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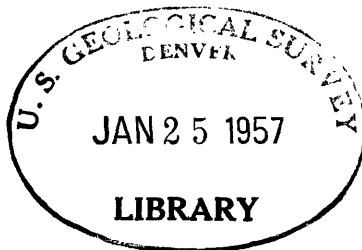
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THE USE OF AROMATIC COMPOUNDS OF
ARSENIC IN CHEMICAL ANALYSIS, PART I

By
A. I. Portnov

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CHEMISTRY

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ANALYSIS, PART I

By

A. I. Portnov

ABSTRACT*

The purpose of this study is to evaluate the analytical properties of aromatic arsonic acids and thus to establish a basis for their broader utilization in chemical analysis. The constants of dissociation have been determined for the phenylarsonic, arsanilic, acetarsanilic, p-oxyphenylarsonic, p-methylphenylarsonic, o-nitrophenylarsonic, m-nitrophenylarsonic, and p-nitrophenylarsonic acids. A study has been made of the effects of the replacing radicals on the constants of dissociation of arsonic acids. The conditions of the precipitation of a number of cations by means of arsonic acids were investigated. The dependence of the solubility of salts of arsonic acids upon the polarizing effects of replacing radicals was brought to light.

1. Introduction

Previous investigations

The following investigations antedate our work. In 1926 Rice, Fogg, and James (1) showed that in strongly acid solutions the zirconium ion forms with phenylarsonic acid a white sediment. These authors found that in strong solutions of hydrochloric acid, sulfuric acid, or nitric acid,

* This abstract was prepared by the translator and is based on the author's conclusions.

phenylarsonic acid precipitates niobium and tantalum quantitatively in the form of a white flakelike sediment, even though the solutions contain tartaric acid, citric acid, oxalic acid, or salicylic acid. The composition of this sediment was not determined by the authors. In the medium of tartaric acid such reactions are produced only by zirconium, hafnium, and tin.

In 1933 Knapper, Craig, and Chandlee (2) suggested the use of phenylarsonic acid as a precipitating agent for quadrivalent tin.

In 1936 Syrokonskii and Pil'niak (3) recommended a gravimetric method for the determination of small quantities of tin in ores by means of phenylarsonic acid.

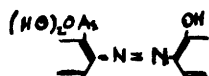
In 1937 Alimarin and Frid (4) as well as Miller (5) published the results of their investigations. Later Alimarin and Vezhenkov (6) criticized the method for the determination of tin proposed by Syrokonskii and Pil'niak; they reached the conclusion that this method cannot be used for the analysis of sulfide ores in the form suggested by these authors and must be further perfected. In the same year Kaufman (7) proposed phenylarsonic acid for a determination of thorium.

In the years 1938 through 1944 several articles dealt with the application of aromatic compounds of arsenic (8, 9, 10, 11).

In 1940 Kuznetsov (12) published an investigation of the causes of differences between the results obtained by various workers in determinations of tin by means of phenylarsonic acid.

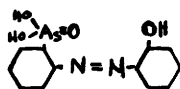
In 1941 Kuznetsov (13) wrote a paper on chromatic reactions to thorium, uranium, and other elements. In this work the author generalizes certain facts and arrives at the conclusion that ortho hydroxyazo compounds, having

an arsono group in the ortho position to the azo group thus having the grouping:



can precipitate a number of elements in an acid medium and this process is accompanied by a strong change of color. In the same year Richter (14) proposed p-oxyphenylarsonic acid as a reagent for titanium.

In 1944 Kuznetsov (15) offered phenylarsonic acid for the precipitation of scandium and its separation from the other rare-earth elements. The author considers that a still more convenient reagent for scandium is a Schiff base, formed by p-aminophenylarsonic acid and salicylic aldehyde,



In 1945 Kuznetsov (16) proposed anthraquinone α -arsonic acid for the determination of tin in the presence of large amounts of tungsten, antimony, copper, and other metals.

Purpose of present study

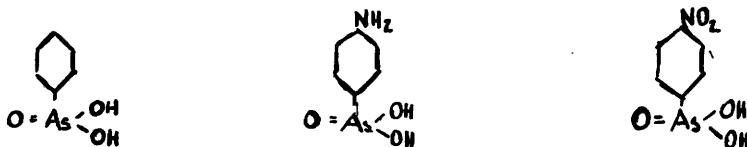
A common feature of all these investigations is their disconnected character. Aside from Feigel, Kuznetsov, and Alimarin, none of the authors pursued objectives contributing to the broader study of this problem. If the small number of these investigations is also taken into account, it becomes entirely clear that it is not possible, on the basis of this work alone, to draw conclusions concerning the wider use of aromatic compounds of arsenic in chemical analyses.

