn. (M)
$TiF_4 \cdot 2THF$	10	5.3	0	1.3	2.6	0.013
$TiF_3Cl \cdot 2THF$	85	44.7	14.9	14.9	29.9	0.150
$TiF_2Cl_2 \cdot 2THF$ (F or H)	64	33.7	33.7	16.8	33.7	0.169
$TiF_2Cl_2 \cdot 2THF$ (J)	16	8.4	8.4	4.2	8.4	0.042
$TiFCl_3 \cdot 2THF$	15	7.9	23.7	7.9	15.8	0.079
$TiCl_4 \cdot 2THF$	0	0	19.3	4.8	9.6	0.048

Table 19. Equilibrium calculations for 0.32 *M* $TiF_2Cl_2 \cdot 2THF$ and 0.17 *M* $TiF_3Cl \cdot 2THF$ at -60°C.

Compound	Measured Intensity	Relative Amount Fluorine	Relative Amount Chlorine	Molar Ratio	Mole Per cent	Equilibrium Concn. (*M*)
$TiF_4 \cdot 2THF$	50	16.0	0	4.0	9.4	0.046
$TiF_3Cl \cdot 2THF$	160	51.3	17.1	17.1	40.2	0.197
$TiF_2Cl_2 \cdot 2THF$ (**F** or **H**)	71	22.8	22.8	11.4	26.8	0.131
$TiF_2Cl_2 \cdot 2THF$ (**J**)	20	6.4	6.4	3.2	7.5	0.037
$TiFCl_3 \cdot 2THF$	11	3.5	10.5	3.5	8.2	0.040
$TiCl_4 \cdot 2THF$	0	0	13.2	3.3	7.8	0.038

$$K_9 = \frac{[\mathrm{TiFCl_3 \cdot 2THF}]}{[\mathrm{TiCl_4 \cdot 2THF}]^{\frac{3}{4}}]\mathrm{TiF_4 \cdot 2THF}]^{\frac{1}{4}}}$$

$$K_{10} = \frac{[\mathrm{TiF_2Cl_2 \cdot 2THF}\ (\mathbf{F}\text{ or }\mathbf{H})]}{[\mathrm{TiF_2Cl_2 \cdot 2THF}\ (\mathbf{J})]}$$

The following experimental equilibrium constants, K^E, are calculated for sample 1 (Table 17).

$$K_3^E = \frac{(0.22)^{\frac{1}{2}}(0.529)^{\frac{1}{2}}}{(0.026)^{\frac{1}{2}}(0.180)^{\frac{1}{2}}} = 5.0 \text{ at } -70^\circ\mathrm{C}$$

$$K_5^E = \frac{(0.22)}{(0.026)^{\frac{1}{2}}(0.529)^{\frac{1}{2}}} = 1.9 \text{ at } -70^\circ\mathrm{C}$$

$$K_6^E = \frac{(0.529)}{(0.22)^{\frac{1}{2}}(0.18)^{\frac{1}{2}}} = 2.7 \text{ at } -70^\circ\mathrm{C}$$

$$K_7^E = \frac{(0.22)}{(0.026)^{\frac{3}{4}}(0.046)^{\frac{1}{4}}} = 7.3 \text{ at } -70^\circ\mathrm{C}$$

$$K_8^E = \frac{(0.529)}{(0.026)^{\frac{1}{2}}(0.046)^{\frac{1}{2}}} = 15 \text{ at } -70^\circ\mathrm{C}$$

$$K_9^E = \frac{(0.180)}{(0.026)^{\frac{1}{4}}(0.046)^{\frac{3}{4}}} = 4.5 \text{ at } -70^\circ\mathrm{C}$$

$$K_{10}^E = \frac{(0.452)}{(0.077)} = 5.9 \text{ at } -70^\circ\mathrm{C}$$

For sample 2 (Table 18) the following values are obtained.

