ion for which $K_{101} = 10^{26.60 \pm 0.15}$. Converting K_{101} to Schwarzenbach's form according to equation 11 yields $K_b = 10^{14.60 \pm 0.15}$. The decrease in the value of F_{2b} beyond a *p*H of 10.5 may be due in part to the presence of a potassium complex. However the irreversible behavior may also be due to the tendency of the mercury to precipitate in very alkaline solutions. In conclusion, the equilibrium of mercury(II) with ethylenediaminetetraacetic acid as a function of *p*H is similar to that observed for other metal complexes of this acid.

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COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Hydrolytic Polymerization of Zirconium in Perchloric Acid Solutions[1]

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By employing the first aqueous complex of zirconium and 2-thenoyltrifluoroacetone as a spectrophotometric indicating reaction, the hydrolysis and polymerization of zirconium(IV) perchlorate was studied in one and two molar perchloric acid solutions at 25°. The monomeric zirconium species at these acidities was indicated to be the unhydrolyzed Zr^{+4}. Hydrolysis polymers commenced to form at approximately 5×10^{-4} *M* zirconium in two molar acid and at 10^{-4} *M* zirconium in one molar acid. Up to 0.02 *M* zirconium concentrations the data could be interpreted in terms of trimer(s) and at least one higher polymer—probably tetramer(s). Their average degree of hydrolysis was found to correspond to about 4 and 8 hydroxide groups, respectively, for the trimer(s) and the tetramer(s). No evidence was found for the formation of dimers. Interpretation of the data beyond 0.02 *M* zirconium concentrations was not attempted because of the uncertainty in activity coefficient changes.

Introduction

Because of extensive hydrolysis and polymer formation even in solutions of high acidity, the aqueous chemistry of zirconium(IV) is extremely complex. A variety of physicochemical methods have been employed in recent years in attempts to identify the various zirconium species in solution.[2–7] The result has been a confusing, and often contradictory, array of postulated monomeric and polymeric hydrolysis products. In the present work a method similar to that used in reference 3, but which permitted greater accuracy, was employed to study the zirconium polymer species existing at moderate acidities in non-complexing aqueous media. McVey[4] has applied essentially the same method to a study of the hydroxide dependence of the hydrolysis.

In brief a spectrophotometric indicating reaction was utilized to follow the equilibrium concentration of monomeric zirconium as a function of total metal ion and hydrogen ion concentrations. The formation of the first aqueous complex between zirconium and 2-thenoyltrifluoroacetone (hereafter abbreviated as TTA in the text and as HK in equations) was used as the indicating reaction. Assuming for the moment that the zirconium is unhydrolyzed and unpolymerized, this equilibrium can be represented as

$$Zr^{+4} + HK = ZrK^{+3} + H^+ \qquad (1)$$

Through the use of suitable blanks and the known molar extinction coefficients of TTA and ZrK^{+3}, it was possible to obtain the concentration of ZrK^{+3} by spectrophotometric methods. The equilibrium concentration of free TTA could then be obtained by direct difference from the known initial concentration, and this was done in a number of experiments. However, for the most part better experimental accuracy was obtained by employing a two phase, benzene–aqueous system wherein the concentration of free TTA could be calculated from the known TTA in the benzene phase and the benzene–aqueous distribution constant. In the latter case experimental conditions were controlled so that the amount of zirconium extracted into the benzene phase as the neutral TTA chelate[2,3] was negligible.

Experimental

Procedures.—Two main series of experiments were performed: one in 2 *M* $HClO_4$ and the other in 1 *M* $HClO_4$ plus 1 *M* $LiClO_4$. In addition a few runs were carried out in 1 *M* $HClO_4$ plus 1 *M* $NaClO_4$. Unless otherwise stated all optical density measurements were made using a Beckman model DU spectrophotometer with the absorption cell compartment thermostated at 25.0 ± 0.1°. All optical density values are defined as

$$D_\lambda = \log I^0/I = \epsilon_\lambda lc \qquad (2)$$

where I^0 and I represent intensities of incident and transmitted light of wave length λ, ϵ_λ the molar extinction coefficient at a wave length λ expressed in millimicrons, l the cell length in cm., and c the molar concentration of the absorbing species. The common logarithm is used. All concentrations are reported in terms of moles per liter of solution, designated by the symbol *M* or by ( ).

In a typical experiment equal volumes of benzene containing a known amount of TTA and of an aqueous phase containing perchloric acid (and lithium or sodium perchlorate in the low acid series) and a known concentration of zirconium perchlorate were placed in an opaque flask. The flask was then shaken vigorously for 16 to 24 hours in a water-bath thermostated at 25.0 ± 0.1°. An aqueous phase sample of suitable size was then removed, centrifuged and analyzed spectrophotometrically. In the majority

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[1] Based on a dissertation submitted to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Research performed under the auspices of the United States Atomic Energy Commission.

[2] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

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

[4] W. H. McVey, United States Atomic Energy Commission HW-21487, June, 1951.

[5] B. A. J. Lister and L. A. McDonald, *J. Chem. Soc.*, 4315 (1952).

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

[7] E. M. Larsen and P. Wang, *ibid.*, **76**, 6223 (1954).

of the experiments a second sample was removed after an additional 24 hours of shaking to demonstrate that equilibrium had been attained. The same procedure was followed with the one phase experiments with the exception that the aqueous phase then also contained the known initial concentration of TTA.

Materials.—Water redistilled from alkaline permanganate was used to prepare all solutions. The benzene was C.P. grade, thiophene free. Perchloric acid solutions were prepared by diluting the G. F. Smith double vacuum distilled product.

Stock solutions of lithium and sodium perchlorate were prepared by treating the respective carbonates with perchloric acid. The sodium carbonate was primary standard grade. Lithium carbonate, containing sulfate as the principal impurity, was purified by the method of Caley and Elving.[8] Both solutions were standardized by evaporating aliquots to dryness in the presence of excess sulfuric acid and weighing the residue as the respective sulfates.[9] The lithium perchlorate stock tested free of sulfate when treated with barium nitrate.