It should be also noted that none of these studies gives consideration to the application of arsonic acids in microchemical analysis. Not a single paper touches on the possibility of utilizing the aromatic compounds of arsenic in developing the volumetric methods of analysis, though this aspect of the problem has a dominant role in the improvement of analytical methods in chemistry.

These considerations prompted us to undertake the task of studying the effect of various replacing radicals on some analytical properties of arsonic acids and thus to establish a basis for a broader utilization of arsonic acids in chemical analysis.

2. Investigation of the dependence of constants of dissociation of arsonic acids on the polarizing effects of replacing radicals

Taking into account that a strongly expressed polarity is doubtless a factor in the chemical behavior of substances, and considering the constants of dissociation to be one of the principal criteria of the polarizing effects of replacing radicals, we found it indispensable to determine the constants of dissociation of the arsonic acids studied by us. We also verified the constants of dissociation of those arsonic acids, data on which are already in the literature (17). For this purpose we selected first of all phenylarsonic, arsanilic, and p-nitrophenylarsonic acids.



The constants of dissociation of the indicated acids were determined on the basis of electrical conductivity. The following values of K were obtained:

K_{18}° of phenylarsonic acid	2.6×10^{-4}
K_{18}° of arsanilic acid	4.9×10^{-5}
K_{18}° of p-nitrophenylarsonic acid	1.0×10^{-3}

For the determination of electrical conductivity the samples were cleaned twice by means of recrystallization from an aqueous solution with the addition of animal carbon.

As had been expected, the group NH_2 , displacing the electrons in the direction of the arsenic radical, decreases the constant of dissociation for the phenylarsonic acid; the radical NO_2 , producing a displacement of electrons away from the arsenic radical, increases the constants of dissociation.

The effect of the replacing radicals upon the degree of dissociation of arsonic acids becomes considerably clearer when this problem is examined from the standpoint of resonance. As regards energy, the less advantageous structures are those which have negative charges disposed at a greater distance from NH_2 . Naturally, such structures participate as small weights in the general balance of the structures characterizing these compounds; yet they exercise a rather considerable effect upon the extent of dissociation, because the negative charges are concentrated near the hydrogens of the arsenic radical.

In the case of p-nitrophenylarsonic acid, conditions are favorable for the separation of hydrogen ions because electrons are distant from the arsenic radical and positive charges are concentrated more or less near the arsenic radical. As regards energy, the less advantageous structures are those which have positive charges disposed at a greater distance from NO_2 ; yet, notwithstanding their small weight, these structures exercise a rather strong effect upon the extent of dissociation of p-nitrophenylarsonic acid.

It was natural to expect that the displacement of the electronic cloud should affect also the solubility of the salts of arsonic acids. In order to clarify this question, which has exceptional importance in analytical chemistry, we undertook a series of experiments.

3. Comparison between the solubilities of salts of phenylarsonic, arsanilic, and p-nitrophenylarsonic acids.

Our experiments for comparing the solubilities of the salts of the indicated acids were conducted as follows*.

To a 0.1-percent solution of the tested cation we added a 1-percent solution of the sodium salt of the respective acid. The precipitating agent was introduced in an excessive amount, 2 to 3 times greater than required by a stoichiometric calculation, with fixation of the sediment formed. The formation of the sediment was observed during 15 minutes.

Salts of the following metals were used for the experiments: copper (II), beryllium, magnesium, zinc, aluminum, thallium (I), manganese, and iron (II and III), in the form of sulfates; silver, calcium, strontium, cadmium, barium, mercury (I), bismuth, and lead, in the form of nitrates; mercury (II), and tin (IV), antimony (III), cobalt, and nickel, in the form of chlorides; tantalum and niobium in the form of complex compounds with tartaric acid.

When precipitation was made by means of a solution of phenylarsonic acid, we obtained insoluble compounds in the case of 9 cations (placed in brackets) out of the 22 cations tested: Be, Mg, Al, Ca, Mn, (Fe), Co, Ni, Cu, Zn, Sr, (Nb), (Ag), Cd, (Sn), (Sb), Ba, (Ta), (Hg^I) but not Hg^{II}, Tl, (Pb), (Bi).

* For our purpose,--namely, for a clarification of the effects of various replacing radicals upon the solubility of the salts of arsonic acids, --there was no need of a direct determination of the solubility of each separate arsonate.