$$K_3^E = \frac{(0.150)^{\frac{1}{2}}(0.211)^{\frac{1}{2}}}{(0.013)^{\frac{1}{2}}(0.079)^{\frac{1}{2}}} = 5.6 \text{ at } -60^{\circ}\text{C}$$

$$K_5^E = \frac{(0.150)}{(0.013)^{\frac{1}{2}}(0.211)^{\frac{1}{2}}} = 2.9 \text{ at } -60^{\circ}\text{C}$$

$$K_6^E = \frac{(0.211)}{(0.150)^{\frac{1}{2}}(0.079)^{\frac{1}{2}}} = 1.9 \text{ at } -60^{\circ}\text{C}$$

$$K_7^E = \frac{(0.150)}{(0.013)^{\frac{3}{4}}(0.048)^{\frac{1}{4}}} = 8.3 \text{ at } -60^{\circ}\text{C}$$

$$K_8^E = \frac{(0.211)}{(0.013)^{\frac{1}{2}}(0.048)^{\frac{1}{2}}} = 8.4 \text{ at } -60^{\circ}\text{C}$$

$$K_9^E = \frac{(0.079)}{(0.013)^{\frac{1}{4}}(0.048)^{\frac{3}{4}}} = 2.3 \text{ at } -60^{\circ}\text{C}$$

$$K_{10}^E = \frac{(0.169)}{(0.042)} = 4.0 \text{ at } -60^{\circ}\text{C}$$

Sample 3 (Table 19) gives the following equilibrium constant values.

$$K_3^E = \frac{(0.197)^{\frac{1}{2}}(0.168)^{\frac{1}{2}}}{(0.046)^{\frac{1}{2}}(0.040)^{\frac{1}{2}}} = 4.2 \text{ at } -60^{\circ}\text{C}$$

$$K_5^E = \frac{(0.197)}{(0.046)^{\frac{1}{2}}(0.168)^{\frac{1}{2}}} = 2.2 \text{ at } -60^{\circ}\text{C}$$

$$K_6^E = \frac{(0.168)}{(0.197)^{\frac{1}{2}}(0.040)^{\frac{1}{2}}} = 1.9 \text{ at } -60^{\circ}\text{C}$$

$$K_7^E = \frac{(0.197)}{(0.046)^{\frac{3}{4}}(0.038)^{\frac{1}{4}}} = 4.4 \quad \text{at} \quad -60^\circ C$$

$$K_8^E = \frac{(0.168)}{(0.046)^{\frac{1}{2}}(0.038)^{\frac{1}{2}}} = 4.0 \quad \text{at} \quad -60^\circ C$$

$$K_9^E = \frac{(0.040)}{(0.046)^{\frac{1}{4}}(0.038)^{\frac{3}{4}}} = 1.0 \quad \text{at} \quad -60^\circ C$$

$$K_{10}^E = \frac{(0.131)}{(0.037)} = 3.5 \quad \text{at} \quad -60^\circ C$$

Table 20 presents a summary of the equilibrium constants calculated for these three samples. As expected, agreement for K_5^E, K_6^E, and K_7^E is much better than for K_1^E, K_2^E, and K_3^E. This illustrates the error introduced because the concentration of $TiCl_4 \cdot 2THF$ could not be determined directly. Direct determination of $TiCl_4 \cdot 2THF$, perhaps by visible or ultraviolet spectroscopy, would greatly increase the accuracy of K_1^E, K_2^E, and K_3^E. The low precision of these data makes impossible any firm conclusion regarding the effect of temperature on the equilibrium constant. There does not, however, appear to be any great effect of temperature on the values of the equilibrium constants.

B. Statistical Equilibrium Constants

Equilibrium constants which consider only the entropy-controlled tendency of a system to achieve random order can be calculated from simple probability theory. These statistical equilibrium constants, K^S, assume that enthalpy changes and nonrandom entropy effects are negligible.

Table 20. Summary of equilibrium constants.

	Sample 1 $-70^{\circ}C$ 1.0 $\underline{M}$ $TiF_2Cl_2 \cdot 2THF$	Sample 2 $-60^{\circ}C$ 0.5 $\underline{M}$ $TiF_2Cl_2 \cdot 2THF$	Sample 3 $-60^{\circ}C$ 0.32 $\underline{M}$ $TiF_2Cl_2 \cdot 2THF$ 0.17 $\underline{M}$ $TiF_3Cl \cdot 2THF$	Average
K_3^E	5.0	5.6	4.2	4.9
K_5^E	1.9	2.9	2.2	2.3
K_6^E	2.7	1.9	1.9	2.2
K_7^E	7.3	8.3	4.4	6.7
K_8^E	15	8.4	4.0	9.1
K_9^E	4.5	2.3	1.0	2.6
K_{10}^E	5.9	4.0	3.5	4.5

