sumed to be 500, 530, 570 and 650 mμ, respectively. Another possibility was considered with reference to their $CoCNS^+$ complex: the solutions used in their experiments were 0.05 *M*, while ours have been not more than 0.002 *M*. It therefore seemed possible that a relatively unstable $CoCNS^+$ complex would not have appeared in our experiments with dilute solutions, but might be revealed at the high concentrations. Experiments carried out by the method of continuous variations at a concentration of 0.04 *M* have shown this to be the case (Fig. 7), evidence for the $CoCNS^+$ complex being found at wave lengths below 550 mμ. With absorption in this region, the complex of course does not contribute to the blue color shown by the other thiocyanate complexes. This would be in agreement with the expectation that such a complex should be hexacoördinate and of the "red" type, rather than tetracoördinate "blue" type[2] as is the tetrathiocyanate complex. It should be pointed out that the complex probably should be written $Co(CNS)(ClO_4)\cdot 4$ solvent, since cobalt perchlorate is only partially dissociated in acetone.[1]

It seems hardly necessary to emphasize here, what is true for the several cobalt salts investigated, and probably also is true for many complexes of other metals: when an analytical method depends on maximum complex formation, ketone medium (as contrasted with aqueous or alcoholic) may be expected to give greatest sensitivity. This is especially true for colorimetric procedures in which the extinction coefficients of the highest complex are greater than those of other complexes which may be formed.

Summary

1. In very dilute solution in acetone, cobalt(II) yields trithiocyanate and tetrathiocyanate complexes.

2. In dilute solution in isopropyl or *t*-butyl alcohol, only dithiocyanate and trithiocyanate complexes are found.

3. The extinction coefficient of the tetrathiocyanate complex is about twice that of the trithiocyanate complex.

4. In relatively concentrated solution in acetone, an unstable complex involving a single thiocyanate group can be identified.

CHICAGO 80, ILLINOIS

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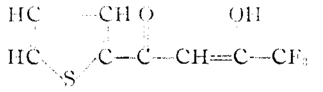
[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Chemistry of Thorium in Aqueous Solutions. I. Some Organic and Inorganic Complexes[1]

BY R. A. DAY, JR.,[2] AND R. W. STOUGHTON

Fry, Barney and Stoughton[3] have recently reported a number of equilibrium constants for the formation of thorium–iodate complex ions. These constants were determined from solubility measurements and solvent extraction data. The solvent extraction method used involved the determination of the distribution ratios between aqueous solutions containing thorium and iodate and benzene solutions containing thenoyl trifluoroacetone (TTA) as a chelating agent. The latter compound has the following structure in the enol form



This method has also been used to determine the equilibrium constants of some zirconium complexes.[4]

The present work was undertaken to determine the stability of complex ions formed between thorium and the anions of several monobasic acids. The acids studied were hydrochloric, nitric, chloric, bromic, hydrofluoric, chloroacetic, dichloroacetic, trichloroacetic, acetic and formic. The TTA extraction method was used throughout. The equation for extraction can be written as

$$Th^{+4} + 4HT_b \rightleftarrows ThT_{4b} + 4H^+ \quad K_T \qquad (1)$$

where HT stands for TTA, T for the enolate ion of TTA, K_T for the equilibrium constant of the reaction, and the subscript *b* indicates that the species involved is in the benzene phase. It is assumed that ThT_4 is the only thorium-containing species in the organic phase and that it exists predominantly in that phase.[5] The work of King and Reas[6] and of Zebroski and Alter[7] shows that 2% of the TTA present is in the aqueous phase under our conditions and that this figure is constant TTA concentration and constant ionic strength in the aqueous phase.

To illustrate the calculations, let us consider the case of thorium complexed by the anion of the weak acid, HX. Considering only two complex ions to be formed, one can write the equations

$$Th^{+4} + HX \rightleftarrows ThX^{+3} + H^+ \quad k_1 \qquad (2)$$

$$Th^{+4} + 2HX \rightleftarrows ThX_2^{+2} + 2H^+ \quad k_2 \qquad (3)$$

where k_1 and k_2 are equilibrium constants for the reactions. The ratio of thorium in the aqueous

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[1] The work covered in this paper was carried out under the auspices of the Atomic Energy Commission at Oak Ridge National Laboratory.