With precipitation by means of a solution of arsanilic acid, a total of 18 cations (placed in brackets) produced insoluble compounds out of the 22 cations tested: (Be), (Mg), (Al), Ca, (Mn), (Fe), (Co), (Ni), (Cu), (Zn), Sr, (Nb), (Ag), (Cd), (Sn), (Sb), Ba, (Ta), (Hg), Tl, (Pb), (Bi).

With precipitation by means of a solution of p-nitrophenylarsonic acid, 8 cations (placed in brackets) gave insoluble compounds out of the 22 cations tested: Be, Mg, Al, Ca, Mn, (Fe), Co, Ni, Cu, Zn, Sr, (Nb), Ag, Cd, (Sn), (Sb), Ba, (Ta), (Hg'), Tl, (Pb), (Bi).

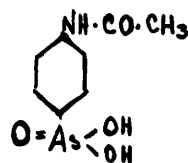
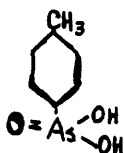
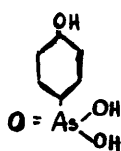
A comparison of these results shows that the greatest number of insoluble compounds is yielded by the arsanilic acid: 18 cations of 22 gave insoluble compounds. The smallest number of insoluble compounds is found in the case of p-nitrophenylarsonic acid: 8 cations of 22 yielded insoluble compounds. An intermediate position is occupied by phenylarsonic acid: 9 cations out of 22 produced insoluble compounds.

These data demonstrate clearly that the radical NH_2 reduces, and the radical NO_2 increases, the solubility of the salts of arsonic acids.

If we now compare the data obtained by the determination of constants of dissociation with the data found on the solubility of the salts of these acids, we clearly see that the factors which affect the constants of dissociation of arsonic acids likewise affect the solubility of the salts of these acids. Namely, an increase in the constants of dissociation of these acids is accompanied by an increase in the solubility of their salts; inversely, a decrease of the constants of dissociation is accompanied by a decrease of solubility.

These findings encouraged us to continue the study of the dependence of the constants of dissociation upon the nature of the replacing radical, and also the dependence of the solubility of the salts of arsonic acids upon

their constants of dissociation. For this purpose we synthesized the following arsonic acids: the p-oxyphenylarsonic, the p-methylphenylarsonic, and the acetarsanilic acid.



We were interested in finding out whether replacing radicals, the polarizations of which did not differ from one another as much as in the case of the amine and nitric derivatives, have in practice an effect on the constants of dissociation of acids and on the solubility of their salts.

The study of this relationship was conducted in the same procedural order as had been used in the first series of experiments. Namely, first, a determination was made of the constants of dissociation of acids, then of the solubility of their salts.

The constants of dissociation of the p-oxyphenylarsonic, the p-methylphenylarsonic, and the acetarsanilic acid were again determined on the basis of their electrical conductivity. The following values of K_{18} were obtained:

K_{18} of p-oxyphenylarsonic acid	8.2×10^{-5} ,
K_{18} of p-methylphenylarsonic acid	1.4×10^{-4} ,
K_{18} of acetarsanilic acid	1.5×10^{-4} .

A comparison of the constants of dissociation for all the studied arsonic acids gives the following picture of the change of these constants in accordance with the polarizing effects of the replacing radicals:

K_{18} of arsanilic acid	4.9×10^{-5}
K_{18} of p-oxyphenylarsonic acid	8.2×10^{-5}
K_{18} of p-methylphenylarsonic acid	1.4×10^{-4}

K_{18} of acetarsanilic acid 1.5×10^{-4}

K_{18} of p-nitrophenylarsonic acid 1.0×10^{-3}

The influence of the -OH radical upon the degree of dissociation is similar to the influence of the NH_2 radical, except that with hydroxy derivatives this influence is weaker. This is so because the formation of oxonium compounds is less advantageous from the energy standpoint than the formation of ammonium compounds.

The influence of the CH_3 radical upon the degree of dissociation of arsonic acids is still weaker than the influence of the -OH radical. The reason lies in the fact that the formation of intra-ionized structures does not in a single case lead to the formation of a surplus bond. Thus, they are less advantageous from an energy standpoint and are represented by smaller weights.

The influence of the NHCOCH_3 radical upon the degree of dissociation of arsonic acids can supposedly be explained likewise by the presence of a number of structures connected with the resonance within the NHCOCH_3 radical itself. It is necessary to consider moreover, that in a large part of these structures the negative charges are concentrated in the replacing radical, namely, at a great distance from the arsenic radical.

