Radiochemical Studies on Ultra-Micro Quantities of Organometallic Compounds. III. On Hydroxyquinolates of Promethium and Yttrium

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Hydroxyquinolates of promethium and yttrium have been studied using radioactive isotopes, promethium-147 and yttrium-90.

The formation of the hydroxyquinolates is confirmed by the facts that both promethium and yttrium are extracted from an aqueous solution into a chloroform solution of 8-hydroxyquinoline while they are not extracted by pure chloroform.

Further, some results are obtained on the composition of the complex compounds according to the method described in the first paper of these studies.[1]

(I) Promethium Hydroxyquinolate

So far there is no report on promethium hydroxyquinolate. The formation and composition of the complex salt are studied using promethium-147.

(A) The Solution of Promethium-147 Used.—Promethium chloride which was imported from the Oak Ridge National Laboratory, U. S. A., is diluted with hydrochloric acid (10% vol.). The resultant solution containing about 1.3 microcurie promethium-147 per cc. is used in the following experiments.

Radiochemical purity.—1 cc. of the solution mentioned above is evaporated up to measure the radioactivity of the residue through aluminum absorber of known thickness. The results are shown in Fig. 1, in which logarithms of the intensities (measured with a Lauritsen electroscope, made by the Scientific Research Institute, Tokyo, and given in divisions per minute) are plotted against thickness of absorber. From the figure we can guess that this radioactivity consists of two components, namely an alpha and a beta activity.

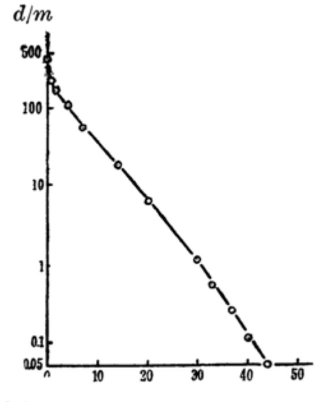

Fig. 1. Absorption curve of "Promethium-149" (Semilog plot).

As contamination of plutonium is described on the certificate sent in the package of the solution of promethium-147, this alpha activity is considered to be due to plutonium.

The beta rays seem to be absorbed entirely by 45–50 mg. Al/cm². Substitution of this value in Glendenin's diagram[2] gives about 0.2 Mev. as the energy of the observed beta rays. This value coincides with that given by Friedlander and Kennedy[3] for the energy of radiation of promethium-147. Therefore, the solution of promethium used is considered to contain promethium-147 and some isotopes of plutonium.

In the following experiments, however, the activity is measured by a Lauritsen electroscope through an aluminum foil (about 8 mg. Al/cm²), so the contamination does not disturb the measurements of the activity of promethium. For this reason the separation of promethium from plutonium has not been tried.

(B) On the Formation of Promethium Hydroxyquinolate. — An aqueous solution (about 8–9 cc.) which contains 1 cc. of the solution of promethium-147 and 5 cc. of the solution of sodium potassium tartrate (5g./30 cc.) or the saturated solution of ammonium acetate is prepared. To adjust pH, ammonium hydroxide is added dropwise to the solution. The solution is made up to 10 cc. with water, and pH of the solution is checked with a pH test paper.

5 cc. of chloroform solution of 8-hydroxyquinoline (61 mg./50 cc.) are added to the aqueous solution and the mixture is shaken vigorously for one minute in a small separating funnel. The chloroform layer is taken and evaporated up under an infra-red lamp. The radioactivity due to promethium in the

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[1] T. Ishimori, This Bulletin, 27, 139 (1954).

[2] L.E. Glendenin, *Nucleonics*, 2, 16 (1948).
cf. G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry", John Wiley & Sons, New York, (1949) p. 164.

[3] ibid., p. 358.

residue is measured by the Lauritsen electroscope. The extractability is calculated by comparing the activity with that of promethium-147 taken into the separating funnel.

