[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Complex Compounds of Zirconium(IV) and Hafnium(IV) with Ethylenediaminetetraacetic Acid[1]

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Zirconium(IV) and hafnium(IV) perchlorate solutions were stabilized toward precipitation with sodium hydroxide by reaction with salts of ethylenediaminetetraacetic acid. Reaction probably proceeded through addition of reagent to hydrolytic polymers of sufficient complexity that essential equivalence of individual units could be assumed. In competitive reaction experiments the stability constant of the 1:1 zirconium(IV) complex was found to be 12.5 times that of the copper(II) chelate at 25°. On the basis of relative ease of hydrolysis, the stability constant of the hafnium(IV) complex was estimated to be approximately one-half that of the zirconium compound. The zirconium(IV) complex compound isolated from aqueous solution at *p*H 6 was found to contain 1.1 ethylenediaminetetraacetate groups per zirconium atom. The precipitate obtained at both extremes of the *p*H range of stability was found to be essentially hydrous zirconium oxide. The over-all behavior of hafnium(IV) was sufficiently similar that isolation and identification of hafnium(IV) compounds was not considered to be necessary.

Ions of zirconium(IV) and hafnium(IV) have been shown to be extensively hydrolyzed in aqueous solution.[3–6] Measurements of the equilibrium *p*H of aqueous solutions of $ZrOCl_2$ from 0.0001 to 0.01 M indicate there are about three hydroxyl ions per zirconium in such solutions.[5] Hydrolysis is significantly great even in 1 to 2 molar perchloric acid solutions, the average zirconium species having a charge of +3 to +4 in 3×10^{-4} M solution.[6]

At zirconium concentrations greater than 2×10^{-4} M in 1 M perchloric acid and at lower concentrations in less acid solutions, polymerization has been found to be important.[3,4,7,8] Although there seems to be general agreement that polymerization does occur, there is some argument as to whether the polymers formed are monodisperse or polydisperse[7,8] in the more acid solutions. On the basis of measurements of extraction of zirconium chelate of thenoyltrifluoroacetone into benzene, Connick and Reas have reported the existence of the dimer and higher polymers.[7] Kraus and Johnson favor the existence of the trimer as the single polymeric species present in 0.5 to 2.0 M acid solutions as a result of ultracentrifugation studies.[9,10] As conditions favoring precipitation of hydrous zirconium oxide are approached, polydispersity certainly appears as a precursor to precipitation.

In the absence of complexing agents precipitation begins at *p*H 3 and is essentially complete at *p*H 5 for 10^{-3} M solutions of both zirconium(IV) and hafnium(IV). Both form series of fluoride complexes,[11] which are quite stable in aqueous solution[6] and precipitation occurs at somewhat higher *p*H values in fluoride solutions. Precipitation of the hydrous oxide of zirconium from approximately 4% oxalate and 8% citrate solutions, containing 7.5 mmoles zirconium(IV) per liter, occurred at *p*H 8–10 and 10–12, respectively.[12] In solutions of substances capable of forming well-defined complex ions or chelate species, it is presumed that stability of the compound formed prevents complete hydrolysis and precipitation does not occur until high concentrations of hydroxide ions are provided. The structures of the complex species formed are not known.

It has been observed in this Laboratory that precipitation of zirconium(IV) and hafnium(IV) may be prevented at *p*H values up to 9–10 by addition of salts of ethylenediaminetetraacetic acid. The present research was undertaken to characterize the species formed in such solutions. There was particular interest in possible direct participation of polymeric, hydrolyzed species with formation of poly-chelate structures.

Experimental

Ethylenediaminetetraacetic Acid.—Solid ethylenediaminetetraacetic acid (Bersworth Chemical Company) was suspended in distilled water and standard sodium hydroxide solution was added in exactly the amount calculated to form disodium ethylenediaminetetraacetate. Evaporation of the solution caused precipitation of a white crystalline substance whose nitrogen content was that calculated for the tetrahydrate of the disodium salt. Subsequent solutions of the reagent were prepared by dissolving appropriate quantities of this material in water.

Zirconium(IV) Solutions.—Zirconyl nitrate (Amend Drug and Chemical Co.) was weighed out and treated with a mixture of nitric and perchloric acids. The mixture was heated with an infrared heat lamp until dense white fumes (perchloric acid) were evolved, and the mixture was evaporated to small volume. More perchloric acid was added and the solution was fumed to dryness. The crystalline residue was washed carefully and quickly with two small portions of water. The material was then dissolved in one molar perchloric acid solution for further use.

