Anal. Calcd. for $C_{12}H_{10}Cl_2SeO$: equiv. wt. (iodometric),[7] 159.1. Found: equiv. wt., 159.8.

p,p'-Dimethoxydiphenyl Selenoxide.—Ten grams of p,p'-dimethoxydiphenyl selenide was dissolved in 30 ml. of warm dioxane. The temperature of the solution was brought to 80°, and small portions of a 30% solution of hydrogen peroxide were carefully added to the hot solution. The foaming and oxygen evolution following each addition was allowed to cease before adding a subsequent portion. After a total of 40 ml. of peroxide solution had been added, the mixture was evaporated to cloudiness on a hot-plate. The crystals formed upon letting the solution cool overnight were filtered off, dried for a few hours in air, and dissolved in boiling benzene. The hot benzene solution was treated with anhydrous magnesium sulfate and Norite, then filtered. The white prisms which separated on cooling were twice recrystallized from benzene; yield 6.5 g. (63%); m.p. 144° (dec.).

Anal. Calcd. for $C_{14}H_{14}O_3Se$: Se, 25.5; equiv. wt. (iod.), 154.5. Found: Se, 25.5; equiv. wt., 154.1.

p,p'-Diethoxydiphenyl selenoxide was prepared as described for the methoxy compound; yield 58%; m.p. 150° (dec.).

Anal. Calcd. for $C_{16}H_{18}O_3Se$: Se, 23.4; equiv. wt. (iod.), 168.5. Found: Se, 23.4; equiv. wt., 169.0.

Oxidation of p,p'-Dimethoxydiphenyl Selenide with Peracetic Acid.—Ten grams of the diaryl selenide was added in small portions to 25 ml. of a 40% solution of peracetic acid in glacial acetic acid. The reaction was quite vigorous. The mixture was carefully heated to boiling, then quickly cooled. The solution was carefully made basic by addition of concentrated ammonium hydroxide, whereupon a considerable quantity of oil separated. The oil solidified after standing one hour; the dark-colored solid was filtered off, dissolved in boiling benzene, and the benzene solution treated with anhydrous magnesium sulfate and Norite, then filtered. Cooling yielded a white solid which was recrystallized from benzene. The product weighed 4.5 g. and melted at 148.5–149.5. A solution of the solid in alcohol did not oxidize acidified potassium iodide solution, indicating that the product was not a selenoxide.

Anal. Calcd. for $C_{14}H_{14}O_4Se$: Se, 24.3. Found: Se, 23.9.

Oxidation of p,p'-diethoxydiphenyl selenide in the same way yielded a similar product, melting at 176–177°.

Anal. Calcd. for $C_{16}H_{18}O_4Se$: Se, 22.5. Found: Se, 22.4.

When either of the above two products was mixed with an equimolar quantity of any of the three mercury(II) halides and the mixture of solids dissolved in a minimum quantity of boiling ethanol, cooling the solution yielded no complex. Instead one of the starting materials crystallized. In the case of the mixtures with mercury(II) bromide or chloride, the product first separating was the selenium-containing compound. In the case of the mixtures with mercury(II) iodide, the first product separating was the yellow form of HgI_2 which changed upon standing to the familiar red form.

Preparation of the Complexes.—A mixture of one millimole of the halide and 1.10 millimoles of the selenoxide was dissolved in a minimum quantity of boiling 95% ethanol. Cooling the solution yielded the desired complex; in those cases where no solid complex was formed, one or both of the starting components separated instead. The complex could usually be distinguished from either of its components or a mixture of both of them by differences in crystalline form. In doubtful cases, a constant composition corresponding to that of $Ar_2SeO \cdot HgX_2$ retained by the solid after successive recrystallizations was taken as a criterion of complex formation. The complexes formed from mercury(II) bromide and mercury(II) chloride are colorless, those of mercury(II) iodide a bright yellow color.

Analytical Methods.—Iodometric equivalent weights of the complexes were obtained by dissolving a weighed sample in warm methanol, adding an excess of acidified potassium iodide solution in water, and titrating the triiodide ion released with standard sodium thiosulfate solution, using the starch end-point. It was found that addition of a few ml. of chloroform to the solution being titrated when the triiodide color became indistinct sharpened the end-point and increased the reliability of the titration.

The analyses for the selenium content were carried out as follows: the sample was thoroughly digested in a mixture of nitric and sulfuric acids, and the resulting solution was diluted with water. Excess nitrous acid was destroyed by addition of urea, and excess potassium iodide was added. The triiodide formed from the reaction of the selenious acid and the iodide was titrated by a method previously described.[7] This method could not be applied to complexes containing iodine since treatment with the sulfuric–nitric acid mixture oxidized a portion of the iodine in the complex to iodate, thus invalidating the titration. A more detailed description of this method, together with an evaluation of its applicability toward other types of organoselenium compounds, will appear in a subsequent communication.

