The Precipitation Reaction of Various Metallic Ions with Phenylarsonic Acid and its Derivatives

By Hisakazu NAKATA, Yuzuru KUSAKA and Shigeaki KIKKAWA

(Received May 11, 1962)

Phenylarsonic acid and its derivatives have been used extensively as precipitation reagents to separate and determine zirconium, titanium, thorium, bismuth, iron, tin and so on[1-4]. In these separation procedures it is very important to keep a sample solution at an appropriate acidity in order to complete the separation. For ortho, meta and para derivatives of aminophenylarsonic acid and nitrophenylarsonic acid, the pH values at which precipitation begins to occur have been reported for forty elements[3,4]. In these reports, however, the experimental conditions, such as the concentration of reagents and metallic ions and the precipitation procedure, were not described. Moreover, the exact acidities less than a pH value of 1 in which zirconium, titanium, tin and so on are precipitated were not reported.

We have studied the precipitation reactions of about twenty-five metallic elements with phenylarsonic acid and its derivatives. Under definite experimental conditions, the acidities in which the precipitation began and was then completed were measured and compared with each other. The acidities to be measured were over a broad region, such as from 12 N in hydrochloric acid to almost neutral. Phenylarsonic acid, *p*-hydroxy, *p*-amino, *o*-nitro, *m*-nitro, *p*-nitro and *p*-hydroxy-*m*-nitrophenylarsonic acid were used as the reagents. The results obtained are reported here.

Experimental

Materials.—*Phenylarsonic Acid and its Derivatives.*—These were synthesized in our laboratory, phenylarsonic acid by the Palmer-Adams method[5],

---

[1] J. F. Flagg, "Organic Reagents Used in Gravimetric and Volumetric Analysis", Interscience Publisher, New York (1948), p.107.

[2] F. J. Welcher, "Organic Analytical Reagents", Vol. IV, D. Van Nostrand Co., Princeton (1948), p. 49.

[3] R. Pietsch, *Mikrochim. Acta*, 1955, 954.

[4] R. Pietsch, ibid., 1955, 1019.

[5] C. S. Palmer and R. Adams, *J. Am. Chem. Soc.*, **44**, 1356 (1922).

p-hydroxy phenylarsonic acid by the Jacobs-Heiderberger method[6], *p*-aminophenylarsonic acid by the Jacobs-Heiderberger-Rolf method[7], and *o*-, m- and *p*-nitrophenylarsonic acid by the Bart method[8]. Only *p*-hydroxy-*m*-nitrophenylarsonic acid was obtained already intact from Prof. Risaburo Nakai of Kyoto University. All were purified by the conventional recrystallization method.

Metallic Salts. — The usual analytical-grade reagents were used. Most of them were chlorides, except for the silver, lead, uranium and thorium as nitrates.

Measurement Instruments.—A photometric Titrator PT-1 of the Yanagimoto Co. and a pH meter M-3 of the Horiba Inst. Co. were used for the measurements. In the former, a red filter was used when the sample solution was colorless. When the solution had some color, as in the case of copper, a filter whose color was the same as that of the solution was used in the experiment. The pH meter was calibrated by Sörensen buffer solutions, solutions mixed with various ratios of 0.1 N hydrochloric acid and 0.1 M sodium citrate.

Precipitation Procedures. — For the elements which were precipitated by an arsonate reagent in pH 1.0~9.0, 8 ml. of 0.05 M metallic ion solution in 0.1 N hydrochloric acid was mixed with 24 ml. of a 0.05 M solution of the arsonate reagent in 0.1 N hydrochloric acid*. Then, by adding a 2.7 N ammonium hydroxide solution drop by drop until the pH value of the solution became 3, the precipitation phenomenon was observed. For the neutralization in more than pH 3, 0.54 N ammonium hydroxide solution was used. As the volume of these ammonia to be added did not exceed 4 ml. in all the experiments, the concentration of metallic ions in the precipitation system was in the range of 0.011~0.013 M.

The formation and the completion of precipitation were investigated with a photometric titrator which measured the transparency or the turbidity of the solution. The pH value of the solution was measured with the pH meter.

