the equilibrium constant, per mole of diborane, is

$$\log_{10} K_{1p\,(\mathrm{atm})} = 7.478 - 6205/T$$

The measured kinetic constants which were cited by the various authors in the form of $(k_x K_{\mathrm{eq}}^{1/2})$ now can be evaluated separately. These have been assembled in Table I for ready reference, expressed in the form $10^A \exp(-E/RT)$, with concentration units in [moles cc.$^{-1}$].

ITHACA, N. Y.

[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

Investigation of the Complexes of Mercury(II) with Ethylenediaminetetraacetic Acid Using the Mercury Electrode

BY JAMES I. WATTERS, JOHN G. MASON[1] AND O. E. SCHUPP, III

RECEIVED JULY 2, 1956

Mercury(II) forms complexes with ethylenediaminetetraacetate ion which are reversibly reduced at the dropping mercury electrode in the acidic *p*H range and to a *p*H of 10 if a relatively large excess of the ligand is present. The composite anodic–cathodic polarographic waves with excess ligand have slopes of 0.030 volt corresponding to a reversible 2 electron transfer. The relative magnitudes of the anodic and cathodic diffusion currents as well as the 0.030 volt shift in the wave for a tenfold change in the ethylenediaminetetraacetic acid concentration prove the complexes contain one mercury(II) and one ethylenediaminetetraacetate ion. The mercury pool electrode rapidly reaches equilibrium with the complexes in solutions containing excess ligand from a *p*H of 10 to at least 2. The potential of the electrode as a function of *p*H and ligand concentration has permitted the interpretation of the equilibrium and the evaluation of the equilibrium constants. Below a *p*H of 3.5, the association of one hydrogen ion by the bound ligand occurs while above a *p*H of 8, the association of one hydroxyl ion occurs. The predominant species in the *p*H range of 4 to 8 is $\mathrm{Hg(enta)^{2-}}$, with $K_{100} = 10^{21.64 \pm 0.02}$ at 25° and $\mu = 0.1$. In more acidic solutions $\mathrm{Hg(Henta)^-}$ also occurs with $K_{110} = 10^{14.62 \pm 0.10}$. In more basic solutions the second species is $\mathrm{Hg(OH)(enta)^{3-}}$ with $K_{101} = 10^{26.60 \pm 0.15}$.

Introduction

After the completion of the polarographic portion of the present investigation a similar study was reported by Matyska and Kossler.[2] In agreement with our results they found three complexes $\mathrm{Hg(enta)^{2-}}$, $\mathrm{Hg(Henta)^-}$ and $\mathrm{Hg(OH)(enta)^{3-}}$ where enta indicates the ethylenediaminetetraacetate ion. However, their complexity constants were consistently smaller than ours. It was concluded that the difference was caused by an unreliable saturated mercury(I) sulfate reference electrode to which they assigned a potential of 0.417 volt instead of the theoretical 0.65 volt. More recently Goffart, Michel and Duychaerts[3] as well as Schwarzenbach, Gut and Anderegg[4] have studied the complex polarographically. The former authors studied the system by the conventional polarographic method in the *p*H range of 4.5 to 9.2. Their data indicated a single complex $\mathrm{Hg(enta)^{2-}}$ in this *p*H range with a complexity constant of $10^{22.15}$ at 25° and $\mu = 0.065 \pm 0.02$. Schwarzenbach, Gut and Anderegg[4] obtained polarograms of a solution containing two metal ions and insufficient enta to completely complex them. From the wave height of one metal ion in the uncomplexed form the known complexity constant of one of the complexes, and the known total concentrations, they calculated the concentrations of all metal species and finally the unknown equilibrium constant. In this way the complexity constants for a large number of cations were calculated. Although the method did not succeed for mercury(II), they included equilibrium constants presumably calculated on the basis of the shift of half wave potential. For the simple and the acid complexes of mercury(II) at $\mu = 0.1$ and 20° their values, $K_{100} = 10^{21.80}$ and $K_{110} = 10^{14.64}$, are in good agreement with ours.