BROOKLYN, N. Y. RECEIVED JANUARY 8, 1951

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[7] J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Anal. Chem.*, **18**, 638 (1946).

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Zirconium Chloranilate Complexes

BY B. J. THAMER[1] AND A. F. VOIGT

Spectrophotometric measurements at 25° in 1 to 2 M perchloric acid solutions of ionic strength of 2 have shown the equilibria: $Zr(IV) + H_2Ch \rightleftarrows Zr(IV)Ch^{++} + 2H^+$, $K_1 = (5.69 \pm 0.08) \times 10^{+5}$, $Zr(IV)Ch^{++} + H_2Ch \rightleftarrows Zr(IV)Ch_2 + 2H^+$, $K_2 \simeq 6000$, where Zr(IV) represents the zirconium monomer, H_2Ch undissociated chloranilic acid and the constants are in terms of concentrations. A precipitate that forms in these solutions with concentrations of the reactants of roughly 5×10^{-4} molar is shown to have a Zr:Ch ratio of 1 to 1.24. A spectrophotometric method is developed for determining zirconium at formalities of 2×10^{-6} to 5×10^{-5} using chloranilic acid and measurement at 3400 Å. The color reaction proceeds rapidly and yields a true solution that is stable indefinitely. The characteristics of chloranilic acid as a colorimetric reagent for zirconium are compared briefly with those of other such reagents.

During a study of various organic complexing agents for zirconium it was found that chloranilic acid gave a bright magenta solution with low concentrations of zirconium even in concentrated acid. Since this reaction had potential practical value as an analytical reaction for zirconium and considerable theoretical interest, the formulas of the products and the formation constants were determined spectrophotometrically.

Non-complexing solutions with constant ionic strength were prepared using perchloric acid plus lithium perchlorate to give a constant total perchlorate concentration of two molar and perchloric acid concentrations from 1 to 2 molar. Measurements were made at 25 ± 1°. Under these conditions and at the zirconium concentrations em-

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[1] Taken from part of the Ph.D. thesis of B. J. Thamer, Iowa State College, 1950.

ployed, the zirconium is reported to be present as an uncomplexed monomer.[2]

Materials and Apparatus

Zirconium perchlorate was prepared from a pure grade of extensively recrystallized zirconyl chloride octahydrate kindly supplied by Dr. K. A. Walsh. Zirconium hydroxide was precipitated from 0.03 *M* $ZrOCl_2$, washed until only a trace of chloride was detectable in the washes, and dissolved in 2.003 *M* perchloric acid. The latter solution was assayed for zirconium by precipitation of the hydroxide and ignition to the oxide. A suitable aliquot was diluted to 1.033×10^{-3} *M* zirconium(IV) in 2.003 *M* perchloric acid. Chloranilic acid purified as described elsewhere[3] was made up to the same concentration in perchloric acid of the same strength.

All solutions were prepared with conductivity water. The stock perchloric acid was prepared using appropriate dilutions of commercially double vacuum distilled perchloric acid.[4] It was standardized against carbonate-free sodium hydroxide for which potassium acid iodate[4] was used as a primary standard. Commercially available lithium perchlorate even after recrystallization was found to contain sufficient sulfate to complex zirconium to an appreciable extent. Consequently the lithium perchlorate was prepared by either of the following methods both of which yielded products free of complexing anions. (1) Lithium metal from the Belmont Smelting and Refining Works was converted to the hydroxide by reaction with water in a platinum dish. After neutralization with diluted perchloric acid,[4] the solution was slightly acidified, allowed to stand for 15–20 hours and filtered free of any silica. If necessary the solution was made alkaline and filtered to remove iron. The solution was finally brought to a *p*H of 7, and aliquot portions were assayed for lithium perchlorate by ignition at 280° and weighing as $LiClO_4$.[5] The solution was then diluted to 2.003 *M*, the exact concentration of the "two molar" perchloric acid. (2) Commercial lithium perchlorate was heated at 270–280° in a stream of dry air for four hours.[5] Sulfate was expelled as sulfuric acid due to the presence of a small amount of acid in the salt. The solution of the desired strength of lithium perchlorate was made up directly from the anhydrous salt.

A Model 12 Cary Recording Spectrophotometer was used in all work except the analytical studies for which a Beckman Model DU Spectrophotometer was employed. Matched silica cuvettes were used throughout and the instrument in use was always zero-adjusted immediately before measurement.