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[3] Fry, Barney and Stoughton, "Atomic Energy Commission Report," AECD-2429 (1948).

[4] Connick and McVey, THIS JOURNAL, **71**, 3182 (1949).

[5] Work of Connick and co-workers indicate this assumption to be valid for other tetravalent cations. Also W. C. Waggener and R. W. Stoughton (private communication) have found that the dependence of thorium extraction on both TTA and hydrogen ion is fourth power in the range of 0.1 to 0.5 *M* $HClO_4$ and an ionic strength of 0.5. Thus since all thorium is in the +4 state, the extracted species must be ThT_4.

[6] King and Reas, "Atomic Energy Commission Report," BC-69, July, 1947.

[7] Zebroski and Alter, private communication

and organic phases, $R^{a}{}_{b}$, can then be shown to be given by the expression

$$\begin{aligned} R^{a}{}_{b} &= \left\{ \frac{(\mathrm{Th}^{+4})}{(\mathrm{ThT}_4)_b} \right\} \left\{ 1 + \frac{(\mathrm{ThX}^{+3})}{(\mathrm{Th}^{+4})} + \frac{(\mathrm{ThX}_2{}^{+2})}{(\mathrm{Th}^{+4})} \right\} \\ &= \left\{ \frac{(\mathrm{H}^+)^4}{K_{\mathrm{T}}(\mathrm{HT})_b{}^4} \right\} \left\{ 1 + k_1 \frac{(\mathrm{HX})}{(\mathrm{H}^+)} + k_2 \frac{(\mathrm{HX})^2}{(\mathrm{H}^+)^2} \right\} \end{aligned} \quad (4)$$

If R_0 represents the distribution ratio in the absence of complexing agent, then

$$\frac{R^{a}{}_{b}}{R_0} = 1 + k_1 \frac{(\mathrm{HX})}{(\mathrm{H}^+)} + k_2 \frac{(\mathrm{HX})^2}{(\mathrm{H}^+)^2} \quad (5)$$

Thus the constants k_1 and k_2 may be determined by measuring the ratio of thorium in the aqueous to organic phases as a function of concentration of complexing agent, while holding constant the hydrogen ion and TTA activities and the activity coefficients of the other species. It is assumed that the HT activity and the ThT_4 activity coefficient are constant at a fixed value of the HT concentration, and that the hydrogen ion activity and the activity coefficients of the other aqueous species remain approximately constant at a given hydrogen ion concentration and a constant ionic strength.

Equation (5) reduces to the equation of a straight line when the term involving k_2 is negligible. From the slope of the line obtained by plotting $R^{a}{}_{b}$ against $(\mathrm{HX})/(\mathrm{H}^+)$, the constant k_2 is easily obtained. When the term involving k_2 is not negligible, the curve obtained by plotting $R^{a}{}_{b}$ against $(\mathrm{HX})/(\mathrm{H}^+)$ can be fitted by the method of least squares and the constants k_1 and k_2 evaluated.

When the complexing agent is the anion of a strong acid, equations (2), (3) and (5) simplify to

$$\mathrm{Th}^{+4} + \mathrm{X}^- \rightleftarrows \mathrm{ThX}^{+3} \quad k_1' \quad (2')$$

$$\mathrm{Th}^{+4} + 2\mathrm{X}^- \rightleftarrows \mathrm{ThX}_2{}^{+2} \quad k_2' \quad (3')$$

$$R^{a}{}_{b}/R_0 = 1 + k_1'(\mathrm{X}^-) + k_2'(\mathrm{X}^-)^2 \quad (5')$$

Experimental

Both aqueous and benzene phases were made up in 25.0-ml. volumes from which four 5.0-ml. aliquots of each phase were added to four 15-ml. glass-stoppered centrifuge tubes for equilibration. The remaining 5-ml. portion was used for preparing counting standards and, in some cases, for analyses. Changes in acidity on addition of some complexing agents were determined with a Beckman model G pH meter. Iodate and bromate concentrations were determined by standard titration with sodium thiosulfate. All volumetric apparatus was calibrated.

