Radiochemical Studies on Ultra-Micro Quantities of Organometallic Compounds. I. On the Determination of the Composition of an Organometallic Compound in an Ultra-Micro Amount

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The composition of an organometallic complex compound is usually determined by the chemical analysis of the pure crystals of the complex compound. For the determination of the composition of a complex compound in a minute amount, some optical or electrochemical methods are available, but these methods are not applicable for a complex salt in an ultra-micro amount. However, there are many complex compounds which can be prepared only in extremely minute quantities, e.g. organometallic compounds of much rarer elements such as polonium, promethium and so on.

Recently the present author[1] reported the formation of polonium dithizonate by the dithizone extraction method. The dithizonate has been used in the determination of radium A and radium F in waters of some strongly radioactive hot springs. Also in Europe, G. Bouissieres et al.[2] purified polonium by means of the extraction of polonium dithizonate. Further, radium B content of waters of hot springs was determined by the extraction in the form of lead (radium B) dithizonate.[3]

Such being the circumstances, the author attempted to determine the composition of organometallic compounds which are difficult to prepare in a large amount and devised a method suitable for this purpose. In the present paper, the theoretical basis of the method and the results of the experiments with lead (thorium B) dithizonate and lead (thorium B) hydroxyquinolate, both of the well known compositions, are described.

(A) Theoretical Basis of the Method.

In 1941, I. M. Kolthoff and E. B. Sandell[4] studied the extraction of zinc dithizonate quantitatively and gave an equation relating the extraction coefficient of the metallic dithizonate, the *p*H of the aqueous solution being extracted and the concentration of the chloroform solution of dithizone used for the extraction.

Recently the principles of solvent extraction were outlined by M. Calvin.[5] Basing his results on his theory, Furman determined

1) T. Ishimori and H. Sakaguchi, *J. Chem. Soc. Japan*, **71**, 327 (1950).

2) G. Bouissieres and C. Ferrandini, *Anal. Chem. Acta*, **4**, 610 (1950).

3) H. Umemoto, *Japan Analyst*, **2**, 201 (1953).

4) I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, **63**, 1906 (1941).

5) M. Calvin, *Experientia*, **6**, 135 (1950); *Manhattan Project Report* CN-2486, December 19, 1944; cf. A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compunds", N. Y., Prentice Hall Inc., 1952, p. 451.

the chemical formulea of various dithizonates.[6] Moreover, also in Sweden, comprehensive studies on thorium acetylacetonate seem to be carried out from the theoretical points of view.[7]

In a similar way the present author studied the equilibrium between the aqueous solution of a definite pH containing a tracer amount of radioisotope of a metallic element and the chloroform solution of an organic reagent, both being in mutual contact.

In such a system the following equilibria are established after thorough shaking and standing:

(organic solvent phase) (aqueous phase)

$$HR \overset{p_r}{\rightleftarrows} HR \overset{k_r}{\rightleftarrows} H^+ + R^-$$

Here, an organic reagent, HR, is considered as a weak acid and k_r and p_r respectively indicate the dissociation constant and the partition coefficient as given by Eq. 1 and 2:

$$k_r = [H^+]_w \cdot [R^-]_w / [HR]_w \quad (1)$$

$$p_r = [HR]_w / [HR]_o \quad (2)$$

Here the suffixes, r, w, and o respectively represent the organic reagent, aqueous phase, and organic solvent phase, and the square bracket represents concentration.

Further, the reaction of the metal ion, M^{n+}, with the organic anion and the partition of the organometallic compound, MR_n, between two liquid phases are written as

organic solvent phase) (aqueous phase)

$$MR_n \overset{p_c}{\rightleftarrows} MR_n \overset{k_c}{\rightleftarrows} M^{n+} + nR^-$$

Therefore, the equilibrium constant for this reaction is

$$k_c = [M^{n+}]_w \cdot [R^-]^n_w / [MR_n]_w, \quad (3)$$

and the partition coefficient of the complex compound between the aqueous and organic phases is

$$p_c = [MR_n]_w / [MR_n]_o. \quad (4)$$

In these equations, the suffix c represents the complex compound.