A sample of the crystalline material was dried under high vacuum and analyzed for both zirconium and perchlorate. The former was precipitated as the hydrous oxide with ammonium hydroxide, converted to the dioxide by high temperature ignition, and weighed. Perchlorate was analyzed for by reduction to chloride with titanium(III) sulfate in the presence of iron(II) sulfate and subsequent determination of chloride titrimetrically.[13] Results were as follows:

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[1] Taken from a dissertation presented to the faculty of the Graduate School of the University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Deceased August, 1954.

[3] M. Adolf and W. Pauli, *Kolloid-Z.*, **29**, 173 (1921).

[4] G. Jander and K. F. Jahr, *Kolloid-Beihefte*, **43**, 295 (1935).

[5] A. W. Laubengayer and R. B. Eaton, THIS JOURNAL, **62**, 2704 (1940).

[6] R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).

[7] R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).

[8] B. A. Lister and L. A. McDonald, *J. Chem. Soc.*, 5315 (1952).

[9] K. A. Kraus and J. S. Johnson, THIS JOURNAL, **75**, 5769 (1953).

[10] J. S. Johnson and K. A. Kraus, private communication, to be published.

[11] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, Longmans, Green and Co., New York, N. Y., 1927, p. 137, 171.

[12] M. Haissinsky and Yang Jeng-Tsang, *Anal. Chem. Acta*, **3**, 422 (1949).

[13] Pennsylvania Salt Manufacturing Co., Technical Report to the Office of Naval Research (Contract Nonr-372(00)), February, 1951.

Anal. Calcd. for $ZrO(ClO_4)_2 \cdot 8H_2O$: Zr, 20.3; ClO_4^-, 44.3. Found: Zr, 20.6; ClO_4^-, 46.0.

Hafnium(IV) Solutions.—Hafnium(IV) dioxide (A. D. Mackay, Inc.) was fused with sodium hydrogen sulfate in a platinum crucible. The cooled melt was dissolved in water and hafnium was precipitated as the hydrous oxide upon addition of ammonium hydroxide. The freshly precipitated oxide was dissolved in perchloric acid and fumed to dryness several times. After cautious washing with water the crystalline perchlorate was dissolved in one molar perchloric acid solution. The resulting solution was reasonably stable, but turbidity appeared upon several months standing. It was never possible to prepare a solution having stability toward hydrolysis comparable to that of the zirconium(IV) perchlorate solutions prepared from the nitrate.

Potentiometric Titrations.—Measurements were made using a line operated Beckman Model H-2 *p*H meter. A standard, all-purpose glass electrode was used for measuring *p*H values less than 8; a special blue-glass electrode, for higher values. Beckman *p*H 7 and *p*H 10 buffers were used for standardization of the instrument. Titrations were carried out in a 5-necked, round-bottom flask, which was thermostated at 25 ± 0.5°. One neck of the flask was used for introduction of a mercury-seal stirrer; one, for nitrogen input; two, for measurement electrodes; one, for addition of reagent. Nitrogen was passed through the solution in order to provide a carbon dioxide-free atmosphere and to stir the solution. In all experiments reported the titrant was approximately 0.01 *N* standardized sodium hydroxide or perchloric acid solution. Titrant was added in increments with calibrated micro-pipets. After addition of each increment the solution was allowed to attain constant *p*H before addition of more titrant. In some cases solutions were allowed to stand for 24 hours; in others, a steady *p*H was reached in 5 minutes. In all experiments the ionic strength was maintained constant at 0.1 with sodium perchlorate.

Spectrophotometric Measurements.—A Model DU Beckman Spectrophotometer was used in absorption spectral measurements. The instrument was operated at constant sensitivity. Cells were Corex and provided a 5 cm. light path.