Crude zirconyl chloride was obtained from City Chemical Corporation and was recrystallized four times from 8 *M* HCl, the product separating out as large crystalline needles of $ZrOCl_2 \cdot 8H_2O$. The final product was found to be spectrographically pure with the exception of 0.3–0.4 mole % of hafnium. Stock solutions of zirconium perchlorate were prepared by repeated fumings of the zirconyl chloride with excess perchloric acid. The clear solution so obtained did not show a Tyndall beam and tested free of chloride when treated with silver nitrate. The excess perchloric acid in this stock solution was determined by treating aliquots with an excess of sodium fluoride and titrating with standard base.[3] The zirconium concentration was determined by precipitating the hydroxide and igniting to zirconium dioxide.

TTA was obtained from the Dow Chemical Company and purified by a series of crystallizations from redistilled hexane. On the basis of the change in melting point with the fraction melted, the purity of the final product was estimated to be between 99.8 and 99.9 mole %. Because of the slow decomposition of aqueous TTA solutions observed by Zebroski[10] and Mattern,[11] fresh solutions were prepared for each experiment from a weighed amount of TTA.

The Zirconium–TTA Complex

McVey[4] has reported the first zirconium–TTA chelate to be the 1-1 complex, ZrK^{+3}, with a maximum light absorption at 366 mμ. By the use of 4 *M* perchloric acid solutions, which afford a fairly wide working range of zirconium concentrations where the monomer is the only important species, McVey was able to determine the formation constant of reaction (1)

$$K = \frac{(ZrK^{+3})(H^+)}{(Zr^{+4})(HK)} \tag{3}$$

and the maximum molar extinction coefficient of ZrK^{+3}. His reported values, all at 25°, are $K = 1084$ and $\epsilon_{366} = 2.34 \times 10^4$.

In order to obtain an independent check of the ZrK^{+3} peak molar extinction coefficient at the ionic strength of two used in this research, the following method was employed. Optical density measurements were made on two sets of solution pairs. The first set consisted of all aqueous solutions. One solution of each pair contained zirconium perchlorate, and the initial TTA concentration of both was identical. Assuming free TTA and the 1–1 complex as the only absorbing species, the difference in optical density of two such solutions is given by

$$\Delta D_1 = l[\epsilon_{ZrK} - \epsilon_{HK}](ZrK^{+3}) \tag{4}$$

Utilizing the optical density at the 366 mμ peak and the ΔD value at any other fixed wave length λ, the ratio of the ΔD values for the same solution pair is a constant

$$\frac{\Delta D_1^{366}}{\Delta D_1{}^{\lambda}} = \frac{\epsilon_{ZrK}^{366} - \epsilon_{HK}^{366}}{\epsilon_{ZrK}^{\lambda} - \epsilon_{HK}^{\lambda}} = k_1{}^{\lambda} \tag{5}$$

The second set of solution pairs consisted of equal volume, benzene–aqueous systems. Again each pair contained identical amounts of TTA and differed only in that one contained added zirconium. The distribution constant for TTA between a benzene and aqueous system is defined as

$$\beta = (HK)_b/(HK)_{aq} \tag{6}$$

For each solution pair in such a system it is readily shown that the ratio of the optical density differences of the equilibrium aqueous phases is again a constant. Thus

$$\frac{\Delta D_2^{366}}{\Delta D_2{}^{\lambda}} = \frac{(\beta + 1)\epsilon_{ZrK}^{366} - \epsilon_{HK}^{366}}{(\beta + 1)\epsilon_{ZrK}^{\lambda} - \epsilon_{HK}^{\lambda}} = k_2{}^{\lambda} \tag{7}$$

By simultaneous solution of equations 5 and 7, it was then possible to calculate ϵ_{ZrK}^{366}. To obtain a reliable average value for this constant, optical density measurements to complement the 336 mμ values were made at 266, 292 and 314.1mμ. The latter three wave lengths correspond to the two TTA absorption peaks and the wave length where $\epsilon_{HK} = \epsilon_{ZrK}$. This last value is indicated by a ΔD value of zero in equation 4.

All aqueous solutions were 2 *M* in perchloric acid, and six independent solution pairs were employed in both the one and two phase runs. The zirconium concentration varied roughly from 0.01 to 0.04 *M* and the initial TTA concentration from 0.7 to 2 × 10^{-5} *M* and 3 to 5 × 10^{-4} *M*, respectively, in the one and two phase experiments. The values of ϵ_{HK} employed in the calculations were 0.0856, 4.07, 7.83 and 10.02 × 10^3 for 366, 314.1, 292 and 266 mμ. These values were readily obtained by direct measurement. Values of β are presented in Table II. A summary of the results is presented in Table I. The ± values represent average deviations for k_1 and k_2 and the corresponding calculated probable uncertainties for the molar extinction coefficient.

TABLE I

DETERMINATION OF ϵ_{ZrK}^{366} IN 2 *M* $HClO_4$ AT 25°

λ(mμ)	$-k_1$	k_2	$\epsilon_{ZrK}^{366} \times 10^{-4}$
314.1	∞	6.04 ± 0.11	2.39 ± 0.06
292	9.68 ± 0.41	5.15 ± .14	2.56 ± .09
266	3.80 ± .07	7.11 ± .43	2.42 ± .18

Weighted av. 2.45 ± 0.07

Once the value of the peak molar extinction coefficient has been determined, eq. 5 allows the determination of the ZrK^{+3} absorption spectrum by the one phase, k_1 experiments only. This spectrum was thus obtained by running suitable solu-

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(8) "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 1.

(9) W. W. Scott, "Standard Methods of Chemical Analyses," Vol. I, D. Van Nostrand Co., New York, N. Y., 5th ed., 1939, pp. 878, 888.

(10) E. L. Zebroski, United States Atomic Energy Commission BC-63, July, 1947.

