CONTRIBUTION FROM THE WM. A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

The Reaction of Titanium Tetrafluoride with Diisopropylamine, Diethylamine, Pyridine, and Triethylamine[1]

BY JOHN A. CHANDLER AND RUSSELL S. DRAGO

Received November 15, 1961

The reactions of titanium tetrafluoride with diisopropylamine, diethylamine, pyridine, and triethylamine have been investigated. Products have been characterized and conductometric titrations carried out in the solvent acetone. The results can be interpreted by a sequence of reactions in which the added base reacts with the most acidic species in the solution. The acid materials during various portions of the reaction are TiF_4, $R_2NHTiF_3^+$, $Ti_2F_9^-$, and TiF_5^-. Secondary amines yield dialkylamidotitanium(IV) trifluorides and dialkylammonium hexafluorotitanates. Addition compounds are formed with tertiary amines. The results of the conductometric titrations of titanium tetrafluoride with these bases lend additional support to a reaction scheme previously proposed. In this scheme the initial reaction occurring in TiF_4-rich solutions leads to a high conductance and is represented by the equation: $3TiF_4 + R_2NH \rightarrow TiF_3R_2NH^+ + Ti_2F_9^-$. In this study we report that pyridine undergoes a similar initial reaction. This result supports our scheme, because conductance is observed in TiF_4-rich solutions in a system where proton loss is not possible.

Introduction

In a previous article[2] we have reported a detailed study of the reaction of TiF_4 with di-*n*-propylamine. Under all conditions employed, extensive aminolysis occurred, yielding TiF_3NR_2 and $(R_2NH_2^+)_2TiF_6^{=}$. A conductometric titration and a continuous variation study yielded results leading to a proposed reaction sequence. This article reports the extension of these experiments to other secondary amines and to two tertiary amines. Additional information is provided in support of the aminolysis scheme previously proposed. The tertiary amines behave quite analogously to the secondary amines except that reactions involving proton loss are not possible.

Experimental

Purification of reagents and general experimental detail have been discussed previously.[2] Elemental analyses for carbon, hydrogen, and nitrogen were performed by the University Microanalytical Laboratory. The presence of fluoride and the extreme hygroscopicity of the samples affected the accuracy of the hydrogen analyses.

The presence of the dialkylammonium hexafluorotitanates in several of the samples was detected by comparison of the X-ray powder diffraction patterns and infrared spectra with known compounds.[3]

Conductance measurements were made with the apparatus and by the procedure previously described.[2] The conditions are similar.

Reaction with Diisopropylamine.—The addition of excess diisopropylamine to either a saturated chloroform or acetonitrile solution of titanium tetrafluoride produces a precipitate of diisopropylammonium hexafluorotitanate.

Anal. Calcd. for $C_{12}H_{32}N_2TiF_6$: C, 39.40; H, 8.80; N, 7.65. Found: C, 39.80; H, 8.88; N, 7.58.

Attempts to recover the pure titanium amidotrifluoride from the filtrate were unsuccessful. Complex residues which are mixtures result from evaporation.

When excess amine is added to an acetone solution of titanium tetrafluoride, a white solid (I) results. The infrared spectrum,[3] X-ray powder diffraction pattern,[3] and elemental analyses indicate that solid I is a mixture of approximate composition $2TiF_3N(C_3H_7)_2$ to $1[(C_3H_7)_2NH_2]_2TiF_6$.

Anal. Calcd. for $2TiF_3N(C_3H_7)_2 + [(C_3H_7)_2NH_2]_2TiF_6$: C, 37.12; H, 7.79; N, 7.22. Found: C, 36.69; H, 8.44; N, 7.03.

Attempts to separate solid I into its components by recrystallization or solvent extraction techniques were not successful. Heating solid I under vacuum resulted in a slow decrease in the amount of hexafluorotitanate present. After 48 hr. at 130°, no further changes occurred. A small amount of material identified as diisopropylammonium hydrogen fluoride[3] was collected on a cold finger kept at 20°. No further material was condensed in a trap kept at $-80°$.[4] The solid residue (II) appears to be a 1:1 mixture of $TiF_3N(C_3H_7)_2$ and $TiF_4 \cdot NH(C_3H_7)_2$. The analysis, the lack of an X-ray pattern, and the presence of NH stretching frequencies but no NH_2 bending frequencies in the infrared all support this formulation. Attempts to separate this mixture were not successful.

Anal. Calcd. for $TiF_3NC_6H_{14} + TiF_4NC_6H_{15}$: C, 33.60; N, 6.53. Found: C, 33.67; N, 6.52.

Reaction with Diethylamine.—The addition of excess di-

---

[1] Abstracted in part from the Ph.D. thesis of John A. Chandler, University of Illinois, 1959.

[2] J. A. Chandler, J. E. Wuller, and R. S. Drago, *Inorg. Chem.*, **1**, 65 (1962).

[3] J. A. Chandler, R. S. Drago, and R. Latham, Jr., *J. Inorg. & Nuclear Chem.*, **21**, 283 (1961).