The 1:1 Complex.—The 1:1 complex was identified using Job's method of continuous variations[6] at a total concentration of 1.033×10^{-4} molar in 2.003 molar perchloric acid. The second complex was present in negligible amount at these concentrations. The solutions were scanned in a 10 mm. cuvette in the ultraviolet. The plot at several wave lengths of $(D - (x/10)D_{x=10})$ *versus* x as shown in Fig. 1 gave a maximum or minimum at $x = 5$ thus indicating the zirconium-to-chloranilate ratio to be unity in this complex.

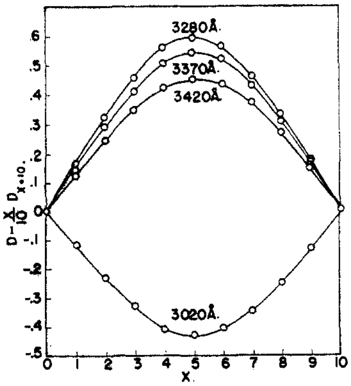

Fig. 1.—The identification of the 1:1 zirconium chloranilate complex: $x/10$ = fraction of chloranilic acid.

A series of solutions was scanned in order to demonstrate that the 1:1 complex obeyed Beer's law. The solutions were prepared in 2.003 molar perchloric acid having a 1.033×10^{-3} molar excess of zirconium in order to prevent the formation of any of the second complex which was later shown to have a lower zirconium-to-chloranilate ratio. The chloranilic acid was more than 99% in the form of the 1:1 complex in this series of solutions. At all wave lengths tested, 2900–3500 Å., Beer's law was obeyed. Similar data for chloranilic acid verified that it also obeyed Beer's law at the concentrations used.

All equilibria reported in this paper were studied solely in terms of concentrations because of the difficulty of obtaining activity coefficients for the zirconium monomer and its complex ions. In studying the formation constant of the 1:1 complex the formality of the chloranilic acid was kept at 1.033×10^{-5} and that of the zirconium was varied from 1.033×10^{-5} to 1.033×10^{-3}. The concentration of the second complex was negligibly low. Three series of experiments were performed, at perchloric acid concentrations of 2.003, 1.502 and 1.001 molar. At concentrations of zirconium at which the equilibrium was measurable the zirconium was entirely in the form of the monomer as could be shown from the data of Connick and Reas.[2] From their data the formula of the monomer will be taken as Zr^{+4} and the effect of its possible hydrolysis to $Zr(OH)^{+3}$ will be discussed later. The formation of the 1:1 complex proceeds according to

$$Zr^{+4} + H_2Ch \rightleftarrows (ZrH_{2-n}Ch)^{+4-n} + nH^+ \quad (1)$$

where H_2Ch represents undissociated chloranilic acid.

Representing 1.033×10^{-5} by c and assuming αc to be the concentration of the 1:1 complex, the formality of uncombined chloranilic acid is $c(1 - \alpha)$. The latter quantity is related to the actual concentration of chloranilic acid by

$$[H_2Ch] = \frac{c(1 - \alpha)}{1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}}$$

where k_1 and k_2 are the dissociation constants (in terms of concentrations) of chloranilic acid. The values are $k_1 = 0.083$ and $k_1k_2 = 3.17 \times 10^{-4}$ determined in 2.003 molar perchloric acid–lithium perchlorate solutions.[3] The term $k_1k_2/[H^+]^2$ can be neglected in the present studies. Expressing the total formality of the zirconium as cy, that of uncomplexed zirconium is $c(y - \alpha)$. The formation constant is then

$$K_1 = \frac{1}{c}[H^+]^n\left(1 + \frac{k_1}{[H^+]}\right)\cdot\rho \quad (2)$$

where

$$\rho = \frac{\alpha}{(y - \alpha)(1 - \alpha)} \quad (3)$$

The optical density D can be shown to be

$$D = \alpha D_{11} + (1 - \alpha)D_0 \quad (4)$$

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(2) R. E. Connick and W. H. Reas, THIS JOURNAL, **73**, 1171 (1951)

(3) B. J. Thamer and A. F. Voigt, *J. Phys. Colloid Chem.*, in press.

(4) Obtained from the G. Frederick Smith Chemical Co.

(5) T. W. Richards and H. H. Willard, THIS JOURNAL, **32**, 4 (1910).

(6) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

where D_{11} is the optical density of the solution when the chloranilic acid is completely in the form of the 1:1 complex and D_0 is the optical density with no zirconium present. Since D_{11} and D_0 can be easily evaluated, α can be obtained from equation 4 in the form

$$\alpha = (D - D_0)/(D_{11} - D_0) \qquad (5)$$

The absorption curves shown in Fig. 2 are representative of the data that were obtained. The 1:1 complex ($y = 25$) showed an absorption maximum at 3280 Å. and uncombined chloranilic acid ($y = 0$) showed a peak at 3020 Å. Both wave lengths were used in the calculations. Values of D_{11} were estimated within 0.5% accuracy from solutions having 99% or more of the chloranilic acid in the form of the 1:1 complex.

