of the molecular relaxation times are longer than would be expected from viscosity differences alone, but some of the times are roughly proportional to the viscosities, which may themselves be influenced by dipole–dipole interaction.

The values of the distribution coefficients show no distribution of relaxation times for the nearly spherical molecules in the pure liquid state, in agreement with previous observations[6] and an apparently considerable distribution only for the solutions of 2,2-dinitropropane in the paraffin oil and 2,2-dichloropropane in heptane. This is in accord with a previously noted tendency toward distribution in solution, possibly attributable in some cases to increased experimental error.

These results and those of the preceding paper[13] of this series point to a rough proportionality between molecular relaxation time and macroscopic viscosity when molecules of similar size and shape are compared. Extreme deviations from proportionality may occur when very different molecules are involved, as in the case of the viscous paraffin oil used as solvent.

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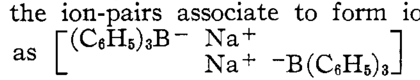
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Triarylboron Anions. I. Magnetic and Cryoscopic Studies of Monovalent Trimesitylboron Anion Solutions[1a,b]

BY TING LI CHU AND THEODORE J. WEISMANN

RECEIVED JULY 11, 1955

Trimesitylboron reacts with sodium in tetrahydrofuran forming a blue solution of the monosodium salt, NaTMB, which is monomeric in the concentration range 0.05–0.15 *M* at 25°, having one unpaired electron. Blue crystals, which are diamagnetic, separate from a tetrahydrofuran solution of NaTMB indicating the association of ion-pairs into ion clusters by coulombic forces. NaTMB is red and diamagnetic in benzene or cyclohexane solution due to polymerization, having association numbers 5.7 ± 0.4 and 5.0 ± 0.4, respectively, as determined by molecular weight measurements. NaTMB formed in ether solution is initially monomeric but gradually associates as indicated by changes in color and magnetic susceptibility. However, NaTMB is monomeric and stable in a 1:1 by weight benzene–tetrahydrofuran mixture which has the same dielectric constant as ether, demonstrating the role of solvation in stabilization of the monomer.

The reaction of the triarylborons with the alkali metals in ether solution, involving the transfer of one or two electrons from the alkali metal atoms to one molecule of the triarylboron, forming colored salts was first studied by Krause and his co-workers.[2] In a solvent of low dielectric constant, the salt exists largely in the form of ion-pairs. The monovalent triaryl-boron anion has an odd number of electrons and is isoelectronic with the corresponding triarylmethyl radical. The sodium salt of the monovalent triphenylboron anion (hereafter NaTPB) was found to be diamagnetic in tetrahydrofuran solution by magnetic susceptibility and paramagnetic resonance absorption measurements, and exhibited no resemblance to triphenylmethyl in spectroscopic behavior.[3] In the absence of molecular weight data on NaTPB, it is assumed that the ion-pairs associate to form ion clusters such as  $\begin{bmatrix} (C_6H_5)_3B^- & Na^+ & \\ & Na^+ & {}^-B(C_6H_5)_3 \end{bmatrix}$ which are diamagnetic. Since the units are held together by electrostatic forces, the dielectric constant of the medium is an important factor in determining the extent of the association; the higher the dielectric constant, the smaller the electrostatic attraction between the ion-pairs and hence the greater the probability of the existence of NaTPB in the monomeric form. However, NaTPB is unstable in such a medium. On the other hand, the importance of the steric effect of ring substituents on the homolytic dissociation of the hexaarylethanes has been well established and would lead one to expect that the replacement of the phenyl groups of NaTPB by bulky aromatic groups may cause the ion clusters to dissociate with the formation of free radicals. In this and subsequent papers, some physico-chemical properties of a series of triarylboron anions containing large aromatic groups will be described.

