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Reaction of Titanium Tetrafluoride with DI-N-Propylamine in Acetonitrile

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REACTION OF TITANIUM TETRAFLUORIDE
WITH DI-N-PROPYLAMINE
IN ACETONITRILE

BY
ROGER NASS

HONORS PROGRAM
SAINT JOHN'S UNIVERSITY
COLLEGE OF ARTS AND SCIENCES
1967

ACKNOWLEDGEMENT

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CHAPTER I

INTRODUCTION

Reactions between Lewis acids and Lewis bases have been investigated extensively in recent years. Products of such reactions frequently are not those predicted by simple application of Lewis acid-base theory when the reactants are complex in nature. In particular, products and mechanisms of reactions of metal fluorides with secondary amines are often of uncertain or undetermined nature.

Reactions of titanium tetrafluoride with secondary amines have been investigated recently (1). Reaction products were separated and identified, and a general reaction mechanism was proposed. The presence of intermediate species in titanium-rich mixtures was demonstrated. This thesis deals with an extension of the original investigation, and is directed toward identification of intermediates in the reaction of titanium tetrafluoride with di-*n*-propylamine in acetonitrile solution. The choice of acetonitrile as a solvent was made for the following reasons: 1) titanium tetrafluoride is readily soluble in acetonitrile thus making it possible to study the reaction in concentrated solution; 2) solutions of titanium tetrafluoride in acetonitrile seem quite stable; 3) n.m.r. techniques have failed to identify intermediate species involved in the reaction of titanium tetrafluoride with secondary amines in acetonitrile (2).

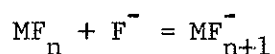
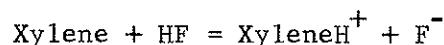
In order to accomplish the scientific goals of this project numerous experimental and theoretical difficulties were overcome. It was necessary to construct a controlled atmosphere apparatus as well as several other devices. Reagents and other chemicals had to be prepared and purified, which necessitated the acquiring of various specialized laboratory techniques. It was necessary to become acquainted with various theoretical concepts pertaining to the system being studied. Conductance measurements and I.R. spectra had to be obtained, and this experimental

data had to be converted into useful information. Hypothetical reaction schemes had to be compared with experimental observations in an effort to discover what was actually happening on a molecular level. Through the course of this work numerous related experiments have been thought out which would develop more insights into both the nature of this reaction system specifically and acid-base theory in general.

CHAPTER II
HISTORICAL

In contrast to the abundance of literature on the reactions of titanium tetrachloride, relatively little has been reported on the reaction of titanium tetrafluoride. The reactions of titanium tetrafluoride may be classified into two general categories: fluorinations and "Lewis Acid" reactions. Fluorinations reported generally involve either direct reaction of metals with titanium tetrafluoride or halogen exchange (3-5).

McCaulay, Higley, and Lien measured acid strengths of metal fluorides by their relative abilities to extract *m*- and *p*-xylenes from *n*-heptane into liquid hydrogen fluoride (6). The following equilibria are involved:



Titanium tetrafluoride was found to be a strong acid, while silicon tetrafluoride was found to be a weak acid. Since two moles of titanium tetrafluoride were required to extract one mole of xylene, it was concluded that the anion involved was Ti_2F_9^- .

Molecular addition compounds of titanium tetrafluoride were first reported in 1903 (2). All early work is of doubtful significance (4). More recently, products of reactions of titanium and zirconium tetrahalides with several bases have been reported (4). Titanium tetrafluoride reacts with pyridine to form a 1:2 adduct. Titanium tetrafluoride forms 1:1 compounds with acetonitrile, propionitrile, benzonitrile, methylamine, ethylamine, aniline, acetaldehyde, benzaldehyde, 3-pentanone, nitromethane, and nitrobenzene. Dissociation pressures of the pyridine, acetonitrile, and benzonitrile compounds were measured over the temperature range 80-130°. The titanium compounds studied were more stable than the corresponding zirconium compounds, but fluoride adducts were less stable than the corresponding chloride,

bromide and iodine adducts.

Pyridine forms a solid 1:1 complex with titanium tetrafluoride in dimethoxyethane. When excess pyridine is present, products of intermediate stoichiometry (approximately 1.6:1) can be isolated (7). Since $TiF_4 \cdot 2Py$ has a dissociation pressure of 3 mm. at 60° (4), this report seems reasonable.

Titanium tetrafluoride forms 1:2 complexes with acetonitrile, dimethylsulfoxide, acetone, acetic acid, alcohols, tetrahydrofuran, tetramethylurea, acetoxime, dimethylacetamide and dimethylformamide. Titanium tetrafluoride forms 1:1 complexes with acetonitrile, trimethylamine, 2,4-dimethylpyridine, dimethylaniline, tetramethylethylenediamine, tetra-(dimethylamino)-ethylene, $C_2H_5N(CH_2CH_2)_2O$, 8-hydroxyquinoline, dioxane, dimethoxyethane, nitromethane, and nitrobenzene (7).

Ethers and thioethers generally give tarry products when reacted with titanium tetrafluoride. Ammonia and protonic amines give fluorotitanates when reacting with ethereal solutions of titanium tetrafluoride. The author reports that ethers may play a role in the dehydrofluorination (7).

The 1:1 complex with acetonitrile is believed to be a dimer. However, the relatively intractable solid insoluble 1:1 complexes with tertiary amines are probably polymeric. Steric repulsions between these large ligands and fluoride ions probably render 1:2 complexes less stable than condensed 1:1 complexes in which octahedral coordination is preserved by fluorine bridging (7). (Amine bridging seems unlikely because of steric repulsions. Self-association of molecular titanium tetrafluoride is well known.)

Low temperature F^{19} magnetic resonance spectra of solutions of various 1:2 titanium complexes in ether or in excess base give fairly conclusive evidence for octahedral symmetry and for a preferred stereochemistry. The presence of two triplets of equal intensity indicate that base molecules occupy positions cis to each other (7,8).

Infrared spectra of the 1:2 complex with pyridine and of the 1:1 complexes with acetonitrile, propionitrile, and benzonitrile

in the 400-800 cm^{-1} region have been determined. The appearance of several bands (rather than one or two bands) in this region of the spectrum of $\text{TiF}_4 \cdot 2\text{Py}$ indicates that this compound has the cis structure (9).

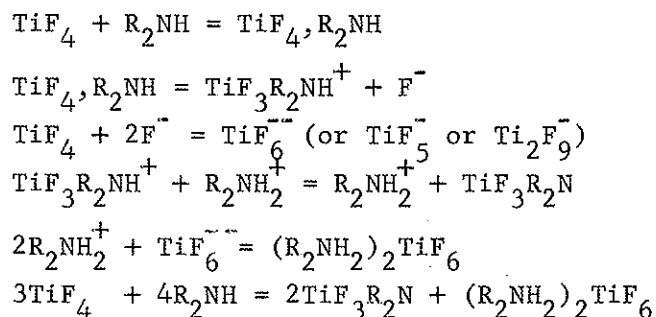
Conclusive evidence for oxygen coordination in certain amide complexes is obtained from infrared spectra. Carbonyl bands in these complexes are 50-80 cm^{-1} lower than in the free amides (7).

Chandler recently investigated reactions of titanium tetrafluoride with several secondary and tertiary amines (1). On adding a secondary amine to a chloroform or acetone solution of titanium tetrafluoride, the corresponding ammonium hexafluorotitanate and amidotrifluoride are formed. Infrared spectra and x-ray diffraction patterns of several ammonium hexafluorotitanates have been reported (10). The reaction of titanium tetrafluoride with any of these amines in the absence of solvent led to considerable reduction of the titanium to a titanium (III) species (1). This reduction occurred even when the reaction was carried out at -78° .

Products of reactions of titanium tetrafluoride solutions with pyridine were similar to those isolated by earlier investigators. The reaction between titanium tetrafluoride and triethylamine in acetone solution gave amorphous solid mixtures.

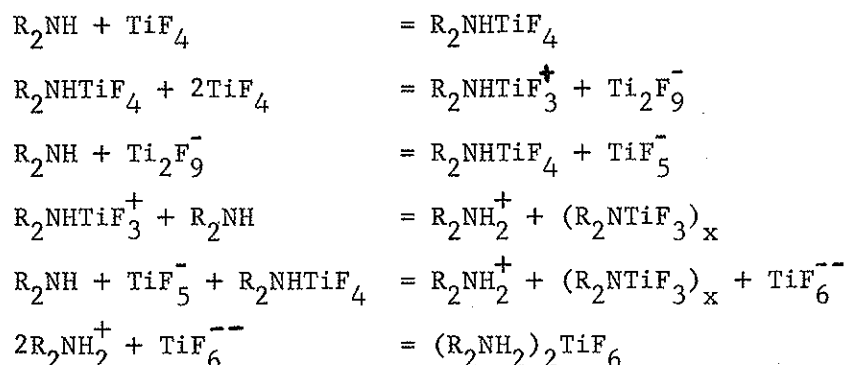
Conductometric titrations of acetone solutions of titanium tetrafluoride with amines showed that conducting intermediate species were formed.

The general reaction scheme proposed by Chandler for reaction of titanium tetrafluoride solutions with di-n-propylamine, diisopropylamine and diethylamine is:



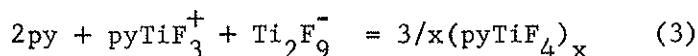
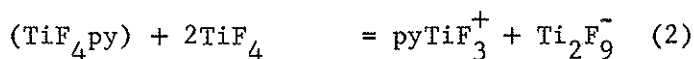
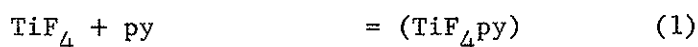
The reaction of titanium tetrafluoride with di-n-propylamine in acetone solution produces di-n-propylammonium hexa-

fluorotitanate and polymeric di-n-propylamidotrifluorotitanium (11). Di-n-propylammonium and hexafluorotitanate ions are not present at low amine:titanium tetrafluoride mole ratios. A conductometric study of the interaction of titanium tetrafluoride and di-n-propylammonium hexafluorotitanate in acetone solution was carried out by the method of continuous variation. Results of this study indicate that anionic species with stoichiometries corresponding to the formulas $Ti_2F_9^-$ and TiF_5^- are relatively stable. The following sequence of reaction correlates conductances observed in the conductometric titrations with those observed in the continuous variation plot and also accounts for the stoichiometries at which both the onset and completion of precipitation occur, as well as the absence of di-n-propylammonium and hexafluorotitanate ions at low amine:titanium tetrafluoride mole ratios:



The conductometric titration curves for the reactions of titanium tetrafluoride with diethylamine and diisopropylamine are similar to the reported curves for di-n-propylamine (12).

The proposed mechanism for the reaction in excess titanium tetrafluoride would predict a conductance increase with a tertiary amine base, whereas those mechanisms based upon proton removal would not. The results obtained in the titration of acetone solutions of titanium tetrafluoride with pyridine demonstrate the predicted conductance increase (Fig. 1) which lends further support to the proposed mechanism. The pyridine curve can be explained by the sequence (py = pyridine)



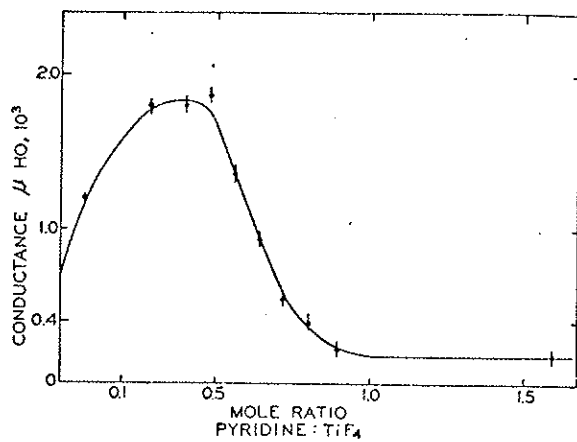


Fig. 1.—Conductometric titration curve for the titration of TiF_4 by pyridine in acetone ($0.18 M \text{TiF}_4$ solution).