TABLE I

THE 1:1 COMPLEX WITH 2.003 *M* ACID

	At 3280 Å. $D_{11} = 0.947$, $D_0 = 0.050$		At 3020 Å. $D_{11} = 0.406$, $D_0 = 1.043$	
y	D	ρ	D	ρ
1.00	0.448	1.437	0.762	1.411
1.10	.472	1.408	.743	1.416
1.20	.499	1.429	.730	1.369
1.25	.505	1.384	.715	1.445
1.50	.560	1.411	.685	1.369
2.00	.638	1.420	.625	1.420
99.0	.939	...	.411	...

TABLE II

THE 1:1 COMPLEX WITH 1.502 *M* ACID

	At 3280 Å. $D_{11} = 0.938$, $D_0 = 0.050$		At 3020 Å. $D_{11} = 0.396$, $D_0 = 1.016$	
y	D	ρ	D	ρ
1.00	0.528	2.52	0.696	2.20
1.10	.552	2.43	.669	2.36
1.25	.600	2.58	.647	2.24
2.00	.717	2.42	.552	2.37
74.0	.930	..	.402	..

TABLE III

THE 1:1 COMPLEX WITH 1.001 *M* ACID

	At 3280 Å. $D_{11} = 0.936$, $D_0 = 0.051$		At 3020 Å. $D_{11} = 0.394$, $D_0 = 1.010$	
y	D	ρ	D	ρ
1.00	0.620	5.04	0.606	5.54
1.10	.651	5.00	.583	5.55
1.20	.682	5.14	.564	5.56
1.30	.710	5.27	.546	5.58
25.0	.927	..	.400	..

The data obtained at the three acidities have been summarized in Tables I, II and III.

The average values of ρ and their standard deviations are shown in Table IV. Values calculated for n using pairs of ρ values and equation (2) were 1.87, 1.975 and 2.05, the average being 1.97. This was so close to 2 that n was assumed to be exactly 2 in calculating the average values of K_1 shown in the table.

TABLE IV

AVERAGE VALUES OF ρ AND K_1

$[H^+]$	ρ	$\bar{K}_1 \times 10^{-5}$
2.003	1.410 ± 0.023	(5.71 ± 0.09)
1.502	2.39 ± 0.12	(5.52 ± 0.28)
1.001	5.34 ± 0.24	(5.62 ± 0.25)

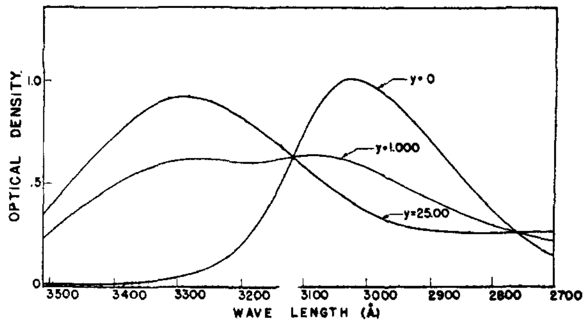


Fig. 2.—Absorption curves of chloranilic acid plus zirconium in 1 *M* $HClO_4$ + 1 *M* $LiClO_4$; length of cuvette 50.00 mm.

The three values of $\bar{K}_1$ gave a grand mean value of

$$\bar{\bar{K}}_1 = (5.69 \pm 0.08) \times 10^{+5}$$

Since n was found to be 2, $\bar{\bar{K}}_1$ presumably refers to

$$Zr^{+4} + H_2Ch \rightleftarrows ZrCh^{+2} + 2H^+ \qquad (6)$$

and

$$K_1 = \frac{[H^+]^2[ZrCh^{+2}]}{[Zr^{+4}][H_2Ch]} \qquad (7)$$

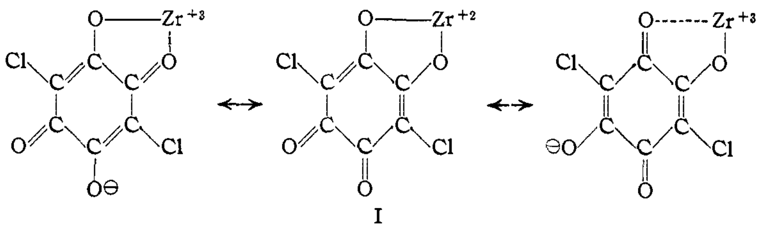
Data of Connick and Reas indicate that the uncomplexed zirconium monomer would be present principally as Zr^{+4} in these solutions. However, hydrolysis of Zr^{+4} and $ZrCh^{+2}$ might proceed as