Trimesitylboron (TMB) reacts readily with sodium in tetrahydrofuran, forming a dark blue solution of the monosodium salt, NaTMB. With 40% sodium amalgam, the reaction proceeds quantitatively to completion within a few minutes. It is probable that the solvation energy of the sodium ion by tetrahydrofuran and the moderate polarity of the medium (dielectric constant 7.39 at 25°), favor this electron transfer process. Unlike the sodium salt of the monovalent tri-α-naphthylboron anion,[4] NaTMB is resistant to further reaction with sodium in solutions of concentration greater than 10^{-4} *M*. This behavior simplifies considerably the experimental investigation of NaTMB. NaTMB is reactive toward oxygen. In the oxygen absorption experiment, 0.7198 mmole of NaTMB in tetrahydrofuran solution absorbed 0.7275 mmole of oxygen at an initial oxygen pressure of 337 mm., yielding a light yellow solution from which TMB was recovered quantitatively after hydrolysis. In another experiment, the oxygenated product, obtained from 0.7186 mmole of NaTMB under similar conditions, regenerated Na-

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(1a) Presented before the Division of Physical and Inorganic Chemistry at the 128th A.C.S. Meeting, Minneapolis, Minn., September, 1955. (b) This paper represents a part of the dissertation to be submitted by T. J. Weismann to the Graduate School of Duquesne University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) E. Krause and H. Polack, *Ber.*, **59**, 777 (1926); **61**, 271 (1928); E. Krause and P. Nobbe, *ibid.*, **63**, 934 (1930); **64**, 2112 (1931).

(3) T. L. Chu, THIS JOURNAL, **75**, 1730 (1953).

(4) H. E. Bent and M. Dorfman, *ibid.*, **54**, 2132 (1932).

TMB quantitatively on treating with sodium, and, on hydrolysis, liberated 1.417 mmoles of sodium hydroxide. These experiments indicate that the monovalent TMB anion does not form a peroxide and that NaTMB probably forms sodium superoxide and TMB with oxygen according to the equation

$$\mathrm{NaTMB} + O_2 = \mathrm{NaO_2} + \mathrm{TMB}$$

The magnetic susceptibility of NaTMB in tetrahydrofuran solution was measured at 25° at various concentrations ranging from 0.05 to 0.15 *M;* six determinations yielding an average value of $(1210 \pm 30) \times 10^{-6}$ c.g.s. units. Assuming that the orbital moment makes no contribution and that Curie's law and Wiedemann's additivity rule are obeyed, NaTMB is monomeric in the concentration range studied, having one unpaired electron. NaTMB in tetrahydrofuran solution is stable over a period of several days as is indicated by the reproducibility of its magnetic susceptibility. In relatively concentrated solutions of NaTMB, say 0.15 *M*, blue crystals separate from the solution on cooling or prolonged standing and the mixture becomes almost diamagnetic. The blue crystals dissolve on gentle warming with quantitative restoration of the original paramagnetism. These crystals are most likely ion clusters (solvated to a lesser extent than the ion-pairs), as mentioned previously for NaTPB, formed by the association of NaTMB ion-pairs due to coulombic forces. The ion clusters dissociate reversibly in tetrahydrofuran solution.

In benzene or cyclohexane solution, the reaction between TMB and sodium takes place extremely slowly and only to a slight extent, as expected. These solutions are dark red and diamagnetic. The evaporation of the tetrahydrofuran solution of NaTMB and prolonged pumping of the residue yields a dark red solid. This red solid also forms red solutions in benzene, cyclohexane and tetrahydrofuran which are diamagnetic within experimental error. The hydrolysis of these solutions regenerates TMB quantitatively. On comparing the absorption spectra (Fig. 1), it is obvious that the solution of dried NaTMB (obtained by preparation in tetrahydrofuran and evaporation of the solvent) in benzene or tetrahydrofuran contains the same light absorbing species as that obtained by direct reaction of sodium with TMB in benzene solution. In non-polar solvents, the interaction of ions or ion-pairs with solvent molecules is negligible and the interaction between ions or ion-pairs under the influence of coulombic forces is greatly enhanced. In this investigation, the red species appeared likely to be polymeric and a molecular weight determination seemed necessary for confirmation. Since the reaction between sodium and TMB is slow and incomplete in benzene or cyclohexane, the red solid obtained from the tetrahydrofuran solution of NaTMB, after thorough drying, was dissolved in benzene or cyclohexane and the solution used for the molecular weight determination by a vacuum freezing point depression method. 1.016 mmoles of the red solid in 13.15 g. of benzene gave a freezing point depression of 0.07 ± 0.004°, giving an apparent molecular weight of 5.7 ± 0.4 times the formula weight of NaTMB. The red solid is only partially soluble in cyclohexane; 0.3236 mmole in 12.77 g. of cyclohexane gave a freezing point depression of 0.10 ± 0.004°, yielding an apparent molecular weight 5.07 ± 0.4 times the formula weight of NaTMB. It is likely that the red solution contains a mixture of polymers such as the tetramer, hexamer, octamer, etc.; the polymers of higher molecular weight are less soluble in cyclohexane than in benzene. They do not redissociate into monomeric NaTMB in tetrahydrofuran, presumably from insufficient solvation energy to overcome the coulombic attractions operating in the polymer.