The extractability, E, namely the ratio of the radioactivity due to the total amount of the radioactive metallic cation taken into the system and that extracted into the organic phase, is written as

$$E = [MR_n]_o \cdot v_o / ([MR_n]_o \cdot v_o + [MR_n]_w \cdot v_w + [M^{n+}]_w \cdot v_w), \quad (5)$$

where v_o and v_w represent respectively the volumes of the organic and aqueous phases. Introducing values from Eqs. 2, 3 and 4, Eq. 5 beomes

$$E = p_c^{-1} \cdot [MR_n]_w \cdot v_o / [MR_n]_w \cdot \{(p_c^{-1} v_o + v_w) + k_c v_w [R^-]_w^{-n}\}. \quad (6)$$

Because p_c and k_c are constant at a definite temperature and v_o and v_w can be kept constant in a series of experiments, Eq. 6 is simplified as

$$E = 1/(A + B'[R^-]_w^{-n}) \quad (7)$$

or

$$E^{-1} = A + B'[R^-]_w^{-n}, \quad (8)$$

where A and B' are constants.

In Eq. 7 or 8, $[R^-]_w$ is difficult to determine experimentally, but in these cases we consider, $[R^-]_w$ is proved to be proportional to the amount of the organic reagent, (HR), taken into the system. Namely in the equation

$$(HR) = [HR]_o v_o + n[MR_n]_o v_o + [HR]_w v_w + n[MR_n]_w v_w + [R^-]_w v_w, \quad (9)$$

the total amount of metal is so small that second and fourth terms on the right hand side can be neglected. Therefore, Eq. 9 becomes

$$(HR) = [HR]_o v_\bullet + [HR]_w v_w + [R^-]_w v_w. \quad (10)$$

Introducing values from Eq. 1 and 2, Eq. 10 is rewritten as

$$(HR) = [R^-]_w \{k_r^{-1}(p_r^{-1} v_o + v_w)[R^+]_w + v_w\}, \quad (11)$$

where all quantities in the right hand side except $[R^-]_w$ are kept constant. Thus $[R^-]_w$ is proved to be proportional to (HR), and Eq. 8 is rewritten as

$$E^{-1} = A + B(HR)^{-n}, \quad (12)$$

in which A and B are constants.

According to Eq. 12, we can determine the value of n, the ratio between the number of organic anions and that of metallic cation, in the following manner.

An aqueous solution of a definite hydrogen ion concentration containing a known amount of the radioactive tracer of a metal is prepared. In a small separating funnel known volumes of this aqueous solution and an organic solvent containing a known quantity of an organic reagent are shaken together until the equilibrium is established. The organic solvent is then separated and dried in a glass dish. The radioactivity of the residue is measured and the extractability, E is calculated.

Similar procedures are repeated for a series of varying amounts of the organic reagent. The values of E^{-1} are plotted against $(HR)^{-n}$, taking for n the values 1, 2, 3 and so on, so that we can find out the integer, n, which gives the best linearity between E^{-1} and $(HR)^{-n}$.

Thus we can determine the actual value of n, but this method does not give any

6) cf. Martel and Calvin, ibid p. 463. The present author can not find where this paper appeared originally.

7) J. Rydberg, *Arkiv für Kimi*, 5, 517 (1953). This is the eleventh report of Rydberg's study. The rest of this series have not been accesible to the present author.

knowledge concerning the water bound to the complex molecule. Moreover it can not be adopted in the case where two or more kinds of organometallic compounds are formed, and also in the case where the formation of radiocolloids prevents the establishment of the equilibria underlying the derivation of Eq. 12.

In addition to these defects, we can not estimate the effects of impurities introduced into the system by chemicals used in the experiment. Any way the amount of these impurities is supposed to be much greater than the radiochemical amount of the metallic cation taken into the system.

(B) Experimental Examination of the Validity of the method.

As mentioned above, there are many uncertain facts which may disturb the results of the method. Therefore, the author intended to check the validity of the above reasoning for some organometallic compounds such as lead dithizonate and lead hydroxyquinolate, the composition of which are known already. In these experiments carrier-free radioisotope of lead, thorium B, is used.

(1) Preparation of thorium B solution.

According to the usual method recommended by O. Hahn[8], the radioactive deposits of thoron are collected on a platinum plate. About 50 g. thorium nitrate is placed in a closed metal container into which an insulated, negatively charged (250 volts) platinum plate is also introduced. The active deposit proceeding from the emanation, i. e. thorium B with its disintegration products, is collected on the platinum plate for about 24 hours, and then dissolved into hot dilute nitric acid (1 : 15). The solution is made up to 25cc. and divided into aliquot portions for both the preparation of the standard specimen of thorium B and the following experiments.

The radiochemical purity is examined by the measurement of the decay curve shown in Fig. 1, in which the logarithm of the activity is plotted against the time elapsed. From this figure the apparent half-life of the activity is calculated as about 10.5 hours. So we can conclude that the "thorium B" will not have any detectable radiochemical impurity except its daughter, thorium C group, in an equilibrium amount.