The aqueous phase was normally prepared to be 1.0 × 10^{-6} M in Th^{+4}, 0.500 M in H^+, and to have an ionic strength of 0.50. The ionic strength and hydrogen ion concentration were maintained with perchloric acid except where otherwise stated. The solution also contained known concentrations of complexing agent and known amounts of tracer UX_1 (Th^{234}) activity.

The benzene phase was made 0.250 M in TTA by direct weighing of the latter. This solution was then shaken overnight on an electric shaking machine with an equal volume of 0.1 M perchloric acid to convert the TTA to the equilibrium mixture of monohydrate and unhydrated forms.[8]

Chemicals of C. P. grade were used throughout. Chloric and bromic acids were prepared from barium chlorate and barium bromate by dissolving the salts in water and precipitating barium sulfate upon addition of sulfuric acid. The solutions were left with a slight excess of barium ion in order to reduce the remaining sulfate ion concentration to a low value. The TTA was obtained from M. Calvin of the University of California and used without further purification.

The tracer was purified by extracting from an aqueous solution of pH 3.0 into 0.01 M TTA in benzene and then back-extracting into a perchloric acid solution of pH 1.0.

Equilibrations of the two phases were carried out by shaking the tubes end-over-end in a water-bath held at 25.0° for 1 to 2.5 hours. Upon removal from the shaking machine, the tubes were immediately centrifuged and aliquots of both phases taken for beta counting. The samples were counted with a G–M counter through a 20.7 mg./sq. cm. aluminum absorber, whereby only the 2.3 Mev. beta of UX_2 (1.1 minute Pa^{234} daughter of UX_1) was counted. By elimination of the weak UX_1 beta more reproducible results were obtained, since the counting of weak betas is very dependent on the amount of extraneous material present in a sample.

It was found that equilibrium between the two phases was obtained within about 15 minutes in the absence of complexing agents; hence it was felt that an equilibration time of one hour or greater should certainly be sufficient. Nevertheless, in order to detect a possibly slower reaction in the presence of complexing agents, equilibrations were made in most cases over both 1-hour and 2.5-hour intervals. No noticeable difference in the results was observed for these different times except for those solutions containing bromic acid. In this case some reaction appeared to be taking place with the TTA (probably an oxidation). Consistent results could be obtained, however, when the solutions were shaken no longer than 30 minutes.

The values obtained for the distribution ratios were usually reproducible to ± 5% and the values reported here are averages of eight different sets of data. Good material balances were normally obtained; that is, the added beta activity was equal to that found in the two phases to within a few per cent. No run was considered reliable unless the material balance was greater than 90%.

Some of the values obtained for solutions containing hydrofluoric acid were also checked in a platinum container. No significant difference was found, indicating that hydrogen fluoride did not appreciably attack the Pyrex glass vessels under the conditions being used.

Results and Discussion

The extraction results obtained in this study are given in Tables I, II and III. A summary of the constants is given in Table IV. These constants are concentration (not activity) constants and hence they contain as factors the activity coefficients of the various species involved. In the case of complexing by nitrate, chloride, chlorate and bromate (Table I) the medium changes from 0.5 M perchloric acid to 0.5 M complexing agent, and one might expect that the various activity coefficients would vary somewhat with the change of medium. Nevertheless a plot of $R^{a}{}_{b}$ against nitrate, chloride or chlorate concentration gives a straight line, indicating a single complex in each case. This further indicates that the activity coefficient factors in the constants do not change appreciably with the varying medium. It is possible, of course, that the effect of a second complex in each case just compensates the effect of varying activity coefficients. The values reported here may be

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[8] Zebroski, "Atomic Energy Commission Report," BC-63, July 1 1947.

looked upon as average values in the varying media. In the case of bromate, greater complexing power is shown and (as with hydrofluoric acid, iodate and di- and trichloroacetic acids) evidence for higher complexing is expected under the conditions employed.