Theoretical

The general mathematical procedure used in the present study was presented in an earlier paper.[5] Since all of the complexes contained mercury(II) and the ligand in a (1:1) ratio, the calculations were relatively simple. The various equilibria involving the association of hydrogen ion with the bound ligand were first considered in terms of the concentration of ethylenediaminetetraacetate ion and the activities of hydrogen ions, instead of ions such as $\mathrm{Henta^{3-}}$ and $\mathrm{H_2enta^{2-}}$, since this greatly simplified the calculations. These constants, indicated by primes, were finally converted to the desired forms.

In the following equations, parentheses indicate concentrations while brackets indicate activities.

$$\mathrm{Hg^{2+} + enta^{4-} \rightleftharpoons Hg(enta)^{2-}};\quad K_{100} = \frac{(\mathrm{Hg(enta)^{2-}})}{(\mathrm{Hg^{2+}})(\mathrm{enta^{4-}})} \quad (1)$$

$$\mathrm{Hg^{2+}} + s\mathrm{H^+} + \mathrm{enta^{4-}} \rightleftharpoons \mathrm{Hg(H_{\mathit{s}}enta)^{(2-\mathit{s})-}};\quad K'_{1s0} = \frac{(\mathrm{Hg(H_{\mathit{s}}enta)^{(2-\mathit{s})-}})}{(\mathrm{Hg^{2+}})[\mathrm{H^+}]^s(\mathrm{enta^{4-}})} \quad (2)$$

$$\mathrm{Hg^{2+}} + t\mathrm{OH^-} + \mathrm{enta^{4-}} \rightleftharpoons \mathrm{Hg(OH)_{\mathit{t}}enta^{(2+\mathit{t})-}};\quad K_{10t} = \frac{(\mathrm{Hg(OH)_{\mathit{t}}enta^{(2+\mathit{t})-}})}{(\mathrm{Hg^{2+}})[\mathrm{OH^-}]^t(\mathrm{enta^{4-}})} \quad (3)$$

In terms of these equilibria, eq. 8 for Leden's[6]

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[1] Presented in part before the Division of Physical and Inorganic Chemistry, American Chemical Society, at Kansas City, Mo., April 1, 1954. Taken in part from a thesis by J. G. Mason submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1955.

(2) B. Matyska and I. Kossler, *Collection Czech. Chem. Commun.*, **16**, 221 (1951).

(3) J. Goffart, G. Michel and G. Duychaerts, *Anal. Chim. Acta*, **9**, 184 (1953).

(4) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 939 (1954).

(5) J. I. Watters and John G. Mason, THIS JOURNAL, **78**, 285 (1956).

(6) I. Leden, *Z. physik. Chem.*, **188A**, 160 (1941).

function, F_0, of the previous paper[5] becomes

$$F_0(\text{enta}^{4-}, \text{H}^+, \text{OH}^-) = \left(\text{antilog}\,\frac{(E_0' - E)}{S}\right) C_m - 1 =$$
$$K_{100}(\text{enta}^{4-}) + K'_{110}(\text{enta}^{4-})[\text{H}^+] + K'_{120}(\text{enta}^{4-})[\text{H}^+]^2$$
$$[\text{H}^+]^2 + \ldots$$
$$+ K_{101}(\text{enta}^{4-})[\text{OH}^-] + K_{102}(\text{enta}^{4-})[\text{OH}^-]^2 + \ldots \quad (4)$$

The following expressions of Leden's equations which are obtained readily by the subtraction of K_{100} and division by $[\text{H}^+]$ or $[\text{OH}^-]$ proved to be the most useful.

$$F_1 = F_0/(\text{enta}) = K_{100} + K'_{110}[\text{H}^+] + K'_{120}[\text{H}^+]^2 + \ldots$$
$$+ K_{101}[\text{OH}^-] + K_{102}[\text{OH}^-]^2 + \ldots \quad (5)$$

$$F_{2a} = (F_1 - K_{100})/[\text{H}^+] = K'_{110} + K'_{120}[\text{H}^+] + \ldots\ldots\ldots$$
$$+ K_{101}[\text{OH}^-]/[\text{H}^+] + K_{102}[\text{OH}^-]^2/[\text{H}^+] \ldots (6)$$

$$F_{2b} = (F_1 - K_{100})/[\text{OH}^-] = K_{101} + K'_{110}[\text{H}^+]/[\text{OH}^-] + \ldots$$
$$+ K_{102}[\text{OH}^-] + \ldots \quad (7)$$