$$Zr^{+4} + H_2O \rightleftarrows Zr(OH)^{+3} + H^+$$
$$h_0 = [H^+][Zr(OH)^{+3}]/[Zr^{+4}]$$
$$ZrCh^{+2} + H_2O \rightleftarrows Zr(OH)Ch + H^+$$
$$h_0 = [H^+][Zr(OH)Ch^+]/[ZrCh^{+2}]$$

where h_0 and h_1 are the hydrolysis constants. The observed values $\bar{K}_1$ are related to K_1 of Equation (7) by

$$\bar{K}_1 = \frac{h_1 + [H^+]}{h_0 + [H^+]} K_1$$

Since $\bar{K}_1$ was observed to be independent of acidity and h_0 is definitely less than 1 judging from the data of Connick and Reas,[2] h_1 and h_0 must be roughly equal or both must be quite small with respect to 1. Thus the 1:1 complex must be largely $ZrCh^{+2}$ the structure of which is represented by I.

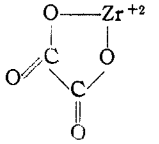


I

The zirconium atom is very likely close enough to each of the adjacent oxygen atoms to make the middle resonance structure of I the most important.

Because of the difference in charge on the zirconium atom in Zr^{+4} and $ZrCh^{+2}$, it is unlikely that these two species should have similar degrees of hydrolysis. Therefore it can reasonably be assumed that both h_0 and h_1 are negligibly small and that the observed equilibrium is that represented by equation 6 with K_1 of equation 7 equal to $(5.69 \pm 0.08) \times 10^{+5}$.

It is of interest to note that Connick and McVey found that oxalic acid strongly complexed zirconium in 2 *M* perchloric acid but that malonic, succinic and glutaric acids complexed zirconium to a much smaller extent.[7] If the oxalate complexing were due to $Zr(C_2O_4)^{+2}$ (II), the structural resemblance (III) to $ZrCh^{+2}$, and the similar formation constant $(\sim 1 \times 10^{+6})$ would be most striking. The $ZrCh^{+2}$ complex and probably the zirconium oxalate complex are examples in which the structure III is more stable than that of IV. Perhaps the zirconium atom utilizes its low-lying *s* and *d* orbitals to form angular *ds* bonds[8] that are more strain-free in the former.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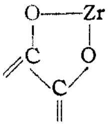
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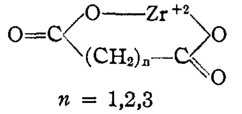
IV

The Second Complex.—The second complex was too unstable with respect to the 1:1 complex to be identified by Vosburgh and Cooper's modification[9] of Job's method.[6] Instead it was necessary to see how well trial values for the Zr to Ch ratio fitted the data. For this purpose a series of solutions was prepared having a zirconium formality *c* of 1.033×10^{-4} or 2.066×10^{-4} and a chloranilic acid formality of *rc* where *r* was varied between 1 and 10. Larger concentrations could not be employed because of the appearance of a precipitate under those conditions. The measurements were made in the visible using 50 mm. cuvettes.

At each acidity it was found that the data could best be interpreted in terms of a second complex having a Zr:Ch ratio of 1:2. Thus the formation of the second complex was assumed to be

$$ZrCh^{+2} + H_2Ch \rightleftarrows ZrH_{2-m}CH_2^{+2-m} + mH^+ \quad (8)$$

$$K_2 = \frac{[H^+]^m[ZrCh_2]}{[ZrCh^{+2}][H_2Ch]} \text{ or } \frac{cK_2}{[H^+]^m} = \frac{c[ZrCh_2]}{[ZrCh^{+2}][H_2Ch]} \quad (9)$$

The expression for the optical density and the equations of material balance can be combined to give

$$D = rD_0 + \frac{1}{c}\left[(Lc\epsilon_{12} - 2D_0)[ZrCh_2] + (Lc\epsilon_{11} - D_0)[ZrCh^{+2}]\right] \quad (10)$$

in which the ϵ's are the extinction coefficients of the two complexes and D_0 is the optical density of chloranilic acid at concentration *c*. By choosing a wave length (3847 Å.) where $Lc\epsilon_{11} = D_0$, equation 10 can be simplified to

$$[ZrCh_2] = \frac{(D - rD_0)c}{Lc\epsilon_{12} - 2D_0} \quad (11)$$

Expressions for the other two absorbing species can be obtained by combining previous equations and discarding some negligible quantities

$$[ZrCh^{+2}] = \frac{c - [ZrCh_2]}{1 + \dfrac{[H^+]^2}{K_1[H_2Ch]}} \text{ and} \quad (12)$$

$$[H_2Ch] = \frac{rc - 2[ZrCh_2] - [ZrCh^{+2}]}{1 + \dfrac{k_1}{[H^+]}} \quad (13)$$

Equations 11, 12 and 13 were used to obtain values for $cK_2/[H^+]^m$ of equation 9. The data are shown in Table V.