Naturally, the small difference between the constants of dissociation, which we have found for the methylphenylarsonic and the acetarsanilic acid, is not to be taken into consideration. Thus, there is no reason to expect a marked influence on the solubility of their salts. The findings on precipitation by means of the three last-named arsonic acids are given below.

The results of precipitation by means of p-oxyphenylarsonic acid showed that, out of the 22 cations tested, 16 (sic) cations yielded insoluble

compounds: Mg, (Be), (Al), Ca, (Mn), Fe, (Co), Ni, (Cu), (Zn), Sr, (Nb), (Ag), (Cd), (Sn), (Sb), Ba, (Ta), (Hg), Tl, (Pb), (Bi). Thus, the oxyphenylarsonic acid occupies the second place after the arsanilic acid as regards the number of insoluble compounds formed.

The results of precipitation by means of methylphenylarsonic acid showed that 14 cations, out of the 22 tested, yielded insoluble compounds: Be, Mg, (Al), Ca, (Mn), (Fe), (Co), Ni, (Cu), (Zn), Sr, (Nb), (Ag), Cd, (Sn), (Sb), Ba, (Ta), (Hg), Ti, (Pb), (Bi). Thus, the methylphenylarsonic acid occupies the third place after the arsanilic acid. This is also in full agreement with the data obtained by the determination of constants of dissociation.

The results of precipitation by means of acetarsanilic acid showed that 16 out of the 22 cations tested yielded insoluble compounds with this acid: (Be), Mg, (Al), Ca, (Mn), (Fe), (Co), Ni, (Cu), (Zn), Sr, (Nb), (Ag), (Cd), (Sn), (Sb), Ba, (Ta), (Hg), Ti, (Pb), (Bi). It must be supposed that small deviations from the indicated relationship are due in this case to the influence of additional factors which we did not take into consideration.

Table 1 presents the constants of dissociation for all the tested acids and the results of precipitation by means of these acids.

Table 1.

Name of the acid	Constant of dissociation at 18° C	Number of insoluble salts	Note
p-Nitrophenylarsonic acid	1.0×10^{-3}	8	As has been indicated above, a small deviation is found only in the case of acetarsanilic acid.
Phenylarsonic acid	2.6×10^{-4}	9	
p-Methylphenylarsonic acid	1.4×10^{-4}	14	
p-Oxyphenylarsonic acid	8.2×10^{-5}	16	
p-Acetarsanilic acid	1.5×10^{-4}	16	
p-Arsanilic acid	4.9×10^{-5}	18	

The results of precipitation by means of the arsonic acids, indicated in table 1, show that an increase of electronic density in the acid residue affects considerably the solubility of the salts of these acids.

4. The effect of the replacing radical, expressed in its dependence on the position that the radical occupies in the molecule of phenylarsonic acid.

In all the described experiments we studied the effect of the replacing radicals in the p-position. As can be seen from the data, the effect of the replacing radical upon the solubility of the salts of arsonic acids is rather noticeable even when the difference between the constants of dissociation is small.

There is, naturally, a considerable interest in the effect exerted by one and the same replacing radical according to whether it occupies one or the other position in the molecule of phenylarsonic acid. In order to clarify this question we selected -NO_2 as the replacing radical.

In addition to obtaining in the first series of experimental data on the effect of this radical in its para position, we now studied its effect in the ortho and meta positions. For this purpose we synthesized the o- and the m-nitrophenylarsonic acid.

The constants of dissociation for these acids were determined by us on the basis of electrical conductivity, as for the previous derivatives. The following values of K were obtained:

K_{18} of o-nitrophenylarsonic acid	3.0×10^{-4}
K_{18} of m-nitrophenylarsonic acid	7.9×10^{-4} .

A comparison of the constants of dissociation for all the three isomers of nitrophenylarsonic acid shows the following relations:

K_{18} of o-nitrophenylarsonic acid	3.0×10^{-4} ,
K_{18} of m-nitrophenylarsonic acid	7.9×10^{-4} ,
K_{18} of p-nitrophenylarsonic acid	1.0×10^{-3} .

The data from our verification of the solubility of the salts of ortho- and meta-nitrophenylarsonic acids are given below. The experiments were conducted under the same conditions as those used for the precipitation of the previously described derivatives of phenylarsonic acid.