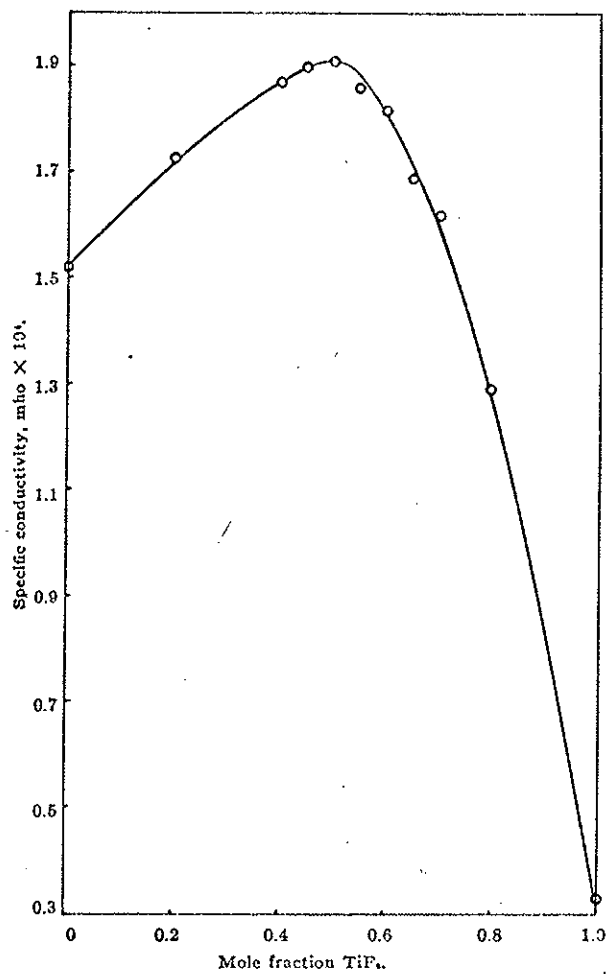


Fig. 2.—A continuous variation study for the system TiF_4 - $[(n\text{-C}_5\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{-2}$ in ethanol (sum of TiF_4 + TiF_6^{-2} = $0.02 M$).

Steps 1 and 2 occur concurrently upon pyridine addition. The high conductance obtained at a Ti/N ratio of 0.3 supports the formulation of $Ti_2F_9^-$. Heavy precipitation begins at a Ti/N ratio of 0.25 and continues throughout the reaction. This precipitation indicates that step 3 is initiated before steps 1 and 2 are completed. (A mole ratio of 0.33 is required for completion of steps 1 and 2.) Concurrent occurrence of steps 1, 2, and 3 results in a flat maximum and a slightly lower conductance than that expected for complete conversion to $Ti_2F_9^-$ at a mole ratio of 0.33.

In order to establish the nature of the species formed in the reaction between titanium tetrafluoride and di-n-propylammonium hexafluorotitanate, a continuous variation study was carried out in absolute ethanol (2). The maximum obtained (Fig. 2) corresponds to the empirical formula TiF_5^- . A n.m.r. study confirmed the presence of an octahedral (six-coordinate) TiF_5^- species and indicated that a molecule of solvent occupied the sixth position. For all molar ratios studied, titanium tetrafluoride and hexafluorotitanate were observed in the n.m.r. spectra as well as the new pentafluorotitanium complex. Pentafluorotitanium complexes undoubtedly can be formed with other Lewis bases but low solubility or side reaction may limit such studies. Efforts to use acetone, acetonitrile, and nitromethane as solvents did not give satisfactory results. (Results obtained were not published.)

The titanium compounds $Ti(NR_2)_4$, where R is methyl, ethyl, n-propyl or butyl, were prepared either by treating the metal chloride with the appropriate lithium dialkylamide or by aminolysis involving a tetrakisdialkylaminotitanium compound and another dialkylamine (13).

CHAPTER III
EXPERIMENTAL APPARATUS AND TECHNIQUES

A. Special Apparatus.

1. Reaction Vessel.

The reaction vessel was a 100 ml. three-necked flask. One neck was used for a gas inlet, another was fitted with a burette or pipette adapter to permit liquid additions and the third held a conductivity cell.

The reactions were carried out in a nitrogen atmosphere. Reactions involving amine addition were carried out using a burette or a 1 ml. pipette fitted with a Propipette addition control.

2. Preparation of Standard Solutions.

A standard solution of di-n-propylamine was not prepared. Molarity of the pure liquid was calculated using its molecular weight and density, and measured amounts of the pure liquid were used.

Solutions of titanium tetrafluoride in acetonitrile and nitromethane were prepared immediately before use. These solutions seemed quite stable for short periods of time. Several hours delay between preparation and use did not result in gross abnormalities in conductivity. Titanium tetrafluoride dissolved readily and completely in acetonitrile. Nitromethane solutions of titanium tetrafluoride were filtered through glass filter disks in a dry atmosphere to remove insoluble matter (about 5 per cent of the original weight).

3. Dry Box.

A dry atmosphere was needed for preparation of titanium tetrafluoride samples and solutions. For ease in carrying out these operations a controlled atmosphere enclosure ("dry box") was constructed (Fig. 3).

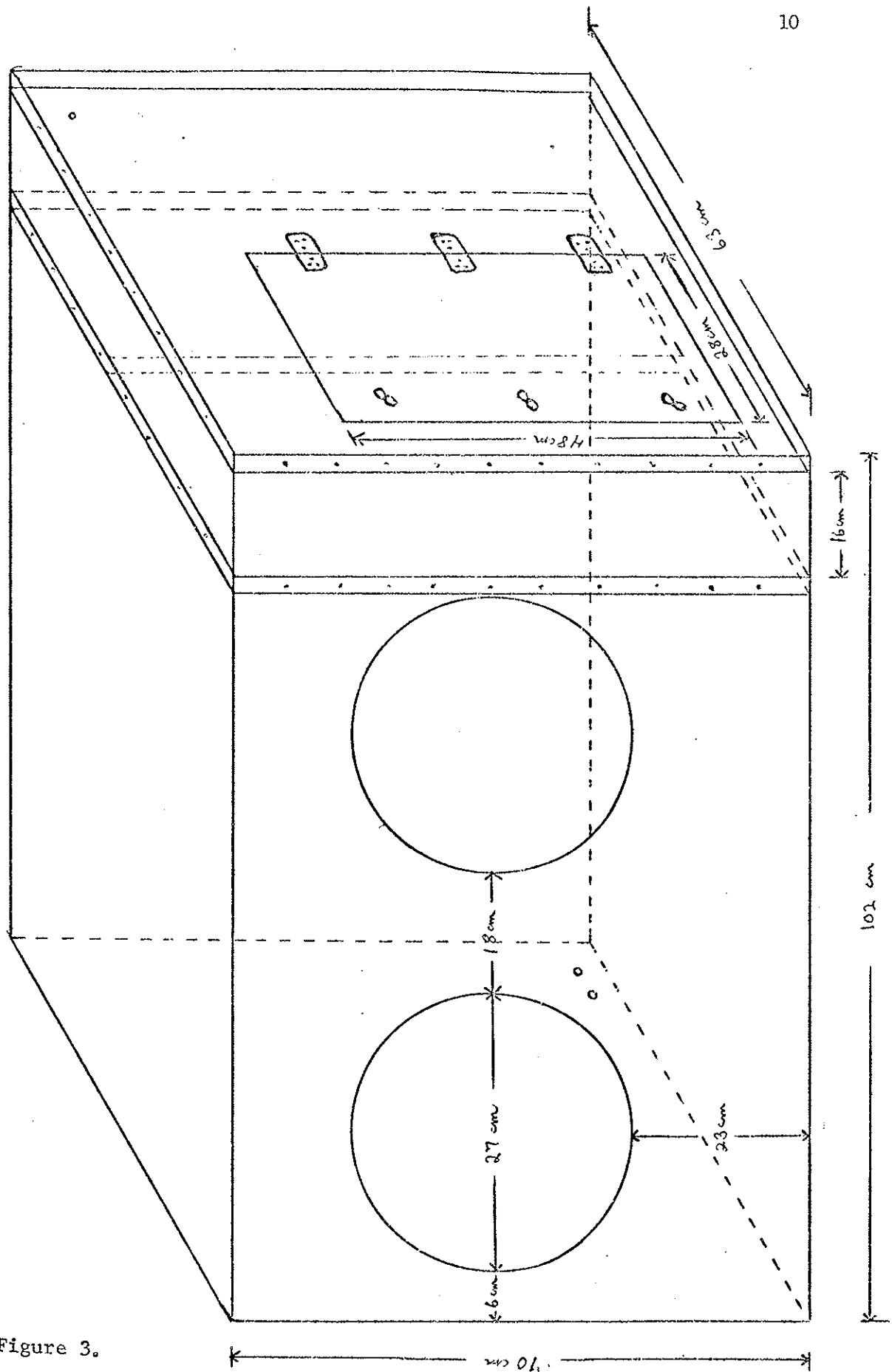


Figure 3.

The "dry box" constructed consists of two chambers, the main working chamber and the air-lock. These chambers are separated by a sliding window which is loose enough to permit desired air flow into the air-lock. Entry into the air-lock is made through a hinged door which is held shut by three wing-nuts. This end is made of wood while the other sides of the enclosure are constructed of plexiglass. The plexiglass provides maximum visibility and adequate strength. The edges of the dry box were fastened by drilling pilot holes and then tapping these holes for standard machine screws. Working access in the main chamber is through two circular ports fitted with large metal rings upon which surgical rubber gloves are attached. All joints in the box were sealed with Silastic.

Compressed air is passed through a column of Drierite 250 cm. long and 8 cm. in diameter. The dried air passes through a small inlet port in the base of the main chamber. This air then circulates through the chamber and eventually passes through the air-lock and out a specially provided exit tube. Air is continually added to maintain a slight positive pressure, minimizing moist air diffusion into the box. There is another inlet at the base of the main chamber which can be used for vacuum filtrations within the main chamber. This air inlet is easily adaptable to permit introduction of nitrogen or other gases.

B. Infrared Absorption Spectra.

A Perkin-Elmer Model 137 instrument fitted with sodium chloride optics was used to obtain absorption spectra.

C. Conductance Measurements.

All conductance measurements were made at a frequency of 1000 cycles per second. The conductance bridge used was conventional in design (Fig. 4).