TABLE V

OBSERVED OPTICAL DENSITY DATA IN THE REGION OF THE SECOND COMPLEX

$[H^+] = 2.002$ $c = 2.066 \times 10^{-4}$		$[H^+] = 1.401$ $c = 1.033 \times 10^{-4}$		$[H^+] = 1.001$ $c = 1.033 \times 10^{-4}$	
r	*D*	*r*	*D*	*r*	*D*
0.00	0.129	0.00	0.065	0.00	0.068
1.00	.171	2.00	.270	2.00	.303
1.50	.332	3.00	.421	2.40	.373
2.00	.500	4.00	.550	3.00	.470
2.50	.662	5.00	.665	3.40	.528
3.00	.794	6.00	.765	4.00	.608
3.20	.862	..	...	6.00	.822
3.50	.930	..	...	9.00	1.098
3.70	.985	..	...	..	...
4.00	1.058	..	...	..	...

Unfortunately the second complex was too unstable to allow the direct measurement of $Lc\epsilon_{12}$. The value of $cK_2/[H^+]^m$ is a constant at each acidity. Hence the correct value of $Lc\epsilon_{12}$ was taken as the one for which a plot of $cK_2/[H^+]^m$ *versus* *r* would be a horizontal straight line as shown by the method of least squares.

The best values calculated for $Lc\epsilon_{12}$ from the data of Table V but expressed in terms of $c = 1.003 \times 10^{-4}$ for all acidities were 0.804, 0.716 and 0.769 for 2.002, 1.401 and 1.001 molar acid. The average of these ($Lc\epsilon_{12} = 0.763$) was used in obtaining

$$K_2 = 1472(2.02)^m$$
$$K_2 = 3500(1.401)^m$$
$$K_2 = 5100(1.001)^m$$

The least squares technique used to obtain the most constant value of K_2 when plotted against acidity gave $m = 1.84 \pm 0.5$. Since this was 2 within experimental error, the true value of K_2 was taken to be exactly 2 and the resulting values for K_2 were thus 5900, 6870 and 5110. The average value was $K_2 \pm 5960 \pm 720 \simeq 6000 \pm 700$. Hence the equilibrium was

$$ZrCh^{+2} + H_2Ch \rightleftarrows ZrCh_2 + 2H^+ \quad (13)$$

and

$$K_2 = \frac{[H^+]^2[ZrCh_2]}{[ZrCh^{+2}][H_2Ch]} = 6000 \pm 700 \quad (14)$$

Curves calculated with $K_2 = 6000$ and $Lc\epsilon_{12} = 0.763$ (for $c = 1.033 \times 10^{-4}$) are shown in Fig. 3 with the experimental points.

Analogous calculations assuming other Zr:Ch ratios for the second complex gave much less consistent values. The best of these was a 2:3 ratio for which the relative errors were twice those obtained assuming a 1:2 ratio. Thus the principal species of the second complex is believed to be $ZrCh_2$ which may have either of the following structures.

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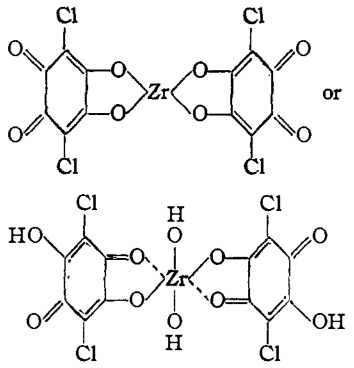
[7] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

[8] G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

[9] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).



A Zirconium Chloranilate Precipitate.—Solutions having greater than 5 × 10^{-4} formal zirconium and chloranilic acid were found to give a gelatinous, blue-gray precipitate in 2 molar perchloric acid. The precipitate was prepared for analysis with concentrations such that the solubility of the chloranilic acid was not exceeded. In order not to alter its composition, the precipitate was not washed but was air-dried for 1 hour after filtration. The moist precipitate was then thoroughly mixed and aliquots were taken to determine its zirconium and chloranilate content.