The function F_1 is useful since its value remains constant in the range where Hg(enta)^{2-} predominates. The functions F_{2a} and F_{2b} are useful since they remain constant in the acidic and basic ranges where Hg(Henta)^- and HgOH(enta)^{3-}, respectively, predominate. Functions F_1, F_{2a} and F_{2b} were adequate for evaluating the complexity constants for the three complexes found. The constant for the acid complex was converted to that for the equilibrium

$$\text{Hg}^{2+} + \text{Henta}^{3-} \rightleftharpoons \text{Hg(Henta)}^-;$$
$$K_{110} = \frac{(\text{Hg(Henta)}^-)}{(\text{Hg}^{2+})(\text{Henta}^{3-})} \quad (8)$$

$$K_{110} = \frac{(\text{Hg(Henta)}^-)K_4}{(\text{Hg}^{2+})(\text{H}^+)(\text{enta}^{4-})} = K'_{110} \times K_4 \quad (9)$$

where K_4 is the fourth dissociation constant of ethylenediaminetetraacetic acid.

Schwarzenbach expresses the equilibrium for the acidic complex in eq. 8 thus

$$\text{Hg enta}^{2-} + \text{H}^+ \rightleftharpoons \text{Hg Henta}^-$$
$$K_a = \frac{(\text{Hg Henta}^-)}{(\text{Hg enta}^{2-})[\text{H}^+]} = K'_{110}/K_{100} \quad (10)$$

which is the reciprocal of the acidity constant of Hg Henta^-. For the alkaline equilibrium he writes

$$\text{Hg}^{2+} + \text{enta}^{4-} + \text{H}_2\text{O} \rightleftharpoons \text{Hg(OH) enta}^{3-} + \text{H}^+$$
$$K_b = \frac{(\text{Hg(OH) enta}^{3-})[\text{H}^+]}{(\text{Hg}^{2+})(\text{enta}^{4-})} = K_{101} \times K_w \quad (11)$$

For this conversion and for the calculation of tetraacetate ion concentration, the acidity constants determined by Schwarzenbach and Ackermann[7] were used. For the successive hydrogen ion dissociations at 20° in 0.1 N KCl they reported $pK_1 = 1.996$, $pK_2 = 2.672$, $pK_3 = 6.161$ and $pK_4 = 10.262$. Since one ligand molecule is complexed throughout the range investigated, the concentration of completely dissociated enta ion is

$$(\text{enta}^{4-}) =$$
$$\frac{(C_1 - C_{\text{Hg}})K_1K_2K_3K_4}{K_1K_2K_3K_4 + K_1K_2K_3[\text{H}^+] + K_1K_2[\text{H}^+]^2 + K_1[\text{H}^+]^3 + [\text{H}^+]^4} \quad (12)$$

where C_1 and C_m are the total concentrations of ethylenediaminetetraacetic acid and mercury(II) ion, respectively, and K_n is the nth acidic dissociation constant of the acid.

Experimental

The potentiometric and polarographic apparatus, the general experimental method and the preparation of the mercury(II) solution were described in a previous publication.[5] The cell was separated from the saturated calomel electrode by a salt bridge containing 0.1 M KNO_3 in 3% agar agar. All experiments were performed at 25 ± 0.1° using solutions containing 0.1 M KNO_3 to produce an ionic strength of 0.10 ± 0.01.

The ethylenediaminetetraacetic acid solutions were prepared on a weight basis from C.P. grade acid, Versenes Inc. The molarity was verified by titrating with standard HCl using the glass electrode. Solutions of intermediate pH were prepared by mixing in various ratios the acidic and basic solutions having the same concentration of mercury(II) and ethylenediaminetetraacetic acid. Potassium hydroxide and freshly boiled nitric acid were used to adjust the pH of the acidic and basic stock solutions.

The capillary used for determining the polarographic diffusion current constant had a drop time of 5.89 sec. and delivered 1.278 mg. of mercury per second at the potential of the S.C.E. corresponding to a capillary characteristic, $m_0^{2/3}t_0^{1/6}$, of 1.664 mg.$^{2/3}$ sec.$^{1/2}$.