The conductance cell consisted of two platinum plates 0.5 X 0.5 cm. separated a distance of 0.5 cm. These plates were spot-welded to platinum wires. The wires were sealed in glass tubes which were fused together. These tubes were then attached to a 19/22 ground glass joint and inserted in one of

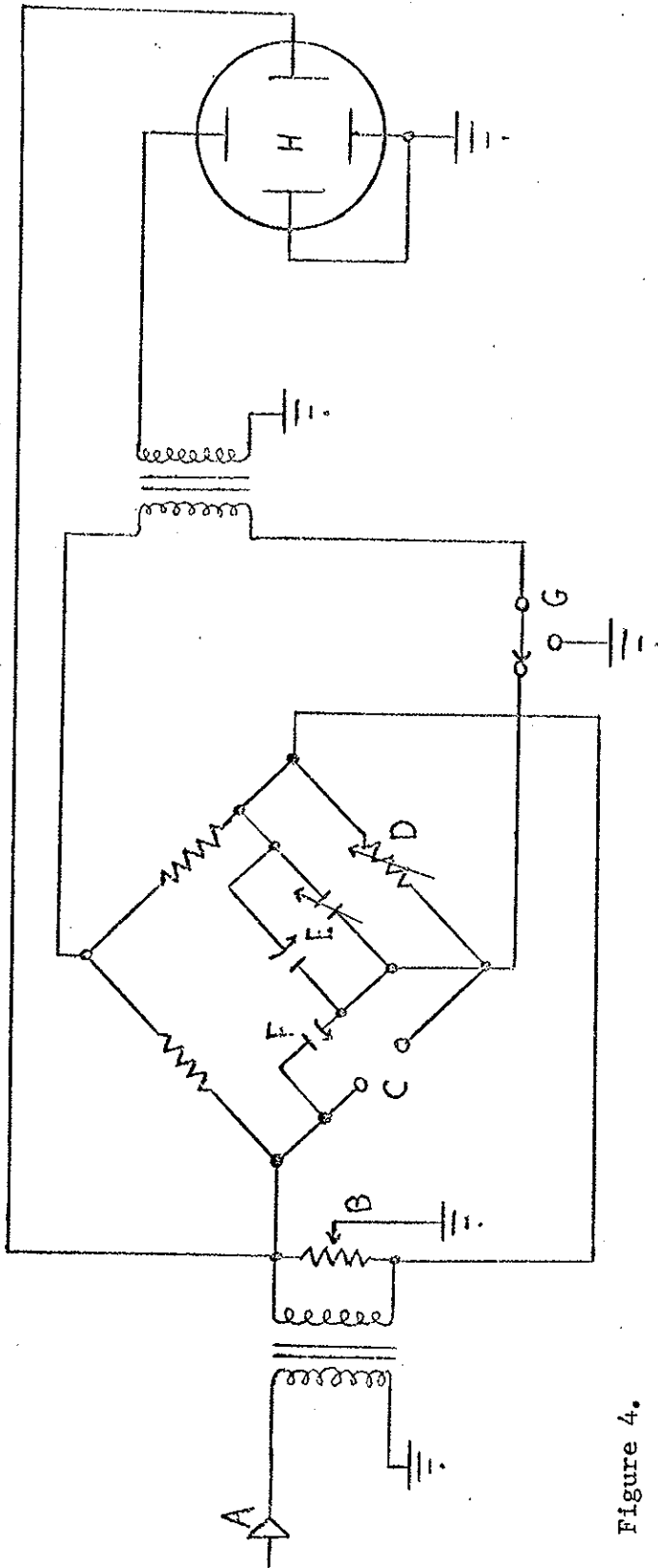


Figure 4.

A. Audio oscillator, type 1311-A, General Radio Company.

B. Wagner ground, ten turn one thousand ohm potentiometer.

C. Conductivity cell.

D. Six decade resistor, type 1432-X, General Radio Company.

E. Variable capacitance, 100 micro microfarad.

F. Variable capacitance, 100 picofarad.

G. Wagner ground selector.

H. Heathkit oscilloscope, model 10.

three necks on the reaction vessel. A variation used for solutions of high conductance involved inserting separate electrodes through different necks (providing a spacing of 3 cm.)

The conductance measurements were carried out in a constant temperature oil bath apparatus which was maintained at $25.0 \pm 0.1^\circ \text{C}$.

Capacitance effects were balanced across the cell and across a six decade variable resistance by 100 picofarad and 100 microfarad capacitors respectively. At very low resistance a Heathkit three decade variable capacitance (0.111 microfarad maximum) and up to 0.26 microfarad of fixed capacitance were attached in parallel with the six decade variable resistance. This enabled the balancing of capacitance effects down to approximately two hundred ohms. Resistance measurements of lower values than this had an unknown error but relative changes in resistance could still be easily observed.

D. Purification of Materials.

1. Solvents.

High quality acetonitrile (Eastman Organic Chemicals or Matheson, Coleman and Bell) was refluxed over anhydrous calcium sulfate or barium oxide and distilled to remove traces of water.

Nitromethane (Commercial Solvents Corp.) was refluxed over anhydrous calcium sulfate for several hours and then fractionally distilled through a column packed with glass beads. The product was redistilled before use from anhydrous calcium sulfate.

2. Amines.

Di-n-propylamine (Eastman Kodak Co. White Label) was refluxed over anhydrous calcium sulfate for six hours and fractionally distilled. The product was redistilled from anhydrous calcium sulfate before use.

3. Titanium Tetrafluoride.

Titanium tetrafluoride (purity 97 per cent) was used as supplied by Alfa Inorganics, Inc. Titanium tetrafluoride cannot be purified because of its polymeric and intractable nature. Samples

were completely soluble in acetonitrile. At most about 5 per cent of any sample was insoluble in nitromethane. All insoluble material was removed by filtration in the dry box.

4. Other Material.

Di-n-propylammonium perchlorate was prepared by mixing 70 per cent perchloric acid and a slight excess of chilled di-n-propylamine. The precipitate was vacuum dried at a moderate temperature to give crystals decomposing over 225° C.

Di-n-propylammonium hexafluorotitanate was prepared by mixing 52 per cent hydrofluoric acid with a slight excess of chilled di-n-propylamine and then adding a sufficient quantity of an acetone solution of titanium tetrafluoride. The oil which resulted crystallized when a small amount of pentane was added. The mixture was filtered and the residue was washed with acetone, dried at 120° C., washed again with acetone and dried at 120° C. The crystals obtained melted at 192-5° C.

CHAPTER IV

RESULTS

A. Conductometric Titrations in Acetone.

Preliminary reactions of di-n-propylamine with titanium tetrafluoride were carried out in acetone in an attempt to reproduce literature values (11). These experiments showed that a Serfass conductivity bridge was inadequate. Large capacitance effects were encountered which obscured the balance point of the Serfass bridge. Therefore the conductivity apparatus described earlier, which incorporates a variable capacitance device to compensate for the capacitance effects, was adopted. Conductivities of these solutions were found to vary significantly with temperature change. This necessitated the use of a constant temperature oil bath, which was maintained at 25° C. All conductivities were measured with the conductivity cell immersed in the bath.

B. Conductometric Titrations in Nitromethane.

Nitromethane was chosen as the next reaction solvent. Nitromethane has a bulk dielectric constant somewhat higher than that of acetone (Table I).

Table I

Dielectric Constants

| Substance | ϵ | t° C |
|--------------|------------|------|
| acetonitrile | 37.5 | 20 |
| nitromethane | 37.4 | 20 |
| ethanol | 24.3 | 25 |
| acetone | 20.7 | 25 |
| benzene | 2.28 | 20 |

The experimentally obtained conductivity curves for nitromethane (Fig. 5) were somewhat like those for acetone. The conductivity maximum occurred in the same vicinity, but it was not as

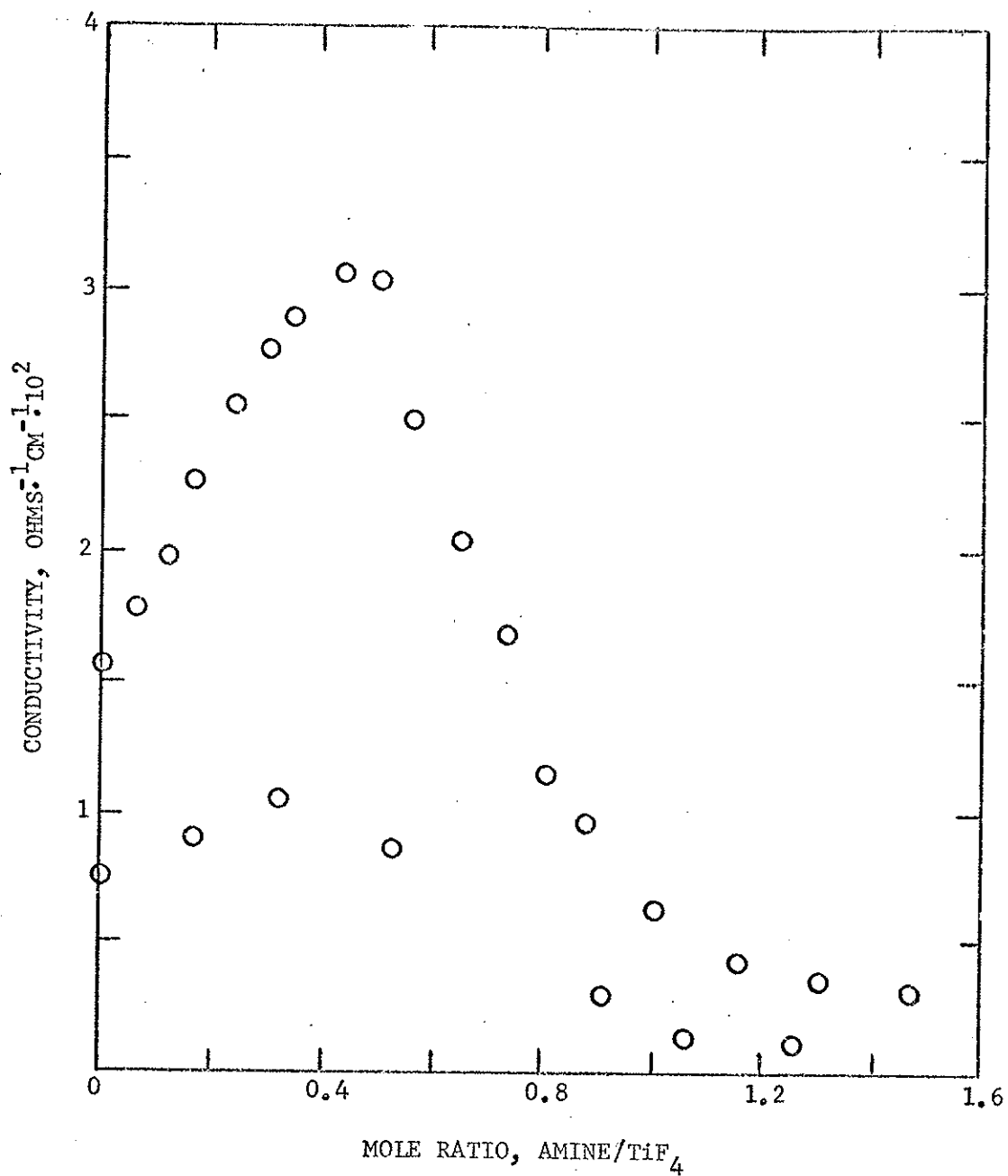


Figure 5. Conductometric Titration of a 0.07 M and 0.25 M Titanium Tetrafluoride Solution in Nitromethane with Di-n-propylamine.

pronounced. The conductivity values were an order of magnitude greater. No precipitation occurred during the reaction. Approximately 5 per cent of titanium tetrafluoride samples were insoluble in nitromethane. This insoluble matter was removed by filtration as discussed earlier.