(11) K. L. Mattern, United States Atomic Energy Commission UCRL-1407, Jan., 1951.

tion pairs on a Cary recording spectrophotometer. The curve shown in Fig. 1 is the average of two such determinations. The absorption spectrum of TTA is presented for comparison.

Results

The initial concentration of TTA in both the one and two phase experiments is always represented as $(HK)^\circ$. In the two phase experiments, all the TTA was initially in the benzene phase. The equilibrium aqueous phase concentrations of TTA and the zirconium–TTA complex are designated by (HK) and (ZrK^{+3}). The formal initial and equilibrium concentrations of zirconium perchlorate, *i.e.*, that uncomplexed by TTA, are represented by ΣZr° and ΣZr. The ratio of aqueous to benzene phase volumes is signified by α.

The data are presented in terms of a complexing coefficient E defined as

$$E = \frac{(ZrK^{+3})}{(HK)\Sigma Zr} \qquad (8)$$

In the case of the two phase experiments, the distribution constant of eq. 6 can be presented as

$$\beta = \frac{(HK)^0 - \alpha(HK) - \alpha(ZrK^{+3})}{(HK)} \qquad (9)$$

From optical density measurements of the equilibrium aqueous phase at 366 mμ

$$(ZrK^{+3}) = \frac{D/l - (HK)\epsilon_{HK}}{\epsilon_{ZrK}} \qquad (10)$$

The concentration of uncomplexed zirconium is obtained by

$$\Sigma Zr = \Sigma Zr^0 - (ZrK^{+3}) \qquad (11)$$

Simultaneous solution of eq. 9–11 allows calculation of the E values. In the case of the one phase experiments, eq. 9 is replaced by

$$(HK) = (HK)^0 - (ZrK^{+3}) \qquad (12)$$

All necessary values of β and ϵ_{HK} for these calculations are listed in Table II. The distribution constants were obtained from aqueous phase TTA concentrations as measured by light absorption at the 292 mμ peak. Equilibrium was approached from both sides and in all cases the TTA benzene concentration was kept sufficiently low for its activity coefficient to be unity.[12] The ± values represent average deviations of 7, 6 and 3 experiments, respectively.

TABLE II

VALUES OF ϵ_{HK}^{366} AND β AT 25°

Aqueous phase	ϵ_{HK}^{366}	β
2 M $HClO_4$	85.6 ± 0.3	35.7 ± 0.1
1 M $HClO_4$ + 1 M $LiClO_4$	77.8 ± .4	46.5 ± .5
1 M $HClO_4$ + 1 M $NaClO_4$	67.4 ± .3	48.1 ± .4

The zirconium–TTA complexing coefficient data are presented in Tables IIIa–IIIc. Five cm. cells were employed for all optical density measurements in 1 M acid; and unless otherwise noted, 2 cm. cells were used for the 2 M acid series. Except where otherwise indicated, the values $\alpha = 1$ and $\alpha = 2.4$ apply, respectively, to the 2 and 1 M acid experiments. In certain of the two phase experiments where high TTA concentrations were employed, it was necessary to make small corrections for zirconium extracted into the benzene phase as ZrK_4. These corrections were made by successive approximations utilizing the data of Connick and Reas.[3]

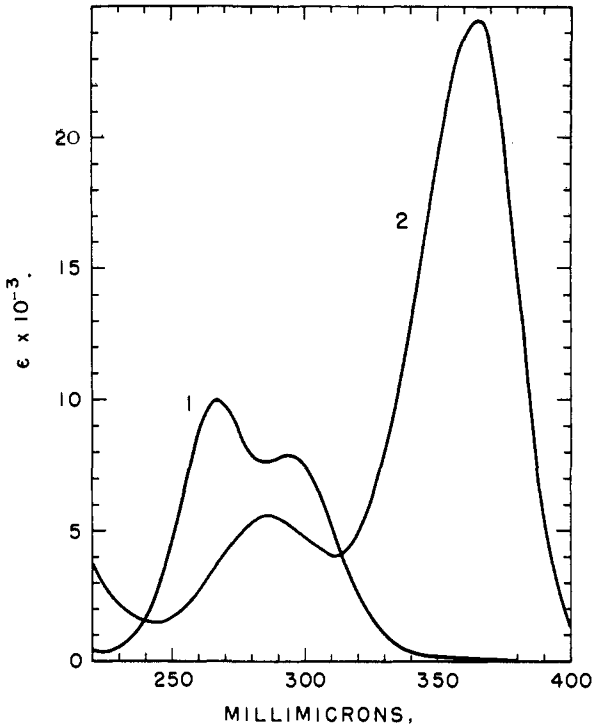

Fig. 1.—Absorption spectrum of: (1) TTA and (2) ZrK^{+3} in 2 M $HClO_4$.

TABLE III

a. COMPLEXING COEFFICIENTS IN 2 M $HClO_4$ AT 25°

ΣZr^0, moles/l. $\times 10^3$	$(HK)^0$ moles/l. $\times 10^4$		D_{366}			E
0.02069	11.99	a	0.974	0.971	c	186
.03211	8.994		.941	.941		185
.03924	6.314		.752	.749		177.5
.06419	5.996		1.009	1.011		179.5
.09505	25.25		0.318	0.323[d]		166[e]
.1956	1.263[a]		.543	.545[c]		171.5
.3153	23.87		.843[d]	...		159.5[e]
.5208	0.5052[a]		.516	.516	c	169
1.299	3.680	b	.241	.237		155.5
2.597	3.680		.421	.416		138.8
3.871	3.680		.5395	...		121
6.278	1.459		.1202	...		99.4
6.297	3.879		.3125	.3095		96.5
12.44	1.459		.1645	...		69.2
12.46	5.071		.578	...		69.9
13.09	4.964		.573	...		67.3
18.10	4.784		.617	...		54.6
24.19	4.784		.7185	...		47.8
24.69	3.879		.5855	...		47.1
26.18	3.310		.502	...		44.6
31.03	5.071		.832	...		40.9
39.28	3.310		.585	...		34.8
61.98	3.879		.821	.805		26.4
154.8	2.070		.655	.647		16.2
310.1	2.070		.955	.952		12.28

