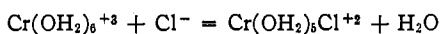| Medium	Q_1° (25°)	ΔH_1° ($\times$ mole kcal.$^{-1}$)	ΔS_1° ($\times$ mole deg. cal.$^{-1}$)
1.0 M HClO$_4$	2.9 ± 0.1	4.3 ± 0.3	16.7 ± 1
3.7 M HClO$_4$	10.7 ± 1	3.4 ± 0.3	16.1 ± 1

The value of ΔS_1° for 3.7 M perchloric acid can be compared directly with the value $\Delta S_1^\circ = 17.2$ cal. mole^{-1} deg.$^{-1}$ for the reaction

$$Cr(OH_2)_6^{+3} + Cl^- = Cr(OH_2)_5Cl^{+2} + H_2O$$

in the same medium.[8] The similarity of these values suggests very strongly that the iron(III) reaction, like the chromium(III) reaction, involves no change in the coördination number of the metal ion.

To what extent does close agreement of values of ΔS_1° for the iron(III) and chromium(III) reactions indicate that the conventions adopted in treating the electromotive force data have resulted in defining the monochloroiron(III) ion produced in reaction 1 as the inner-sphere complex Fe-$(OH_2)_5Cl^{+2}$? If there is such an entity as a well-defined outer-sphere complex, which does not seem at all certain, ΔS° for the reaction

$$Fe(OH_2)_6^{+3} + Cl^- = Fe(OH_2)_6^{+3}\cdot Cl^-$$
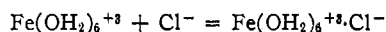
would be expected to be less positive than ΔS° for the reaction forming the inner-sphere com-

plex. The value of ΔS° for formation of one mole of monochloroiron(III) ion, x moles of which is outer-sphere species and $(1 - x)$ moles of which is inner-sphere species is

$$\Delta S_1^\circ = x\Delta S_{1,o}^\circ + (1 - x)\Delta S_{1,i}^\circ - R(x \ln x + (1 - x) \ln (1 - x))$$

in which $\Delta S_{1,o}$ and $\Delta S_{1,i}$ are values of the entropy change for reactions forming outer-sphere and inner-sphere complexes, respectively. Calculated values of $(\Delta S_1^\circ - \Delta S_{1,i}^\circ) \times$ cal.$^{-1}$ deg. mole are

$\{\Delta S^\circ_{1,i} - \Delta S^\circ_{1,o}\}$ $\times$ deg. cal.$^{-1}$ mole	$x = 0.25$	$x = 0.50$	$x = 0.75$
4	$+0.1$	-0.6	-1.9
6	-0.4	-1.6	-3.4
8	-0.9	-2.6	-4.9

Because of the entropy of mixing term, inclusion of outer-sphere species in what monochloroiron-(III) ion comprises does not have much effect upon ΔS_1° unless the outer-sphere species is the predominant monochloroiron(III) species. The presence of an appreciable amount of monochloroiron(III) ion as outer-sphere species cannot, therefore, be ruled out on the basis of the similarity of the entropy changes in the iron(III) and chromium(III) reactions.

The Reaction of Titanium Tetrafluoride with Di-*n*-propylamine

BY JOHN A. CHANDLER,[1] JEROME E. WULLER, AND RUSSELL S. DRAGO[2]

The reaction of di-*n*-propylamine with titanium tetrafluoride has been investigated in detail. In all cases studied an aminolysis reaction occurred resulting in $(R_2NH_2^+)_2TiF_6^-$ and R_2NTiF_3. Product isolation, results from conductometric titrations, and an infrared study can be interpreted to eliminate several reaction schemes. A sequence of reactions is proposed which is consistent with the experimental results. A continuous variation study on the system $(R_2NH_2^+)_2TiF_6^-$–TiF$_4$ gives rise to both formulas for the species and conductance data that can be employed to explain the sequence of reactions of TiF$_4$ with the amine.

Introduction

In contrast to the abundance of literature on the reactions of titanium tetrachloride, relatively little is reported on titanium tetrafluoride. Surprisingly, it is reported that titanium tetra-

fluoride forms 1:1 addition compounds with methylamine, ethylamine, and aniline.[3] A compound containing two molecules of base to one of TiF$_4$ is reportedly formed with ammonia and both 2:1 and 1:1 addition compounds are reported to form with pyridine.[4] In most of this earlier

(1) Abstracted in part from the Ph.D. Thesis of John A. Chandler, University of Illinois, 1959.
(2) Author to whom correspondence should be addressed.