To determine the significance of conductivity data it was necessary to determine experimentally the conductivities of nitromethane solutions of various salts of known concentration. Figure 6 shows the conductivities of solutions of $(n\text{-C}_3\text{H}_7)_2\text{NH}_2^+\text{ClO}_4^-$ and $[(n\text{-C}_3\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{--}$ in nitromethane. The results indicate that ion pairing occurs quite readily with the TiF_6^{--} ion. The low conductivity of this species could explain the large decrease in conductivity in the later stages of the reaction.

C. A Continuous Variation Study in Nitromethane.

In order to establish the nature of the anion present, a continuous variation study (14) was carried out on the binary system $\text{TiF}_4 - [(n\text{-C}_3\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{--}$ in the solvent nitromethane. The study was carried out at a total concentration of 0.20 M (TiF_4 plus $[(n\text{-C}_3\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{--}$). The conductivity of the freshly prepared 0.20 M titanium tetrafluoride solution increased at a rate of approximately eight ohms per minute for nearly thirty minutes after preparation. This increase in conductivity was accompanied by a decrease in the amount of capacitance needed to balance the bridge. This behavior suggests that a less polarizable species is being produced as disproportionation of TiF_4 occurs. The conductometric curve (Fig. 7) shows a conductivity maximum at approximately a 4.5 F/Ti ratio. This maximum corresponds to the empirical formula Ti_2F_9^- . This stoichiometry is in agreement with the species found for solutions of titanium tetrafluoride in liquid HF (5). Because of limitations inherent in a continuous variation study (15), the existence of other species of the general formula $[(\text{TiF}_4)_x\text{F}^-]_n$ cannot be ruled out by this study. No insoluble product at any mole ratio was encountered in the study.

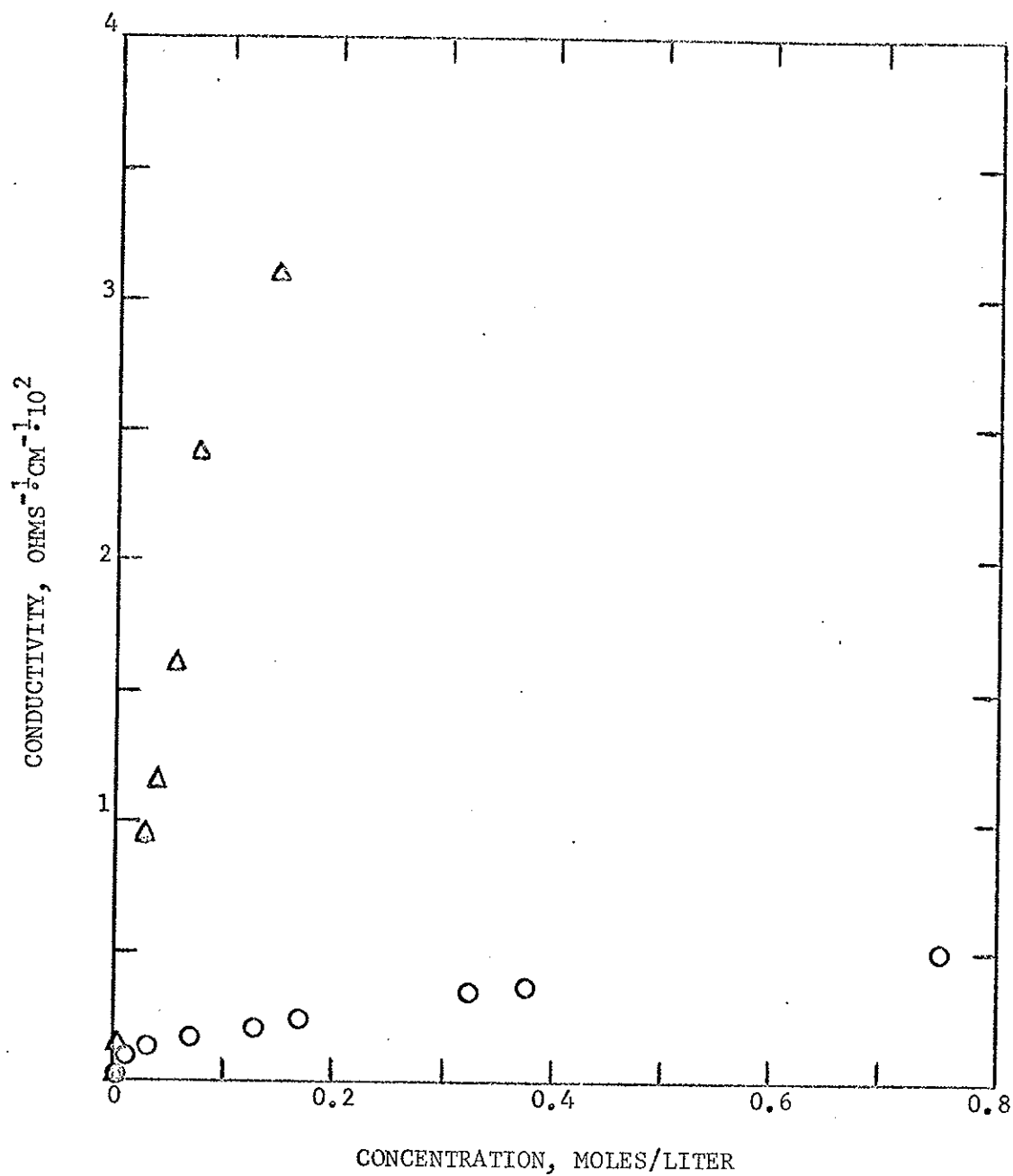


Figure 6. Conductivity of Di-n-propylammonium hexafluoro-titanate (o) and Di-n-propylammonium perchlorate (Δ) in Nitromethane.

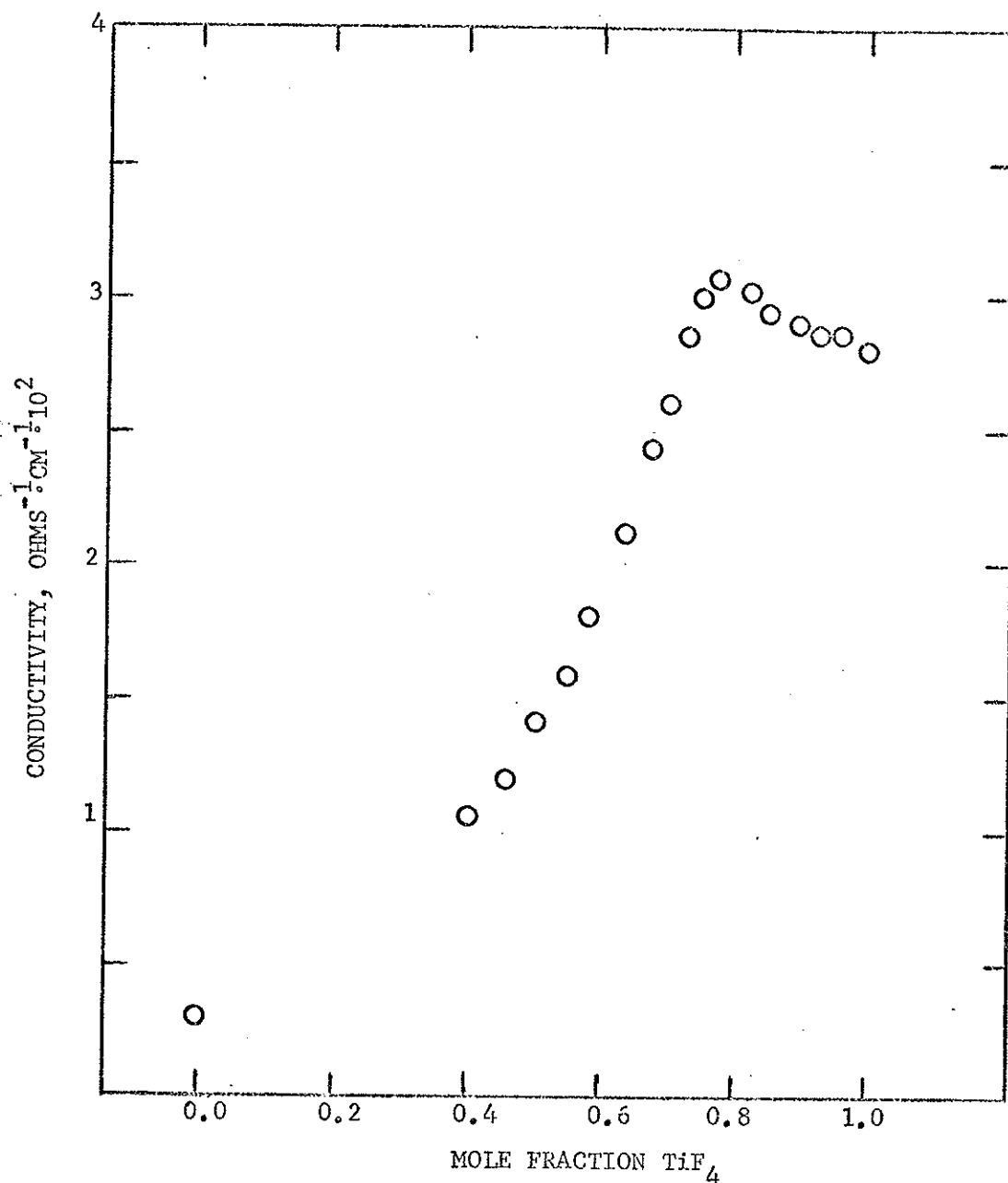


Figure 7. A Conductometric Study of the interaction of a 0.20 M TiF_4 Solution with a 0.20 M $(\text{Pr}_2\text{NH}_2)_2\text{TiF}_6$ Solution in Nitromethane.

D. Conductometric Titrations in Acetonitrile.

Conductometric titrations were next carried out in acetonitrile. Acetonitrile has approximately the same bulk dielectric constant as nitromethane, hence specific solvation effects could be compared.

Conductometric titration of 0.11 M, 0.22 M, 0.26 M, 0.30 M and 0.66 M solutions of TiF_4 with di-n-propylamine were carried out in the solvent acetonitrile. The curves obtained in dilute and moderately concentrated solutions (up to 0.25 M TiF_4) were similar in shape (Fig. 8). At concentrations greater than 0.25 M TiF_4 there was evidence of a slow reaction up to mole ratio 0.40 which tended to lower conductivity values. This phenomenon produced a relative minimum at a mole ratio of approximately 0.30 if the reaction was carried out rapidly. The following portions of the conductivity curve were similar in shape at all TiF_4 concentrations. A rapid increase in conductivity occurs upon addition of amine to titanium tetrafluoride solution until an amine: TiF_4 ratio of 0.4 is obtained. All ratios are amine: TiF_4 mole ratios unless otherwise stated. The curve flattens and a rapid decrease in conductance is observed in the region of ratios of 0.5 to 1.0. In the region 1.0 to 1.5 the conductivity decreases less rapidly. No precipitate is formed during the course of the reaction.

To determine the significance of conductivity data it was necessary to determine experimentally the conductivities of acetonitrile solutions of various salts of known concentrations. Figure 9 shows the conductivities of solutions of $(\text{n-C}_3\text{H}_7)_2\text{NH}_2^+\text{ClO}_4^-$ and $[(\text{n-C}_3\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{--}$ in acetonitrile. The conductivities of these species were comparable to those obtained in nitromethane, although somewhat higher. These results indicate that ion pairing occurs quite readily with the TiF_6^{--} ion in acetonitrile. The low conductivity of TiF_6^{--} could explain the large decrease in conductivity in the later stages of the reaction.