This procedure is repeated for several known pH values of the aqueous solution. The results are shown in Table I, in which we can see the remarkable transference of promethium into the phase of chloroform in the experiment at about pH 9. The similar procedure is repeated further with pure chloroform at about pH 9, but no promethium is extracted. So we may conclude that the formation of a new complex salt between promethium and 8-hydroxyquinoline at about pH 9 is proved by these experimental facts.

TABLE I
FORMATION OF PROMETHIUM 8-HYDROXYQUINOLATE

From the solution containing	pH	Extractability
Sodium potassium tartrate	9.2	23 %
,,	7.4	0.5
,,	3.4	...*
Ammonium acetate	5.6	0.4
,,	4.4	0.0

* tartaric acid is pptd.

(C) On the Composition of Promethium Hydroxyquinolate.—The composition of the hydroxyquinolate is determined according to the method described in the first paper[1] of this series.

When a definite volume of an aqueous solution of promethium is shaken, at constant value of pH, with a known volume of a chloroform solution of 8-hydroxyquinoline until the equilibrium is established, the following equation is expected based on the theoretical consideration of the chemical system.

$$E^{-1}=A\,(\mathrm{HO}_x)^{-n}+B.$$

E: Extractability, the ratio of the activities due to promethium extracted and total promethium taken into the system.

(HO_x): The amount of 8-hydroxyquinoline added to the system.

A and B: Constants.

n: The number of the anion of 8-hydroxyquinoline bound to one atom of promethium.

Therefore, if several experiments are repeated with chloroform solutions of 8-hydroxyquinoline in varying concentration (keeping the other conditions constant) and their results are plotted in the $E^{-1}-(\mathrm{HO}_x)^{-1,2,3\ldots\ldots}$ diagrams, n is determined by finding out $(\mathrm{HO}_x)^{-n}$ which is linear to E^{-1}.

(1) The Absorption of the beta Rays of Promethium.—In the experiments for the determination of the composition, precise measurement of the activity is earnestly desired. As promethium-147 is an emitter of considerably soft beta rays (0.20 MeV.), the absorption by 8-hydroxyquinoline which may come into the layer of chloroform must be considered.

Fortunately most 8-hydroxyquinoline seems to have been eliminated during the evaporation of chloroform solution under an infrared lamp. This is proved in two ways. The first is based on weighing the residue of chloroform solution of 8-hydroxyquinoline, namely the residue of 5 cc. solution (101 mg. 8-hydroxyquinoline/50 cc.) is less than 1 mg. Secondly, known volumes of the chloroform solution are evaporated in a glass dish containing the residue of 1 cc. of promethium solution and the radioactivity is measured. Table II shows the results in which we can see that no serious error will occur by the absorption of the beta rays. The glass dishes used for measurements have a diameter of about 4 cm.

TABLE II
ABSORPTION OF BETA RAYS BY 8-HYDROXYQUINOLINE

mg. 8-hydroxyquinoline (added)	0.00	1.01	2.02	3.03	5.05	6.06	10.1
% Radioactivity	100	100	98	102	97	92	100

(2) Experimental Procedure. — A solution which contains 5 g. sodium potassium tartrate and 10 cc. of promethium-147 solution is made alkaline by adding ammonium hydroxide dropwise and finally made up to 100 or 50 cc. The pH value of the solution is checked by indicator paper. 10 cc. of the resultant solution is mixed with 5 cc. of a

TABLE III
RESULTS OF FIRST SERIES (pH=9.3)

(HO_x)	$(\mathrm{HO}_x)^{-1}$	$(\mathrm{HO}_x)^{-2}$	$(\mathrm{HO}_x)^{-3}$	$(\mathrm{HO}_x)^{-4}$	$(\mathrm{HO}_x)^{-5}$	E^{-1}
10 mg.	0.10	0.01	0.001	10^{-4}	10^{-5}	1.35
4	0.25	0.06	0.016	0.004	10^{-4}	3.78
3	0.33	0.11	0.037	0.012	0.004	6.88
2.7	0.37	0.14	0,051	0.019	0.007	11.6
2.4	0.42	0.17	0.073	0.030	0,013	16.4

TABLE IV
RESULT OF SECOND SERIES (pH=9.6)