[4] It has been reported that liquid nitrogen is needed to efficiently trap titanium tetrafluoride vapor under vacuum conditions. E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, *J. Electrochem. Soc.*, **105**, 275 (1958).

ethylamine to an acetone solution of titanium tetrafluoride produces a white solid. The infrared spectrum, X-ray powder diffraction pattern, and elemental analyses indicate the solid is a mixture of approximate composition $2TiF_3N(C_2H_5)_5$ to $1[(C_2H_5)_2NH_2]_2TiF_6$.

Anal. Calcd. for $2TiF_3NC_4H_{10} + TiF_6C_8H_{24}N_2$: C, 28.99; H, 6.69; N, 844. Found: C, 28.62; H, 7.52; N, 8.01.

Addition of an acetone solution of titanium tetrafluoride to diethylamine produced a solid product. The X-ray diffraction pattern indicated a trace of diethylammonium hexafluorotitanate was present. The infrared spectrum showed only a very weak NH_2 band. The inherently less intense NH bonds were not present. The analysis corresponded to $TiF_3N(C_2H_5)_2$.

Anal. Calcd. for $TiF_3NC_4H_{10}$: C, 27.10; N, 7.91. Found: C, 27.08; N, 8.18.

Addition of an acetone solution of diethylamine (0.75 mole amine/mole of titanium tetrafluoride) produces a slightly less pure material very similar to the solid from pure amine. *Anal.* Found: C, 26.97; N, 7.46.

Attempts at further purification of the diethylamine reaction products were not successful.

Reaction with Pyridine.—Depending upon reaction conditions, two products were obtained from the reaction of TiF_4 and pyridine; a 2:1 and a 1:1 addition compound.[5] The 1:1 addition compound is a stable adduct, but the 2:1 addition compound slowly loses pyridine on standing in a dry atmosphere. This is in agreement with results previously reported.[6,7] Though the 1:1 compound is stable, the 2:1 compound does not form the 1:1 compound as it loses pyridine.[8] Difficulty was encountered in the analysis of the 2:1 compound because of the volatility of pyridine. Most compositions were intermediate between 1.5 and 2 to 1.

Preparation of the 2:1 Compound.—The 2:1 compound is prepared by the addition of a large excess of pyridine to an ethanol or chloroform solution of TiF_4. The reverse mode of addition also results in the 2:1 compound.

Preparation of the 1:1 Compound.—The 1:1 addition compound is prepared by the slow addition of a slight excess of pyridine in acetone to an acetone solution of TiF_4. The white solid which precipitates is recovered by filtration and dried *in vacuo* over $CaCl_2$.

Anal. Calcd. for $TiF_4C_5H_5N$: C, 29.6; N, 6.9. Found: C, 30.9; N, 6.6.

Reaction with Triethylamine.—The reaction of triethylamine and TiF_4 in acetone gives rise to a complex reaction product which we were unable to separate into pure compounds by recrystallization, solvent extraction, or sublimation. Depending upon conditions, the product can be formulated as a mixture of 1:1 and 2:1 or 1:1 and 3:2 addition compounds. In all samples a small amount of triethylammonium hexafluorotitanate was detected by faint lines in the X-ray powder patterns.[3] A typical preparation involves the addition of a large excess of triethylamine to a titanium tetrafluoride solution in acetone. A white solid precipitates which is collected by filtration and dried *in vacuo* over calcium chloride. A product containing more amine can be obtained by addition of an acetone solution of TiF_4 to liquid triethylamine.

Results and Discussion

Secondary Amine Reactions.—The conductometric titration curves for the reactions of titanium tetrafluoride with diethylamine and diisopropylamine were similar to that reported for di-*n*-propylamine[2] and are not reproduced here. The significant features of the curve can be summarized briefly: there is a rapid increase in conductance upon addition of amine until an amine: TiF_4 ratio of 0.25 is obtained; the curve flattens; and in the region 0.45 to 0.8 a rapid decrease in conductance is observed. Through the remainder of the curve there is a gradual decrease in conductance. Between mole ratios of 0.7 and 1.3 precipitation occurs.

The results from the conductometric titration curve, infrared spectra, and a continuous variation study were interpreted as evidence for the reaction scheme[9]

$$R_2NH + TiF_4 \longrightarrow [R_2NHTiF_4] \quad (1)$$

$$[R_2NHTiF_4] + 2TiF_4 \longrightarrow R_2NHTiF_3{}^+ + Ti_2F_9{}^- \quad (2)$$

$$R_2NHTiF_3{}^+ + R_2NH \longrightarrow R_2NH_2{}^+ + (R_2NTiF_3)_x \quad (3)$$

$$R_2NH + Ti_2F_9{}^- \longrightarrow R_2NHTiF_4 + TiF_5{}^- \quad (4)$$

$$R_2NH + TiF_5{}^- + R_2NHTiF_4 \longrightarrow R_2NH_2{}^+ + TiF_6{}^= + (R_2NTiF_3)_x \quad (5)$$

$$2R_2NH_2{}^+ + TiF_6{}^= \longrightarrow (R_2NH_2{}^+)_2TiF_6{}^= \quad (6)$$

Solids isolated at the completion of reactions of the three secondary amines studied closely approximate a mixture of $2TiF_3R_2N + [R_2NH_2]_2TiF_6$. The yields are near quantitative. The same interpretation of the conductance curve reported for diisopropylamine[2] applies to both diisopropyl and diethylamine.