(3) H. J. Emeleus and G. S. Rao, *J. Chem. Soc.*, 4245 (1958).
(4) O. Ruff and R. Ipsen, *Ber.*, **36**, 1777 (1903).

work the concern has been the preparation of a large number of compounds rather than a more complete study of the products of a few reactions. The absence of reports of hexafluorotitanates as products in the methylamine and ethylamine reactions bears this out. Subsequent to our initiation of research in this area an exhaustive study of some molecular addition compounds of titanium tetrafluoride was reported.[5] Only very brief mention is made to indicate that protonic amines react in ether to produce hexafluorotitanates. In this article we report an extensive investigation of the reaction of TiF_4 with the protonic amine, di-*n*-propylamine. Isolation of products, conductometric titrations, and infrared investigation of solutions of TiF_4 containing amine are reported. A reaction scheme is proposed to account for the results of these experiments. Under all conditions employed di-*n*-propylammonium hexafluorotitanate is shown to be one of the principal products of the reaction of this secondary amine with TiF_4.

Experimental

Reagents.—Titanium tetrafluoride obtained from the General Chemical Division of Allied Chemical and Dye Corporation was used without purification. The container was opened in a dry box and the entire contents were transferred to glass ampoules and sealed. Control experiments using the middle fraction of titanium tetrafluoride obtained from sublimation in a nitrogen atmosphere gave results identical with those obtained with this sample of commercial grade titanium tetrafluoride. The sublimation of TiF_4 was carried out in a glass apparatus containing a monel liner.

Prepurified nitrogen was employed in all experiments. The solvents used in this study, chloroform and acetone, were purified by standard techniques.[6] Di-*n*-propylamine was dried over barium oxide for several days, shaken with activated alumina for one hr., and then fractionated from barium oxide. The reaction between amine and titanium tetrafluoride was carried out under a variety of conditions. In all instances, transfers of material were carried out in a dry box.

Conductance Measurements.—Electrical conductance was measured with an Industrial Instruments Model RC 16 B2 conductance bridge. The cell used for the conductometric titrations consisted of a three-necked flask equipped with a buret, platinum disk electrodes, and a nitrogen inlet-outlet system. Duplicate readings were taken after each amine addition to ensure that the conductivity was constant with time.

Other Measurements.—Infrared spectra were obtained with a Perkin–Elmer Model 21 instrument fitted with so-

dium chloride optics. The spectra of solid samples were obtained as mulls in Nujol and hexachlorobutadiene. Powder diffraction patterns were taken with a Hull–Debye–Scherrer type camera mounted on a Picker X-ray unit using copper $K\alpha$ radiation and a nickel foil filter. Elemental analyses for carbon, hydrogen, and nitrogen were performed by the University microanalytical laboratory. The presence of fluoride in several samples and their hygroscopicity affected the accuracy of the hydrogen analyses.

Reactions of Di-*n*-propylamine with Titanium Tetrafluoride.—The presence of di-*n*-propylammonium hexafluorotitanate in several of the products was detected by X-ray powder diffraction. The syntheses of a series of ammonium hexafluorotitanates were carried out for comparison purposes and their infrared spectra and diffraction patterns have been reported.[7]

The Reaction in Pure Amine.—When titanium tetrafluoride, precooled to $-78°$, is added to solid di-*n*-propylamine, also at $-78°$, and the mixture is allowed to warm slowly to room temperature under a dry nitrogen atmosphere, considerable reduction of the titanium tetrafluoride to titanium(III) species occurs. No attempt was made to establish the nature of the products containing the titanium(III). Di-*n*-propylammonium hexafluorotitanate was identified as a product.

Reaction in the Solvent Chloroform.—Addition of excess di-*n*-propylamine to a chloroform solution of TiF_4 results in an exothermic reaction. TiF_4 is only very slightly soluble in chloroform. No precipitate is formed, but a solid (solid I) is obtained by the addition of hexane to the solution. The infrared spectrum, X-ray powder diffraction pattern, and elemental analysis for nitrogen indicate that solid I is a mixture of approximate composition 2 $TiF_3 \cdot N(C_3H_7)_2$ to $1[(C_3H_7)_2NH_2]_2TiF_6$.

Anal. Calcd.: N, 7.22. Found: N, 7.14.

Solid I can be resolved into the two components by evaporation of a chloroform solution at reduced pressure. The hexafluorotitanate precipitates out in a nearly pure state. Washing with a small amount of chloroform produces the pure material. Yields are near quantitative.