The probability of forming any component containing $\underline{n}$ fluorine atoms, where $\underline{n} = 0, 1, 2, 3$, or 4, is given by the expression

$$P_{4,\underline{n}} = \frac{4!}{\underline{n}!\,(4-\underline{n})!} \quad [F]^{\underline{n}}[Cl]^{(4-\underline{n})}$$

where [F] is the mole fraction of total halide that is fluorine and [Cl] equals the mole fraction of the total halide that is chlorine. Solving this expression for the case of equal molar amounts of chlorine and fluorine gives a ratio of components at equilibrium of $TiF_4{\cdot}2THF : TiF_3Cl{\cdot}2THF : TiF_2Cl_2{\cdot}2THF : TiFCl_3{\cdot}2THF : TiCl_4{\cdot}THF = 1:4:6:4:1$.

Using these values, statistical equilibrium constants can be calculated for equations 3, 5, 6, 7, 8, and 9. These calculated values follow.

$$K_3^S = \frac{(6)^{\frac{1}{2}}(4)^{\frac{1}{2}}}{(1)^{\frac{1}{2}}(4)^{\frac{1}{2}}} = 2.45$$

$$K_5^S = \frac{(4)}{(1)^{\frac{1}{2}}(6)^{\frac{1}{2}}} = 1.63$$

$$K_6^S = \frac{(6)}{(4)^{\frac{1}{2}}(4)^{\frac{1}{2}}} = 1.50$$

$$K_7^S = \frac{(4)}{(1)^{\frac{1}{4}}(1)^{\frac{3}{4}}} = 4$$

$$K_8^S = \frac{(6)}{(1)^{\frac{1}{2}}(1)^{\frac{1}{2}}} = 6$$

$$K_9^S = \frac{(4)}{(1)^{\frac{3}{4}}(1)^{\frac{1}{4}}} = 4$$

Discussion

A comparison of the experimental and statistical equilibrium constants is given in Table 21. Free energy values were calculated from the equation $-\Delta G = -RT \ln K$ ($T = 213^{o}K$). The ratio of the experimental equilibrium constant to the statistical equilibrium constant, K^{E}/K^{S}, indicates stabilization of the complex from factors other than random scatter entropy effects. These other factors include changes in the enthalpy of reaction and nonrandom entropy effects. The effect of these factors is clearly indicated by $\Delta(\Delta G)$ which is the difference in the experimental free energy of reaction and the statistical free energy change expected for random ordering. Positive values for $\Delta(\Delta G)$ indicate increased stability and negative values indicate decreased stability per mole of reaction product from that expected for random ordering, negligible nonrandom entropy effects, and no change in the enthalpy of reaction. All ΔG values are per mole of reaction product. The stability increase appears to be in the order:

$TiF_3Cl \cdot 2THF > TiF_2Cl_2 \cdot 2THF > TiFCl_3 \cdot 2THF$.

It is interesting to note that $TiF_3Cl \cdot 2THF$ and $TiF_2Cl_2 \cdot 2THF$ are increased in stability whereas $TiFCl_3 \cdot 2THF$ is decreased in stability from that expected for random ordering. This may indicate stronger molecular bonding forces as the number of fluorine atoms in the molecule increases and would result in enthalpy changes. The small deviation from randomness

Table 21. Statistical and experimental equilibrium constants.

	Statistical		Experimental		Calculated	
Equation	K^S	$-\Delta G$ cal/mole	K^E	$-\Delta G$ cal/mole	K^E/K^S	$\Delta(\Delta G)$ cal/mole
(3)	2.45	380	4.9	680	2	+300
(5)	1.63	210	2.3	350	1.4	+140
(6)	1.5	175	2.2	335	1.5	+160
(7)	4	590	6.7	810	1.7	+220
(8)	6	760	9.1	940	1.5	+180
(9)	4	590	2.6	410	0.65	-180

could also be easily accounted for on the basis of nonrandom entropy effects. The deviation in the experimentally determined equilibrium constants with temperature is not sufficient, considering the low precision of the data, to allow for any conclusions regarding the importance of enthalpy. It is known that nonrandom entropy changes, such as differences in solvation entropies of reactants and products, could account for significantly greater deviation from the statistically expected values than were observed for this system.