E. A Continuous Variation Study in Acetonitrile.

In order to establish the nature of the anion present, a continuous variation study (14) was carried out on the binary

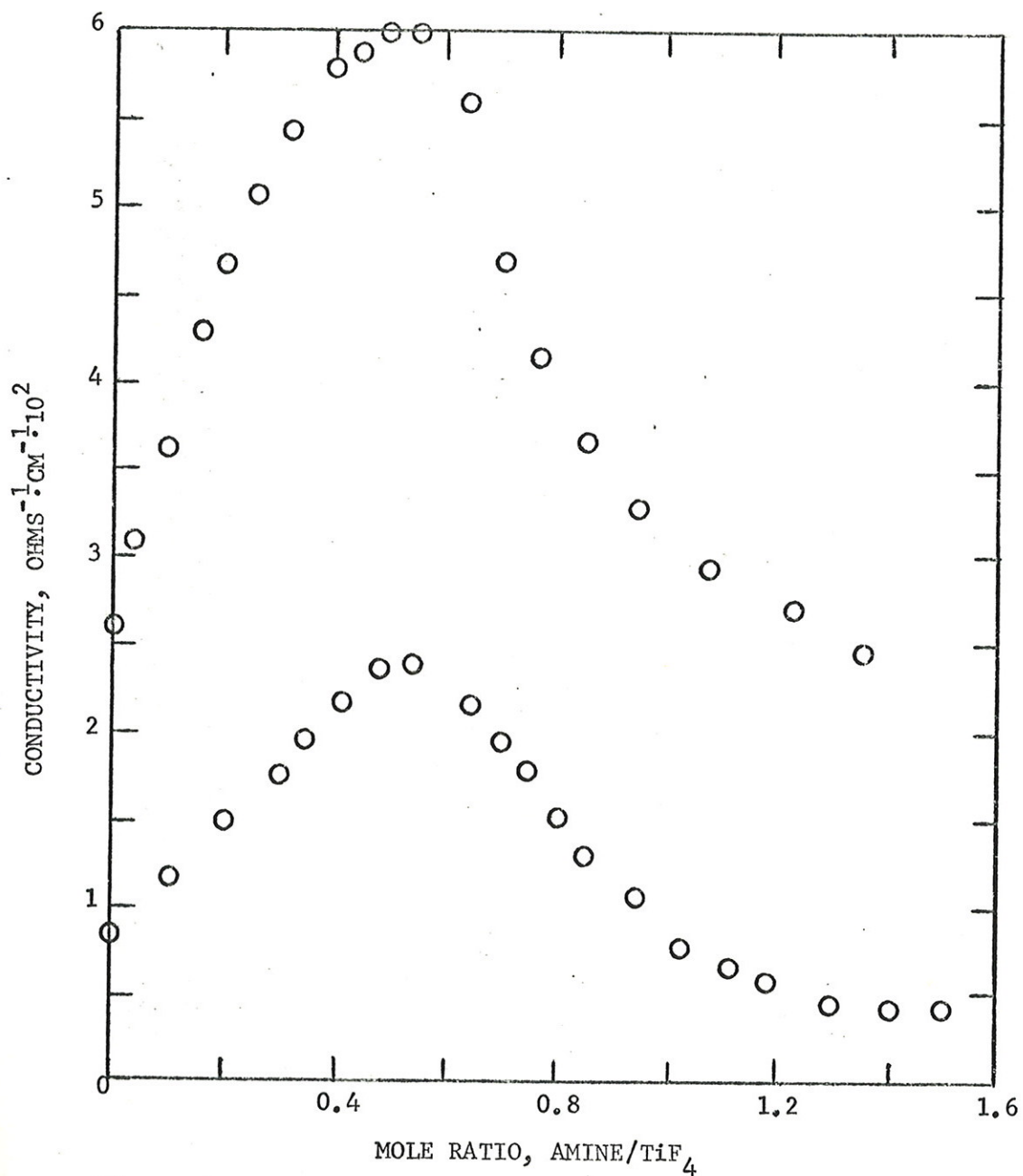


Figure 8. Conductometric Titrations of 0.11 and 0.66 M Titanium Tetrafluoride Solutions in Acetonitrile with Di-n-propylamine.

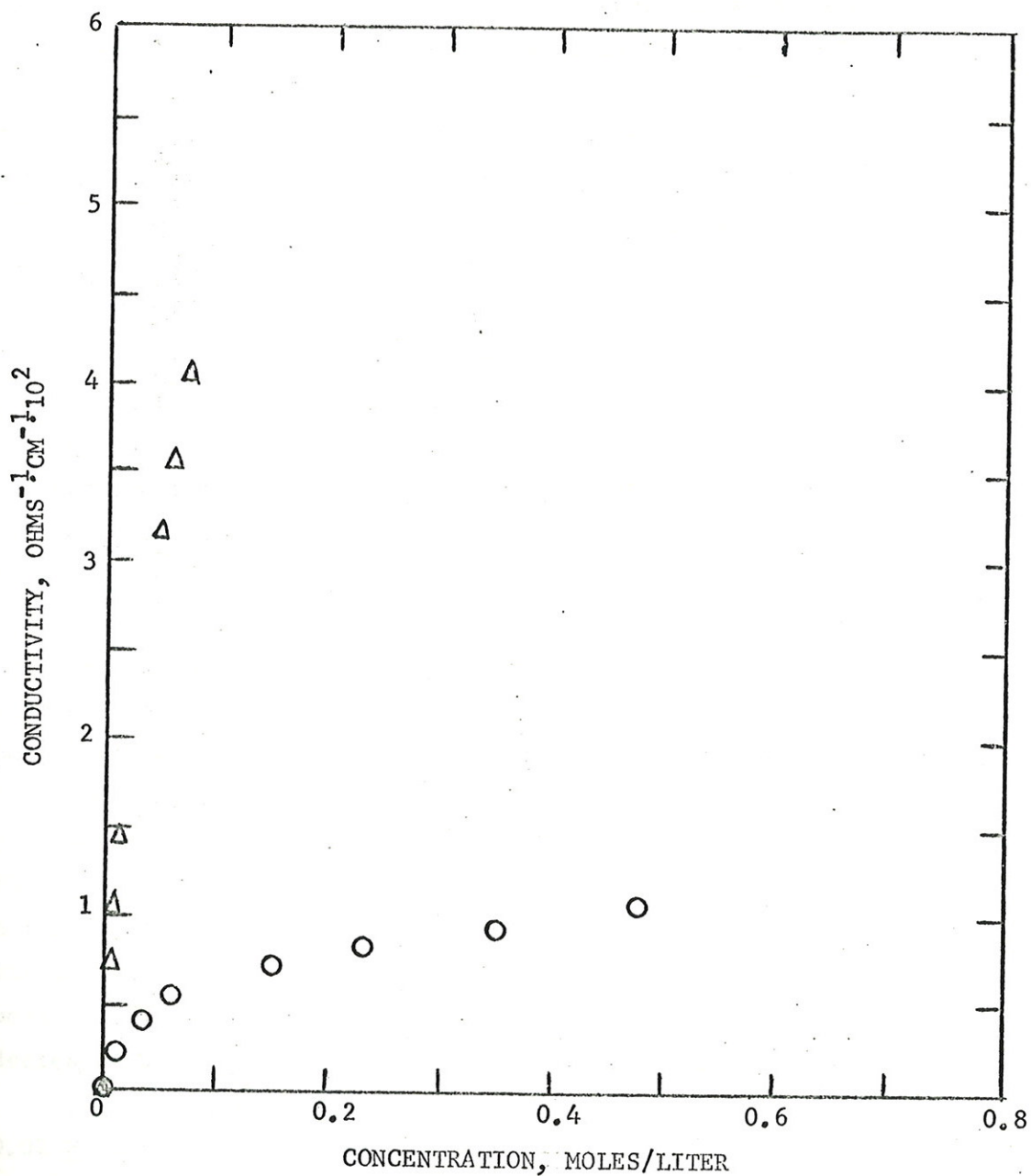


Figure 9. Conductivities of Di-n-propylammonium hexafluorotitanate (o) and Di-n-propylammonium perchlorate (Δ) in Acetonitrile.

system $\text{TiF}_4 - [(\underline{n}\text{-C}_3\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{--}$. The results, as illustrated in Figure 10, show that the same general curve is obtained at both concentrations. The ratio at which maximum conductivity occurs corresponds to a 4.5 F/Ti ratio in both instances. This maximum corresponds to the empirical formula Ti_2F_9^- . This stoichiometry is in agreement with the species found for solutions of TiF_4 in liquid HF (5). Because of limitations inherent in a continuous variation study (15), the existence of other species of the general formula $[(\text{TiF}_4)_x\text{F}^-]_n$ cannot be ruled out by this study. No insoluble product at any mole ratio was encountered in the study.

F. Conductometric Titrations in 25% Acetonitrile and 75% Benzene.

A conductometric titration of a 0.22 M solution of titanium tetrafluoride with di-n-propylamine was carried out in the mixed solvent system 25 per cent acetonitrile - 75 per cent benzene. Benzene was used because of its low bulk dielectric constant (Table I) and its miscibility with acetonitrile. Because the bulk dielectric constant of the mixed solvent is relatively low, ionic material produced in the reaction would be likely to precipitate. The reaction curve can be summarized briefly. There was a rapid conductivity increase up to mole ratio 0.2. A flat conductivity maximum was found in the region between mole ratios 0.2 and 0.5. The conductivity decreased rapidly from mole ratios 0.5 to 1.0. Beyond the mole ratio 1.2 the conductivity decreased slowly. No precipitate formed throughout the reaction.

$[(\underline{n}\text{-C}_3\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{--}$ was found to be less soluble than 0.02 M in the mixed solvent system.

Pure benzene could not be employed as a reaction solvent because titanium tetrafluoride is not soluble in benzene.