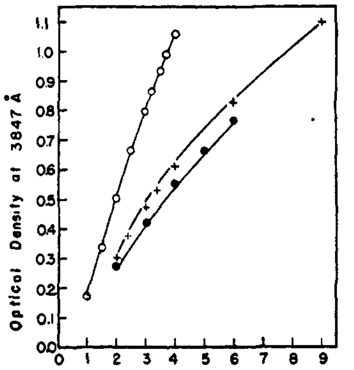


Fig. 3.—Optical densities with excess chloranilic acid present: ○, $[H^+]$ = 2.003, c = 2.066 × 10^{-4}; ●, $[H^+]$ = 1.401, c = 1.033 × 10^{-4}; +, $[H^+]$ = 1.001, c = 1.033 × 10^{-4}. Curves are calculated.

The chloranilate content was obtained by metathesizing the aliquot to $Zr(OH)_4$ and chloranilate ion with dilute sodium hydroxide, adding perchloric acid to dissolve the $Zr(OH)_4$, diluting to a fixed volume in 10^{-3} M excess zirconium and 2 M perchloric acid, and measuring the optical density of the 1:1 complex at 5500 Å. in a 50-mm. cuvette. A solution of similar composition but known chloranilate content served as the standard. The zirconium content was determined by a similar metathesis and solution of another aliquot followed by the addition of sufficient chloranilic acid to make the total chloranilic acid formality 1.033 × 10^{-4} upon dilution to a fixed volume in 2 M perchloric acid. Measurement was made at 3400 Å. in a 10-mm. cuvette. The zirconium formality (2–4 × 10^{-5}) was obtained from the standardization curve shown in Fig. 4.

Table VI shows the results of the analyses of the precipitate which is designated as $ZrCh_n$. Columns two and three represent the initial concentrations of the reactants. Each analytical value was determined with a separate aliquot. Discrepancies between pairs of values for zirconium or chloranilate are attributed mainly to non-representative sampling. The average value of n was 1.24 ± 0.09 thus indicating a zirconium to chloranilate ratio different from that of the 1:1 complex or the second complex. Its value suggests that the precipitate probably is composed of one or more of the species: $Zr_3(OH)_4Ch_4$, $Zr_4(OH)_6Ch_5$, $Zr_5(OH)_8Ch_6$ and/or $Zr_6(OH)_{10}Ch_7$.

TABLE VI

ANALYSES OF THE $ZrCh_n$ PRECIPITATE

$[Zn^{+4}]$ × 10^{+3}	$[H_2Ch]$ × 10^{+3}	10^{+4} × no. millimoles/mg. of ppt. Zr (found)	Zr (av.)	H_2Ch (found)	H_2Ch (av.)	n
2.0	2.6	4.12	4.11	5.40	5.08	1.24
		4.09		4.75		
2.0	2.6	3.57	3.68	4.92	4.91	1.33
		3.80		4.91		
1.0	2.0	7.42	7.25	7.94	7.90	1.09
		7.07		7.86		
3.0	2.0	5.40	5.39	6.44	6.63	1.23
		5.38		6.81		

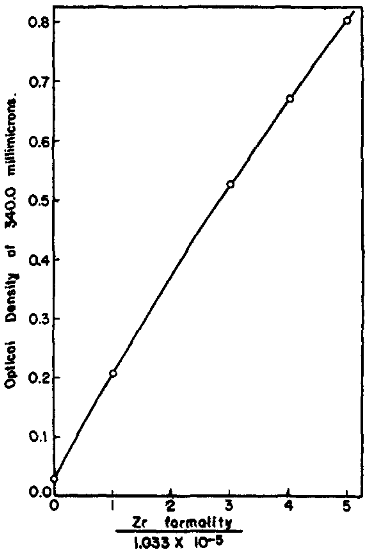


Fig. 4.—Standardization curve for zirconium; length of cuvette = 10.00 mm.

Chloranilic Acid as a Colorimetric Reagent for Zirconium.—As illustrated in Fig. 4, 10^{-4} M chloranilic acid may be used in determining zirconium at concentrations of 2 × 10^{-6} to 5 × 10^{-5} molar. Since the color is principally due to the 1:1 complex the absorption curves of Fig. 2 indicate that measurements could be made at any fixed wave length from 3300 to 3500 Å. depending upon the desired sensitivity. The final optical densities are reached within 15 minutes from the time of mixing of the zirconium and chloranilic acid solutions. The solutions are indefinitely stable true solutions. One molar, instead of 2 molar, perchloric acid could be employed safely and higher concentrations of chloranilic acid could be used if desired. Accuracies within 1% should be obtainable.