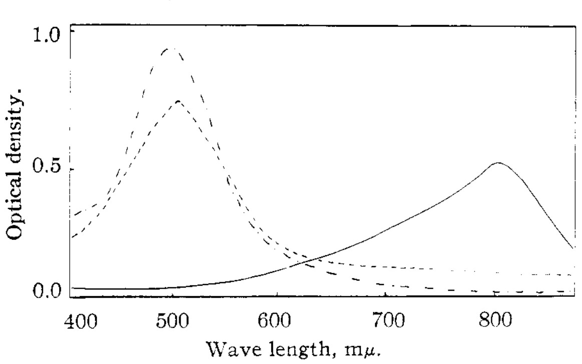

Fig. 1.—Absorption spectra in visible region of: ——, NaTMB in tetrahydrofuran; – – – – –, NaTMB polymer (prepared in benzene) in benzene; —·—·—, NaTMB polymer (prepared in tetrahydrofuran) in benzene. (The spectrum of NaTMB polymer (prepared in tetrahydrofuran) in cyclohexane is identical with —·—·—·).

In ether solution, the reaction between TMB and sodium also takes place readily, yielding initially a dark blue solution which gradually turns to purple and then red. In a typical run, a 0.09554 *M* solution of NaTMB in ether solution has a molar susceptibility of $(1240 \pm 20) \times 10^{-6}$ c.g.s. units measured immediately after preparation of the sample, indicating the monomeric nature of NaTMB in ether. Associated with the color change of the solution on standing is a parallel decrease in molar susceptibility to $(1100 \pm 20) \times 10^{-6}$ after 80 minutes, $(812 \pm 30) \times 10^{-6}$ after 220 minutes and to $(105 \pm 30) \times 10^{-6}$ after two days, when the solution becomes quite red. Evidently polymerization sets in when the ether solution of NaTMB is allowed to stand. It has been mentioned that the stability of monomeric NaTMB is determined mainly by the dielectric constant of the medium as well as by the solvation energy of the sodium ion by the solvent molecules. The dielectric constant of ether, 4.35 at 25°, is lower than that of tetrahydrofuran, favoring the association process. Since the solvation of the sodium ion by ether is electrostatic in character and the ethyl group is sterically rather bulky, there is a reduction in solvation energy and stability of monomeric NaTMB. In order to determine the relative importance of these two factors, several tetrahydrofuran solutions of NaTMB were made and various amounts of benzene added. The magnetic susceptibility of these solutions was measured and their stabilities studied. These magnetic susceptibilities, together with the dielectric constants of the solvent mixtures are summarized in Table I.

TABLE I

MOLAR SUSCEPTIBILITIES OF NaTMB IN BENZENE–TETRAHYDROFURAN MIXTURES AND THE DIELECTRIC CONSTANTS OF THE SOLVENTS

Run	Concn. of NaTMB, *M*	Wt. fraction of C_6H_6 in solvent mixture	Dielectric constant of solvent at 25° [a]	Molar susceptibility $\times 10^6$ at 25 ± 1°
1	0.07447	0.40	5.05	1260 ± 20
2	.03563	.50	4.35	1200 ± 30
3	.04694	.70	3.65	1080 ± 30
4	.05703	.86	2.88	420 ± 20

[a] T. L. Chu, N. C. Li and T. J. Weismann, unpublished results.

In the first two runs, no color change was observed when benzene was added to the tetrahydrofuran solution of NaTMB and NaTMB remained monomeric as indicated by the susceptibility data. These solutions were as stable as those in tetrahydrofuran. Although no color change was noticeable in the third run, the molar susceptibility of NaTMB is slightly lower than that corresponding to one unpaired electron, indicating partial association of the ion-pairs. A solvent with high weight fraction of benzene was used in the fourth run; the tetrahydrofuran solution of NaTMB turned red within a short time after the addition of benzene and the susceptibility was measured after the association had reached equilibrium. In the second run, where the solvent mixture has the same dielectric constant as ether, NaTMB undergoes no appreciable association, whereas considerable association takes place in the ether solution. It is thus clear that in using ether as solvent, solvation is the predominating factor in enhancing the association of NaTMB.

