large "humps" in the *j* curves with well marked positive deviations from the theoretical limiting law. Eight of the alkali salts show no positive deviation at all, and that of lithium chloride is less than one-tenth of that of the ammonium salts. The behavior of the ammonium salts is still unexplained, but the present work shows conclusively that it is not due to a systematic error in our measurements. To make doubly sure on this score, since ammonium bromide showed the largest "hump," the alkali bromides were purified and their concentrations were determined by the same method as had been used for the ammonium salt.

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[CONTRIBUTION FROM THE PENNSYLVANIA SALT MANUFACTURING COMPANY CHEMICAL RESEARCH DEPARTMENT]

Addition of 8-Hydroxyquinoline by Thorium and Uranium 8-Hydroxyquinolates

BY FRANCIS J. FRERE

Introduction

F. Hecht and W. Reich-Rohrwig[1] have outlined an analytical procedure for the determination of thorium and uranium by means of 8-hydroxyquinoline. It was stated that uranium formed a compound of the formula $UO_2(C_9H_6NO)_2 \cdot C_9H_6NO$, which was stable up to about 200°.

As regards thorium, Hecht and Reich-Rohrwig[1] stated that this element formed a compound containing water of crystallization which did not start to dehydrate until at about 155°, and at 160 to 170° lost its water of crystallization rapidly and could be dried to constant weight at this temperature. The dried precipitate was dissolved and brominated and was found to contain four moles of 8-hydroxyquinoline, from which it was concluded that thorium formed a compound of the formula $Th(C_9H_6ON)_4$.

Hecht and Reich-Rohrwig later observed that when brominating the thorium precipitate, without drying, somewhat high results were obtained. This was claimed to have been overcome by washing the precipitate with 25% alcohol.

An investigation of this work found some of the above statements in error and has led to a rather interesting phenomenon.

Experimental

Materials Used.—C. P. reagent grade thorium nitrate and uranyl acetate were used in these experiments. The thorium nitrate solution was standardized by precipitating as oxalate, igniting and weighing as the oxide. The uranyl acetate solution was standardized by reducing in a Jones reductor and titrating with potassium permanganate. Pipets and burets certified by the U. S. Bureau of Standards were used throughout this work.

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[1] Hecht and Reich-Rohrwig, *Monatsh*, **53–54**, 596 (1929).

A series of experiments was first made in order to determine whether or not thorium 8-hydroxyquinoline formed a compound containing water of crystallization. The following general procedure was used throughout for precipitating both thorium and uranium.

The solution was treated with 4 to 5 ml. of 2 *N* acetic acid heated to 90° and an excess of a 2.5% solution of 8-hydroxyquinoline was added; the solution was heated to boiling and about 15 ml. of 2 *N* ammonium acetate was added. After allowing to cool to room temperature, the precipitate was filtered on a weighed Gooch crucible, washed with cold water, and dried for two hours at 130 to 140°. The precipitate was then dissolved in hydrochloric acid and the quinolate titrated with a potassium bromide–bromate solution.[2] It seems quite obvious from the results given in Table I that thorium does not form a hydrated salt with 8-hydroxyquinoline and that the high results obtained by Hecht and Reich-Rohrwig cannot be attributed to this cause.

TABLE I

COMPOSITION OF THORIUM 8-HYDROXYQUINOLINE PRECIPITATE

Precipitate, g.	0.1015	0.1012	0.1024	0.1010	0.1012
C_9H_6NOH found, g.	.0744	.0745	.0751	.0744	.0744
Total found, g.	.1015	.1016	.1022	.1015	.1015
Diff., g.	.0	+ .0004	− .0002	+ .0005	+ .0003

TABLE II

DETERMINATION OF THORIUM RESULTS CALCULATED ON THE BASIS OF $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$

ThO_2 added, g.	0.0062	0.0062	0.0062	0.0123	0.0123	0.0123	0.0309	0.0309
ThO_2 found, g.	.0062	.0061	.0061	.0123	.0123	0.0122	.0309	.0310

The amount of 8-hydroxyquinoline which combines with thorium and uranium was determined by precipitating both cations as outlined above, dissolving the precipitates in hydrochloric acid and titrating with potassium bromate. It will be seen from Table II and Table III that both elements combine quantitatively with one additional mole of 8-hydroxyquinoline in excess of their normal valence.

Washing the thorium precipitate with 25% alcohol, as recommended by Hecht and Reich-Rohrwig, proved unsuccessful and no reliable results were obtained.

TABLE III

DETERMINATION OF URANIUM: RESULTS CALCULATED ON THE BASIS OF $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$

U_3O_8 added, g.	0.0056	0.0056	0.0056	0.0112	0.0112	0.0112	0.0279	0.0279
U_3O_8 found, g.	.0056	.0056	.0055	.0111	.0111	.0111	.0278	.0278

Another series of experiments was made in order to determine the stability of the thorium and uranium 8-hydroxyquinolates at various temperatures and to find, if possible, at what temperature the additional mole of 8-hydroxyquinoline could be driven off. Both compounds were found to be quite stable at 100 to 110°. At 130 to 140° the thorium salt slowly decreased in weight while the uranium salt remained practically constant. When the temperature was raised to 160 to 170°, the thorium salt completely lost the additional mole of 8-hydroxyquinoline in about three hours, and, upon further heating at this temperature, continued slowly to decrease in weight. The uranium salt slowly decreased in weight at 160 to 170°, but at 200° the additional mole of 8-hydroxyquinoline was liberated in about two hours. The residue consisting of the compound

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[2] R. Berg, *Pharm. Z.*, **71**, 1542 (1926). See also Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, New York, 1929, Vol. II.

containing two moles of 8-hydroxyquinoline was found to be quite stable at this temperature.