Investigations of Other Workers

Ligand exchange between metal acetylacetonates, $M(acac)_4$, and metal trifluoroacetylacetonates, $M(tfac)_4$, has been studied by both ^{19}F and proton NMR (1,2,38). Pinnavaia and Fay (38) found that formation of the mixed ligand zirconium complexes, $Zr(acac)_3(tfac)$, $Zr(acac)_2(tfac)_2$, and $Zr(acac)(tfac)_3$ was favored over that expected on the basis of statistical scatter. Equilibrium constants corresponding to K_4^E, K_5^E, and K_6^E were determined and found to be approximately 1.58 times larger than the statistical equilibrium constants. A study of the temperature dependence of the equilibrium constants lead the authors to conclude that the enthalpy changes for all three reactions are zero. Differences in solvation entropies of reactants and products was suggested to account for the observed nonstatistical distribution. In a study of the same system, Adams and Larsen (1,2) concur with Pinnavaia and Fay and have calculated equilibrium constants corresponding to K_7^E, K_8^E, and K_9^E and found these values to be 4.5, 8.5, and 6.0 times larger than the expected statistical equilibrium constants.

Conclusion

It is clear that either enthalpy or nonrandom entropy changes or a combination of both could account for the deviations from the statistical equilibrium constant values. The question cannot be answered without a more detailed study of the temperature dependence of the equilibrium constants and the determination of more precise experimental values.

CONCLUSION

The $TiCl_4 \cdot 2THF$--$TiF_4 \cdot 2THF$ system has been investigated in THF solution by ^{19}F magnetic resonance spectroscopy. At room temperature no spectral detail was observed because of rapid donor molecule and halide exchange. The presence of the three mixed chloride fluoride complexes, as well as the tetrafluoride complex, was confirmed by the well-resolved spectrum at -60°C.

Approximate equilibrium constants were calculated for the formation of each mixed halide complex from its parent compounds. The difference in the free energy values calculated from the experimental equilibrium constants and the free energy values calculated from statistical equilibrium constants expected for random distribution were +220, +180, and -180 cal/mole for $TiF_3Cl \cdot 2THF$, $TiF_2Cl_2 \cdot 2THF$, and $TiFCl_3 \cdot 2THF$. This relatively small deviation from random order could be due to either nonrandom entropy effects or small changes in the enthalpy of reaction. The experimental results were not sufficient to determine the magnitude of possible enthalpy changes.

A detailed analysis has been made of the low temperature ^{19}F magnetic resonance spectra in an attempt to determine specifically what isomers were present. The following conclusions are based on spectra that were obtained at -60°C.

<u>$TiF_4 \cdot 2THF$</u>: The <u>cis</u> isomer strongly predominates with a <u>cis</u> to <u>trans</u> ratio of approximately 33 to 1. Two equal intensity triplets are observed for the <u>cis</u> isomer with $\delta_{F_\alpha F_\beta}$ = 60 ppm and $J_{F_\alpha F_\beta}$ = 37.7 Hz. The <u>trans</u> isomer gives a singlet approximately 12 ppm upfield from the high field triplet of the <u>cis</u> isomer.

<u>$TiF_3Cl \cdot 2THF$</u>: Only one isomer is observed for this compound. The ^{19}F NMR data strongly suggest that this isomer contains THF groups <u>cis</u> to each other and two fluorines <u>trans</u> to each other. This isomer gives rise to a low field triplet and a higher field doublet in 2 to 1 intensity ratio with $\delta_{F_\alpha F_\beta}$ = 67 ppm and $J_{F_\alpha F_\beta}$ = 33.1 Hz.

<u>$TiF_2Cl_2 \cdot 2THF$</u>: Two isomers are observed for this compound. The presence of an enantiomorph isomer with similar ligands <u>cis</u> to each other is conclusively established by virtue of its unique splitting pattern. Two equal intensity doublets are observed for this isomer with $\delta_{F_\beta F_\gamma}$ = 76 ppm and $J_{F_\beta F_\gamma}$ = 45 Hz. The second isomer, with an approximate ratio to the enantiomorph isomer of 5 to 1, appears as a singlet about 6 ppm downfield from the high field doublet of the enantiomorph isomer. The position of this peak suggests that it arises from an isomer with <u>cis</u> fluorine and either <u>cis</u> chlorine and <u>trans</u> THF or <u>cis</u> THF and <u>trans</u> chlorine. The former is somewhat more consistent with the observed data and is therefore slightly favored.