Experimental

Materials.—Trimesitylboron was prepared by the reaction of mesitylmagnesium bromide with boron trifluoride according to the procedure of Dodson.[5] The product was purified by sublimation, giving a white crystalline product with melting point 190.5 to 191.5°.

Mallinckrodt A.R. grade benzene and ether and Fisher Reagent grade cyclohexane were dried over sodium–potassium alloy and used without further purification. Eastman Kodak Co. tetrahydrofuran was fractionated, b.p. 65–66°, and dried over sodium–potassium alloy.

Reaction of TMB with Sodium or Sodium Amalgam.—A weighed amount of TMB in tetrahydrofuran or other solvent containing excess sodium was sealed off in a tube under vacuum. After prolonged shaking, the solution was hydrolyzed and titrated with standard hydrochloric acid using a Beckman Model G *p*H meter. The composition of the reaction product was obtained by comparison of the weight of TMB originally used and the amount of alkali liberated on hydrolysis. In a typical run, 0.1097 g. (0.2981 mmole) of TMB in 10 ml. of tetrahydrofuran, after reaction with sodium and hydrolysis, yielded 0.2989 mmole of sodium hydroxide with quantitative recovery of TMB.

When 40% sodium amalgam was used instead of sodium, the reaction was carried out in the following manner. A weighed amount of TMB was placed in a reaction flask of approximately 50-ml. capacity, the neck of which was connected to another flask of similar capacity through a fritted glass disk. After thorough evacuation of the apparatus, tetrahydrofuran was distilled into the reaction flask and excess 40% sodium amalgam, prepared in a vacuum dumper, introduced. The reaction flask was sealed off from the vacuum line, the contents shaken for a few minutes and filtered into the second flask. The reaction flask was thoroughly rinsed by repeatedly distilling solvent back from the second flask, and the contents in the latter hydrolyzed and titrated with standard hydrochloric acid. The results showed a 1:1 mole ratio of TMB/NaOH, indicating the completeness of the reaction between sodium amalgam and TMB in tetrahydrofuran in a short time interval. In benzene solution, however, the reaction between sodium amalgam and TMB proceeded only to a limited extent even after prolonged shaking. For instance, 0.1971 g. (0.5351 mmole) of TMB, after two days treatment with excess 40% sodium amalgam and hydrolysis, yielded only 0.0866 mmole of sodium hydroxide.

Magnetic Susceptibility Measurements.—The magnetic susceptibility of solutions of NaTMB was measured by the Gouy method. The apparatus, consisting of a General Electric Isthmus Electromagnet and an Ainsworth microbalance, has already been described.[6] A double ended compensation tube, similar to the one used by Freed and Kasper,[7] was calibrated and used for all susceptibility measurements, which were made at 25 ± 1°. The tube was calibrated in terms of $A(H_1^2 - H_2^2)/g$ by measuring Δw, the apparent change in weight of the sample tube on application of a magnetic field of definite strength, of (1) the tube with both compartments evacuated and (2) the tube with the lower compartment evacuated and the upper compartment filled to a definite height with distilled water, outgassed and sealed off under vacuum. The difference between these two measurements is related to the volume susceptibility of water taken as -0.720×10^{-6} c.g.s. unit at 25°.

The susceptibility of NaTMB in tetrahydrofuran or ether was measured in the following manner. The lower compartment of the sample tube was filled with the solvent and sealed off under vacuum; the upper portion of the tube was outfitted with a ground joint and constricted approximately 20 cm. from the partition. A weighed amount of the purified TMB was placed in the tube and a piece of sodium above the constriction. The tube was attached to a vacuum line and thoroughly evacuated. A measured amount of pre-dried solvent was distilled in from a graduated pipet so that the height of the column of solution at room temperature was the same as that of the water used in calibration. The sodium was melted carefully and allowed to pass through the constriction (surface impurities of the sodium remained above the latter) to a position on the side of the tube slightly above the solution. The tube was sealed off at the constriction while under vacuum. Δw was measured before and after the reaction of the solution with sodium. If it is assumed that the diamagnetic contribution of the TMB anion does not differ appreciably from that of TMB, the net difference in the two measurements is proportional to the paramagnetic susceptibility of the anion as well as the diamagnetic susceptibility of the sodium ion, which is negligibly small. The paramagnetic volume susceptibilities of the anion solutions were obtained by the relation