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[12] E. L. King and W. H. Reas, THIS JOURNAL, 73, 1806 (1951).

b. COMPLEXING COEFFICIENTS IN 1 M $HClO_4$ + 1 M $NaClO_4$ AT 25°

ΣZr^0, moles/l. × 10^4	$(HK)^0$, moles/l. × 10^4		D_{366}		E
0.7775	2.387	a	0.751	0.749	325.5
1.295	1.492		.754	.751	323.8
1.944	0.5959		.433	.433	315

c. COMPLEXING COEFFICIENTS IN 1 M $HClO_4$ + 1 M $LiClO_4$ AT 25°

ΣZr^0, moles/l. × 10^3	$(HK)^0$, moles/l. × 10^4		D_{366}		E	
0.02097	10.06	a	0.875	0.875	232	
.03920	6.289		.986	.984	293.5	
.05223	2.516		.541	.541	301	
.07811	1.529		.487	.488	314.5	
.1302	0.956		.500	.501	327	
.1953	0.956		.718	.720	327	
.3255	18.52		.489	.471	317	e
.3255	17.90		.471	.452	314.5	
.4672	18.52		.649	.625	296	
.4673	17.90		.623	.603	294	
.6486	18.52		.787	...	265	
.6487	17.90		.779	.770	269.5	
1.038	7.246		.4125	.4095	218	
1.619	7.246		.5195	.4955	173.5	
3.209	7.246		.6695	.6625	115.5	
5.187	5.010		.555	.553	86.4	
7.758	5.010		.620	.617	64.8	
12.90	3.999[b]		.588	.593	47.0	
19.40	5.010		.855	.854	36.2	
32.28	3.999[b]		.824	.835	26.75	
48.28	2.016		.489	.505	21.35	
64.32	3.999[b]		1.084	1.089	17.85	
80.17	2.016		0.603	0.609	15.88	
128.6	2.016		0.749	0.750	12.4	

[a] One phase experiment, $\alpha = \infty$. [b] $\alpha = 2.5$. [c] Cell length = 5 cm. [d] Cell length = 10 cm. [e] Corrected for ZrK_4 in benzene phase.

As will be shown shortly in the theoretical treatment, at constant acidity E must approach a constant value as the zirconium concentration is decreased. This condition is met fairly well in the 2 M acid series, but in 1 M $HClO_4$ plus 1 M $LiClO_4$ the E values reach a maximum and then commence to decrease. Exactly this same behavior was observed previously by Connick, *et al.*,[2,3] and it has been attributed to the complexing of a small amount of zirconium by an impurity in the solutions. This impurity remains unidentified but there is some evidence that it is leached off glass surfaces.[3] As a precaution, a careful cleaning procedure was used on all glassware, and in addition all glass vessels and pipets were coated with Dri-Film, $(CH_3)_2SiCl_2$. Apparently this procedure met with some success since no evidence of the impurity was observed in 2 M acid and the effect in 1 M acid was less than that encountered previously.[2,3]

A quantitative correction for this impurity effect was made by assuming that the amount of zirconium complexed by the impurity was constant in all the 1 M $HClO_4$ plus 1 M $LiClO_4$ experiments. If this is the case, then over the zirconium concentration range where the complexing coefficient is constant (corresponds to zirconium monomer as the only important species)

$$E^0 = \frac{E\Sigma Zr}{\Sigma Zr - X} \qquad (13)$$

where E^0 is the true (constant) value of the complexing coefficient, E is the experimentally observed value, and X represents the constant concentration of zirconium "lost" to the impurity complex. Equation 13 can be rearranged to give

$$\Sigma Zr = X + E\Sigma Zr/E^0 \qquad (14)$$

Thus a plot of ΣZr *vs.* EΣZr should be linear with slope equal to $1/E^0$ and intercept equal to X. The excellent straight line obtained with such a plot is illustrated in Fig. 2. The five points correspond to the five runs at lowest zirconium concentration in the 1 M $HClO_4$ plus 1 M $LiClO_4$ series. At higher zirconium concentrations polymerization of the zirconium becomes appreciable. Utilizing the least squares technique, the following values and standard deviations were calculated for the slope and intercept of Fig. 2: $E^0 = 341 \pm 2$ and $X = (0.530 \pm 0.042) \times 10^{-5}$ M. This value of X was used to correct the six points at lowest zirconium concentration in the 1 M $HClO_4$ + 1 M $LiClO_4$ series of Fig. 3.

Discussion

The general case of combined hydrolysis and polymerization of zirconium is represented by the reaction(s)

$$nZr^{+4} + mH_2O = Zr_n(OH)_m{}^{+4n-m} + mH^+ \qquad (15)$$

and the corresponding concentration equilibrium constant(s)

$$K_{nm} = (Zr_n(OH)_m{}^{+4n-m})(H^+)^m/(Zr^{+4})^n \qquad (16)$$

Consideration is thereby given to all possible integral values of n, commencing with one, and all corresponding m values, starting with zero, for each n.

The total (formal) concentration of zirconium is obtained by solving 16 for the concentration of $Zr_n(OH)_m{}^{+4n-m}$ and summing over all values of n and m

$$\Sigma Zr = \sum_{n,m} nK_{nm}(Zr^{+4})^n(H^+)^{-m} \qquad (17)$$

Substitution of (3) and (8) into equation 17 yields

$$\Sigma Zr = \sum_{n,m} nK_{nm}\,(E\Sigma Zr)^n\,K^{-n}(H^+)^{n-m} \qquad (18)$$

By partial differentiation of (18) with respect to ΣZr at constant (H^+) and constant values of the K's

$$\left(\frac{\partial \log E}{\partial \log \Sigma Zr}\right)_{(H^+)} = -1 + \frac{\Sigma Zr}{\sum\limits_{n,m} n^2(Zr_n(OH)_m{}^{+4n-m})} = -1 + \frac{1}{\Sigma nf_{n,m}} \qquad (19)$$

where each f_{nm} represents the fraction of the total zirconium which exists in a polymer containing n zirconium atoms and m hydroxide groups. The weighted summation of all such groups, as designated by Σnf_{nm}, is the weight average degree of polymerization and represents the size of the polymer in which a zirconium ion will be found on the average.