Anal. Calcd. for $[(C_3H_7)_2NH_2]_2TiF_6$: C, 39.40; H, 8.80; N, 7.65. Found: C, 39.48; H, 8.77; N, 7.60. The hexafluorotitanate melts at $180-184°$ with decomposition.

Continued evaporation of solvent from the solution remaining after removal of most of the hexafluorotitanate produces an extremely hygroscopic, light tan solid that decomposes slowly around $80°$. The solid is most probably polymeric and is amorphous to X-rays. The infrared spectrum of this product is similar to that of di-*n*-propylammonium hexafluorotitanate except for the absence of ammonium ion $(R_2NH_2^+)$ stretching and bending modes.

Anal. Calcd. for $TiF_3 \cdot (C_3H_7)_2N$: C, 35.20; N, 6.84. Found: C, 35.01; N, 6.81.

This represents our best result from several attempts to isolate this material. Reproducibility was difficult but in all instances the infrared spectra showed a pronounced decrease in the NH_2^+ vibrations in this most soluble fraction. Attempts to separate compounds from solid I by sublimation failed.

Reaction in the Solvent Acetone.—Solutions of TiF_4

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

(6) (a) W. T. Richards and J. H. Wallace, *ibid.*, **54**, 2705 (1932); (b) J. W. Williams and F. Daniels, *ibid.*, **46**, 903 (1924); (c) J. Timmermans and L. Gillo, *Roczniki Chem.*, **18**, 812 (1938).

(7) J. A. Chandler, R. S. Drago, and R. Latham, Jr., *J. Inorg. & Nuclear Chem.*, accepted for publication.

in acetone range in color from colorless to yellow to ruby red, depending on the concentration of the acid and aging time. Concentrated solutions normally possess a red color if prepared at room temperature. However, they are colorless to light yellow when prepared at −78°. The qualitative and quantitative aspects of the reaction of amine with TiF₄ are independent of the color of the solution. Addition of equivalent quantities of amine to the TiF₄ solutions in acetone causes the color to disappear. The change from red to colorless is reversible. The red color is not due to Ti^{+3}. Attempts to isolate the red material indicate the presence of only a small amount of a highly chromophoric species which was not identified.

When an excess of a dilute solution of di-*n*-propylamine in acetone is added to a dilute solution of titanium tetrafluoride in acetone, a white precipitate forms. Titanium is almost quantitatively removed from solution. The product is the same as that obtained in chloroform solution and precipitated by hexane.

Anal. Calcd. for 2TiF₃NC₆H₁₄ + [(C₃H₇)₂NH₂]₂TiF₆: C, 37.12; H, 7.79; N, 7.22. Found: C, 36.89; H, 8.27; N, 7.10.

A sample of the product was shaken with a large volume of di-*n*-propylamine for one day. No change in composition occurred.

Results and Discussion

In an attempt to formulate a reaction scheme for this reaction, conductometric titrations of 0.04 *M*, 0.12 *M*, and 0.40 *M* solutions of TiF₄ with di-*n*-propylamine were carried out in the solvent acetone. The curves obtained in concentrated and dilute solution are identical in shape (Figure 1). Dilution of the amine with acetone and titration with this solution did not affect the results. The significant features of these
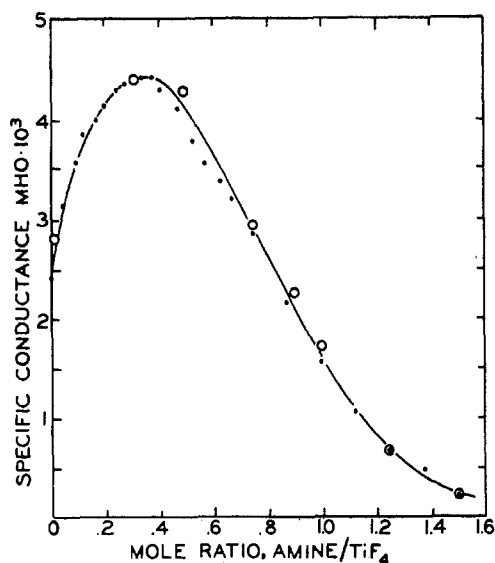

Fig. 1.—Conductometric titration of a 0.4 *M* TiF₄ solution in acetone with di-*n*-propylamine: ● Experiment 1; ○ Experiment 2.

curves are similar for all concentrations and can be summarized briefly. There is a rapid increase in conductance upon addition of amine until an amine:TiF₄ ratio[8] of 0.25 to 1 is obtained.