<u>$TiFCl_3 \cdot 2THF$</u>: A single ^{19}F resonance observed for this compound indicates the presence of only one isomer. Assignment of this resonance to a specific isomer is very tenuous. The most consistent data is obtained by ascribing this resonance to the isomer containing <u>trans</u> THF groups. A close second and third choice would be the isomer having <u>cis</u> THF and <u>trans</u> chlorine and the isomer having <u>cis</u> THF and <u>cis</u> chlorine.

SIGNIFICANCE

Prior to this investigation it was believed that donor molecule exchange alone was responsible for the observed temperature dependence of the ^{19}F NMR spectra for $TiF_4 \cdot 2L$ and similar complexes. Halogen exchange between octahedral complexes was unknown. This research has conclusively established that halogen exchange does take place in the $TiCl_4 \cdot 2THF$--$TiF_4 \cdot 2THF$ system and it strongly suggests that intermolecular fluoride exchange takes place in $TiF_4 \cdot 2L$ and similar complexes. A mechanism by which halogen exchange can occur has been suggested.

The accuracy of the equilibrium constants calculated for the $TiCl_4 \cdot 2THF$--$TiF_4 \cdot 2THF$ system is not precise but it is sufficient to indicate that formation of the mixed halide complexes does not deviate markedly from that expected for random ordering. This indicates that there is nothing unusual about the bonding or structure for the mixed halide complexes. The qualitative stability order has been found to increase with increasing fluorine as might be expected.

The ability to resolve the observed spectra into their components for each of the six species present indicates that the Ti--F system is ideal for ^{19}F NMR studies. A first order spectrum was observed for each isomer. This is attributed to a $3d^0$ configuration which permits strong $p\pi \longrightarrow d\pi$ interactions and causes significant differences in the paramagnetic shielding of fluorine atoms in different environments in the complex. The only titanium isotopes with nuclear spin are ^{47}Ti (7.4% abundance) with I = 5/2 and ^{49}Ti (5.5% abundance) with I = 7/2. The only observed coupling is therefore between fluorine atoms. The advantages of the Ti--F system over the Sn--F system are clearly evident. This research will undoubtedly stimulate other researchers to investigate titanium compounds and complexes by NMR techniques.

The greatest significance of this research rests in the ability to determine absolute stereochemical configurations for the octahedral complexes observed. This investigation carries with it theoretical implications that should be of interest to NMR spectroscopists, coordination chemists, and stereochemists. The present study does not provide all the answers, but it does provide a beginning and some interesting theories which can be built on, amplified, and modified during future studies. Confirmatory evidence is added to the theory first proposed by Ragsdale that groups bonded <u>trans</u> to fluorine in an octahedral complex control the tendency toward π bonding for fluorine and therefore strongly affect its shielding constant. The present study suggests that the magnitude of this π bonding is exhibited both by chemical shift and by coupling constant values. Future investigations may allow the NMR spectroscopist to predict accurately the positions of resonance peaks for octahedral complexes as well as the approximate magnitude of chemical shift and coupling constant values. The coordination chemist may then be able to determine quantitatively the π bonding strengths for a large number of ligands. Finally, the stereochemist--with knowledge of the configurations of many octahedral complexes--may be able to develop a theory to account for these observed configurations.

RECOMMENDATIONS FOR FUTURE WORK

1. More precise values of the equilibrium constants should be determined. This could be accomplished by first isolating $TiCl_4 \cdot 2THF$ and $TiF_4 \cdot 2THF$ and then combining these in the desired proportions. Alternatively, samples for NMR study could first be prepared by any convenient method and then analyzed for their chlorine to fluorine ratios.

2. Once high precision has been achieved in the calculation of equilibrium constants, a very careful temperature dependence study should be conducted to determine the magnitude of enthalpy changes.