Thus by a plot of log E *vs.* log ΣZr at constant hydrogen ion concentration, a direct measure of the degree of polymerization is obtained. At low zirconium where the monomer is the only important species, $\Sigma n f_{nm}$ equals one and eq. 19 demands a zero slope. As the zirconium concentration is increased and polymers begin to form, the slope should become negative, approaching minus one as a limiting value if the polymers are of infinite size.

All of the complexing coefficient data in 1 and 2 M acid are presented in Fig. 3 in such a plot. Nearly all points represent the average of two or more experimental values. As discussed earlier, certain of the points in 1 M acid at low zirconium concentration have been corrected for the impurity complex. The smooth curves represent calculated values that will be discussed shortly.

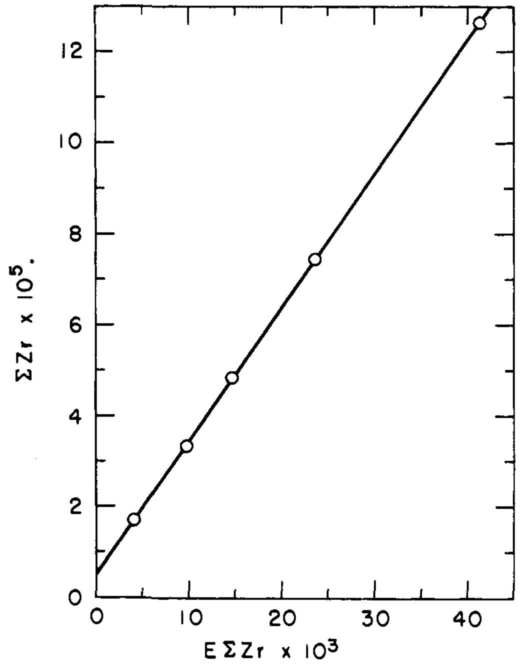

Fig. 2.—Zirconium-impurity complex in 1 M HClO$_4$ + 1 M LiClO$_4$.

Formula of the Monomer.—The limiting values of the complexing coefficient, designated as E^0, at low zirconium concentration in 1 and 2 M acid allow a calculation of the degree of hydrolysis of the monomeric species relative to the chelate. Assuming the chelate to be ZrK^{+3}, we obtain from eq. 18

$$K/E^0 = (H^+) + K_{11} + K_{12}/(H^+) + \ldots K_{1m}/(H^+)^{m-1} \quad (20)$$

Equation 20 indicates the complex nature of E^0 as a function of hydrogen ion concentration when a number of hydrolysis products of comparable importance are present. An unambiguous conclusion for data at but two acidities can be drawn if, and only if, E^0 is observed to have an inverse first power dependence on hydrogen ion concentration. This corresponds to Zr^{+4} as the monomeric species and is indicated to be the case in Fig. 3 where the theoretical curves have been drawn with E^0 values of 341 in 1 M acid and 170.5 in 2 M acid. The value of K is then 341 compared to McVey's value of 1084 in 4 M HClO$_4$.[4]

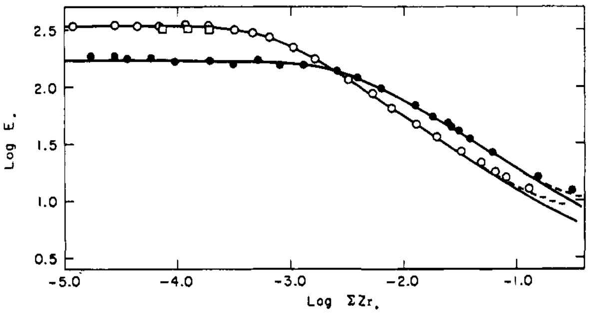

Fig. 3.—Zirconium–TTA complexing coefficients: ● 2 M HClO$_4$; ○ 1 M HClO$_4$ + 1 M LiClO$_4$; □, 1 M HClO$_4$ + 1 M NaClO$_4$.

It is to be noted that the impurity complex correction was applied to the 1 M acid data. It is assumed that this correction was made with fair accuracy; however, even without the correction, the estimated extrapolated value of E^0 in low acid would be approximately the same. This is indicated by the three points in 1 M HClO$_4$ plus 1 M NaClO$_4$ solutions where *no* correction was applied for an impurity complex.

In interpreting the data chelate complexes beyond the first were ignored because the ratio of zirconium chelate to monomeric zirconium was always small. It is possible that the slight rise of the points at the lowest zirconium concentrations above the curve for the 2 M HClO$_4$ solutions is due to the presence of a small amount of the second chelate, since the conditions for its formation were most favorable at the lowest zirconium concentrations.

In interpreting the effect of acidity here and in the next section, it was assumed that activity coefficient ratios remained constant in going from 2 M HClO$_4$ to 1 M HClO$_4$ plus 1 M LiClO$_4$ (or NaClO$_4$). All of the equilibria involve either positive ions or neutral molecules. Because the activity coefficient of a positive ion is determined primarily by the negative ion,[13,14] and the latter was fixed in the present case, the assumption of cancellation seems reasonable for effects arising from ionic charges.

That there are significant activity coefficient changes for the neutral TTA molecule is shown by the values of β of Table II. Assuming the activity coefficient in the benzene layer to be constant, that in the aqueous phase must increase 30% in replacing 2 M HClO$_4$ by 1 M HClO$_4$ plus 1 M LiClO$_4$.[15] At first sight it might seem better to use the concentration of TTA in the benzene layer and thus correct for the change of activity coefficient of TTA. Actually such is not the case. The concentration of TTA always occurs in the equations in the form (HK)/(ZrK^{+3}). It has been shown by Larsson and Adell[16] that the activity coefficients of the negative ions of large organic acids can be con-

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[13] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

[14] J. N. Brönsted, THIS JOURNAL, **44**, 877 (1922).