G. Preparative Reactions.

A 2.65 M solution of titanium tetrafluoride in acetonitrile was prepared. After a few minutes a presumed addition complex precipitated which would not redissolve with heating. Cold di-n-propylamine was added slowly with stirring to the mixture. The liquid turned dark brown and the precipitate went into solution. Di-n-propylamine was added until an amine: TiF_4 ratio

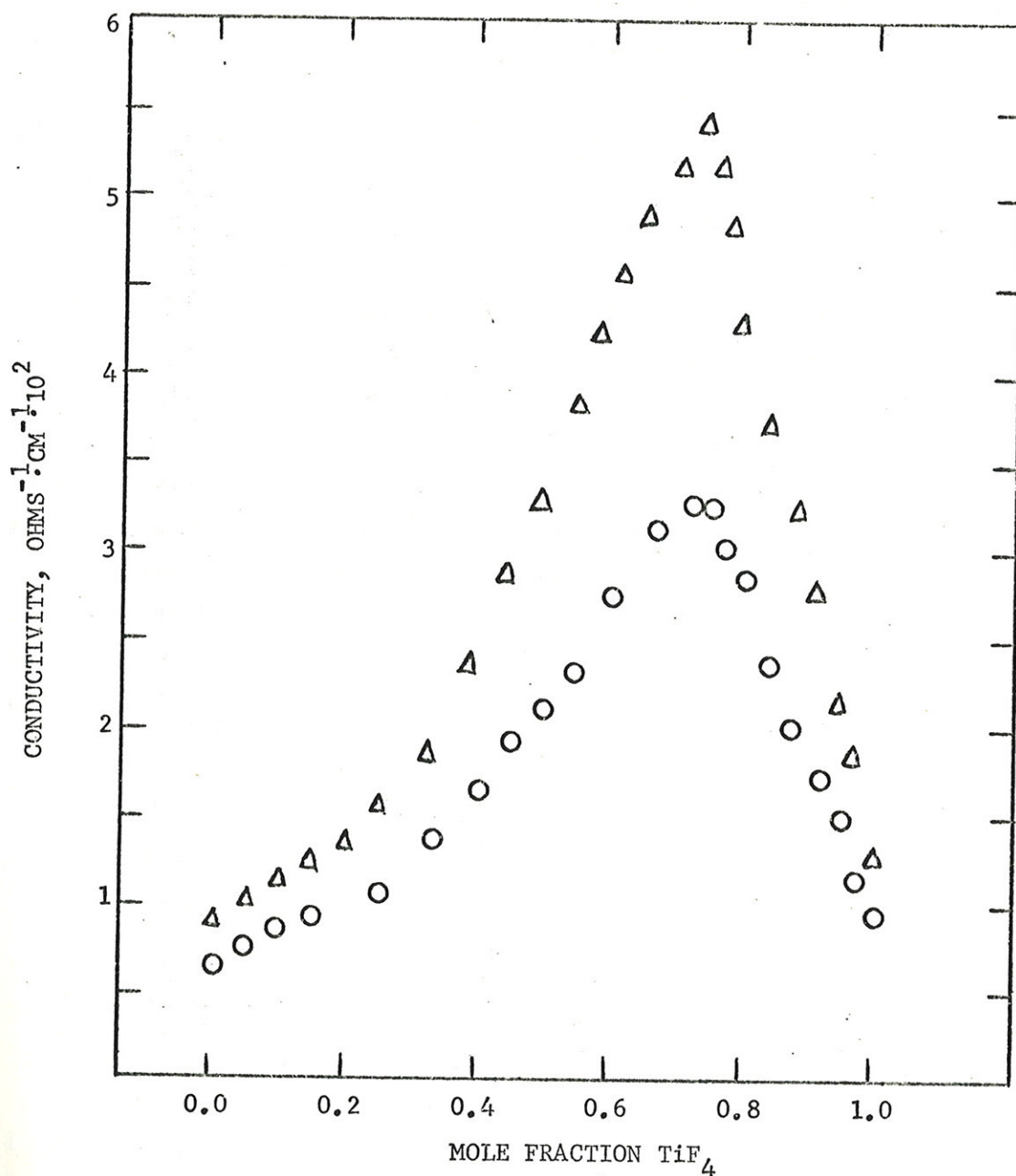


Figure 10. A Conductometric Study of the Interaction of 0.11 (o) and 0.22 (Δ) M TiF_4 Solutions with 0.11 and 0.22 $\text{M (Pr}_2\text{NH}_2)_2\text{TiF}_6$ Solutions in Acetonitrile.

of 1.5 was reached. The solution remained dark brown with no precipitate. Equal volumes of benzene and pentane were added which produced no change. An infrared spectrum was made of this solution. A strong absorption band at about 1600 cm.^{-1} indicated the presence of a moderate amount of di-n-propylammonium ion. (Benzene and di-n-propylamine have weak absorption bands in this region. Pentane has no absorption band in this region.) A portion of the solution was placed in a rotary vacuum evaporator where the solvent was removed. A dark very viscous liquid remained. Crystallization did not occur. The character of this material did not change on standing at room temperature for several weeks. Acetone was added to another portion of the solution producing an oily material as well as light tan crystals which melted at $185\text{-}190^\circ\text{ C}$. These crystals were soluble in acetonitrile but not in acetone. Crystals could not be obtained by treatment of portions of the solution with ether, benzene or pentane.

CHAPTER V

DISCUSSION

A. Theoretical Considerations.

The reaction of titanium tetrafluoride (TiF_4) with secondary amines is not a simple reaction that is the same in all solvents. A variety of mechanisms for the reaction of TiF_4 with amines have been proposed. Added amine is expected to react preferentially with the most acidic species present in a TiF_4 solution. Species such as solvated TiF_4 , Ti_2F_9^- , and TiF_5^- should be appreciably different in acidity. In general, acidity of a titanium species is a function of: (1) solvent character; (2) ligands; (3) base employed as reference.

(1) Solvent character affects the relative thermodynamic stabilities of reactants and products. The stabilities of different sets of products will be affected differently by change in solvent. Solvent molecules can also serve as ligands, effecting new equilibria and species.

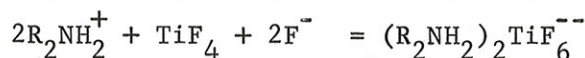
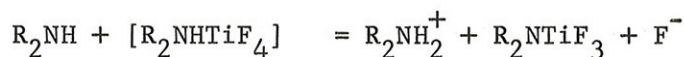
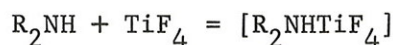
(2) The assumption is made that acidity of a titanium-containing species in solution is inversely proportional to the number of amine and F^- ligands. Acidity should also be affected by the net ionic charge on the species. The acidity of solvated species would be expected to have the following order; $\text{TiF}_3^+ > \text{R}_2\text{NHTiF}_3^+ \geq \text{TiF}_4 > \text{R}_2\text{NHTiF}_4 \geq \text{TiF}_5^- \gg \text{TiF}_6^{--}$. (Presence of an R_2N^- ligand should depress acidity significantly.) The position of Ti_2F_9^- in this series cannot be predicted because bridging fluorines cannot be considered equivalent to monocoordinated fluorides. The effect of positive ionic charge would be to increase acidity somewhat. Conversely, the effect of negative ionic charge would decrease acidity somewhat.

(3) Excessive steric requirements of a given amine may diminish thermodynamic stability of various species, especially those containing amine ligands cis to each other. Specific

factors involved in variations of amine basicity towards titanium(IV) cannot be discussed in detail here.

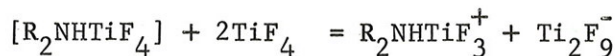
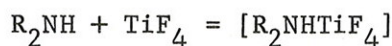
If the various species present in reaction mixtures would be appreciably different in acidity, reaction involving these species would proceed in a stepwise manner where each step would be essentially completed before the beginning of the next step. Presumed intermediate species such as $Ti_2F_9^-$ and TiF_5^- or $Ti_2F_{11}^{--}$ have not been isolated. Thermodynamic stability of $Ti_2F_9^-$ is considered to be the driving force in TiF_4 -amine reactions in acetone (11) but this species is presumably not present in ethanol (2).

Reaction mechanisms have been proposed in which deprotonation of coordinated amine is of utmost importance (12).



Deprotonation must occur, since $R_2NH_2^+$ has been isolated from appropriate reaction mixtures. Since the observed reactions involve dehydrohalogenation and formation of relatively stable polyfluorotitanate ions, it cannot be determined with certainty that deprotonation is the driving force for such reactions.

A reaction mechanism which depended on proton removal would not predict a conductivity increase on addition of a tertiary amine to TiF_4 . A reaction mechanism such as the following (12):



(etc.)

does predict a conductivity increase for both secondary and tertiary amines. The reaction of TiF_4 with pyridine in acetone (Fig. 1) shows a conductivity increase with addition of amine. This gives support to the latter mechanism for secondary amines. However, this evidence cannot be used against the idea of facile deprotonation. Dehydrohalogenation could proceed by either

route, i.e., through $R_2NHTiF_3^+$ or through $R_2NTiF_4^-$, with the same net results.

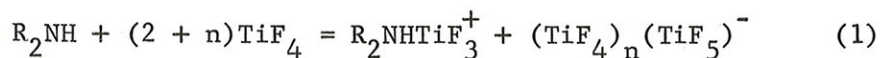
Stability of the coordinated fluoride ion is much greater than the stability of coordinated solvent molecules, as shown by the fact that TiF_6^{--} is stable in various solvents. (Fluoride ion should have a conductivity similar to ClO_4^- . Figure 9 shows that the TiF_6^{--} ion has a much lower conductivity. Hence it is concluded that TiF_6^{--} is stable in the solvent acetonitrile.) Stability of coordinated amine is also greater than that of coordinated solvent, since exothermic reaction occurs when an amine is added to a titanium tetrafluoride solution. The fluoride ligand is presumably somewhat more stable than an amine ligand since addition of excess amine to hexafluorotitanates and to various amine-rich crude reaction mixtures does not increase conductivity appreciably. (The electrostatic attraction of fluoride ion to Ti(IV) apparently outweighs the greater polarizabilities of amines.) Therefore, order of ligand stability for our system is $(F^-) > (R_2NH) > (solvent)$.

B. Proposed Reaction Mechanisms.

Theoretical reaction mechanisms coupled with continuous variation studies can be utilized to give theoretical reaction curves. These reaction curves can then be compared with experimental curves. Various theoretical curves can be combined to give hybridized theoretical curves that are closer approximations to actual reaction curves. By this method insights into the actual reaction mechanism can be gained and various alternatives eliminated from consideration.

In order to obtain a set of theoretical reaction curves an assumed reaction mechanism is proposed and various assumptions are made. The following pattern of thought leads to the curves in Figure 11.