(HO_x)	$(HO_x)^{-1}$	$(HO_x)^{-2}$	$(HO_x)^{-3}$	$(HO_x)^{-4}$	$(HO_x)^{-5}$	E^{-1}
10 mg.	0.10	0.01	0.001	10^{-4}	10^{-5}	1.23
4	0.25	0.06	0.016	0.004	10^{-3}	2.00
3.12	0.33	0.10	0.033	0.011	0.0034	3.23
2.68	0.38	0.14	0.055	0.021	0.0078	5.64

chloroform solution of 8-hydroxyquinoline (known concentration) and treated as described in (B). The procedure is repeated for several varying concentrations of 8-hydroxyquinoline in chloroform. Two series of experiments are carried out; the first is done at about pH 9.3 and the second is done at about pH 9.6.

(3) **Results Obtained.**—The results of these experiments are shown in Tables III and IV.

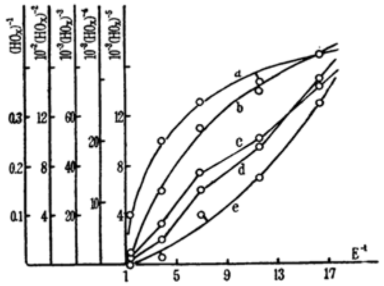

Fig. 2. Results of 1st series (pH=9.3).
a; $E^{-1}-(HO_x)^{-1}$, b; $E^{-1}-(HO_x)^{-2}$,
c; $E^{-1}-(HO_x)^{-3}$, d; $E^{-1}-(HO_x)^{-4}$,
e; $E^{-1}-(HO_x)^{-5}$,

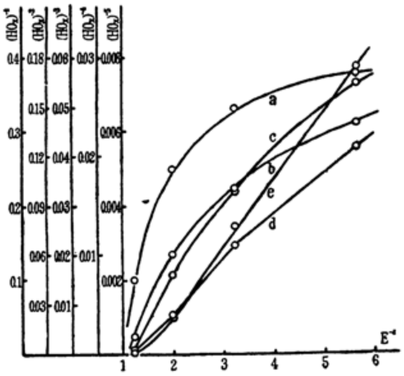

Fig. 3. Results of 2nd series (pH 9.6).
a; $E^{-1}-(HO_x)^{-1}$, b; $E^{-1}-(HO_x)^{-2}$,
c; $E^{-1}-(HO_x)^{-3}$, d; $E^{-1}-(HO_x)^{-4}$,
e; $E^{-1}-(HO_x)^{-5}$,

In Fig. 2 and 3 the diagrams of $E^{-1}-(HO_x)^{-1,2,3,4 \text{ and } 5}$ are given.

In these diagrams, figures of curve vary more slowly against the variation of n than in the cases previously reported by the author where the best linearity is got for $n=2$. So the determination of n becomes more difficult than the cases of lead dithizonate, lead hydroxyquinolate or polonium dithizonate.[1,4] Fig. 2a and b and Fig. 3a and b are clearly convex, and Fig. 2e and Fig. 3e are probably concave. So the best linearity is expected for $2<n<5$. However, we can not decide the value of n which gives the best linearity in E^{-1} vs. $(O_x)^{-n}$ diagram, because Fig. 2c and d and Fig. 3d are broken to a considerable extent. (We may assume that Fig. 3c is slightly convex.)

There is no generally accepted formula about the oxidation state of promethium in an aqueous solution, but according to its position in the periodic table, it belongs to the rare earth elements and it is most likely to assume trivalent cation of promethium. Based on this assumption, we can guess that the formula of the complex will probably be written as $Pm(O_x)_3$ or $Pm(O_x)_3(HO_x)$.[5] As the example of hydroxyquinolate of the latter type, thorium hydroxyquinolate, $Th(O_x)_4(HO_x)$, is known.[6]

(II) Yttrium Hydroxyquinolate

There is no description on yttrium hydroxyquinolate, except a report on its formation in an acetic acid solution[7]. In the present paper, the formation and composition of the complex salt of yttrium and hydroxyquinoline in chloroform medium, are studied using yttrium-90 which is easily prepared from strontium-90.