[15] Such a difference in salt effects is not unreasonable for large organic molecules. See, for example, F. A. Long and W. F. McDevit *Chem. Revs.*, **51**, 119 (1952).

[16] E. Larsson and B. Adell, *Z. physik. Chem.*, **A156**, 381 (1931); **A157**, 342 (1931).

sidered to be made up of the product of two terms: one representing the interaction of the charge with its environment and the other the interaction of the uncharged organic part of the ion with its environment. To a fair approximation the activity coefficient change arising from this second term is just cancelled by the activity coefficient of the undissociated acid. The experimental evidence for this statement is that the values of $\gamma_{H^+}\gamma_{A^-}/\gamma_{HA}$ for a wide variety of organic acids in a given salt solution are nearly equal, even though the activity coefficient of the acid varies considerably. Similarly, the change in activity coefficient of HK would be expected to be cancelled to a large degree by a corresponding change in the activity coefficient of ZrK^{+3} arising from the uncharged part of the chelate ion.[17]

The error introduced by the above assumptions cannot be estimated reliably. The belief that it is small is supported by the fact that a solution containing 1 *M* $NaClO_4$ plus 1 *M* $HClO_4$ gave the same result as a solution containing 1 *M* $LiClO_4$ plus 1 *M* $HClO_4$.

Should the chelate itself be hydrolyzed, the limiting results of Fig. 3 indicate that the monomer and chelate contain the same number of hydroxide groups per zirconium. Since it is unlikely that the chelate with its negatively charged oxygens attached to the zirconium would be as hydrolyzed as the monomer itself, it is reasonable to conclude that neither is hydrolyzed and that the monomer is primarily Zr^{+4} in one to two molar perchloric acid solutions.

Previous work is in agreement with this conclusion. Thus extraction experiments[3] with TTA, using an entirely different equilibrium for measurement, yielded similar results and conclusions.[18] The work of McVey,[4] using the present method but varying the acidity, is consistent with the present work. Larsen and Wang[19] found that ion-exchange equilibria with zirconium at low concentrations were also best fitted by the assumption of monomeric Zr^{+4}.

Polymeric Species.—The weight average degree of polymerization, as calculated from the slopes of Fig. 3 by eq. 19, can be analyzed in terms of possible species in solution; and this method was used by Connick and Reas[3] in their treatment of zirconium–TTA extraction coefficients. Since the measurement of slopes from non-linear curves is liable to a good deal of error, a more analytical treatment of the data is made here.

Equation 18 can be rewritten and expanded as

$$1/E = a_1 + a_2(E\Sigma Zr) + \ldots a_n(E\Sigma Zr)^{n-1} \quad (21)$$

where each a_n is defined by

$$a_n = nK^{-n}\sum_m K_{nm}(H^+)^{n-m} \quad (22)$$

At constant hydrogen ion concentration all a_n values of eq. 21 can be considered as constant coefficients. Thus a plot of $1/E$ *vs.* $E\Sigma Zr$ gives a simple polynomial curve whose terms and coefficients are directly related to the polymeric species in solution. Analysis of the data by means of such plots revealed that for zirconium concentrations up to 0.013 and 0.018 *M* for the one and two molar acid series, respectively, $1/E$ represents a cubic equation in $E\Sigma Zr$, corresponding to the tetramer as the highest polymer present at appreciable concentrations under these experimental conditions. In addition it was found that the value of a_2, the coefficient of the dimer term, is negligibly small. Thus assuming the polymeric species to consist of a trimer–tetramer mixture only, eq. 21 can be placed in the linear form

$$(1/E - a_1)(E\Sigma Zr)^{-2} = a_3 + a_4(E\Sigma Zr) \quad (23)$$

and a plot of the left hand member of 23 *vs.* $E\Sigma Zr$, at constant acidity, should give a straight line with intercept equal to a_3 and a slope equal to a_4. The value of a_1 is simply $1/E^0$.

Such plots for the 1 and 2 *M* acid data are shown in Fig. 4. Only a somewhat limited range of zirconium concentrations is covered for two reasons. First, because of the $(1/E - a_1)$ term in eq. 23, the amount of polymerization must be appreciable before any reasonable accuracy can be obtained. Second, a definite trend at high zirconium concentrations is believed caused by a combination of increased acidity due to hydrolysis and an increase in the ionic strength with the addition of zirconium perchlorate. The latter two effects cause a rapid fall off of the experimental points from the extrapolated linear plots of Fig. 4. They are also indicated by the marked upward curvature of the data of Fig. 3 at high zirconium concentrations.

For these reasons the range of zirconium concentrations covered in Fig. 4 is roughly 3×10^{-4} to 0.018 *M*. Nearly all the points represent the average of two or more experimental values. Uncertainties in the individual points are indicated by vertical lines and are based on an estimated possible error of 3% in the *E* values and of 5% in each a_1. The linear plots were obtained by least squares analysis of all points shown in the figure.

The effect that would be produced in Fig. 4 by appreciable quantities of the dimer and/or higher polymers than the tetramer can be seen by expanding eq. 23 in its full form

$$(1/E - a_1)(E\Sigma Zr)^{-2} = a_2/(E\Sigma Zr) + a_3 + \ldots a_n(E\Sigma Zr)^{n-3} \quad (24)$$

Therefore if a_2 is not negligibly small, the ordinate term of Fig. 4 would commence to increase at low values of $E\Sigma Zr$. Higher polymers than the tetramer would be indicated by an upward curvature at high values of $E\Sigma Zr$. An estimated upper limit for a_2 may be made by plotting the quantity $(1/E - a_1)(E\Sigma Zr)^{-1}$ *vs.* $E\Sigma Zr$, which should have an ordinate intercept equal to a_2. Within the limits of experimental error, the observed value is a zero intercept; but on the basis of estimated possible errors, the limit on a_2 (in 1 *M* acid) was approximately placed as no greater than 5×10^{-4}. By the use of

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[17] Additional discussion of such canceling of activity coefficients and its occurrence in the iodide–iodine–triiodide equilibrium is presented by L. I. Katzin and E. Gebert, THIS JOURNAL, **77**, 5814 (1955).