TABLE I

DISTRIBUTION RATIO, $K^a{}_b$, AS A FUNCTION OF COMPLEXING AGENT CONCENTRATION AT IONIC STRENGTH 0.5

M complex. agent	NO_3^-	Cl^-	ClO_3^-	BrO_3^-	$ClCH_2$-COOH
0.00	0.63	0.63	0.63	0.63	0.63
.05	..	..	..	0.87	..
.10	0.94	.74	.75	1.04	.81
.20	1.24	.86	.86	1.67	.98
.30	1.54	.95	.98	2.22	1.12
.40	1.84	1.07	1.09	3.05	1.29
.50	2.14	1.18	1.21	3.98	.

TABLE II

DISTRIBUTION RATIO, $R^a{}_b$, AS A FUNCTION OF COMPLEXING AGENT CONCENTRATION AT IONIC STRENGTH 0.5 IN PERCHLORATE MEDIUM

M HIO_3 [a]	$R^a{}_b$	*M* Cl_2-CHCOOH	$R^a{}_b$	*M* Cl_3-CCOOH	$R^a{}_b$
0.00	0.63	0.00	0.63	0.00	0.63
3.1×10^{-4}	0.71	.022	.78	.014	.74
		.028	.84	.024	.82
2.1×10^{-3}	1.27	.044	.95	.035	.90
8.3×10^{-3}	3.31	.054	1.06	.041	1.00
2.06×10^{-2}	13.37	.068	1.21	.064	1.22
		.082	1.34	.073	1.30
3.1×10^{-2}	30.8	.099	1.51	.081	1.45
				.094	1.56

[a] Molarity of added HIO_3; *M* of IO_3^- = 0.44 × *M* added HIO_3.[3]

TABLE III

DISTRIBUTION RATIO, $R^a{}_b$, AS A FUNCTION OF CONCENTRATION OF HYDROFLUORIC ACID AT IONIC STRENGTH 0.5 IN NITRATE AND PERCHLORATE MEDIA

M $HF \cdot 10^5$	HNO_3 medium $R^a{}_b$	$HClO_4$ medium
0.00	2.14	0.63
1.00	2.80	1.22
2.00	3.52	1.83
3.00	4.19	2.27
4.00	4.78	2.94
6.00	...	4.08
8.00	...	5.50
10.0	9.66	6.94
20.0	19.0	14.6
30.0	30.3	24.0
60.0	...	60.4
80.0	144	...
100	174	133
200	509	...

TABLE IV

EQUILIBRIUM CONSTANTS FOR THORIUM COMPLEXES AT IONIC STRENGTH 0.5

Reaction	Constant
$Th^{+4} + HF = ThF^{+3} + H^+$	4.3×10^4
$Th^{+4} + 2HF = ThF_2^{+2} + 2H^+$	3.1×10^7
$Th^{+4} + IO_3^- = Th(IO_3)^{+3}$	7.6×10^2
$Th^{+4} + 2IO_3^- = Th(IO_3)_2^{+2}$	6.2×10^4
$Th^{+4} + 3IO_3^- = Th(IO_3)_3^{+}$	1.4×10^7
$Th^{+4} + BrO_3^- = Th(BrO_3)^{+3}$	6.4
$Th^{+4} + 2BrO_3^- = Th(BrO_3)_2^{+2}$	8.2
$Th^{+4} + ClO_3^- = Th(ClO_3)^{+3}$	1.84
$Th^{+4} + NO_3^- = Th(NO_3)^{+3}$	4.73
$Th^{+4} + Cl^- = ThCl^{+3}$	1.76
$Th^{+4} + ClCH_2COOH = Th(ClCH_2COO)^{+3} + H^+$	1.33
$Th^{+4} + Cl_2CHCOOH = Th(Cl_2CHCOO)^{+3} + H^+$	5.74
$Th^{+4} + 2Cl_2CHCOOH = Th(Cl_2CHCOO)_2^{+2} + 2H^+$	12.7
$Th^{+4} + Cl_3CCOOH = Th(Cl_3CCOO)^{+3} + H^+$	8.23
$Th^{+4} + 2Cl_3CCOOH = Th(Cl_3CCOO)_2^{+2} + 2H^+$	26.7