3. The relative π bonding order of chlorine and tetrahydrofuran should be determined and the structural assignments for the titanium(IV) chloride fluorides should be confirmed. A study of the $TiBr_4$--TiF_4--THF system would result in the replacement of chlorine with a weaker π bonding atom, bromine. The effect of this on the ^{19}F resonance should be clearly evident and should support one of the π bonding orders. Examination of the $TiCl_4$--TiF_4 system in a bidentate solution should insure <u>cis</u> chelation and would eliminate from consideration a number of structures involving <u>trans</u> coordination, thereby simplifying the system. A number of other systems could be studied which should provide enough

information for conclusively establishing the structures of all the octahedral complexes observed. The $TiCl_6^{--}$--TiF_6^{--} system could be studied in concentrated hydrochloric acid. It should be possible to establish clearly the π bonding strength of chlorine and THF by comparing the spectrum of $TiF_4Cl_2^{--}$, $TiF_3Cl_3^{--}$, and $TiF_2Cl_4^{--}$ with those already obtained for $TiF_4 \cdot 2THF$, $TiF_3Cl \cdot 2THF$, and $TiF_2Cl_2 \cdot 2THF$. The addition of methanol to the $TiCl_4$--TiF_4--THF system should provide for the replacement of chlorine with methoxo- groups and thereby provide additional information.

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APPENDICES

APPENDIX I

Reaction of TiF_4, TiF_3Cl, and TiF_2Cl_2 with $(C_6H_5)_3SiOH$

A reaction was observed to take place between $(C_6H_5)_3SiOH$ and TiF_4, TiF_3Cl, or TiF_2Cl_2 in chloroform. Numerous solid samples were isolated from these reactions, but none in pure form. Most of the solids were insoluble in common solvents and ranged in color from pink to black. Some samples gave fairly simple X-ray diffraction patterns.

Filtration of the original reaction mixture usually gave clear yellow to orange filtrates. Addition of pentane or hexane to these solutions caused the formation of solids which could not then be redissolved. Evaporation of the yellow-orange solution produced a gummy orange material or yellow oil that could not be dried further. Addition of wet solvents to the yellow-orange solutions or exposure of these solutions to the atmosphere caused the formation of a white solid which was identified as tetrakis(triphenylsiloxy)titanium, $[(C_6H_5)_3SiO]_4Ti$, by its infrared spectrum. Infrared evidence indicated that some of the solid samples contained C_6H_5-Si, Si-O-Ti, and Ti-F bonds. The anticipated reaction products $(C_6H_5)_3SiOTiF_3$ and $[(C_6H_5)_3SiO]_2TiF_2$ were not isolated.

A reaction was also observed between titanium(IV) chloride fluorides and $(C_6H_5)_3SiOH$ in tetrahydrofuran.

Addition of $(C_6H_5)_3SiOH$ to yellow $TiCl_4$--TiF_4--THF solutions caused them to become colorless. Evaporation of these solutions gave only gummy materials and oils.

APPENDIX II

Automatically Controlled Constant Pressure Dry Box

A Kewaunee Scientific Company dry box was modified to maintain a constant internal pressure of nitrogen slightly above atmospheric pressure. This served several purposes:

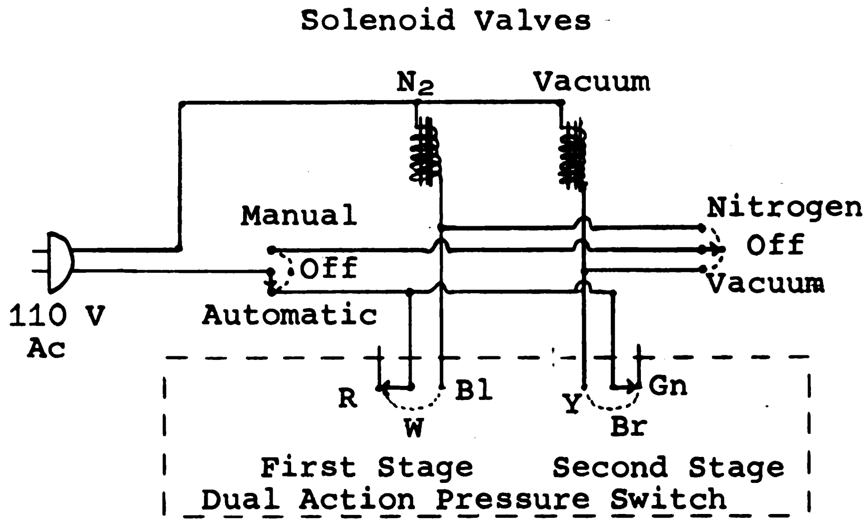
1. The effect of any leaks in the system would be minimized by an outward flow of nitrogen.