Results and Discussion

Reversible anodic–cathodic polarograms were obtained for solutions containing mercury(II) ion with a small excess of enta using 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ at pH 8.5 as the supporting electrolyte with 0.005% gelatin added as a maximum suppressor. The anodic–cathodic polarogram of a solution 0.5×10^{-3} M in Hg^{2+} and 1.0×10^{-3} M in enta furnished considerable information concerning the nature of the complex. Since the anodic and cathodic diffusion currents were approximately equal it was evident that the complex must contain the mercury(II) and the enta in a (1:1) ratio. The excellent continuity of the wave across the zero current axis indicated a reversible electrode reaction. In the absence of mercury in the solution well shaped anodic waves with similar half wave potentials were obtained. With the same concentration of enta, 1.0×10^{-3} M but with the mercury(II) ion absent the anodic diffusion current was, as expected, twice as large as in the former polarogram.

The value of $\Delta E/\log(i_{d_0} - i)$ in both the anodic–cathodic and the anodic waves was 0.032 v., proving the electrode reaction to be essentially a reversible two-electron transfer. Similar waves were obtained in more alkaline solutions and below a pH of 4. However, approaching a pH of 7 the slope increased to more than double this value. Similar results were obtained in unbuffered solutions 1 M in KNO_3 in which the pH was adjusted with nitric acid or potassium hydroxide.

When the enta concentration was increased to 0.1 M the wave became continuous across the zero current axis. There was no constant anodic diffusion current region due to the large enta concentration. The slope of 0.030 v., obtained throughout the pH range of 2 to 12, indicates a reversible 2-electron transfer. Another advantage of the excess ligand concentration is the buffering capacity in the absence of foreign anions other than nitrate. In 0.1 M KNO_3 the diffusion current constant of the Hg enta^{2-} complex was 3.09 microamperes millimolar^{-1} mg.$^{-2/3}$ sec.$^{-1/2}$ in the pH range of 6 to 9.

The reversibility of the electrode was further tested by measuring the spontaneous potential of the dropping mercury electrode and of a quiet mercury pool in solution in which the mercury(II) and

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(7) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

the enta concentrations as well as the *p*H were varied independently over at least a tenfold range. The two electrodes yielded essentially the same potential except for the iR_{cell} drop due to the charging current of the dropping electrode. No drift in potential was observed with either electrode. Because the potentials of the quiet mercury pool *versus* the saturated calomel electrode were measured with greater precision, these values presented in Fig. 1 and Table I were used in the calculations.

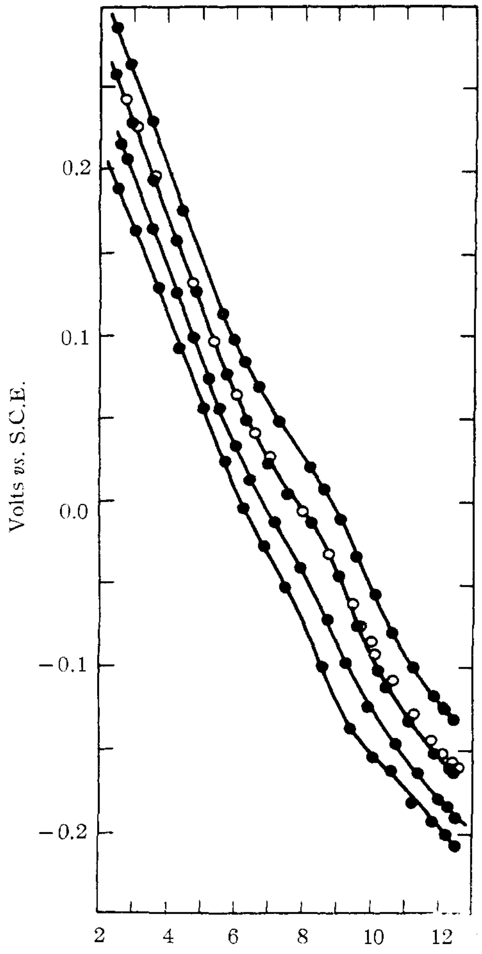

Fig. 1.—Effect of varying the *p*H on the potential of the mercury pool in the following solutions: (1) 1 × 10^{-5} *M* $Hg(NO_3)_2$, 1 × 10^{-2} *M* enta, 0.1 *M* KNO_3; (2) 1 × 10^{-4} *M* $Hg(NO_3)_2$, 1 × 10^{-2} *M* enta, 0.1 *M* KNO_3; (3) (solid circles) 1 × 10^{-3} *M* $Hg(NO_3)_2$, 1 × 10^{-2} *M* enta, 0.1 *M* KNO_3; (3) (open circles) 1 × 10^{-4} *M* $Hg(NO_3)_2$, 1 × 10^{-3} *M* enta, 0.1 *M* KNO_3; (4) 5 × 10^{-4} *M* $Hg(NO_3)_2$, 1 × 10^{-3} *M* enta, 0.1 *M* KNO_3.