Results

Potentiometric Titrations.—Titration experiments were done using solutions of the free chelating agent, zirconyl and hafnyl perchlorates, and mixtures of the salts and chelating agent. Stable solutions of zirconium(IV) and hafnium(IV) were obtained in the *p*H range 3–9 in the presence of at least equimolar concentrations of ethylenediaminetetraacetate. Precipitation occurred at both extremes and the precipitate formed in each case was found not to contain nitrogen, carbon or perchlorate. Once precipitated, zirconium(IV) and hafnium(IV) hydrous oxides could not be dissolved in solutions of the chelating agent in a measurable time. Accordingly, the complex compounds were formed at *p*H 6 by addition of zirconyl or hafnyl perchlorates to solutions of the chelating agent at the desired concentration and *p*H. During addition of the salt solutions, which were initially 1 *M* in perchloric acid, *p*H was maintained constant by simultaneous addition of dilute sodium hydroxide solution. Titrations were then carried out using sodium hydroxide or perchloric acid solutions.

Both zirconyl and hafnyl perchlorates exhibited titration curves typical of a strong acid. Precipitation occurred upon addition of the first portions of base and continued until the end-point was reached at two equivalents of base added. The titration curve obtained for ethylenediaminetetraacetic acid corresponded very closely to that reported in the literature,[14] with end-points at two and at three equivalents of added base. Titration of equimolar mixtures of zirconyl or hafnyl perchlorates and chelating agent gave results similar to those from titration of the free chelating agent, but with the curves shifted in the direction of larger titrant volumes. In each case two end-points were observed, as for the free acid, at *p*H 4–5 and at *p*H 7–8, while precipitation occurred at *p*H 9–10. For comparison, the curve obtained for copper(II) chelate with ethylenediaminetetraacetic acid was similar to that of a strong acid with a single end-point at four equivalents of base added.

The zirconyl and hafnyl complex titration curves may best be interpreted in terms of the behavior of free acid. Differential curves are given in Fig. 1, in which the difference between the number of equivalents of base required to achieve a given *p*H in ethylenediaminetetraacetic acid solutions in the presence and absence of metal ions was plotted against *p*H. If it is assumed that two acetate groups were associated with metal ion in each complex and that the other two were virtually unaffected, then the number of equivalents of base represents the number of hydroxide groups which became associated with the metal ions (hydroxyl number minus two, since the metal ions were in the zirconyl and hafnyl forms already). On the low *p*H side, precipitation occurred at hydroxyl number 3, and on the high *p*H side, at 4. The hydroxyl number of the stable form at *p*H 4 was 2.60, rising to 2.85 at *p*H 6, and remaining constant at that value to *p*H 8.4.

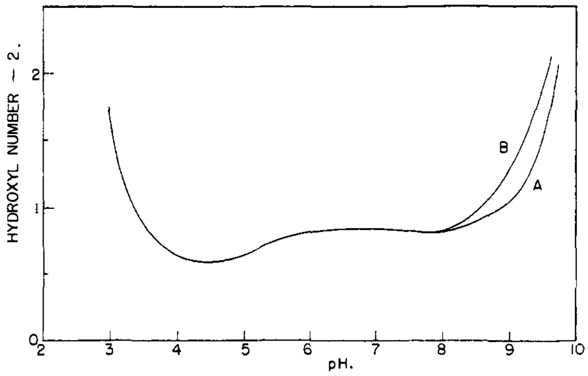

Fig. 1.—Differential titration curves: A, zirconium(IV) complex; B, hafnium(IV) complex.

Titration experiments were also done at several higher concentrations of ethylenediaminetetraacetic acid. In each case the differential curves obtained were essentially identical with those of Fig. 1. With increasing concentration of reagent, precision of the difference measurements decreased so that those presented for the equimolar solutions represent the most precise data.

The hydrolytic behavior of hafnium(IV) complex and zirconium(IV) complex differed somewhat in the *p*H region 8–10. The *p*H for half-reaction was 0.3 higher for the zirconium compound, suggesting that the reaction constant in that case was a factor of 2 higher. The reaction constant in each case included the hydrolysis constant for the metal ion and the stability constant of the complex compounds formed with each.

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[14] *Cf.* A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 537.

Zirconium(IV) complex was isolated from aqueous solution containing an excess of ethylenediaminetetraacetate at *p*H 6. The material was precipitated upon evaporation of the solution and was purified by recrystallization from water. The product obtained was a white crystalline material which decomposed at high temperature to form zirconium(IV) oxide. Analysis for nitrogen by the micro Dumas method gave 3.90% nitrogen. Zirconium concentration was 11.54%. The atom ratio thus found was 2.20 N/Zr.