[18] In this earlier work the question of the activity coefficient correction of HK did not arise because the chelated zirconium species ZrK_4 was present in the benzene phase.

[19] Reference 7. These authors also pointed out the ambiguity in the interpretation of Lister and McDonald[5] of earlier ion-exchange measurements where it had been concluded that Zr^{+4} did not exist. See also reference 21, p. 79.

eq. 22 the sum of the dimerization constants is calculated to be

$$\Sigma_m K_{2m} \leqq 30$$

Although the assumption of trimer and tetramer fits the data of Fig. 4, the assumption of trimer and pentamer fits nearly as well, as would also combinations of these three polymers. However, the points beyond $E\Sigma\text{Zr} = 0.6$ in the 1 *M* acid series show considerably greater deviations from the ideal curves for the assumption of a pentamer than for a tetramer. It is primarily for the latter reason that the interpretation in terms of tetramer is preferred. In the following analysis of the data only the tetramer will be considered although the ambiguity in its choice should be kept in mind.

The values and standard deviations of a_3 and a_4 as calculated by the least squares technique from the linear plots of Fig. 4 are presented in Table IV. The respective values of a_3 and a_4 are observed to have roughly an inverse first and an inverse fourth power hydrogen ion dependence, although the latter is extremely uncertain. As can be demonstrated by expansion of eq. 22, these results taken at face value correspond to the polymeric species[20] $Zr_3(OH)_4^{+8}$ and $Zr_4(OH)_8^{+8}$. The corresponding polymerization constants, K_{34} and K_{48}, have been calculated by means of eq. 22 and are also presented in Table IV. However it should be strongly emphasized that interpretation of the data in terms of but one trimer and one tetramer could easily be an oversimplification of a complicated system. At least the values so obtained represent the average degree of hydrolysis of the polymers as observed in this work,

TABLE IV

TRIMER AND TETRAMER POLYMERIZATION CONSTANTS AT $\mu = 2$ AND 25°

(H^+)	$a_3 \times 10^3$	$a_4 \times 10^3$	$K_{34} \times 10^{-5}$	$K_{48} \times 10^{-8}$
1	18 ± 2	58 ± 4	2.4 ± 0.3	2.0 ± 0.2
2	9.6 ± 1.4	2.7 ± 2.1	2.5 ± .4	1.5 ± 0.2

As mentioned previously, the results at high zirconium concentration are considered uncertain due to ionic strength effects and the increased hydrogen ion formed in the hydrolysis reactions. This is not too unreasonable when it is noted that a typical experimental solution such as ΣZr equal to 0.025 *M* in 2 *M* perchloric acid would actually be 2.1 *M* in perchlorate ion and could be 2.1 *M* in hydrogen ion if the zirconium were completely hydrolyzed. The error due to increased hydrogen ion concentration can be calculated by means of the above values of K_{34} and K_{48} and by combining eq. 3 and 8 to yield

$$E = \frac{K(\text{Zr}^{+4})}{(\text{H}^+)\Sigma\text{Zr}} \qquad (25)$$

The theoretical smooth (solid) curves of Fig. 3 were obtained in this manner. However, the effect produced by increased hydrogen ion was not sufficient in itself to match the upward swing of the experimental points at high zirconium concentrations. Consideration of the possible effect of increased ionic strength was made in the following manner. A value of $K = 1084$ at $\mu = 4$ is available from McVey's work.[4] Zielen,[21] from additional analysis of zirconium hydrolysis experiments conducted by McVey,[4] has obtained values for trimer and tetramer polymerization constants at μ equal 4. Then by assuming a linear variation of *K* and the polymerization constants with perchlorate ion concentration, values of these quantities could be calculated for any given value of ΣZr. The results of these calculations are illustrated in Fig. 3 by the dashed extensions of the theoretical curves at high zirconium concentrations. Obviously such calculations are to be considered as only very crude estimates of the possible ionic strength effect. However, the corrections are in the right direction and could conceivably account for the deviations between experimental and theoretical values of *E* at high zirconium concentrations. The presence of higher polymers than those assumed would have produced deviations in a direction opposite to that observed.

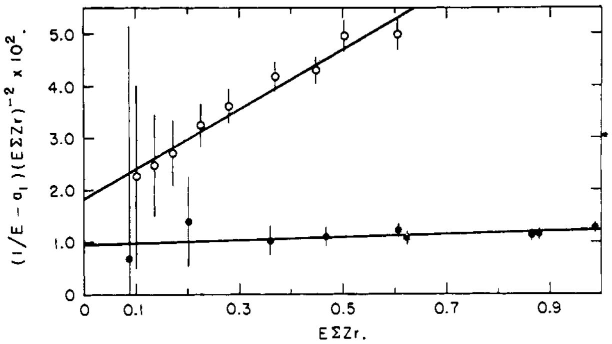

Fig. 4.—Trimer and tetramer zirconium polymers: ○, 1 *M* $HClO_4$ + 1 *M* $LiClO_4$; ●, 2 *M* $HClO_4$.

Comparison with Results of Other Investigators. Connick and Reas[3] concluded from extraction measurements that, in addition to Zr^{+4}, a series of polymers beginning with the dimer exists in one and two molar perchloric acid solutions. Kraus and Johnson,[6] on the basis of ultracentrifugation measurements of 0.05 and 0.12 *M* zirconium in 1 *M* $HClO_4$–1 *M* $NaClO_4$ solutions, calculated a degree of polymerization of approximately 3, with an outside possibility that it might be as high as 4.5. They found no evidence for the higher polymers in this solution reported by Connick and Reas. The present results confirm and extend the conclusions of Kraus and Johnson. Thus in the concentration range investigated there exist both a trimer and a tetramer, and the dimer is not detectable.