The results of precipitation by means of ortho-nitrophenylarsonic acid showed that only 5 (sic) out of the 22 cations tested undergo a practically complete sedimentation, the sixth cation (Sb) being precipitated to a small extent: Be, Mg, Al, Ca, (Mn), (Fe), (Co), Ni, Cu, Zn, Sr, (Nb), Ag, Cd, (Sn), (Sb), Ba, (Ta), Hg, Tl, (Pb), (Bi).

The results of precipitation by means of meta-nitrophenylarsonic acid showed that only 8 out of the 22 cations tested yield insoluble compounds, namely, the same number as in the case of precipitation by means of p-nitrophenylarsonic acid: Be, Mg, Al, Ca, Mn, (Fe), Co, Ni, Cu, Zn, Sr, (Nb), Ag, Cd, (Sn), (Sb), Ba, (Ta), (Hg'), Tl, (Pb), (Bi).

The small difference between the constants of dissociation for meta- and para-nitrophenylarsonic acids does not noticeably affect the number of the insoluble compounds formed by them.

The greatest effect by way of displacing the electrons away from the arsenic radical is produced by the NO_2 radical in the ortho position. Therefore it could be expected that the NO_2 radical produces in the ortho position also the greatest effect by way of increasing the constants of dissociation. However, the experiment showed that among all the three isomers the ortho-nitrophenylarsonic acid has the lowest constant of dissociation. Evidently,

this is to be explained by the formation of an inner hydrogen bond between the nitric radical and the arsenic radical. The process of precipitation by means of ortho-phenylarsonic acid, on the contrary, is affected by the maximum displacement of the electrons away from the arsenic radical; namely, this acid yields the smallest number of insoluble compounds, which fully corresponds to the relationship found by us.

The results of precipitation by means of all the three isomers of nitrophenylarsonic acid and the constants of dissociation for these acids are given in table 2.

Table 2.

Name of the acid	Constant of dissociation at 18° C.	Number of cations, forming insoluble compounds
o-Nitrophenylarsonic acid	3.0×10^{-4}	5
m-Nitrophenylarsonic acid	7.9×10^{-4}	8
p-Nitrophenylarsonic acid	1.0×10^{-3}	8

Our findings show that the influence of replacing radicals on the solubility of salts of arsonic acids is manifested in such a way that an increase of electronic density in the acid residue considerably decreases the solubility of the respective salts, whereas a diminution of electronic density augments the solubility of these salts.

Moreover, it is evident that the effect of this factor is so great that it overshadows some other factors having a definite part in the process of dissolving. Thus, for example, the radicals NH_2 and OH belong in the atomic groups which can form stable solvates, and their introduction into the

molecule of phenylarsonic acid not only does not increase the solubility of the respective salts but considerably diminishes it.

It is also known that the greater the dipole moment of the molecule of the substance dissolved, the greater its solubility when no other factors are operative. If we compare in this respect the influence of two such replacing radicals as NH_2 and CH_3 , we again reach the conclusion that the principal role in the process of dissolving is played by electronic density in the acid residue. Namely, NH_2/μ (an aromatic derivative) = +1.55 decreases the solubility of salts of arsonic acids to a considerably greater extent than CH_3/μ (an aromatic derivative) = +0.45.

Data concerning the influence of replacing radicals on the properties of arsonic acids, such as the described dependence of the solubility of the salts of arsonic acids on the polarizing effects of replacing radicals, open up possibilities of a broad utilization of these acids in chemical analysis. We have found it convenient to unify all the determinations that can be made by means of arsonic acids under the one designation of "arsonate method."

The arsonate method includes all the determinations in which the ion ascertained is precipitated by means of some arsonic acid independently of the other procedures which follow precipitation. In some cases the salt of the respective arsonic acid is quantitatively determined by the bromometric method, and in others by the iodometric method. The latter method of completing determinations is the least advantageous, because it requires a destruction of organic substances which involves very painstaking and lengthy work.

The study of the effects of replacing radicals on the analytical properties of arsonic acids is continuing.

5. Conclusions

1. The constants of dissociation have been determined for the phenylarsonic, arsanilic, acetarsanilic, p-oxyphenylarsonic, p-methylphenylarsonic, o-nitrophenylarsonic, m-nitrophenylarsonic, and p-nitrophenylarsonic acids.

2. A study was made of the effects of the replacing radicals on the constants of dissociation of arsonic acids.

3. The conditions of the precipitation of a number of cations by means of arsonic acids were investigated.

4. The dependence of the solubility of salts of arsonic acids upon the polarizing effects of replacing radicals was brought to light.

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