The measurements of the activities are carried out by a Lauritsen electroscope made by the Scientific Research Institute, Tokyo.

Owing to its relatively short half-life (10.6 hours), the solution of thorium B must be prepared just before each series of experiments so that its radioactivity is measured accurately.

(2) On the composition of lead dithizonate.

5cc. of 50% sodium citrate solution and and 5cc. of 10% potassium cyanide are added to 20cc, of thorium B solution obtained as above. Ammonium hydroxide is added to the mixture dropwise to make it weakly alkaline, and the resultant solution is made up to 100cc. The *p*H of the solution is checked by a *p*H test paper and estimated to be about 9.5.

The stock chloroform solution of dithizone (about 1.25×10^{-4} mol./1.)[9] is diluted successively with chloroform and a series of chloroform solutions of dithizone, 1, 1/5, 1/10, 1/25 and 1/50 times the concentration of the original stock solution, is prepared. Dilution of the solutions is made just before use to prevent the decomposition of dithizone.

To 10 cc. of the aqueous solution prepared as above, 5 cc. of the chloroform solution of dithizone (known concentration) are added in a separating funnel. The system of the two liquid phases is shaken vigorously for one minute and is left to stand aside for a while so that it separates into two liquid phases. The chloroform phase is taken into a glass dish, dried up and left to stand overnight before the measurement of radioactivity. During the overnight standing, thorium B disintegrates to a considerable extent, so it looks unfavorable for the measurement of radioactivity, but it is necessary to make sure the condition of radiochemical equilibrium between thorium B and its daughters, members of thorium C group.

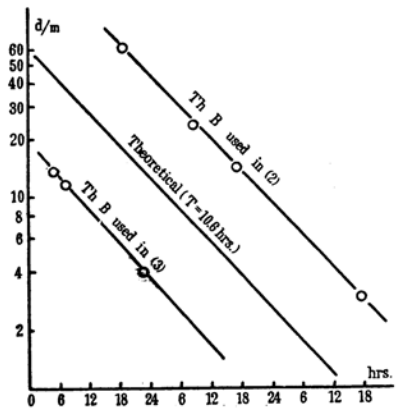

Fig. 1

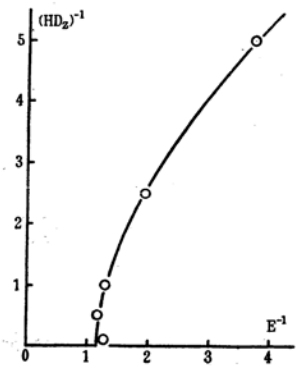

Fig. 2 a

8) Otto Hahn, "Applied Radiochemistry" Cornell Univ. Press, New York, N. Y., p. 44 (1936).

9) The concentration of dithizone in chloroform is determined by titrating a dilute solution of silver nitrate.

Taking the ratio of the activity due to the extracted thorium B to that of the standard specimen of the same age, the extractability, E, is calculated.

Similar procedures are repeated for varying concentrations of dithizone in chloroform.

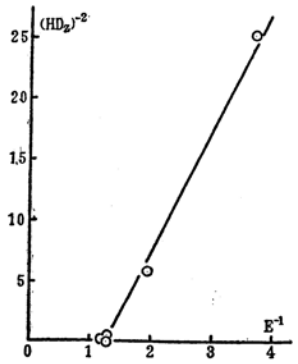

Fig. 2 b

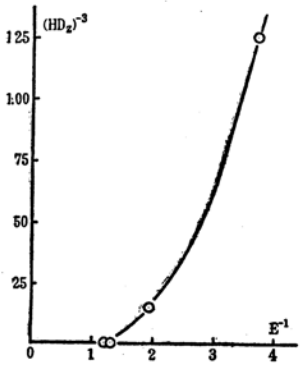

Fig. 2 c

TABLE I

RESULTS FOR LEAD DITHIZONATE

No.	(HDz)	$(HDz)^{-1}$	$(HDz)^{-2}$	$(HDz)^{-3}$	E^{-1}
1	10	0.1	0.01	0.001	1.27
2	2	0.5	0.25	0.125	1.19
3	1	1.0	1.0	1.0	1.30
4	0.4	2.5	6.3	15.6	1.97
5	0.2	5.0	25.	125.	3.72

(HDz): Amount of dithizone in an arbitrary unit in which about 6.3 10^{-7} mol. dithizone corresponds to (HDz)–10

E : Extractability

Results obtained are shown in Table I and Fig. 2 (a, b, c). As can be seen in these figures, E^{-1} is linear to $(HDz)^{-2}$. (cf. Fig. 2 b) So we can conclude that the composition of lead dithizonate is of such a ratio as when one atom of lead is bound to two anions of dithizone, Dz.