The curve flattens and in the region of ratios of 0.45 to about 0.8 a rapid decrease in conductance is observed. Through the remainder of the curve there is a gradual decrease in conductance. Two other observations also should be accounted for by any reaction scheme. Between mole ratios of 0.5 and 0.6 the characteristic red color that develops in concentrated TiF₄ solutions in acetone disappears, and at a mole ratio of 0.7 precipitation begins. Precipitation continues until a ratio of about 1.3.

When titration is carried out in reverse fashion, *i.e.*, when the TiF₄ solution is added to an amine solution, a precipitate forms on first addition, increases in bulk until a nearly equimolar quantity of TiF₄ has been added, then redissolves on addition of excess TiF₄. Conductance values are similar to those for mixtures of equal concentration and stoichiometry prepared by addition of amine to TiF₄ solutions. Di-*n*-propylammonium hexafluorotitanate was isolated from precipitates formed by either mode of addition. This salt is very insoluble in acetone.

The absence of precipitate in TiF₄-rich solutions (ratios lower than 0.7) could be due to the absence of either the hexafluorotitanate ion or the di-*n*-propylammonium ion. Infrared spectra of solutions of 0.5 mole ratio indicated the absence of ammonium ion by the absence in the spectra of absorptions due to the NH₂$^+$ deformation around 1600 cm.$^{-1}$. The titration also was carried out in acetone solution containing added di-*n*-propylammonium perchlorate. Precipitation occurs at the same mole ratio as in the absence of added ammonium ion. The TiF₆$^−$ ion must not exist in solution at amine:TiF₄ mole ratios lower than 0.7 but conductance must arise from other anions probably of the type [F(TiF₄)$_x$$^−$]$_n$. The solution does not contain hexafluorotitanate ion below 0.7 nor appreciable R₂NH₂$^+$ ion below 0.5.

In order to establish the nature of the anion present, a continuous variation study[9] was carried out on the binary system TiF₄–[(*n*-C₃H₇)₂NH₂$^+$]₂-TiF₆$^−$ in the solvent acetone. The results are illustrated in Figure 2. The maximum obtained corresponds to the empirical formula Ti₂F₉$^−$.

(8) All ratios given are amine:TiF₄ ratios.

(9) P. Job, *Ann. chim.*, **9**, 113 (1928); F. Woldbye, *Acta Chem. Scand.*, **9**, 299 (1955); M. M. Jones, *J. Am. Chem. Soc.*, **81**, 4485 (1959).
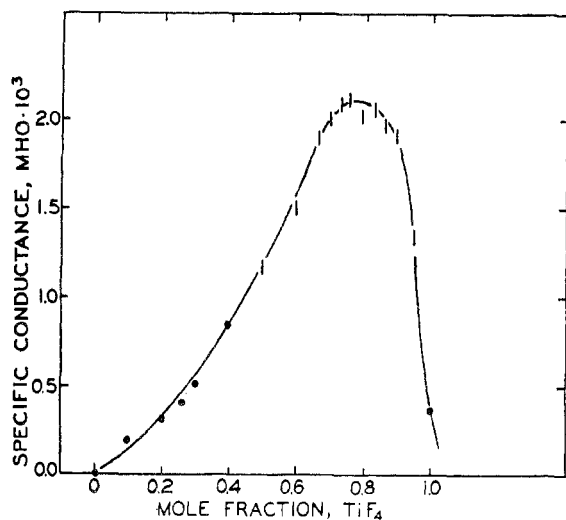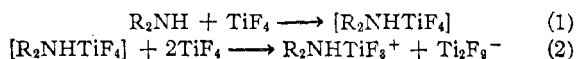
Fig. 2.—A continuous variation study for the system titanium(IV) fluoride-di-n-propylammonium hexafluorotitanate in acetone (*i.e.*, sum of TiF_4 + $(R_2NH_2^+)_2TiF_6^-$ equals 0.12 M).
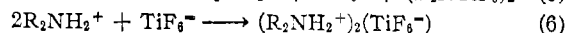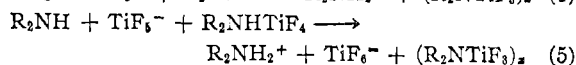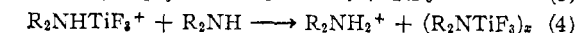
This stoichiometry is in agreement with the species found for solutions of TiF_4 dissolved in liquid HF.[10] Because of weaknesses inherent in a continuous variations study, the existence of other species of the general formula $[(TiF_4)_xF^-]_n$ cannot be ruled out by this study. At mole ratios below 0.55 TiF_4 to 0.45 TiF_6^-, solid $(R_2NH_2^+)_2TiF_6^-$ (m.p. 180–184°) is present but above this ratio all the material present is soluble. This suggests the existence of $(TiF_6^-)_n$.[11]