For the elements which were precipitated in a more acidic medium than with a pH value of 1, the acidities in which the precipitation occured were determined by a two-step method. First, an approximate region of the acidity was determined. Each 1 ml. of a 0.05 M metallic ion solution whose acidities were adjusted to 6, 5, 4, 3, 2 and 1 N for hydrochloric acid was put in a separate test tube, and then 3 ml. of a 0.05 M arsonate reagent solution of the same acidity as that of the metallic ion solution was added. By this technique, an approximate acidity in which the precipitation is occured was determined; for example, zirconium *p*-hydroxy phenylarsonate is precipitated in a 5~4 N hydrochloric acid solution. In the next step, the more accurate acidity was determined by a similar method. For example, 8 ml. of a 0.05 M zirconium chloride solution in 5 N hydrochloric acid was mixed with 24 ml. of a 0.05 M *p*-hydroxy phenylarsonic acid solution in 5 N hydrochloric acid. Then, 13.5 N ammonium hydroxide was added drop by drop. The arsonate precipitation phenomenon was investigated by the photometric titrator, and the acidity in the precipitation was calculated from the amount of ammonia added to the solution.

For the elements which were precipitated in a stronger acidic medium than 6 N in hydrochloric acid, the experiment was performed by almost the same method as has been described above. In this case, however, only an approximate region of the acidity was determined by a method similar to the first step in the above experiment, and the next step of determining a more accurate acidity in the precipitation was ommited, because ammonium chloride was precipitated by adding ammonia in such a strong hydrochloric acid solution.

In all cases, the experiments were performed at room temperature (about 15°C); this temperature did not exceed 20°C even in the evolution of neutralization heat.

Results and Discussion

Typical examples of the results in the experiments of lead and cadmium phenylarsonates in a weak acidic medium and of thorium and uranium *p*-nitrophenylarsonates in a strong acidic medium are shown in Figs. 1 and 2.

As these figures show, the acidities at which the precipitation began and then was completed could be elucidated by measuring the acidity and the transparency depression in the solution. The turbidity was measured only as a subsidiary means to the transparency measurement. For example, when some color change of ions, based on an acidity change in solution, occured, as in the case of chromic ion, the turbidity measurement played an important role.

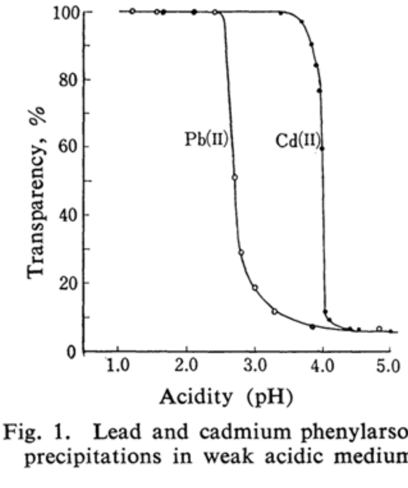

Fig. 1. Lead and cadmium phenylarsonate precipitations in weak acidic medium.

---

[6] W. A. Jacobs and M. Heiderberger, ibid., **41**, 1440 (1919).

[7] W. A. Jacobs, M. Heiderberger and I. P. Rolf, ibid., **40**, 1580 (1918).

[8] H. Bart, *Ann.*, **429**, 106 (1922).

* In the cases of silver and lead, nitric acid was used instead of hydrochloric acid because of their chloride precipitations.

TABLE I. ARSONATE PRECIPITATION IN A STRONG ACIDIC MEDIUM
(Normality of acid)

	Phenyl.	*p*-OH phenyl.	*p*-NH$_2$ phenyl.	*o*-NO$_2$ phenyl.	*m*-NO$_2$ phenyl.	*p*-NO$_2$ phenyl.	*p*-OH-*m*-NO$_2$ phenyl.
Nb(V)	10	9	9	10	11	12	10
	9	8	8	9	9	11	8
Ta(V)	12	7	10	7	7	10	8
	8	6	9	6	6	8	7
Ti(IV)	9	6	0.4	1.8	9	11	8
	8	6	0.3	1.1	8	9	7
Zr(IV)	6	4.9	1.3	0.6	6	6	6
	6	3.7	0.5	0.1	6	6	6
Sb(V)	2.2	2.5	0.5	—	3.5	2.6	2.1
	1.9	2.2	0.3	—	3.4	2.3	1.7
Sn(II)	1.4	0.7	0.5	1.7	3.0	3.0	2.0
	0.5	0.6	0.4	0.7	0.8	0.8	0.02*
Sb(III)	0.6	0.6	0.4	2.0	1.0	1.8	1.1
	0.3	0.3	0.2	1.6	0.8	0.4	0.7
U(VI)	0.2	0.4	0.6	0.2	1.0	1.0	1.0
	0.03	0.3	0.5	0.2	0.5	0.5	0.7
Th(IV)	0.3	0.2	0.2	0.07	1.9	2.3	0.5
	0.01	0.1	0.1	0.07	0.9	0.9	0.06
Bi(III)	0.03	0.4	0.4	0.1	0.03	0.5	0.01
	0.003	0.3	0.3	0.1	0.01	0.5	0.004
Fe(III)	0.1	0.003	0.02	0.005	2.0	2.0	0.2
	0.07	0.002	0.004	0.003	1.0	0.9	0.07
Sn(IV)	2.0	0.5	0.5	1.8	—	—	1.8
	1.4	0.05	0.4*	0.7	—	—	1.1

* Beyond these acidities, these precipitates were dissolved in a more basic region.