Reaction Mechanism I



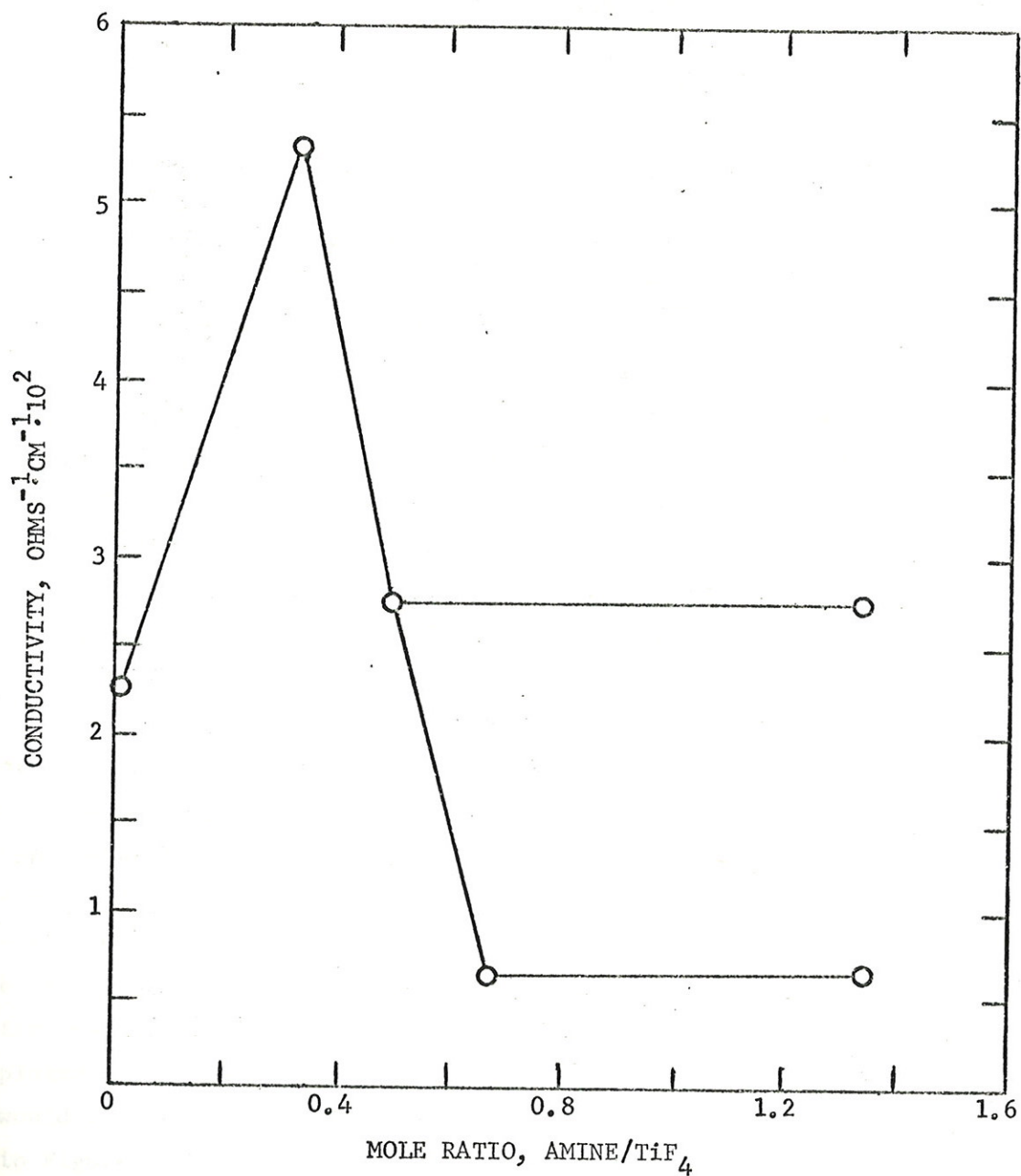
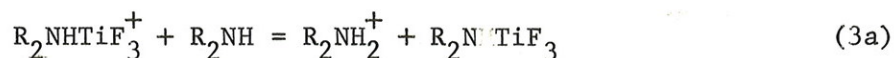
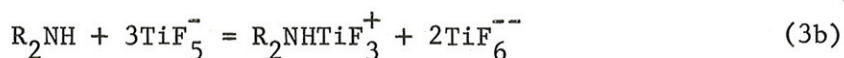


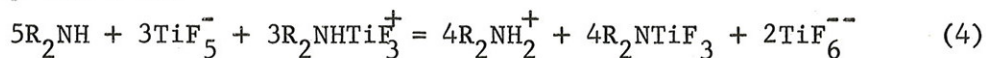
Figure 11. Theoretical Curve for Reaction Mechanism I.



or



or step (3a + 3b)

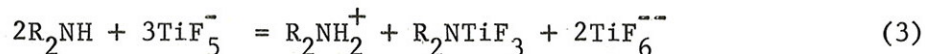
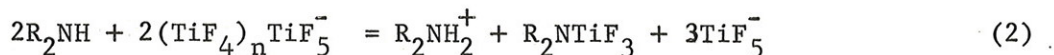
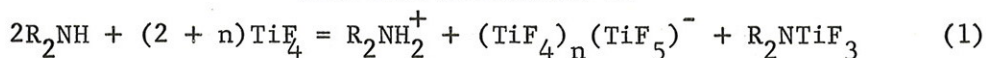


Assume that n equals one. Step (1) should proceed to a mole ratio of 0.33. The initial conductivity of a 0.33 M TiF_4 solution is approximately $2.15 \times 10^{-2} \text{ ohms}^{-1} \text{ cm.}^{-1}$. From the continuous variation study (Fig. 10) the maximum conducting species has the empirical formula $Ti_2F_9^-$. Assuming that this species produces maximum conductivity at a mole ratio of 0.33, the maximum conductivity would be $5.40 \times 10^{-2} \text{ ohms}^{-1} \text{ cm.}^{-1}$, since a 0.33 M TiF_4 solution would give a 0.22 M $Ti_2F_9^-$ concentration. (These conductivity comparisons assume that the conductivity and ion-pairing abilities of $R_2NH_2^+$ and $R_2NHTiF_3^+$ are similar.) Step (2) will proceed to a mole ratio of 0.50. The concentration of TiF_5^- will be 0.165 M at this stage. From the continuous variation study (Fig. 10), at a F/Ti ratio of 5:1, the conductivity of a 0.165 M solution can be determined by interpolation to be approximately $2.76 \times 10^{-2} \text{ ohms}^{-1} \text{ cm.}^{-1}$. After completion of step (2) the reaction may proceed by either step (3a) or (3b) or some combination of both these steps (4). If the reaction proceeds by step (3a) the conductivity change would be negligible. If the reaction proceeded by step (3b) the reaction would be completed at a mole ratio of 0.67 and the resulting conductivity would be that of 0.11 M TiF_6^{--} of $0.65 \times 10^{-2} \text{ ohms}^{-1} \text{ cm.}^{-1}$ as shown in Figure 10. With TiF_6^{--} as a final product step (3a) would continue to a mole ratio of 1.33 with no further change in conductivity. Combinations of steps (3a) and (3b) would give curves intermediate in conductivity values until a mole ratio of 1.33.

The theoretical curve obtained by this method (Fig. 11) is constructed by drawing straight lines between the various determined points. In reality straight lines would not be expected due to such effects as ion-pairing.

Another plausible reaction mechanism is:

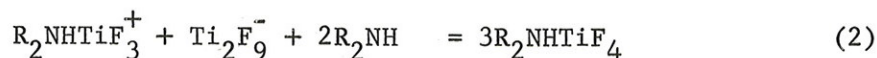
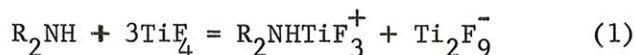
Reaction Mechanism II



For n equal to one, step (1) would proceed to a mole ratio of 0.67. The initial conductivity of a 0.33 M TiF_4 solution would be the same as in the previous example. The conductivity at mole ratio 0.67 would be the same as the conductivity at mole ratio 0.33 in the previous example. Step (2) would proceed to a mole ratio of 1.0 where the conductivity of the TiF_5^- species, $2.76 \times 10^{-2} \text{ ohms}^{-1} \text{ cm.}^{-1}$, would be expected. Step (3) would run to a mole ratio of 1.33. The expected conductivity would be that of the TiF_6^{--} species. The points are again connected by straight lines to give the theoretical reaction curve (Fig. 12). It should be noted that this theoretical curve predicts a conductivity maximum at a mole ratio of 0.67 whereas the previous theoretical curve had a maximum at 0.33. In actuality the conductivity maximum lies between these two points.

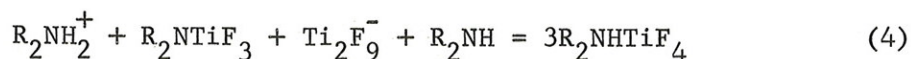
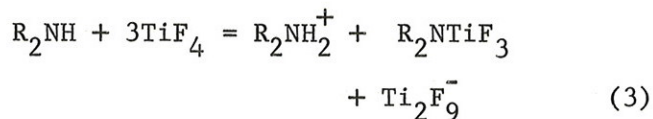
Reaction mechanisms that would produce different products would be the following:

Reaction Mechanism III



or with an alternate path to the maximum:

Reaction Mechanism IV



Reaction mechanism III would produce a conductivity maximum at

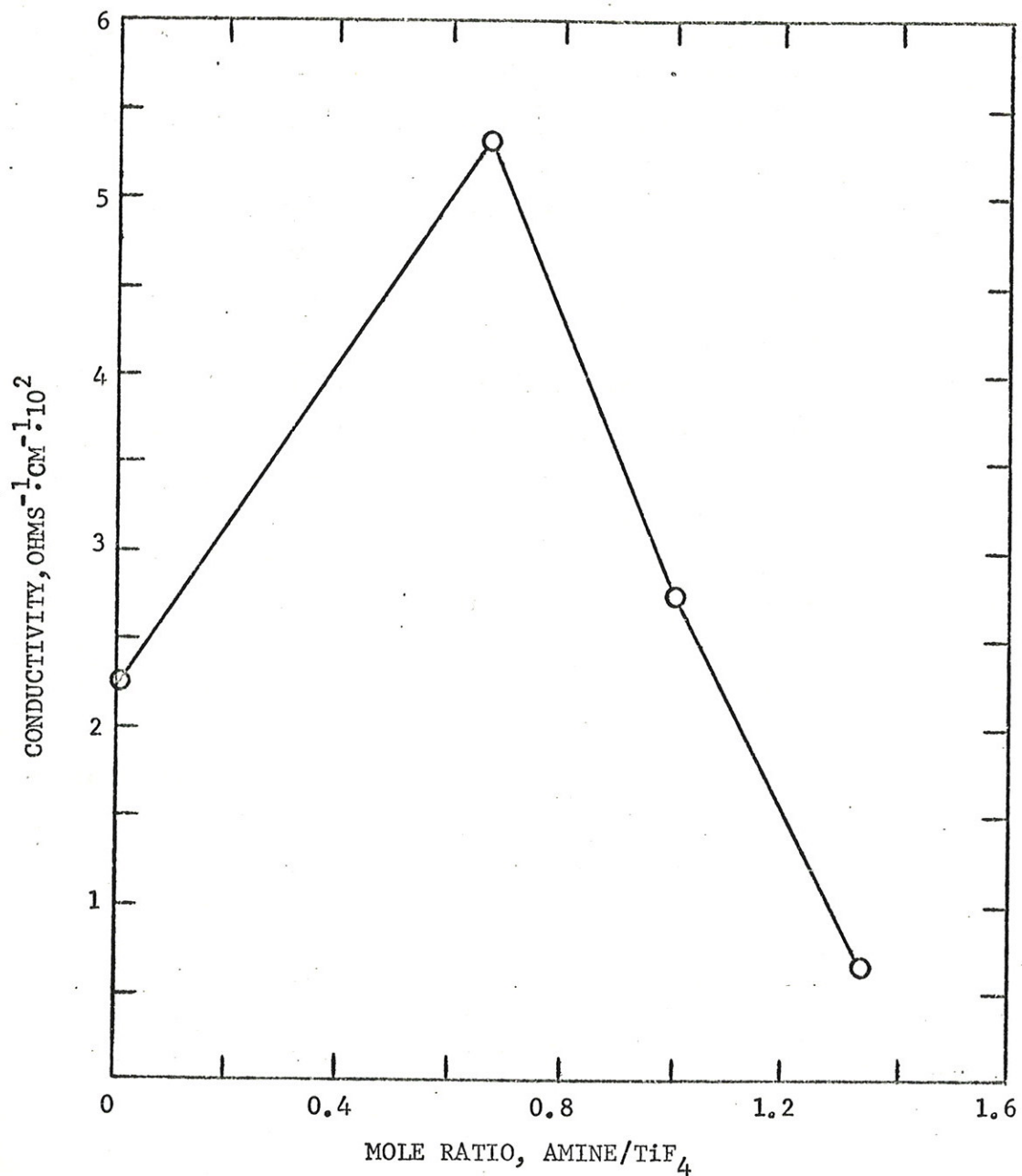


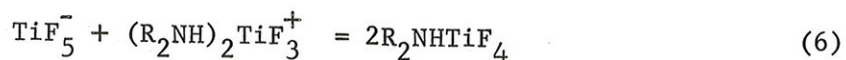
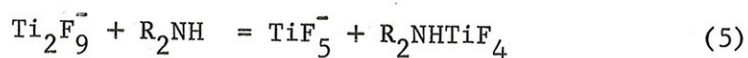
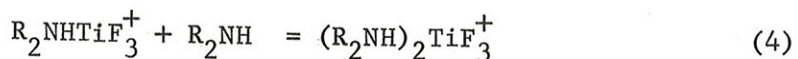
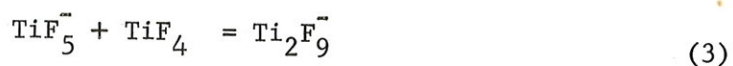
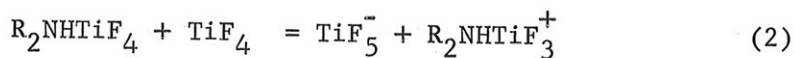
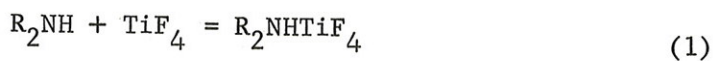
Figure 12. Theoretical Curve for Reaction Mechanism II.