The above information and the conductometric titration curve eliminate several of the many reaction schemes possible for this system. The sequence of reactions numbered 1 to 6 fulfills the following requirements: (1) It correlates conductances observed in the titration with those observed in the continuous variation study; (2) it accounts for the stoichiometries at which the maxima, ammonium ion, the onset and completion of precipitation occur; and (3) it is consistent with the absence of any effect by added ammonium ion on precipitation.

$$R_2NH + TiF_4 \longrightarrow [R_2NHTiF_4] \qquad (1)$$
$$[R_2NHTiF_4] + 2TiF_4 \longrightarrow R_2NHTiF_3^+ + Ti_2F_9^- \qquad (2)$$

(10) D. A. McCaulay, W. S. Higley, and A. P. Lien, *J. Am. Chem. Soc.*, **78**, 3009 (1956).

(11) If these anions are polymeric this could simply amount to TiF_6^- fragments incorporated into a $Ti_2F_9^-$ polymer to give an average composition TiF_5^-. Other anions $[(TiF_4)_xF^-]_n$, where x is greater than 2, probably exist also. In view of the maximum conductance at $Ti_2F_9^-$ and the appearance of precipitate around TiF_6^-, our description of the conductometric titration curve will be simplified by utilizing these empirical formulas. Should the nature of the above species eventually be resolved, the explanation of the conductance curve would be essentially the same; only the description of the anions would need to be changed.
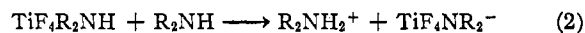
$$R_2NH + Ti_2F_9^- \longrightarrow R_2NHTiF_4 + TiF_5^- \qquad (3)$$
$$R_2NHTiF_3^+ + R_2NH \longrightarrow R_2NH_2^+ + (R_2NTiF_3)_x \qquad (4)$$
$$R_2NH + TiF_5^- + R_2NHTiF_4 \longrightarrow$$
$$R_2NH_2^+ + TiF_6^- + (R_2NTiF_3)_x \qquad (5)$$
$$2R_2NH_2^+ + TiF_6^- \longrightarrow (R_2NH_2^+)_2(TiF_6^-) \qquad (6)$$

In the above scheme the reactions have been simplified by omitting solvent participation. TiF_4 is most certainly solvated[5] and some of the anions may very well be.

The addition compound R_2NHTiF_4 is proposed as an intermediate that instantly reacts with excess TiF_4 to form $Ti_2F_9^-$ (or $(TiF_4)_2F^-)_x$. This is the essential reaction occurring up to the maximum of the conductometric titration curve. The conductance of this solution at the maximum is slightly higher than that of a solution of similar concentration of $(n\text{-}C_3H_7)_2NH_2^+$ $Ti_2F_9^-$. This may be due to the higher conductance of the R_2-$NHTiF_3^+$. The slight conductance decrease that occurs in the range amine:TiF_4 ratio 0.33–0.5 is attributed to step 3. Before step 3 is completed step 4 begins and the conductance falls while steps 3 and 4 occur simultaneously. The initial precipitate which occurs at 0.7 is $(R_2NTiF_3)_x$ and isolation of solid material at this point produces a very hygroscopic light tan material similar to the impure $(R_2NTiF_3)_x$ obtained from the product. Around 0.9 steps 3 and 4 are nearing completion and the conductivity is that expected from the continuous variation study for a solution of $(n\text{-}C_3H_7)_2NH_2^+TiF_5^-$. Further addition of amine initiates step 5 and causes precipitation of $(R_2$-$NH_2^+)_2(TiF_6^-)$. Precipitation can be detected visually and the conductance continues to drop slowly until a 1.2–1.3 mole ratio is reached (1.33 is theoretical for completion of this reaction scheme.)

The excellent agreement between the conductances measured in the continuous variations study and those obtained in the conductometric titration strongly support the existence of the anions proposed in the above reaction scheme. Solubility relationships also are very similar.