(A) **Preparation of Solution of Yttrium-90.**—Solution of "strontium-89" imported from the Oak Ridge National Laboratory, U.S.A., contains strontium-90. In the solution of "strontium-89" which has been left to stand for about 20 days, yttrium-90, the daughter element of strontium-90, is formed in an amount which is in equilibrium with strontium-90. Therefore, yttrium-90 can be isolated by the common chemical methods. Although a method for preparation of yttrium-90 based on radiocolloid of yttrium-90 was reported by G.K. Schweitzer et al.[8] a

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[4] T. Ishimori, This Bulletin, 27, 520 (1954).

[5] The concentration of undissociated 8-hydroxyquinoline in the aqueous solution is proportional to that of the anion of 8-hydroxyquinoline. Therefore, even in a case in which the complex salt is of the mentioned formula, the basis of the method is available.

[6] F.J. Frere, *J. Am. Chem. Soc.*, 55, 4362 (1933).

[7] K. Shiba, *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, 28, No. 8 (1932).

different method was used in the present research.

A solution of non-active strontium chloride (containing about 15 mg. strontium) is added to the solution which contains yttrium-90, strontium-90 and strontium-89 (about 0.5 milli curie strontium-90). After addition of ferric alum (0.1 g.), the resultant solution is made up to about 100 cc. and treated with ammonium chloride and ammonium hydroxide in order to coprecipitate yttrium-90 with ferric hydroxide. The precipitate is filtered off and reprecipitated according to the usual way.

Strontium goes to the filtrate and yttrium remains in the precipitate of ferric hydroxide. The precipitate is dissolved in hydrochloric acid (1 : 1) and iron is extracted into ether according to the Rothe's method. The aqueous solution which contains yttrium-90 is evaporated up and the residue is redissolved with water to obtain 25 cc. of the aqueous solution.

Ammonium chloride which is contained in the resultant solution does not disturb the result of the experiment.

Radioactivity of residue of the yttrium-90 solution thus prepared is strong enough (20–30 div./min. per cc.) for the following experiments and shows the decay as shown in Fig. 4. From the figure the half-life of the radioactivity is calculated as about 60 hours, and this value almost coincides with that described by Friedlander and Kennedy[9].

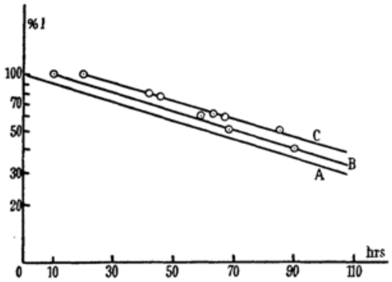

Fig. 4. Decay of Yttrium-90.

A : Theoretical decay for t=60 hrs.

B : Y-90 used in 1st series of experiments.

C : Y-90 used in 2nd series of experiments.

As strontium has a long half-life (19.9 years), yttrium-90 is repeatedly prepared from the filtrate which contains strontium-90.

(B) On the Formation of Yttrium Hydroxyquinolate. -- An aqueous solution which contains 1 cc. of the solution of yttrium-90 and 5 cc. of the solution of sodium potassium tartrate (20%) or 5 cc. of ammonium acetate (20%) is treated in the almost same way as described in I, (B) and the extractability is calculated. This procedure is repeated for several different pH values of the aqueous solution.

The results are shown in Table V, in which we can see that remarkable amounts of yttrium-90 are extracted from weak alkaline solution. Further similar procedure is repeated with pure chloroform at pH 8.6 and 8.8, but no yttrium is extracted. Basing our ideas on these facts, we can conclude that yttrium forms a hydroxyquinolate in an alkaline solution.

TABLE V

EXTRACTION OF YTTRIUM HYDROXYQUINOLINE

Extraction of the complex from the solution containing	pH	Concentration of 8-hydroxyquinoline in $CHCl_3$ (mg./50 cc.)	Extractability
ammonium acetate	3.5	10	0.05%
,,	4.5	,,	0.1
,,	6.8	,,	0.15
,,	8.6	,,	3.6
,,	8.6	1000	53
sodium potassium tartrate	3.5	111	...*
,,	5.8	,,	0.0
,,	8.8	,,	28
,,	8.6	none	0.1
,,	8.8	,,	0.0

* Tartaric acid is pptd.