Spectrophotometric Measurements.—Complex compounds of both zirconium(IV) and hafnium(IV) with ethylenediaminetetraacetate were colorless and their ultraviolet absorption spectra differed little from those of the non-complexed materials, so that direct spectral absorption methods were not useful in their study. It was possible, however, to use spectrophotometric methods in competitive experiments to determine the stability constant for zirconium(IV) complex. The copper(II) chelate with ethylenediaminetetraacetate is an extremely stable substance which absorbs light in the visible region to a much greater extent than does the copper(II) ion. Relative concentrations of the two forms may be established quite easily if the total copper concentration and the relative absorbancy of the solution is known.

In these experiments electrolytic copper metal was dissolved in nitric acid and the resulting solution was twice fumed to dryness with perchloric acid. Copper(II) perchlorate was then dissolved in 0.01 *M* perchloric acid, 0.1 *M* perchlorate solution to the extent of 10^{-3} mole per liter. Ethylenediaminetetraacetic acid was added to aliquots of that solution in amounts varying from 10^{-4} to 10^{-3} mole per liter. On the assumption that all of the added chelating agent reacted with copper(II), the molar absorbance was calculated from the experimental data and was found to be constant in the concentration range used. Absorbances of copper(II) and copper(II) chelate were additive, so that concentrations of both could be determined from optical density data at a given total copper concentration. The complex constant for zirconium(IV) was obtained from data on solutions containing 10^{-3} *M* copper(II) chelate and which varied from 10^{-4} to 10^{-3} *M* in zirconium(IV). Those data are given in Table I. The range of acidity in which it was possible to work without precipitation of some component was very narrow. For that reason measurements were made only at *p*H 2 as described in the preceding discussion.

Table I

Competitive Reaction Data

(10^{-2} *M* $HClO_4$, 10^{-3} *M* $Cu(ClO_4)_2$, 10^{-3} *M* ethylenediaminetetraacetic acid.)

	Concn. ($M \times 10^4$)				
	Cu(II)		Zr(IV)		
Total Zr(IV)	Chelate	Ion	Complex	Ion	*Q*
3.11	7.09	2.95	3.01	0.10	12.5
4.18	5.28	4.76	4.82	.36	12.0
6.25	3.74	6.30	6.36	.89	12.1
8.29	3.16	6.93	6.99	1.30	11.8
9.62	2.48	7.55	7.72	1.90	13.8
10.36	1.67	8.37	8.43	1.93	21.9

It may be calculated from the data of Table I that the ratio of complexed to non-complexed zirconium(IV) was directly proportional to the ratio of chelated to non-chelated copper(II). The direct proportionality constant, *Q*, is given in the last column of Table I. Hydrogen ion dependence could not be determined because of the narrow range of acidities available for experimentation. The results obtained could have been attributable to equilibrium between monomeric species of both copper(II) and zirconium(IV) or, alternatively, between polymeric species having sufficiently high molecular weight that individual polymer units did not display widely different reaction characteristics. The former assumption was not compatible with the previously reported behavior of zirconium(IV). The latter could have applied as a result of further polymerization of acid species of zirconium(IV) upon addition to solution at *p*H 2, if the assumption were made that complexing did not interfere with the process up to a certain point, that point being short of the formation of perceptible colloidal particles. That point of view was considered to be most probable and the formal treatment of data was carried out in the following manner.

An approach similar to that involved in the development of the Langmuir isotherm was used. It was assumed that zirconium(IV) polymers of reasonable size were formed and that complex formation proceeded by interaction of the reagent with the rate constant *k*, while the complex species dissociated according to the rate constant *k'*. Then, if *x* represents the number of units complexed and *m*, the total number of units

$$k'(x/m) = k(1 - x/m)c$$

in which *c* is the concentration of complexing agent in solution. Thus

$$x/m = Kc/(1 + Kc)$$

where

$$K = k/k'$$

and

$$c/(x/m) = (1/K) + c$$

In order to utilize data from Table I, *c* was evaluated in terms of *R*, the ratio of chelated to non-chelated copper(II) species and *K'*, the copper(II) chelate stability constant

$$c = R/K'$$

and (*x*/*m*), in terms of *F*, the fraction of total zirconium(IV) complexed

$$x/m = F$$

Thus

$$(K'/K) + R = R/F$$

The plot of *R*/*F* against *R* is displayed in Fig. 2. The intercept, *K'*/*K*, is reciprocal to the proportionality constant, *Q*, obtained earlier.