$$\kappa = -0.720 \times 10^{-6} \times \frac{\Delta W_{\text{NaTMB soln.}-\text{solvent}} - \Delta W_{\text{TMB soln.}-\text{solvent}}}{\Delta W_{\text{H}_2\text{O}-\text{Vac.}} - \Delta W_{\text{Vac.}-\text{Vac.}}}$$

and the molar susceptibility of NaTMB was calculated according to Wiedemann's additivity rule by using the expression $\chi_n = \kappa W/nd$, where n is the number of moles of NaTMB present in a solution of weight w and d is the density of the solution. The density of the solution was determined under vacuum by means of an expansion pycnometer of about 5-ml. capacity with an expansion neck approximately 10 cm. long.

When benzene or cyclohexane was used as solvent, the apparatus was similar to that described under the "Reaction of TMB with Sodium Amalgam," excepting that the hydrolysis vessel was replaced by a calibrated sample tube. NaTMB, in tetrahydrofuran, was prepared in the reaction flask from a weighed amount of TMB and sodium amalgam, and the solvent evaporated. After thorough evacuation, a measured amount of benzene or cyclohexane was distilled into the flask and the contents of the latter filtered into the calibrated sample tube, which was sealed off after thorough rinsing of the reaction flask to insure complete transfer.

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(5) V. H. Dodson, Ph.D. Thesis, Purdue University, 1952.

(6) T. L. Chu and S. C. Yu, THIS JOURNAL, **76**, 3367 (1954).

(7) S. Freed and C. Kasper, *ibid.*, **36**, 1002 (1930).

The measurement of ΔW of this sample yielded

$$\Delta W_{\text{NaTMB soln.}-\text{solvent}}.$$

$\Delta W_{\text{TMB soln.}-\text{solvent}}$ was obtained by repeating the measurement on a TMB solution containing the same amount of TMB as that used in the preparation of NaTMB.

For solutions of NaTMB in benzene–tetrahydrofuran mixtures, a measured amount of tetrahydrofuran was used for the reaction between TMB and sodium amalgam. Following completion of the reaction, an appropriate amount of benzene was introduced and the solution filtered into the calibrated sample tube. $\Delta W_{\text{TMB soln.}-\text{solvent}}$ was measured as described for using only benzene as solvent.

Molecular Weight Determination.—The apparatus used in the molecular weight determination by the freezing point depression method was as follows. Two dumpers, A and C, were connected in series and the latter attached by means of a T-joint to a reaction vessel E, with a constriction D. The dumper A was provided with a sidearm B, and dumper C with a fritted glass disk. A freezing point tube F (30 mm. diameter and 20 cm. length) containing a Beckmann thermometer G, and a stirrer H, was connected to reaction vessel E at a position slightly below the constriction D. The stirrer was made of a thin Pyrex rod, the upper portion of which was attached to a piece of Pyrex tubing containing a small iron bar. Stirring was effected by applying an intermittent magnetic field outside the tube F. In a typical run, about 2 g. of mercury was placed in dumper A and 2 g. of freshly cut sodium above the constriction in the sidearm B. About 0.5 g. of TMB was introduced into dumper C and the apparatus assembled and attached to the vacuum line. After thorough evacuation, the sodium in sidearm B was melted and allowed to pass through the constriction into dumper A where it combined with mercury to form the amalgam. Predried tetrahydrofuran was distilled into dumper C and the amalgam introduced from A. After shaking for about one hour, the solvent was evaporated and the residue dried by pumping for several hours. A measured amount of benzene or cyclohexane was introduced by distillation from a 25-ml. graduated pipet to dissolve the residue. The red solution was filtered through the sintered glass into the vessel E and the latter sealed off at D. The solvent in E was next distilled into F, which was placed into the Beckmann molecular weight apparatus and the freezing point of the solvent determined. The solid in E was put into solution by transferring the solvent to the vessel E and the freezing point of the solution determined in F.

The molal freezing point constants of benzene and cyclohexane were also determined using purified triphenylmethane. Values of 5.11 and 20.0, respectively, in agreement with the generally accepted values, were obtained.