Of the existing colorimetric reagents for zirconium, p-dimethylaminoazobenzenearsonic acid is somewhat time-consuming,[10] and alizarin and alizarin S give lake suspensions which settle out with time.[11,12] The use of the latter two reagents requires some care in pH adjustment for sensitivities comparable to those obtained with chloranilic acid. Chloranilic acid in 2 M perchloric acid gives roughly the same ZrCh^{+2} color with tetrapositive hafnium, uranium, thorium and stannic tin but only a weak pink color with tetravalent titanium. Ferric ion gives a violet-black color and saturated boric acid gives a light pink color. No visible reaction is observed at this acidity with ferrous, chromic, aluminum, copper, cobalt, manganese, barium or potassium ions. Many of these ions interfere in the use of alizarin or alizarin S, although their effect may be reduced by using higher acidities with consequent loss of sensitivity.[11,13,14]

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[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

Oxidation–Reduction Reactions of Neptunium(IV) and -(V)[1]

BY JOHN R. HUIZENGA AND LAWRENCE B. MAGNUSSON

The rate law for the reaction Np(IV) + Fe(III) ⇄ Np(V) + Fe(II) may be expressed as $d[\mathrm{Np(IV)}]/dt = k_2[\mathrm{Np(V)}][\mathrm{Fe(II)}][\mathrm{H}^+] - k_1[\mathrm{Np(IV)}][\mathrm{Fe(III)}]/[\mathrm{H}^+]^3$. The reactions involve a hydrolytic mechanism. The forward rate constant, k_1, is 3.4 moles^2 liters^{-2} min.$^{-1}$ and the reverse rate constant, k_2, is 4.7 moles^{-2} liters^2 min.$^{-1}$ at 25° in 1.0 M perchlorate solutions. The apparent activation energy of the forward reaction is 35 kcal. mole^{-1}. The forward rate constant is smaller in nitrate solutions as would be expected from spectral evidence for nitrate complexing of Np(IV).

Introduction

The aqueous ions of the +5 and +6 oxidation states of uranium, neptunium and plutonium are oxygenated cations, $\mathrm{MO_2}^+$ and $\mathrm{MO_2}^{+2}$, in non-complexing acidic solutions. The metal to oxygen bonding is strong so that the oxygen is not easily, if at all, removable by reaction with hydrogen ion.[2,3] The oxygenated structure of the +5 and +6 states has a marked influence on the oxidation–reduction kinetics of these elements. The transitions between $\mathrm{MO_2}^+$ and $\mathrm{MO_2}^{+2}$, with the exception of change in hydration, should require only the transfer of an electron between the heavy metal ion and a reducing or oxidizing agent. As might be expected these transitions are rapid with oxidation–reduction couples which do not inherently involve slow processes. The stable ions of the lower oxidation states, +3 and +4, are of the types M^{+3} and M^{+4} in non-complexing acidic solutions. The transitions between M^{+3} and M^{+4} also require only electron transfer as far as the heavy metal ion is concerned and the reactions are usually rapid. Transitions between the lower oxidation states and the +5 or +6 states, however, have been observed to be slow in general.[4,5,6] The relative slowness of these reactions indicates that the rate of electron transfer is dependent on the mechanism for the addition or removal of oxygen.

Neptunium is particularly suited for studies of the M^{+4}–$\mathrm{MO_2}^+$ transition since the +5 oxidation state is stable under a wide range of conditions with respect to disproportionation (self oxidation–reduction to higher and lower states). Oxidizing and reducing agents for reaction with the neptunium may be selected with the aid of the fact that the oxidation potential of the Np(IV)–Np(V) couple is *ca.* −0.7 volt in 1 molar hydrogen ion solution.[7,3] Iron is of interest since the oxidation potential of the ferrous–ferric couple is near the potential of the Np(IV)–Np(V) couple so that oxidation–reduction equilibrium constants can be directly determined. Ferrous and ferric ions, furthermore, react at relatively high, yet measurable, rates with the neptunium ions. A preliminary study of this system in hydrochloric acid has been reported.[5] The rate of reduction of Np(V) by ferrous ion was found to be proportional to about the first power of the hydrogen ion concentration.

Precise measurements of the iron–neptunium system have now been made in perchlorate and nitrate solutions. Forward and reverse rate constants, temperature dependence, hydrogen ion dependence and nitrate effect have been determined. Equilibrium measurements will appear in a subsequent publication.

Experimental

The neptunium stock solutions were prepared by dissolving pure Np(IV) or Np(V) hydroxides, reprecipitated with ammonia from perchlorate solutions and washed free of ammonia, in weighed portions of standardized 8 M perchloric acid. Weighed aliquots of the neptunium solutions were dried on platinum plates for alpha-particle counting. Neptunium concentrations were calculated on the basis of 790 alpha-counts-minute^{-1}-microgram^{-1} specific counting yield for a 50% geometry counting chamber.[8]

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