The data of the present work can be compared directly with those of Connick and Reas. The decrease in activity of the Zr^{+4} caused by polymerization is in agreement within the experimental accuracy for the 2 *M* $HClO_4$ series of the two sets. Serious differences appear only at zirconium concentrations above 0.03 *M* where changes in acidity and ionic strength affect the two types of measurement differently. For the 1 *M* $HClO_4$ series, how-

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[20] In these formulas two hydroxide groups could equally well be replaced by one $O^=$.

[21] A. J. Zielen, United States Atomic Energy Commission UCRL 2268, July, 1953. The reported values of the polymerization constants at μ equal 4 are $K_{35} = 4 \times 10^6$ and $K_{48} = 1.4 \times 10^9$. The difference in hydrogen ion dependence of the trimer was ignored in making the ionic strength correction.

ever, there are discrepancies outside of the experimental precision at low zirconium concentrations in the direction of more apparent polymerization in the earlier results. The source of this difference is unexplained. The present work is accepted because of the much greater precision.

In a recent paper Johnson, Kraus and Holmberg[22] have reported studies on the ultracentrifugation of hafnium dissolved in hydrochloric acid solutions. Comparison with zirconium is justified because of the similarity in the chemistry of these two elements. Although the negative ion was chloride rather than perchlorate, as used in the present work, it is interesting that their results indicate a degree of polymerization between 3 and 4[23] at acidities and metal ion concentrations similar to those used here.

Clearfield and Vaughan[24] in reporting preliminary results on the X-ray investigation of solid $ZrOCl_2 \cdot 8H_2O$ and $ZrOBr_2 \cdot 8H_2O$ have stated that zirconyl ion appears as the tetramer $(ZrO)_4$ in the form of rings. Although the present work relates to perchlorate solutions, it is possible that the same tetramer unit is involved.

McVey[4] has studied zirconium hydrolysis in $HClO_4$–$LiClO_4$ solutions using the same method employed here but varying the hydrogen ion concentration at constant zirconium concentration. His data serve best to indicate the average number of hydroxides per zirconium in the polymers, while the present work indicates best the number of zirconiums per polymer species. A reinterpretation[21] of his results in terms of the three zirconium units found in the present work, *i.e.*, monomer, trimer and tetramer, yielded: zero hydroxides on the monomer, *i.e.*, Zr^{+4}; five hydroxides on the trimer, *i.e.*, $Zr_3(OH)_5{}^{+7}$; and eight hydroxides on the tetramer, *i.e.*, $Zr_4(OH)_8{}^{+8}$. This compares with the less accurate values of 4 and 8 hydroxides for the trimer and tetramer, respectively, found in the present work. It should be noted, however, that McVey's experiments were mostly carried out at lower acidities than used in the present work, so that other polymers may have been present.

Throughout the interpretation perchlorate complexing has been assumed to be absent. Should such complexes be present none of the conclusions about hydrolysis and polymerization are changed as long as the perchlorate concentration was held constant. In the experiments at the highest zirconium concentrations the perchlorate concentration did rise above 2 M and the high values for E found there could in part be explained by preferential complexing of ZrK^{+3} by perchlorate ion. Comparison of McVey's value of K (eq. 3) of 1084 for 4 M $HClO_4$ with the value of 341 for 2 M $HClO_4$ is consistent with the above but would require the unlikely hypothesis that perchlorate ion complexes ZrK^{+3} more than Zr^{+4}.

In summary it is concluded that in the perchloric acid range of one to two molar the principal zirconium species at low zirconium concentrations is the unhydrolyzed monomer, Zr^{+4}. At higher zirconium concentrations, *i.e.*, up to 0.02 M, species containing 3 and probably 4 zirconium atoms are present. The trimer appears to contain approximately four hydroxide groups and the tetramer approximately eight.

NOTE ADDED IN PROOF.—Since submission of this paper for publication an additional paper by Johnson and Kraus has appeared on the ultracentrifugation of zirconium and hafnium solutions (THIS JOURNAL, **78**, 3937 (1956)). The authors deduce from their data a weight average degree of polymerization of *ca.* 3.5 for 0.05 M zirconium in 1 M HCl and conclude that probably a trimer or tetramer is formed (see footnote 23). From two experiments with 0.049 M and 0.12 M zirconium in 1 M $HClO_4$–1 M $NaClO_4$ they deduce a weight average degree of polymerization of *ca.* 3.7 and a charge per zirconium of *ca.* 1.75. Although the authors stated that these latter results were not considered accurate, they agree remarkably well with the corresponding values calculated from the equilibrium constants of this paper, *i.e.*, 3.60 and 3.70, respectively, for the weight average degree of polymerization and a charge of *ca.* 2 per zirconium. The agreement is perhaps fortuitous since Johnson and Kraus assumed monodispersity of the solutions in interpreting their data. Also, the first experiment was run at 24° and the second at 29°, while the work reported here was for 25°.

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[22] J. S. Johnson, K. A. Kraus and R. W. Holmberg, THIS JOURNAL, **78**, 26 (1956).

[23] Although the data indicated a weight average degree of polymerization, N_W, of 3.2 the authors stressed that this number was uncertain because of the numerous approximations made in interpreting the data. From the apparent lack of concentration dependence of N_W the authors concluded that the solution was probably predominantly monodisperse. It is easy to show that this latter conclusion is not justified by the data. The experiment at lowest hafnium concentration (0.008 M) showed evidence of depolymerization and cannot be used. Other experiments ranged from 0.02 to 0.12 M hafnium. If it is assumed that only trimers and tetramers are present, and that N_W is 3.20 for a 0.02 M hafnium solution, one calculates that N_W changes only to 3.30 for a sixfold increase in hafnium concentration. This change is well within their experimental accuracy, especially considering the approximations made in measuring N_W, such as constancy of activity coefficients, approximate monodispersity, constant chloride complexing, constant charge per zirconium, etc.

[24] A. Clearfield and P. A. Vaughan, abstract of paper presented at American Crystallographic Association Summer Meeting, June 22–26, 1953, Ann Arbor, Michigan.