a mole ratio of 0.33. This mechanism would predict a rapid decrease in conductivity from mole ratio 0.33 to 1.0. The final conductivity of the reaction mixture would be a function of the extent of disproportionation of R_2NHTiF_4 . Reaction mechanism IV would predict a conductivity maximum at a mole ratio of 0.67, followed by an extremely rapid decrease in conductivity. The final conductivity would again be a function of the extent of disproportionation of the R_2NHTiF_4 species. The existence of di-n-propylammonium ion at mole ratios near 0.67 should be detectable by infrared absorption techniques.

A combination of reaction mechanisms III and IV could give the correct conductivity maximum. However, a reasonable amount of di-n-propylammonium ion should be present. Detection of this ion by infrared absorption in acetonitrile is difficult but it is thought that relatively little of this species exists in the reaction solution.

A reaction mechanism that satisfies most completely the experimental data found in reactions carried out in acetonitrile is the following:

Reaction Mechanism V



This mechanism gives the flexibility needed to explain position and magnitude of the observed conductivity maximum. This mechanism predicts completion of the reaction at a mole ratio of 1.0, which is the mole ratio experimentally observed as the conductivity ceases to change. Observed conductivities at mole ratio 1.0 can be explained by slight disproportionation of R_2NHTiF_4 .

Consideration of step (1) demonstrates the flexibility of mechanism V. Presence of R_2NHTiF_4 in the early stages of the reaction would depress and delay the conductivity maximum. If half of the reaction mixture at the maximum were R_2NHTiF_4 , the maximum would occur at a mole ratio of 0.67. Depression in height cannot be established from available experimental data with certainty, since the reference solution chosen contains a different cation. However, it is believed that the anions carry most of the current in acetonitrile, and that the conductivities of equimolar solutions containing the same anions and different but similar cations should be similar. The $R_2NHTiF_3^+$ and the $(R_2NH)_2TiF_3^+$ solvated cations are certainly larger and much heavier than the $R_2NH_2^+$ solvated cation, and the specific conductance of the former ions should, if anything, be lower than that of the $R_2NH_2^+$ ion. The fact that experimental conductivities of reaction mixtures in acetone, nitromethane, and acetonitrile solutions approximate those obtained for $R_2NH_2^+$ species indicate strongly that either the conductivities of $R_2NHTiF_3^+$ and $(R_2NH)_2TiF_3^+$ solvated species are similar to those of $R_2NH_2^+$ solvated species or the anions are carrying almost all of the current. (Ion-pairing effects would be expected to be comparable for these solvated species.)

C. Evidence For $Ti_2F_9^-$ as a Reaction Intermediate.

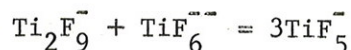
The existence of $Ti_2F_9^-$ as a highly conducting species has been suggested for the acetone solvent system (11). However, continuous variation studies in ethanol have not shown the presence of $Ti_2F_9^-$ as the maximum conducting species (2). Analysis of the continuous variation studies in nitromethane (Fig. 7) and in acetonitrile (Fig. 10) leads to the hypothesis that $Ti_2F_9^-$ is relatively stable and relatively highly conducting in these solvents. Triple fluorine bridge bonding in $Ti_2F_9^-$ should give it sufficient stability to exist in solution. However, this ion has not been isolated. This information plus the fact that its existence has not been detected in ethanol would suggest that it is not extremely stable. The sharp rises in conductivity upon addition of amine to TiF_4 solutions in acetonitrile lead to the

conclusion that Ti_2F_9^- is produced. The results of the continuous variation study in nitromethane indicate that additional species with F/Ti ratios between 4.0 and 4.5 are also formed when amine is added to TiF_4 . A variety of such species can be constructed, e.g., $\text{Ti}_3\text{F}_{13}^-$, $\text{Ti}_4\text{F}_{17}^-$, etc. Analysis shows that several species coexist between mole ratios of 4.0 and 4.5. Analyses of conductivity curves for the reaction of TiF_4 with amine in nitromethane (Fig. 5) give results consonant with this conclusion.

D. Evidence For TiF_5^- as a Reaction Intermediate.

TiF_5^- has been postulated as the maximum conducting species in the continuous variation study using absolute ethanol as a solvent (2). The existence of TiF_5^- species in acetone has not been conclusively demonstrated. The TiF_5^- could amount to TiF_6^{--} fragments incorporated into a Ti_2F_9^- polymer to give an average composition TiF_5^- (11). There has been no positive evidence for the existence of TiF_5^- in acetonitrile.

If TiF_5^- is being produced on the "down slope" in the reaction of di-*n*-propylamine with TiF_4 in acetonitrile then one would predict that addition of TiF_6^{--} ion at the conductivity maximum would produce TiF_5^- according to the equation:



This should result in a slight conductivity decrease. Experimentally the conductivity was found to increase in a linear fashion to a maximum and then to remain constant (correcting for increases in solution volume) thereafter. Thus no positive evidence for TiF_5^- was obtained. A reaction which would predict such a conductivity increase is:



where the highly conducting species Ti_2F_9^- is being produced rather than consumed.

Continuous variation studies in nitromethane and in acetonitrile offer no support to the TiF_5^- hypotheses. A continuous variation study in ethanol in moderately concentrated solutions might lead to somewhat different results than reported.

E. Evidence For $R_2NH_2^+$ as a Reaction Intermediate.

Di-n-propylammonium ion was not found at mole ratios of 0.5 and lower in the TiF_4 -di-n-propylamine reactions in acetone (11). In the latter stages of the reactions, however, the di-n-propylammonium ion combines with the hexafluorotitanate ion to give the precipitate di-n-propylammonium hexafluorotitanate. Attempts to find the di-n-propylammonium ion using infrared absorption spectra in moderately concentrated reaction mixtures in acetonitrile were unsuccessful. This suggests that deprotonation is not a major factor in acetonitrile. This, in turn, would imply that reaction mechanisms which did not include deprotonation more adequately represent the actual course of the reaction in acetonitrile.

F. Evidence For $Ti_2F_{11}^{--}$ as a Reaction Intermediate.

$Ti_2F_{11}^{--}$ appears to be a relatively stable intermediate in the continuous variation study in acetonitrile. Analysis of Figure 10 shows an abrupt, significant change in curve slope at a F/Ti ratio of 5.5. This nonlinearity points to the existence of a relatively stable species with the empirical formula $Ti_2F_{11}^{--}$. There is no published evidence to date for the existence of this species in the reaction of TiF_4 with various amines in different solvents.

In the continuous variation study in nitromethane insufficient data was obtained to permit judgement as to the composition of species between mole fraction TiF_4 of 0 and 0.4. However, the slope of the curve at 0.4 is such that the existence of an intermediate species between 0 and 0.4 must be postulated.

G. Evidence For $(R_2NH_2)_2TiF_6$ or TiF_6^{--} As a Reaction Product.

Di-n-propylammonium hexafluorotitanate has been isolated as an insoluble product of the reaction of TiF_4 and di-n-propylamine in acetone. Di-n-propylammonium hexafluorotitanate is moderately soluble in acetonitrile and in nitromethane, hence precipitation cannot be expected. Conductivities of solutions of this species in acetonitrile and in nitromethane are rather low due to ion-pairing (Fig. 9). Therefore its presence in reac-

tion mixtures cannot be determined conclusively by conductivity measurements.

Numerous attempts have been made in this research to cause precipitation of solid products in the intermediate and final stages of the reaction. Addition of excess benzene and pentane to drastically lower the bulk dielectric constant of the reaction mixture has failed to produce a crystalline product. (Formation of solid di-n-propylammonium hexafluorotitanate in acetone is considered a peculiarity of that solvent.) Oils obtained in attempted preparative reactions do not crystallize when shaken with ether, benzene, pentane, etc., but apparently react with acetone to produce solid di-n-propylammonium hexafluorotitanate (quantity of precipitate increases rapidly with time) and another product which is presumably the polymeric amidotrifluorotitanate.

H. Suggestions For Future Work.

A research project of professional scope and depth necessarily leads to numerous ideas for further work. Various problems arise during the course of the work that could be expanded into new research projects. Time precludes the performance of each and every presumably helpful experiment.

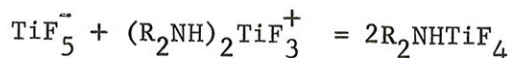
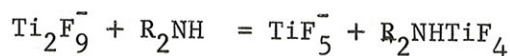
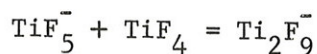
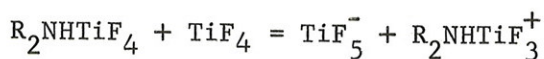
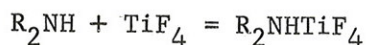
Several logical possibilities for future related work are:

- (1) Titration of " $R_2NH_2^+Ti_2F_9^-$ " with amine.
- (2) Titration of various reaction mixtures with TiF_6^{3-} .
- (3) Determination of thermodynamic and kinetic effects of changing reaction temperature.
- (4) More effort towards isolation of presumed species and intermediates, from "continuous variation" mixtures.
- (5) Determination of the effects of known trace amounts of water and acetone on the reaction of amines with TiF_4 .
- (6) Reaction of tertiary amines with TiF_4 in acetonitrile.
- (7) Extension of this work to other solvent systems.

CHAPTER VI

SUMMARY

Reaction of titanium tetrafluoride with di-n-propylamine was carried out in the solvents acetonitrile and nitromethane. Conductometric studies of the interaction of titanium tetrafluoride and di-n-propylammonium hexafluorotitanate in acetonitrile and nitromethane were carried out by the methods of continuous variation. Results of these studies indicate that anionic species with stoichiometries corresponding to formulas $Ti_2F_9^-$ and $Ti_2F_{11}^{--}$ are relatively stable. Various preparative reactions were carried out in an attempt to isolate reaction products. These reactions resulted in oily substances rather than crystalline solids. Various theoretical reaction mechanisms were postulated and theoretical curves were drawn. These curves were compared with actual experimental reaction curves. The following mechanism correlates conductivities observed in the conductometric titrations with those observed in the continuous variation studies and also accounts for position and magnitude of conductivity maxima, as well as the lack of appreciable amounts of such species as $R_2NH_2^+$, TiF_5^- and TiF_6^{--} .



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