Complexing by Nitrate and Iodate.—The value of the equilibrium constant found for the formation of the $ThNO_3^{+3}$ complex (4.7 for reaction 2 assuming that perchlorate does not form a complex at 0.5 *M* chlorate ion concentration) is unexpectedly high in comparison to the value for the formation of the corresponding plutonium complex, $PuNO_3^{+3}$. The value for the latter constant has been found to be 2.9 at an ionic strength of 2.0.[9] Since the crystal radius of Th^{+4} is appreciably larger than that of Pu^{+4}, 0.95 Å. (compared to 0.86 Å.),[10] one would expect the complexing of thorium to occur to a much smaller extent than in the case of plutonium.

The data reported by Fry, Barney and Stoughton[3] for iodate complexing of thorium were obtained in nitrate media. These workers showed that the iodate ion concentration in these media was given by 0.44 *m*, where *m* is the molarity of iodic acid. On the assumption that the mean activity coefficient is the same in nitric and perchloric acid media at an ionic strength of 0.5, the iodate ion concentrations have been calculated here by the same expression. The results thus obtained in perchloric acid are in good agreement with the results of Fry, Barney and Stoughton after their data are corrected for nitrate complexing. This is strong evidence against the formation of complexes containing both iodate and nitrate ions under the conditions used by these workers.

A more direct way of comparing the two sets of data, and one which will be used in discussing the fluoride results, is as follows. According to equation (4), the distribution ratio in nitrate medium, $(R_0)_n$, in the absence of other complexing agent becomes

$$(R_0)_n = \frac{\{(Th^{+4}) + (ThNO_3{}^{+3})\}}{(ThT_4)_b} = \{1 + k_n(NO_3^-)\}\frac{(H^+)^4}{K_T(HT)_b{}^4} \quad (4a)$$

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[9] Hindman, "National Nuclear Energy Series," Division IV, Vol. 14B, No. 4.5, McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

[10] Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).

where k_n is the constant for equation (2′) when X^- is NO_3^-. Combining equation (4a) with equations (5) and (5′), we get, respectively,

$$\{(R^a{}_b/R_0)_n - 1\}\{1 + K_n(NO_3^-)\} = k_1\,(HX)/(H^+) + k_2\,(HX)^2/(H^+)^2 \quad (6)$$

$$\{(R^a{}_b/R_0)_n - 1\}\{1 + K_n(NO_3^-)\} = k_1'(X^-) + k_2'(X^-)^2 \quad (6')$$

k_1 and k_1' being simply related in terms of the acid constant of HX. In perchlorate medium $(NO_3^-) = 0$, and hence $(R^a{}_b/R_0 - 1)$ is equal to the expressions on the right-hand sides of equations (6) and (6′). Hence, if the observed values of $(R^a{}_b/R_0 - 1)$ obtained in perchlorate medium and the values of $\{(R^a{}_b/R_0)_n - 1\}\{1 + k_n(NO_3^-)\}$ obtained in nitrate medium are both plotted against the concentration of HX or X^-, identical curves should be obtained if the same complexes exist in both media. If additional complexes exist in the nitrate medium over those indicated in equations (6) or (6′), then the nitrate curve will lie above the perchlorate curve when the results are plotted as in Fig. 1. In this figure the two functions mentioned above are plotted against the logarithm of the concentration of added hydrofluoric acid in one case, and of iodate ion in the other.

The identity of the iodate curves is strong evidence against the existence of complexes containing both nitrate and iodate ions. This assumes, as was mentioned above, that the various activity coefficients have essentially the same values in nitric and perchloric acid media.