The stability constant for copper(II) chelate has been reported to be approximately 2×10^{18} at 20°.[15] Using that value as an approximation of the value at 25°, an approximate value of 2.5×10^{19} may be calculated for the zirconium(IV) complex species.

[15] Schwarzenbach and Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951).

Discussion

The individual experimental results given in the preceding discussion are no doubt susceptible to a variety of interpretations. Taken as a group, however, the requirements of consistency limit somewhat the number of possibilities. Thus, data obtained in competitive complex formation experiments were compatible with the assumption of monomeric zirconium(IV) species, or with the assumption of extensively polymerized species; considering the known chemistry of zirconium and hafnium, the former was most unlikely, while the latter was quite probable.

Titration data supported the assumption of reaction of polymeric species and suggested that the formation of complex species probably did not result in decomposition of the basic polymer structure. That conclusion was suggested by the fact that precipitation on the high *p*H side did not occur in either zirconium(IV) or hafnium(IV) systems until a hydroxyl number of 4 had been reached. At low *p*H, where the concentration of ionic reagent was low, precipitation occurred at hydroxyl number 3. It is suggested that even low occupation of zirconium(IV) or hafnium(IV) polymer by the increasingly ionic reagent prevented aggregation until sufficiently high *p*H values were reached for complete replacement of complexing agent with hydroxyl groups.

It is clear from examination of the titration curves that the third and fourth acid groups of the reagent were neither involved in complex formation nor were their ionization constants profoundly affected by the involvement of the other two acid groups in such complex formation. On the other hand, the stability constant calculated for the zirconium(IV) compound and that inferred for the hafnium(IV) compound were sufficiently large to suggest chelate formation. The chelate could not have involved more than a quadridentate structure, as noted in the preceding discussion, as compared to the reported hexadentate structure of copper(II) chelate. In this case as in that of the usual monomeric chelates,[16] the entropy decrease attendant upon formation of the more highly organized structure was offset by the large entropy gain resulting from liberation of the coördinated aquo groups from the metal ions. Additional entropy gain was probably associated with opening up of the polymer structure as a result of creation of charged units in the structure.

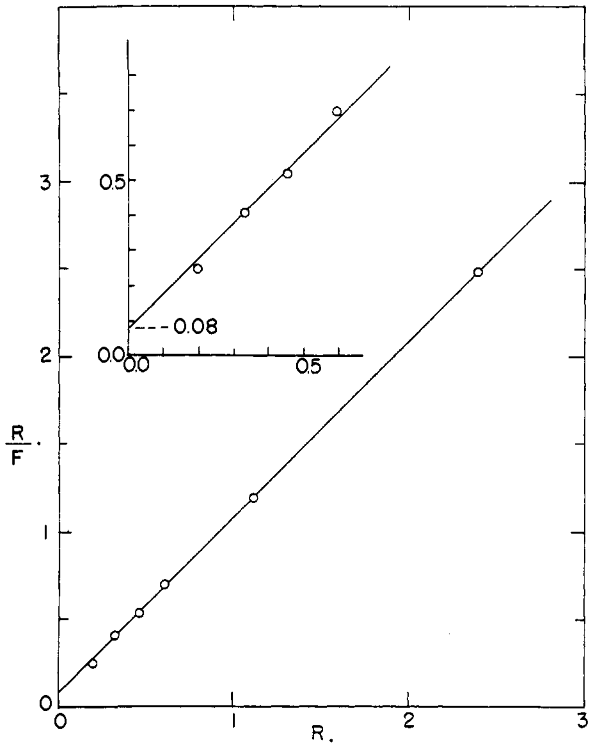

Fig. 2.—Linearity test of polymer-complex formation equation; evaluation of stability constant.

It is suggested that both nitrogens of the reagent were coördinately bound to the central atom of a polymer unit and that two of the acetate groups were ionically associated with the same unit within the coördination sphere. As the third acetic group ionized with increasing *p*H and as additional hydroxyl groups associated with the central atom, the negative charge on the unit increased.

As the number of hydroxyl groups associated with the unit increased further, the complex groups became dissociated. Upon complete removal of the polyvalent groups, aggregation took place and a visible precipitate formed. This material was typical zirconium(IV) or hafnium(IV) hydrous oxide, with no associated ethylenediaminetetraacetate.

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[16] M. Calvin and R. Bailes, THIS JOURNAL, **68**, 949 (1946).