Radiochemical Studies on Ultra-Micro Quantities of Organometallic Compounds. II. On the Composition of Polonium Dithizonate

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Previously the author[1] has reported on the formation of polonium dithizonate which is extracted into a carbon tetrachloride solution of dithizone (diphenylthiocarbazone) from an aqueous solution under some appropriate chemical circumstances. Further there is a literature[2] which shows that the complex salt can be used in the purification of polonium; however, the present author could not find out any report on the composition of polonium dithizonate.

In the present paper, the composition of polonium dithizonate (formed in a solution acidified with nitric acid) is determined according to the method described in the first paper[3] of this series and the author estimates that two anions of dithizone are bound to one atom of polonium in polonium dithizonate.

(A) Preparation of the Polonium Solution.—The polonium solution used is a solution of radium F which is prepared as follows:

1.5 g. powdered pitchblende are dissolved in nitric acid. The undissolved residue is filtered off after the solution is diluted with water. The filtrate is treated with hydrogen sulfide to precipitate polonium (radium F) with lead and some other elements of the hydrogen sulfide group which may occur in the starting material. The precipitate is dissolved in nitric acid, and the residue containing sulfur is filtered off. The filtrate is diluted until the content of nitric acid becomes about 2.5% (vol.), and then extracted successively with some portions of the chloroform solution of dithizone. The combined chloroform solution is shaken with 10 cc. of (1:1) nitric acid to obtain an aqueous solution of polonium. The aqueous solution is separated, diluted to about 20 cc. with water, and preserved as the stock solution.

1) T. Ishimori and H. Sakaguchi, *J. Chem. Soc. Japan*, **71**, 327 (1950).
2) G. Bouissieres and C. Ferrandini, *Anal. Chim. Acta*, **4**, 610 (1950).
3) T. Ishimori, This Bulletin, **27**, 139 (1954).

The resultant solution contains about 25% (vol.) nitric acid and about 10^{-9} curie radium F (about 10^{-12} g. P_0) per 1 cc. The radioactivity due to the alpha emission of the evaporated residue of the solution is measured by an electroscope (gold leaf type) made by the Scientific Research Institute, Tokyo. The decay of the radioactivity shows that the half-life is about 140 days (Fig. 1). On the other hand, the extremely weak beta-rays are detected by a Geiger-Müller counter. Therefore, this solution seems to contain slight contaminations of radium E and other isotopes.

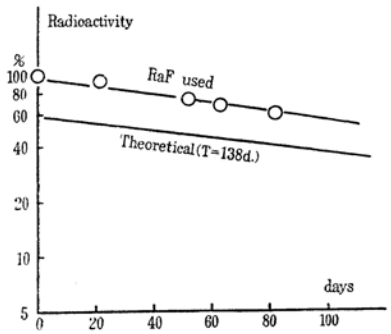

Fig. 1. Decay of RaF

(B) Determination of the Composition of Polonium Dithizonate.—In the first paper[3] of this series, the author gave a method for the determination of the composition of an organo-metallic compound in an ultra-micro amount, basing his conclusions on the following relation:

$$E^{-1}=A+B(HR)^{-n}$$

where, E is extractability, 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, n, the ratio between the number of organic anions and that of the metallic cation, and A and B are constants.

According to the method, the composition of polonium dithizonate is determined by repeating the measurement of extractability for various amounts of dithizone, (HDz), plotting the results in $E^{-1}-(HDz)^{-1,2,3}$ diagrams, and finding out $(HDz)^{-n}$ which is almost linear to E^{-1}. In these experiments, all experimental conditions such as pH and volume of the aqueous phase or volume of the organic phase, must be kept constant. Otherwise the above equation can not be used as the theoretical basis.

(1) Series of Experiments I.—10 cc. of distilled water and 1.0 cc. of the stock solution of polonium are respectively added to six small separating funnels. Though the solutions are not buffered, the pH values are supposed to be fairly constant as they contain about 2.2% (vol.) of nitric acid. Therefore, the necessary condition for a constant pH value[3] is almost satisfied in this case.

5.0 cc. of the dithizone chloroform solutions with various concentrations are prepared by diluting the stock solution of dithizone in chloroform (about 0.4×10^{-3} mol./l.)[4] and added to each separating funnel which contains the diluted aqueous solution of polonium. The funnels are shaken vigorously for a minute.

The separated chloroform layers are evaporated up in glass dishes to measure the radioactivities due to the fractions of radium F which are extracted into the chloroform solution.

The measured intensities[5] are compared with that of the standard specimen which is prepared by evaporating 1 cc. of the stock solution of polonium in a glass dish, and the extractability, E, is calculated.

The results obtained are shown in Table I and Fig. 2(a,b,c).

TABLE I

RESULTS OF (B, 1)

No.	(HDz)	$(HDz)^{-1}$	$(HDz)^{-2}$	$(HDz)^{-3}$	d/m $P_{0\,extd.}$	E^{-1}
1	0.96	1.04	1.09	1.13	11.75	1.31
2	0.42	2.38	5.66	13.5	10.33	1.49
3	0.080	12.5	156	1.95×10^{3}	3.43	4.48
4	0.032	31.2	974	3.04×10^{4}	0.87	17.7
5	0.024	41.7	1740	6.97×10^{4}	0.55	28.0
6	0.000	∞	∞	∞	−0.03	—

E: Extractability; The ratio of radioactivities due to radium F taken (15.39 d/m) and radium F extracted.