(C) On the Composition of Yttrium 8-Hydroxyquinolate.—The composition of yttrium hydroxyquinolate is estimated in a similar way as that described in I, (C). Two series of experiments are carried out at about pH 8.6 and 8.8.

The results of experiments are shown in Tables VI and VII. The $E^{-1}-(HO_x)^{-1,2,3}$

TABLE VI

RESULTS OF FIRST SERIES (pH=8.6)

(HO_x)	$(HO_x)^{-1}$	$(HO_x)^{-2}$	$(HO_x)^{-3}$	E^{-1}
1.0	1.0	1.0	1.0	1.78
0.4	2.5	6.3	15.6	11.9
0.2	5.0	25	125	40.3
0,12	8.3	69	578	100

(HO_x) : Amount of 8-hydroxyquinoline given in an arbitrary unit in which $(HO_x)=1$ corresponds to 8.3 mg. 8-hydroxyquinoline.

E : Extractability.

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[8] G.K. Schweitzer, B.R. Stein and Wm. M. Jackson, *J. Am. Chem. Soc.*, **75**, 793 (1953).

[9] G. Friedlander and J.W. Kennedy, "Introduction to Radiochemistry", John Wiley & Sons, New York, (1949) p. 327.

TBALE VIII

RESULTS OF SECOND SERIES (pH=8.8)

(HO_x)	$(HO_x)^{-1}$	$(HO_x)^{-2}$	$(HO_x)^{-3}$	E^{-1}
11.1	0.09	0.008	0.0008	3.66
4.4	0.23	0.052	0.012	14.8
3.3	0.30	0.092	0.028	35.7
2.6	0.38	0.15	0.057	58.7
2.2	0.46	0.21	0.094	86.0

(HO_x): Amount of 8-hydroxyquinoline given in mg.

E: Extractability.

diagrames are given in Figs. 5 and 6. As can be seen in the figures, $(HO_x)^{-2}$ is linear to E^{-1}. So we can conclude that yttrium hydroxyquinolate contains 8-hydroxyquinoline anion in such a ratio as two anions are bound to one atom of yttrium. Consequently, according to the results of the present study, we may guess that the composition of the complex salt will correspond to a formula such as $Y(O_x)_2X$, where (O_x) represents C_9H_6ON and X represents some monovalent anion other than $(O_x)^-$.

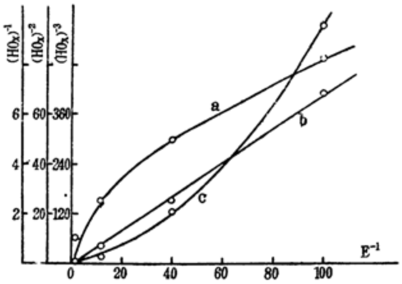

Fig. 5. Results of 1st series (pH=8.6).
a: $E^{-1}-(HO_x)^{-1}$, b: $E^{-1}-(HO_x)^{-2}$,
c: $E^{-1}-(HO_x)^{-2}$

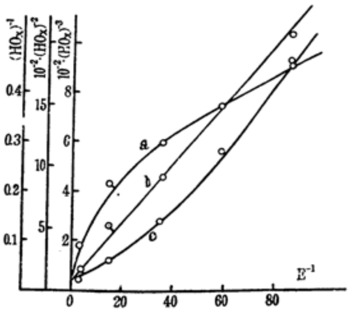

Fig. 6. Results of 2nd series (pH=8.6).
a: $E^{-1}-(HO_x)^{-1}$, b: $E^{-1}-(HO_x)^{-2}$,
c: $E^{-1}-(HO_x)^{-3}$

The studies of the complex in macro amounts is desired, because of possible differences between the composition of the complex compound formed from a concentrated solution and that formed from an extremly dilute solution.

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