TABLE II. ARSONATE PRECIPITATION IN A WEAK ACIDIC MEDIUM
(pH)

	Phenyl.	*p*-OH phenyl.	*p*-NH$_2$ phenyl.	*o*-NO$_2$ phenyl.	*m*-NO$_2$ phenyl.	*p*-NO$_2$ phenyl.	*p*-OH-*m*-NO$_2$ phenyl.
Pb(II)	2.5	1.5	2.5	2.5	2.2	2.1	1.8
	3.3	3.1	2.8	2.9	2.5	3.4	2.5
Zn(II)	3.5	4.4	2.4**	4.3	2.4	2.2	2.9
	4.5	4.7	4.9	4.9	2.6	3.8	3.2
Ag(I)	4.4	4.1	1.6	5.1	3.2	1.0	3.2
	5.1	5.5	2.5	5.4	4.3	1.0	4.5
Ce(III)	3.4	3.3	3.4	2.5	4.5	2.7	3.2
	3.5	3.5	3.9	3.4	6.2	3.3	3.7
La(III)	3.3	3.2	4.1	5.9	2.5	2.6	3.0
	3.5	3.3	4.3	6.5	3.5	3.5	3.4
Cd(II)	3.5	4.4	2.3	7.2	2.5	2.3	1.8
	4.5	5.4	3.0	7.6	2.6	3.2	2.3
Cu(II)	—	3.0	2.5	5.3	2.7	1.7	2.9
	—	3.4	3.5	5.6	3.0	3.1	3.4
Cr(III)	—	4.5	4.0	4.0	2.3	1.5	3.5
	—	5.7	5.2	7.1	3.8	2.5	7.5
Mn(II)	2.1**	5.0	2.4**	—	1.0**	1.0	1.5
	5.0	6.2	5.5	—	4.5	4.4	4.6
Co(II)	6.2	6.5	5.8	8.2	4.4	1.6**	7.0
	6.7	7.4	6.9	9.2	5.0	6.0	7.6
Ni(II)	—	7.0	—	—	—	—	—
	—	7.7	—	—	—	—	—

** Beyond these acidities, a part of the precipitates were dissolved.

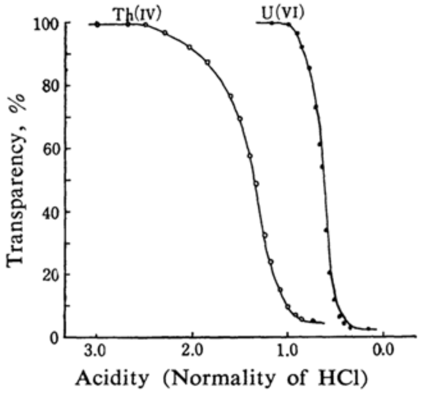

Fig. 2. Thorium and uranium *p*-nitrophenylarsonate precipitations in strong acidic medium.

The experimental results which were obtained for various metallic ions are shown in Tables I and II, in which the former is the precipitation in a strong acidic medium and the latter that in a weak acidic medium. In the tables, the numbers of the first line for each element indicate the acidity at which the precipitation began, and those of the second line indicate that point at which the precipitation is completed.

As the tables show, it seems possible to formurate some general rules on the precipitation of various elements by phenylarsonic acid and its derivatives. Although a few exceptions are found in each reagent, the general order of the elements precipitated from a strong acidic to a weak acidic medium is the order of elements shown in the tables, that is, up to down in the tables.

In each arsonate, especially when they are compared with the phenylarsonates, the nitro derivatives seem to be precipitated in a more acidic medium. In the nitro derivatives, the order is generally from the para and the meta and to the ortho form. The para hydroxy and the para amino derivatives seem to be precipitated in a more basic medium.

The authors wish to express their thanks to Messrs. Hideo Kitai, Mitsuro Tsubosaka, and Mrs. Akiko Ueshima, who contributed to this study by their synthesis of arsonic acid reagents and by their primary study of the precipitations of various metallic ions. Thanks are also due to Mr. Haruo Tsuji for his frequent assistance and to Dr. Risaburo Nakai for his gift of *p*-hydroxy *m*-nitro phenylarsonic acid.

Department of Chemistry
Faculty of Science
Konan University
Higashinada, Kobe