In a reaction as complex as this one many reaction sequences can be considered. Of the many schemes considered the one presented above best describes the experimental results. The conductances obtained are similar to those calculated by considering the concentration of material expected from the reaction sequence and the conductivity measured for the ion in the continuous variation study. The scheme proposed may not represent a unique solution but the data eliminate

several possibilities. For example, the following scheme is eliminated

$$R_2NH + TiF_4 \longrightarrow [TiF_4 \cdot R_2NH] \quad (1)$$
$$TiF_4R_2NH + R_2NH \longrightarrow R_2NH_2^+ + TiF_4NR_2^- \quad (2)$$
$$TiF_4NR_2^- + 2TiF_4 \longrightarrow R_2NTiF_3 + Ti_2F_9^- \quad (3)$$

Continued reaction of $Ti_2F_9^-$ as

in the proposed mechanism   (4)

This scheme can be eliminated, for completion of steps 1, 2, and 3 would produce the maxima in the conductance curve and would require 0.66

mole of base per mole of TiF_4 instead of the 0.33 mole found experimentally. Appreciable quantities of alkylammonium ion at low mole ratios also are required and this species is found to be absent.

Many other schemes can be eliminated by similar reasoning.

Oxygen Tracer Experiments on the Oxidation of Aqueous Uranium(IV) with Oxygen-Containing Oxidizing Agents[1]

BY GILBERT GORDON[2] AND HENRY TAUBE

Oxygen[18] tracer studies have been made on the oxidation of aqueous uranium(IV) with various oxygen-containing oxidizing agents. The reactions studied were the oxidation of U_{aq}^{+4} by solutions of MnO_4^-, CrO_4^-, H_2O_2, and some halogenates; solid samples of PbO_2, MnO_2, and $NaBiO_3$; and gaseous samples of O_2 and O_3. With oxygen or ozone only one of the oxygens in the UO_2^{++} product derives from the oxidizing agent. In the case of PbO_2 or MnO_2 both (very nearly) oxygens in the UO_2^{++} derive from the oxidizing agent. These results are interpreted in terms of oxygen atom transfer accompanied either by hydrolysis with solvent or by oxide ion transfer from the oxidizing agent.

This paper presents the results we have obtained measuring the extent of oxygen transferred when oxy-oxidizing agents react with U^{+4}. The results are of some special interest since they are the first of this kind to be obtained for an oxy-cation of the actinide series. The work[3-5] which has been done on the exchange between UO_2^{++} and water has prepared the way for the present study. UO_2^{++}, at least when the UO_2^+ concentration is kept low,[5] exchanges oxygen with the solvent only slowly, so that with the oxidizing agents suitably chosen meaningful tracer experiments can be done.

Experimental

The steps involved in carrying out a tracer experiment on the oxidation of uranium(IV) were: preparation of

uranium(IV) and of the 'normal' oxidizing agent in oxygen[18]-enriched water; mixing of the reagents to bring about reaction; removal of excess oxidizing or reducing agent or of substances which may interfere in the step following; precipitation of the UO_2^{++} as $(UO_2)_2Fe(CN)_6$; conversion of oxygen in the UO_2^{++} to CO_2; mass spectrometric analysis of the carbon dioxide.

Preparation of Materials.—All of the chemicals used in this work were reagent grade. Uranyl perchlorate pentahydrate was prepared from uranyl nitrate.[4] Uranium(IV) solutions were prepared by electrolytic reduction of UO_2^{++} in $HClO_4$, using a Hg cathode and Pt anode in a compartmented cell. Providing the solution was kept cold (0°), the reduction of U(VI) to U(IV) went to completion. Any U(III) formed was removed by a stream of oxygen. Oxygen only slowly oxidizes acidic solutions of uranium(IV).[6] Uranium(IV) concentrations were determined by ceric sulfate titration at 50° using ferroin as the indicator.[4] The absence of U(III) and U(VI) peaks in the spectrum of the U(IV) solution constituted the criterion for purity of the preparation.[7] The hydrogen ion concentration was determined by titration with standard NaOH after the uranium was removed with an ion-exchange resin column. Cor-

(1) Presented before the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September 1961.

(2) Department of Chemistry, University of Maryland, College Park, Maryland.

(3) H. W Crandall, *J. Chem. Phys.*, **17**, 602 (1949).

(4) G. Gordon and H. Taube, *J. Inorg. & Nuclear Chem.*, **16**, 272 (1961).

(5) G. Gordon and H. Taube, *ibid.*, **19**, 189 (1961).

(6) J. Halpern and J. G. Smith, *Can. J. Chem.*, **34**, 1419 (1956).

(7) D. Cohen and W. T. Carnall, *J. Phys. Chem.*, **64**, 1933 (1960).