On the other hand Liebhasky and Winslow[10] reported that lead dithizonate corresponds to the formula $PbDz$, but Clifford[11] showed that the complex compound is actually $PbDz_2$, whicn is generally accepted by most chemists.[12] The conclusion obtained by the present method also coincides with that of Clifford. Therefore, the present method is considered to be applicable for the determination of the composition of organometallic compounds. And the disturbing factors mentioned above proved to result in no serious error.

(3) On the composition of lead hydroxyquinolate.

To the solution which contains 5g. sodium citrate and 20 cc. thorium B solution described in (1), ammonium hydroxide is added dropwise until *p*H of the solution becomes about 9. The resultant solution is made up to 50 cc.

About 100 mg. 8-hydroxyquinoline is dissolved in 50 cc. chloroform. Diluting this solution with chloroform, a series of solutions of 8-hydroxyquinoline is prepared. Their concentrations are 1, 2/5, 1.5/5, and 1.2/5 times that of the original solution.

Using the aqueous solution of thorium B and the chloroform solution of 8-hydroxyquinoline, a series of experiments is carried out in a similar way as described in the case of lead dithizonate.

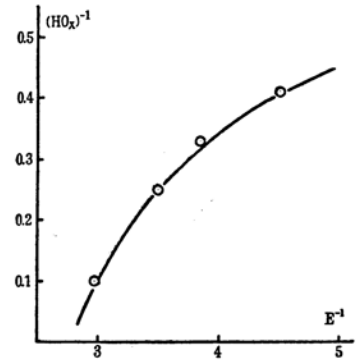

Fig. 3 a

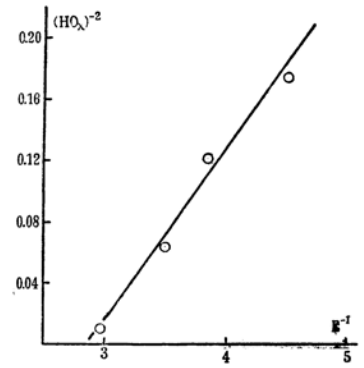

Fig. 3 b

10) H. A. Liebhasky and E. H. Winslow, *J. Am. Chem. Soc.* **59**. 1966 (1937).

11) P. A. Clifford, *J. Official Agr. Chem.* **26**, (1943); *C. A.*, **37**, 3009.

12) The formula given by Clifford which coincides with that of H. Fischer (*Z. anorg. Chem.*, **47**, 685 (1934).) is quoted by F. J. Welcher ("Organic Analytical Reagents", vol. 3, D. van Nostrand Co., Inc., New York, 1947. p. 470.).

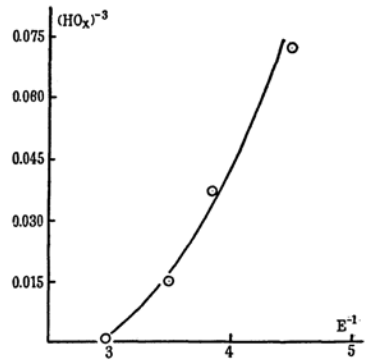

Fig. 3 c

TABLE II.

RESULTS FOR LEAD HYDROXYQUINOLATE

No.	(HOx)	$(HOx)^{-1}$	$(HOx)^{-2}$	$(HOx)^{-3}$	E^{-1}
1	10	0.1	0.01	0.001	2.97
2	4	0.25	0.063	0.015	3.50
3	3	0.33	0.111	0.037	3.84
4	2.4	0.41	0.174	0.072	4.51

(HOx): Amount of 8-hydroxyquinoline in an arbitrary unit in which (HOx) = 10 corresponds to about 10 mg. 8-hydroxyquinoline.

E : Extractability

The results are shown in Table II and in Fig. 3 (a, b, c). In Fig. 3 b, we can see a linear relationship between E^{-1} and $(HOx)^{-2}$. Therefore we can conclude that lead hydroxyquinolate corresponds to the formula $Pb(Ox)_2$. This conclusion agrees with the generally accepted formula[13] for lead hydroxyquinolate, again showing the applicability of the present method method for such a problem.

In the following papers results for some organometallic compounds which have unknown compositions will be reported.

The author has to thank to Professor Tsunetaka Sasaki, Kyushu University, for his encouragement and criticism in several discussions on the theoretical considerations of the present study.

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13) V. Maarson and L. W. Haase, *Chem. Ztg.* **52**, 993 (1928); *C. A.* **23**, 1077 (1928).