Comparing the potentials in curves 1 and 2, the potential shift due to a tenfold increase in mercury ion is +0.029 ± 0.002 v. in the *p*H range of 2 to 10. Comparing curves 2 and 3 (open circles), the shift in potential due to a tenfold increase in enta concentration is close to 0.030 ± 0.002 v. in the *p*H range from 2 to 12. In curve 3 the points for a tenfold dilution (open circles) lie close to those for the more concentrated solutions (solid circles) except in the most alkaline range.

It was not necessary to consider Hg_2^{2+} even at a *p*H of 2 since the addition of HCl to the solutions resulted in no precipitation of Hg_2Cl_2.

Substitution of the data into equation 5 yielded essentially a constant value of $10^{21.64 \pm 0.02}$ for F_1 at 25° and $\mu = 0.1$ in the *p*H range of 4 to 8. This constant value of F_1 is equal to K_{100}. Typical data and results are summarized in Table I. Outside of the *p*H range of 4 to 8 the values of F_1 began to deviate.

TABLE I

*p*H	E_{SCE}	log F_1	log $F_2{}^a$
A. Curve 3 (solid circles), $C_{\text{enta}} = 10^{-2}$ *M*, $C_{\text{Hg}} = 10^{-3}$ *M*			
2.38	0.25801	22.63	24.96
2.94	.22883	22.11	24.87
3.21	.21603	21.93	24.83
3.97	.17471	21.71	24.85
4.80	.12696	21.66	
6.04	.06125	21.63	
7.20	.01752	21.63	
8.25	− .01357	21.60	
9.05	− .04547	21.90	26.50
10.20	− .10135	22.88	26.65
10.22	− .10296	22.92	26.68
10.50	− .11185	23.10	26.59
12.45	− .16371	24.66	26.21
B. Curve 2, $C_{\text{enta}} = 10^{-2}$ *M*, $C_{\text{Hg}} = 10^{-4}$ *M*			
2.60	0.21564	22.35	24.85
2.79	.20630	22.20	24.85
2.99	.19240	22.18	25.02
3.90	.14528	21.80	25.19
4.74	.09908	21.68	
5.51	.05658	21.64	
6.26	.02040	21.63	
7.13	− .01320	21.68	
8.70	− .07164	22.04	27.12
9.49	− .10791	22.45	26.88
10.14	− .13325	22.96	26.80
10.54	− .14152	23.02	26.46
12.52	− .19085	24.53	26.01
C. Curve 3 (open circles), $C_{\text{enta}} = 10^{-3}$ *M*, $C_{\text{Hg}} = 10^{-4}$ *M*			
2.72	0.24255	22.20	24.88
3.00	.22782	22.01	24.78
3,48	.19874	21.91	25.08
4.73	.13156	21.64	
5.35	.09726	21.60	
6.52	.04082	21.64	
7.99	− .00601	21.60	
8.94	− .04728	22.06	26.92
9.73	− .07452	22.28	26.44
10.15	− .09287	22.62	26.42
12.57	− .16064	24.55	25.98

[a] $F_2 = F_{2a}$ in acidic range and F_{2b} in basic range.

The constant value of F_{2a}, $10^{24.88 \pm 0.10}$ below a *p*H of 4, proves the presence of a single complex containing one hydrogen. This value of F_{2a} corresponds to the value of the equilibrium constant K'_{110} shown in eq. 2 and 9. Conversion to the equilibria in equation 8 yields $K_{110} = 10^{14.62 \pm 0.10}$. Converting to Schwarzenbach's acidity expression, eq. 10 yields $K_a = 10^{3.24}$.

The constant value of F_{2b}, $10^{26.60 \pm 0.15}$ in the *p*H range above 8, indicates that the second species in alkaline solutions contains only one hydroxide 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 pH 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 pH 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]

BY A. J. ZIELEN AND ROBERT E. CONNICK

RECEIVED JULY 13, 1956

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.

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