Complexing by Fluoride.—Dodgen and Rollefson,[11] using a potentiometric method, reported values of $k_1 = 4.5 \times 10^4$ and $k_2 = 2.9 \times 10^7$ for equations (2) and (3) where HX = HF. These results were obtained in sodium perchlorate–perchloric acid media at an ionic strength of 0.5. The values obtained here by the extraction method (Table IV) are in good agreement with the results of Dodgen and Rollefson.[12]

Data were also obtained here for fluoride complexing in nitric acid solutions. These are plotted in Fig. 1 in the manner discussed above. It is seen that the curve for extraction from nitric acid medium lies above that for perchloric acid, indicating the existence of additional complexes in the former medium over the latter. Interpreting the nitrate results in terms of thorium–fluoride–nitrate complexes in addition to ThF^{+3} and ThF_2^{+2}, we get in place of k_1 and k_2 in equation (6), two new constants $K_1 = k_1 + k_1^* = 5.3 \times 10^4$, and $K_2 = k_2 + k_2^* = 3.5 \times 10^7$. Knowing k_1 and k_2 from the perchlorate data, k_1^* and k_2^* are readily evaluated. Now, since all the nitrate–fluoride results were obtained at constant nitrate concentration, nothing can be said about the nitrate dependence of the terms containing k_1^* and k_2^*. If it is assumed that the dependence is first power, *i. e.*, that each double complex contains only one nitrate, the constants for the following reactions become

$$Th^{+4} + NO_3^- + HF \rightleftarrows ThFNO_3^{+2} + H^+$$

$$k_{1n} = \frac{k_1^*}{(NO_3^-)} = 2 \times 10^4$$

$$Th^{+4} + NO_3^- + 2HF \rightleftarrows ThF_2NO_3^+ + 2H^+$$

$$k_{2n} = \frac{k_2^*}{(NO_3^-)} = 8 \times 10^6$$

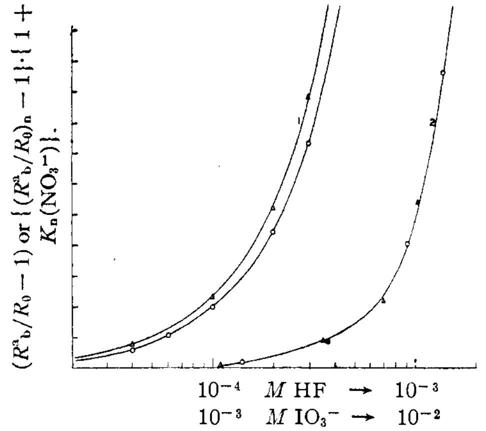

Fig. 1.—1, HF; 2, IO_3^-; Δ, HNO_3 medium; O, $HClO_4$ medium.

It should be pointed out that the difference between the nitrate and perchlorate results may be caused by a difference in activity coefficients of the various species in the two media. Or it may be caused by a reaction between impurities in the nitric acid and the TTA.[13] More difficulty was encountered in obtaining reproducible results in solutions containing nitric acid than in those containing perchloric. However, considerable care was taken to avoid trouble with impurities. Numerous runs were made at different time intervals and no indication of a reaction between impurities and TTA was noted. It is believed that the results reported here are quite reliable.

Complexing by Chloride, Chlorate and Bromate.—Of all the oxygenated anions studied, iodate forms the strongest complexes with thorium, followed by bromate, nitrate and chlorate. The latter two, as well as chloride, showed no tendency to form a second complex in solutions up to 0.5 M in the anions. Chloride shows about the same complexing power as chlorate.

As in the case of nitrate mentioned above, the value of the constant of the thorium complex with chloride is surprisingly high compared to the corresponding value for the plutonium complex. Hindman[14] reported a value of about 0.4 for the

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(11) Dodgen and Rollefson, THIS JOURNAL, **71**, 2600 (1949).

(12) Zebroski, private communication, using the TTA solvent extraction method, reports values of these two constants in substantial agreement with ours.

(13) Connick and co-workers, private communication, state that nitrous acid is known to react with TTA.

(14) Hindman, "National Nuclear Energy Series," Division IV, Vol. 14B, No. 4.7, McGraw-Hill Book Co., Inc., New York, N. Y., 1950; AECD-1893.

formation of the complex $PuCl^{+3}$, at an ionic strength of 2.0. Zebroski and Alter[7] found a value of about 2 for thorium at ionic strength 3.8.