The above scheme is obtained by assuming that each step (except 1, 3, and 4) goes nearly to completion before a subsequent step is initiated. This is expected if the added amine reacts with the most acidic species in solution, and there is an appreciable difference in the acidity of TiF_4, $Ti_2F_9{}^-$, and $TiF_5{}^-$. Other schemes can be proposed if a delicate balance between competing equilibria is assumed. The similarity in the behavior of the three secondary amines which differ in basicity toward a proton and in steric requirements toward Lewis acids supports the assump-

---

(5) All ratios given in the manuscript are amine: TiF_4 ratios.

(6) H. J. Emeléus and G. S. Rao, *J. Chem. Soc.*, 4245 (1958).

(7) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960). These experiments were carried out in our laboratory prior to the appearance of these articles.

(8) This observation was confirmed by comparison to the X-ray powder diffraction patterns of the 1:1 compound and a sample of the 2:1 compound which had lost approximately 1 mole of pyridine.

(9) In the scheme the reactions have been simplified by omitting solvent coördination.

tion that the acidities differ appreciably and each step is nearly completed before a second one begins. This is the significance of the study of these reactions with additional secondary amines.

Mechanisms have been considered which instead of step 2 involve removal of a proton from the addition compound R_2NHTiF_4 by either amine or solvent. These schemes would account for the rise in conductance by the presence of either the $R_2NH_2^+$ or $(CH_3)_2COH^+$ ions. Arguments against these reaction sequences in excess TiF_4 have been presented.[2] When the reaction is carried out by adding a solution of TiF_4 to a solution of the amine, instant precipitation occurs. Under these conditions proton removal may be important and this scheme may be operative

$$R_2NH + TiF_4 \longrightarrow [R_2NHTiF_4] \tag{1}$$

$$R_2NH + [R_2NHTiF_4] \longrightarrow R_2NH_2^+ + R_2NTiF_3^+F^- \tag{2}$$

$$2R_2NH_2^+ + TiF_4 + 2F^- \longrightarrow (R_2NH_2^+)_2TiF_6^= \tag{3}$$

Steps 1, 2, and 3 occur concurrently. The great affinity of TiF_4 for F^- is manifested by the formation of $TiF_6^=$ in the presence of such a large excess of amine.

Tertiary Amine Reactions.—The proposed mechanism for the reaction in excess TiF_4 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 TiF_4 with pyridine (Fig. 1) demonstrate the predicted conductance increase which lends further support to the proposed mechanism. The pyridine curve can be explained by the sequence (py = pyridine)

$$TiF_4 + py \longrightarrow [TiF_4py] \tag{1}$$

$$[TiF_4py] + 2TiF_4 \longrightarrow pyTiF_3^+ + Ti_2F_9^- \tag{2}$$

$$2py + pyTiF_3^+ + Ti_2F_9^- \longrightarrow 3/x(pyTiF_4)_x \tag{3}$$

Steps 1 and 2 occur concurrently upon pyridine addition. The high conductance obtained at 0.3 supports the formulation of $Ti_2F_9^-$.[2] Heavy precipitation begins at 0.25 and continues throughout the reaction. That step 3 is initiated before steps 1 and 2 are completed is evidenced by copious precipitation at 0.25 mole ratio. 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 0.33.

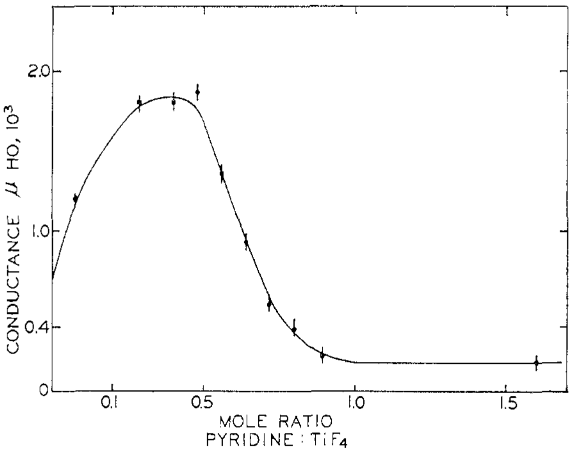

Fig. 1.—Conductometric titration curve for the titration of TiF_4 by pyridine in acetone (0.18 *M* TiF_4 solution).

The compound $py{\cdot}TiF_4$ is most probably a polymeric material consisting of six-coördinate titanium. The polymeric nature explains the insolubility of this material in acetone. The significance of this pyridine titration lies in the existence of conducting species in TiF_4-rich solutions.

Acknowledgment.—The authors wish to acknowledge the generous support of this research by the Titanium Division of the National Lead Corporation.