Oxygen Absorption Measurements on NaTMB.—The apparatus used to determine the oxygen uptake of NaTMB in tetrahydrofuran solution was similar to that described under "Molecular Weight Determination" with the following modification. The freezing point apparatus F was replaced by an open-end mercury manometer equipped with a reservoir of approximately 100 ml. and a stopcock which was attached to the sidearm of E by means of a ball joint.

In performing the experiment, the system was evacuated and dry oxygen introduced through the vacuum line. The manometer stopcock was then closed, and the pressure of oxygen in the manometer and reservoir recorded. The volume occupied by the oxygen was later determined by calibration of the manometer and reservoir with water. The rest of the system, comprised of units A, B, C and E, was thoroughly evacuated and NaTMB in tetrahydrofuran prepared in C using sodium amalgam, by the method previously described. The blue NaTMB solution was transferred quantitatively to E and the latter sealed off at D. E was immersed in a constant temperature bath at 25° for 0.5 hour, the stopcock leading to the reservoir of oxygen opened, and the solution in E gently agitated. After one minute the solution had lost its blue color, turning yellow. The final pressure of the system, which was constant over a period of several hours, was recorded. The volume of the reaction vessel E was determined by calibration with water. In order to account for the amount of oxygen absorbed by the tetrahydrofuran and the contribution of tetrahydrofuran vapor to the final pressure, a second run was made using tetrahydrofuran alone, the volume of which corresponded to that of the solution used in the previous run. The initial and final pressures and volumes of oxygen obtained from these two runs, permitted calculation of the amount of oxygen absorbed by NaTMB.

Acknowledgment.—We wish to thank the Research Corporation for the Frederick Gardner Cottrell grants which enabled us to carry out this work.

Pittsburgh, Pa.

[Contribution from the Oak Ridge National Laboratory, Chemistry Division]

Hydrolytic Behavior of Metal Ions. V. Ultracentrifugation of Hafnium(IV)[1,2]

By James S. Johnson, Kurt A. Kraus and Robert W. Holmberg

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By equilibrium ultracentrifugation hafnium(IV) was found to form a low molecular weight hydrolytic polymer (or polymers) in *ca.* one molar acid solutions with an approximate degree of polymerization N of 3 or 4 (trimer or tetramer). Studies were carried out as a function of initial Hf(IV) concentration (0.008 to 0.1 M), of supporting electrolyte concentration (1 to 2 M), of type of supporting electrolyte (HCl, and HCl with LiCl, NaCl and CsCl), of acidity (0.5 to 2 M H_3O^+) and of temperature (*ca.* 1 to 30°). By combination of these experiments simultaneous evaluation of N and of the charge z of the polymeric ion was attempted.

The hydrolytic behavior of Hf(IV) has received very little attention although generally the assumption is made that the hydrolysis of Hf(IV), as well as its chemistry in general, is very similar to that of Zr(IV), which has been studied rather extensively.[3] Since Zr(IV) was found to polymerize in acidic solutions, polymerization of Hf(IV) was also expected. Although the results regarding polymerization of Zr(IV) have been somewhat contradictory,[3] there appears now to be considerable evidence that low molecular weight polymers are formed in solutions of acidity approximately 1 M. The present centrifugation results indicate that Hf(IV) also forms low molecular weight polymers under these conditions; further, Hf(IV) is either predominantly monodisperse (only one principal polymeric aggregate), or

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(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper, K. A. Kraus and F. Nelson, This Journal, **77**, 3721 (1955).

(3) See for example the following papers, where further references are given: (a) G. Jander and K. F. Jahr, *Kolloid-Beih.*, **43**, 295 (1935); (b) R. E. Connick and W. H. Reas, This Journal, **73**, 1171 (1951); (c) B. A. Lister and L. A. McDonald, *J. Chem. Soc.*, 4315 (1952); (d) K. A. Kraus and J. S. Johnson, This Journal, **75**, 5769 (1953); (e) W. B. Blumenthal, *Ind. Eng. Chem.*, **46**, 528 (1954); (f) in a recent paper E. M. Larsen and A. M. Gammill (This Journal, **72**, 3615 (1950)) point out that Hf(IV) precipitates less readily than Zr(IV). However, the work reported here was carried out in strongly acidic solutions where the observations of Larsen and Gammill do not necessarily apply.