2. Inserting the gloves into the dry box and manipulations in the dry box were made very convenient since the proper working pressure was automatically maintained. Operations such as filtration under vacuum or under nitrogen pressure were easily accomplished.

3. Evacuating and filling the entrance port was greatly simplified. One valve connected the entrance port to the dry box while another connected the entrance port to a vacuum pump. When the entrance port had been evacuated, the connection to the vacuum pump was turned off and the valve leading to the dry box was opened. Since the pressure in the dry box was automatically maintained, the entrance port was automatically filled to the proper pressure.

This automatically controlled constant pressure modification was constructed from one dual action pressure (DAP) switch, two solenoid valves, and two single-pole double-throw (SPDT) center off switches. The system could be operated either automatically or manually. One SPDT switch selected either the automatic or manual mode and also functioned as the main power on--off switch. The second SPDT switch operated only in the manual mode and selected either nitrogen or vacuum. In the manual mode, the selection of nitrogen opened a solenoid valve which allowed nitrogen to enter the dry box, thereby increasing the pressure; the selection of vacuum opened a solenoid valve between the dry box and a vacuum pump, thereby reducing the pressure. In automatic mode the DAP switch automatically controlled operation of the solenoid valves to maintain the desired pressure. When pressure in the dry box was below or equal to atmospheric, the first stage of the DAP switch turned on the nitrogen solenoid valve. Introduction of nitrogen increased pressure in the dry box to a comfortable working pressure (P_1) slightly above atmospheric, at which time the first stage of the DAP switch turned the nitrogen solenoid valve off. At a slightly higher pressure (P_2) caused by insertion of the gloves into the dry box or by various manipulations within the dry box, the second stage of the DAP switch turned on the vacuum solenoid valve, thereby reducing pressure. When the pressure fell to a comfortable working level the second stage of the DAP switch shut off the vacuum solenoid.

A schematic diagram of the control circuit is presented on the following page along with a more detailed description of the DAP switch and solenoid valves.



The circuit diagram is represented in the automatic mode with the dry box at a convenient working pressure (P_1).

Dual Action Pressure Switch: Model D2H-H2, pressure range 0.018--1.7 psi, obtainable from Barksdale Valves, 5125 Alcoa Avenue, Los Angeles, California.

First Stage: Actuated at P_1

Red--Normally open White--Common Blue--Normally closed	At pressures below P_1, the red--white circuit is open and the blue--white circuit is closed. At pressures of P_1 and above, the red--white circuit is closed and the blue--white circuit is open.

Second Stage: Actuated at P_2

Yellow--Normally open Brown--Common Green--Normally closed	At pressures below P_2, the yellow--brown circuit is open and the green--brown circuit is closed. At pressures of P_2 and above, the yellow--brown circuit is closed and the green--brown circuit is open.

Both actuation points may be adjusted to give a suitable working pressure range.

Solenoid Valves: "Alco," Type S115, Maximum pressure 200 psi, obtainable from Alco Valve Co., St. Louis, Missouri.

The dry box was also fitted with a recirculating drying train which operated independently of the automatic constant pressure system. This recirculating system consisted of a Sprayit pressure-vacuum pump Model 906CA18 (available from Thomas Industries, Inc.; Sprayit Division; Sheboygan, Wisconsin) and several drying towers which contained Linde Type 4A molecular sieves. The recirculating line was designed so that a large volume cold trap could also be inserted into the line to remove vapors from the dry box when such solvents as tetrahydrofuran were being handled. An open dish of P_2O_5 in the dry box served as a desiccant and indicated when the molecular sieves needed regenerating. Prepurified nitrogen, which was passed through a cold trap containing molecular sieves and immersed in liquid nitrogen, acted as the nitrogen source for the dry box.

With fresh desiccant in the drying train it was possible to handle $TiCl_4$ for several hours without any observable fuming.