It was noted also that the precipitates had changed from their original color. The thorium precipitate changed from an orange-red to a light yellow and the uranium changed from a deep brick-red to an olive-green.

An attempt was now made to determine whether or not these regenerated precipitates would again recombine with 8-hydroxyquinoline. Known quantities of each precipitate were treated with a few ml. of a 2.5% solution of 8-hydroxyquinoline and digested at a low heat on the hot-plate. It was observed that upon slight warming the precipitates rapidly changed back to their original red color, this being particularly noticeable of the uranium salt. The thorium salt did not recombine with the same degree of ease, and it was found necessary to increase the concentration of 8-hydroxyquinoline from about 3 ml., as in the case of uranium 8-hydroxyquinoline, to about 10 ml. The time of digestion was also slightly longer. However, in no case did it exceed more than ten to fifteen minutes.

It will be seen from Tables IV and V that the recombination of 8-hydroxyquinoline goes nearly to completion. Perhaps the slight differences may be due to inefficient wetting of the precipitates.

TABLE IV

ADDITION OF 8-HYDROXYQUINOLINE BY $Th(C_9H_6NO)_4$

$Th(C_9H_6NO)_4$ taken, mml.	C_9H_6NOH before addition, mml.	C_9H_6NOH after addition, mml.	C_9H_6NOH added, mml.	Conversion $Th(C_9H_6NO)_4$ to $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$, %
0.0234	0.0937	0.1135	0.0189	96.92
.0469	.1877	.2272	.0395	96.84
.0933	.3731	.4514	.0783	96.78
.1244	.4975	.6054	.1079	97.34

TABLE V

ADDITION OF 8-HYDROXYQUINOLINE BY $UO_2(C_9H_6NO)_2$

$UO_2(C_9H_6NO)_2$ taken, mml.	C_9H_6NOH before addition, mml.	C_9H_6NOH after addition, mml.	C_9H_6NOH added, mml.	Conversion $UO_2(C_9H_6NO)_2$ to $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$, %
0.0442	0.0833	0.1277	0.0394	96.37
.0883	.1767	.2577	.0790	96.49
.1325	.2650	.3915	.1265	98.49
.1766	.3533	.5141	.1608	97.00

Results shown in Tables IV and V are the mean of duplicate determinations.

Evidence for an Addition Compound.—Portions of the thorium and uranium 8-hydroxyquinolates which had been previously dried at 100 to 110° were placed in a closed vessel connected to a condenser tube and heated carefully at 170 and 200°, respectively. The sublimation products which were collected gave a melting point of 73 to 74°, which was the same as that of the 8-hydroxyquinoline. This sublimed salt was used for precipitating thorium and uranium and both gave precipitates identical with the original.

The above evidence seems to be sufficient to show that thorium and uranium form molecular complexes and, according to Werner's coördination formula theory, the additional mole of 8-hydroxyquinoline is held by secondary valence.[3]

It may also be noteworthy to mention that of the many elements which form precipitates with 8-hydroxyquinoline, thorium and uranium are the only two known which form an addition compound.

Summary

1. It has been shown that thorium and uranium 8-hydroxyquinolates form an addition compound with 8-hydroxyquinoline.

2. It has been shown that the additional mole of 8-hydroxyquinoline can be driven off by heating and that it will again recombine to nearly its former value.

3. An explanation of these phenomena on the basis of Werner's theory of secondary valence seems plausible.

(3) A. Werner, "New Ideas on Inorganic Chemistry." Translated from second German ed. by E. P. Hedley, Longmans, Green and Co., New York, 1911.

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Magneto-optic Nicol Rotation Method for Quantitative Analysis of Calcium

BY EDNA R. BISHOP, C. B. DOLLINS AND IRENE G. OTTO

The magneto-optic method[1] of analysis detects the presence of minute traces of a compound regardless of the presence of other compounds. A quantitative method[2] for the determination of calcium depending on dilutions has been described. It offers a means of analysis of samples containing less calcium than could be detected by other methods, but the determination is slow and requires a high degree of skill to operate the apparatus and great care to prevent contamination.

Allison and Murphy[3] early investigated the effect of concentration on the amount that the analyzing nicol could be rotated and the minima still be seen. They found an increase in the angle of rotation with increase in concentration of the solution examined but the variation in angle was less than 2° for a change in concentration from 10^{-11} to 10^{-3} g./cc.; hence, it did not lend itself to quantitative use. Similar determinations were made recently with like results.

In the meantime, however, Allison, Christensen and Waldo[4] predicted and found that the characteristic minima could also be produced if the

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(1) Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930); Allison, *Ind. Eng. Chem., Anal. Ed.*, **4**, 9 (1932).

(2) Bishop and Dollins, THIS JOURNAL, **54**, 4585 (1932).

(3) Work unpublished.

(4) Allison, Christensen and Waldo, *Phys. Rev.*, **40**, 1052 (1932).