(HDz): Amount of dithizone denoted in an arbitrary unit in which $(HDz)=1$ corresponds to about 10^{-6} gram mol. dithizone.

4) The concentration of the chloroform solution of dithizone is determined by titrating known quantities of silver nitrate.

5) The radioactivity is measured by the electroscope mentioned above. The absorption of alpha-particles is checked by adding the stock solution of dirhizone on the specimen of polonium and drying it up. The following table shows that the effect of the absorption is negligible.

ml. dithizone solution (added)	0	1	2
radioactivity measured (d/m)	18.8	19.2	19.4

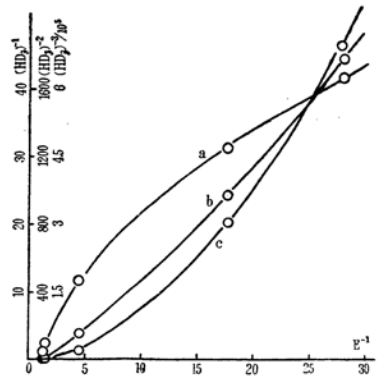

Fig. 2(a, b, c). $(HDz)^{-n}-E^{-1}$ diagram
a: $(HDz)^{-1}-E^{-1}$
b: $(HDz)^{-2}-E^{-1}$
c: $(HDz)^{-3}-E^{-1}$

(2) Series of Experiments II.—Almost the same experiments are repeated, but the procedures are slightly different from that of (1) in the following point: The aqueous solution of polonium is prepared by pipetting 4 cc. of the stock solution of polonium into a 50 cc. volumetric flask, and then adding water to the mark. After mixing thoroughly, 10 cc. of the diluted solution of polonium are taken to each separating funnel respectively. Therefore, the acidity of the aqueous solution is weaker than that of (1).

The results are shown in Table II as well as Fig. 3(a,b,c).

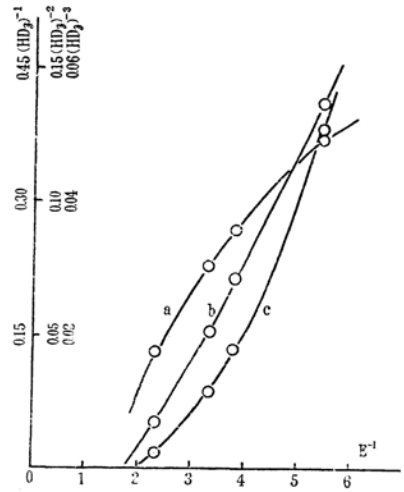

Fig. 3(a, b, c). $(HDz)^{-n}-E^{-1}$ diagram
a: $(HDz)^{-1}-E^{-1}$
b: $(HDz)^{-2}-E^{-1}$
c: $(HDz)^{-3}-E^{-1}$

TABLE II
RESULTS OF (B, 2)

No.	(HDz)	$(HDz)^{-1}$	$(HDz)^{-2}$	$(HDz)^{-3}$	d/m $P_{0\ extd.}$	E^{-1}
1	7.50	0.133	0.0176	0.0024	6.01	2.33
2	4.38	0.228	0.0519	0.0118	4.20	3.34
3	3.75	0.267	0.0713	0.0181	3.44	3.79
4	2.70	0.371	0.137	0.0509	2.39	5.45

E: Extractability; The ratio of radioactivities due to radium F taken (13.00 d/m) and radium F extracted.
(HDz): Amount of dithizone denoted in an arbitrary unit in which $(HDz)=1$ corresponds to about 10^{-8} gram mol. dithizone.

In these two series of experiments, the acidity of the aqueous solution is different. So the values of extractability given by both series do not coincide for a value of (HDz). However, the results of both series agree in the facts that almost linear relation is found between $(HDz)^{-2}$ and E^{-1} (cf. Fig. 2b and 3b), while the curve of $(HDz)^{-1}-E^{-1}$ is convex (cf. Fig. 2a and 3a) and that of $(HDz)^{-3}-E^{-1}$ is concave. Therefore according to the method described in the first paper of this study,[3] polonium dithizonate is supposed to have two anions of dithizone for one atom of polonium.

So far there is no generally accepted knowledge about the form in which polonium is dissolved in aqueous solutions. However G. v. Hevesy et al.[6] reported bivalent cation Po^{++} in hydrochloric acid solution. On the other hand M. Haissinsky[6] reported that PoO_3^{--} or PoO^{++} is prevailing in dilute nitric acid solution. So we can guess that polonium dithizonate will correspond to the chemical formula $PoDz_2$ or $PoODz_2$.

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6) Gmelins Handbuch d. Anorganischen Chemie, 8 Auflage, System Nr. 12 (1941), Verlag Chemie, Berlin, S. 103-104.