Complexing by Formic, Acetic and the Chloroacetic Acids.—Of the chloroacetic acid series under our conditions, the trichloro acid shows the greatest tendency to form a complex, followed by the di- and monochloro acids. In determining the constants and the increase in hydrogen ion concentration caused by the addition of these acids as complexing agents it was necessary to use the dissociation constants of the acids. The values used were 0.2, 0.05 and 0.0014 for the trichloro-,[15] dichloro-[16] and monochloroacetic[17] acids, respectively.

If one compares the complex-forming tendency of the anions of the three chloroacetic acids, *i. e.*, if the values of the constants k_1 (equation 2′) are compared, the above order of decreasing magnitudes is reversed, as expected. The values of these constants become 950, 115 and 41 for the mono-, di- and trichloroacetate ions, respectively.

In the case of formic and acetic acids another factor came into play, making the thorium more extractable. For example, the aqueous/organic distribution ratio was 0.44 in a solution 0.5 *M* in acetic acid and 0.5 *M* in $HClO_4$. In a solution 1.0 *M* in acetic acid and 0.5 *M* in $HClO_4$ the ratio was 0.37. In the absence of complexing agent, however, the ratio was 0.63. No measurable extraction was observed, however, when no TTA was present in the benzene phase. The distribution ratio increased to 0.79 for 0.03 *M* formic acid and then remained essentially unchanged for increased concentrations up to 1.0 *M* formic acid. Some indication of this same effect was noticed with the chloroacetic acids when fairly high concentrations were used. For this reason the constants reported for these acids may be slightly low.

Effect of TTA in the Aqueous Phase.—The effect of the 2% of TTA which goes into the aqueous phase has so far not been considered. Actually the corresponding decrease in the total concentration of chelating agent in the benzene phase causes an 8 to 10% correction in the value of K_T if one uses the amount of TTA added for the amount in the organic phase. However, it does not directly affect the values of the constants of the aqueous complexes. Zebroski,[7] however, has reported the formation of an aqueous thorium–TTA complex

$$Th^{+4} + HT(aq) \rightleftarrows ThT^{+3} + H^+$$

with a value for the constant k_t for the reaction as written of about 5.7 at ionic strength 2.0. From other work of Zebroski a value of roughly 7 is estimated for k_t at ionic strength 0.5.

Taking into account this thorium–TTA complex, the component $(ThT^{+3})/(Th^{+4}) = k_t(HT)_{aq}/(H^+)$ would be added to the expression in the second brackets in equation (4). All the constants in equations (5) and (5′) would then contain the factor $1/\{1 + k_t(HT)_{aq}/(H^+)\}$, as would the constants in equations (6) and (6′), including k_n. Hence the true values for any of these constants would be obtained by multiplying the values given in this paper by $\{1 + k_t(HT)_{aq}/(H^+)\}$, which according to Zebroski's data is about 1.07. Since there is some doubt as to the actual value of k_t at an ionic strength of 0.5, we have not made this correction.

It should be emphasized that the only effect the thorium–TTA complex has on the treatment of the iodate and fluoride data in nitrate and perchlorate media is in changing the values of the constants obtained. The interpretation of the data in terms of double complexes is not altered.

Summary

1. The equilibrium constants for the formation of complex ions of thorium with anions of the acids hydrochloric, nitric, chloric, bromic, hydrofluoric, chloroacetic, dichloroacetic and trichloroacetic have been evaluated at a hydrogen ion concentration of 0.5 *M* and ionic strength of 0.5 using the TTA–benzene solvent extraction method.

2. Evidence is cited for the existence of double complexes of the type $Th(NO_3)F^{+2}$ and $Th(NO_3)F_2^+$ in mixtures of nitric and hydrofluoric acids. No evidence was found for the existence of similar species involving nitrate and iodate ions.

3. It was found that the presence of acetic acid in the aqueous phase increases the extractability of the chelated product formed between thorium and TTA. Some other organic acids also showed a tendency in this direction.

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[15] Deyrup, This Journal, **56**, 60 (1934).

[16] Ostwald, *Z. physik. Chem.*, **3**, 177 (1889).

[17] Wright, This Journal, **56**, 314 (1934).