

New Procedure for Synthesis of p-Hydroxyl Phenyl Arsonicacid.

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An examination of the publication and the patent literature dealing with the preparation of p-hydroxyl phenyl arsonic acid discloses that the method to synthesize the compound is divided into two: Bart's and Bechamp's method.

In Bart's method p-aminophenol is converted into p-hydroxyl phenyl arsonic acid by way of its diazonium salt affording good results, but the p-aminophenol is not so readily available. Bechamp's method¹⁾ consists in direct transformation of phenol into p-hydroxyl phenyl arsonic acid by arsonation, usually gives poor yields, although its procedure is comparatively simple.

In the present study, it is our main concern to devise an improved (or possibly new) method for the synthesis of p-hydroxyl phenyl arsonicacid.

Experiments have been done to find possible catalysts to improve the Bechamp's procedure. Many metals and inorganic compounds were added to the reaction mixture in the Bechamp's method to examine their effects upon the reaction rate and yield of the p-hydroxyl phenyl arsonic acid formed.

Interesting behavior of sulfuric acid was observed in the course of the experiments. That is, for a while after sulfuric acid was added, the presence of phenol sulfonic acid formed by the interaction of phenol and sulfuric acid could be detected. However as the reaction proceeded, it became difficult to detect

it and at last in the course of two hours no magnesium salt of the compound precipitated when magnesium sulfonate was added.

The results show that sulfon radical of p-hydroxyl phenyl sulfonic acid formed in the first stage of the reaction was exchanged by another radical (presumably arsonic radical) in the following stage. The following experiments were done in order to demonstrate the above assumption.

Arsonic acid was heated with p-hydroxyl phenyl sulfonic acid in place of phenol and the quantity of sulfuric and arsonic acid in the reaction mixture was determined quantitatively at the definite intervals of time.

As the reaction proceeded, the quantity of free sulfuric acid which was presented in the reaction mixture at the outset, increased in proportion to the decrease of arsonic acid added,

After a couple of hours, all the sulfon radical was converted into free sulfuric acid, while instead the equivalent amount of arsonic acid was fixed in the form of p-hydroxyl phenyl arsonic acid.

Reaction may be used to prepare p-hydroxyl phenyl arsonic acid, if the yield of the compound could be improved.

In order to examine the optimum condition to obtain satisfactory results, effects of temperature, time, quantity of arsonic and sulfuric acid and concentra-

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tion of these reagents to be added, upon the yield of p-hydroxyl phenyl arsonic acid were examined by determining quantitatively the quantity of sulfuric acid separated during the reaction.

It is quite a troublesome task to prepare p-hydroxyl phenyl sulfonic acid in large quantity and in pure state, and therefore in every experiment the reaction mixture prepared by heating phenol with sulfuric acid was employed in place of p-hydroxyl phenyl sulfonic acid as such. Thus 300g. of phenol was mixed

with 300g. of 96% H_2SO_4 and the mixture was heated at 90° to $100^\circ C.$ for 24 hrs.. Because an excess of sulfuric acid was used, 0.27g. of H_2SO_4 was to remain unconsumed in 10g. of the reaction mixture mentioned above.

A: Effect of temperature.

The temperature varied in the range of 120° - $140^\circ C.$ The reaction occurred quickly at higher temperatures, to afford satisfactory yields.

The results obtained are shown on the following table, and Fig. I.

Fig I

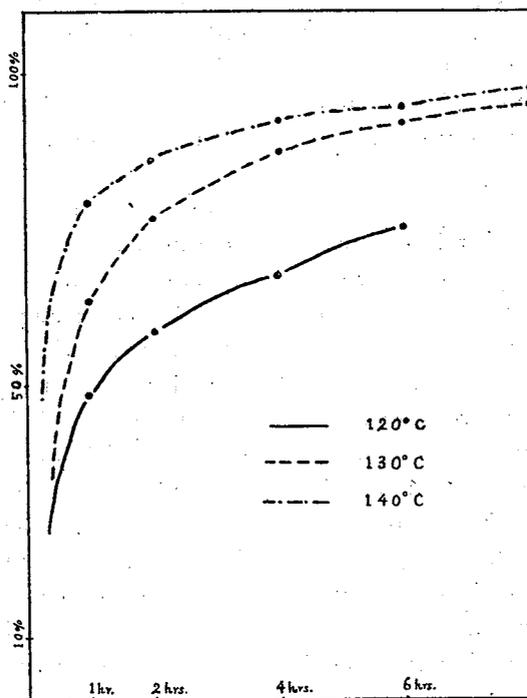


Table I. Quantity of Barium sulfonate precipitated.

Temp. \ Time.	1 hr.	2	4	6	8
120°	5.95g.	7.0	7.9	8.25	—
130	7.5	8.95	10.1	10.6	10.9
140	9.2	9.9	10.6	10.8	11.0

Table II. Quantity of sulfuric acid in terms of per cent.

Temp. \ Time.	1 hr.	2	4	6	8
120°	49.3%	59.0	67.4	70.7	—
130	63.7	77.2	87.8	92.5	95.2
140	79.8	86.0	92.5	94.2	96.2

B: Effect of the quantity of H_3AsO_4
When hydroarsonic acid and phenol were employed in molar ratio of 1 to 2, the best results were obtained, while in less quantity of hydroarsonic acid the

reaction proceeded more slowly, and more quantity of the reagent gave rise to no effect. The results are shown in the following table and Fig. II.

Table III. Quantity of Barium sulfonate precipitated.

H_3AsO_4 \ Time.	1 hr.	2	4	6	8
8.5g.	5.6g.	—	8.2	8.6	—
10	5.8	8.3	9.5	10.1	10.3
11.5	7.0	8.3	9.5	10.1	10.4
12.5	6.9	8.4	9.7	10.05	10.3

Table IV. Quantity of sulfuric acid separated in terms of per cent.

H_3AsO_4 \ Time.	1 hr.	2	4	6	8
8.5g.	46%	—	70.2	73.9	—
10	55.7	70.0	81.0	86.7	88.5
11.5	57.5	70.0	81.0	86.7	88.7
12.5	56.6	70.8	83.0	86.2	88.7

C: Effect of Quantity of sulfuric acid.

When at the starting point of reaction there was added 2.5g. and 5g. of sulfuric acid, the reaction was found to

proceed slowly. Therefore sulfuric acid separated in the reaction, also gave the similar unfavorable results. The results are shown in the following table, and Fig. II.

Table V. Quantity of Barium sulfonate precipitated.

H_2SO_4 \ Time.	1 hr.	2	4	6	8
Contrast	6.8	8.3	9.5	10.1	10.3
2.5g.	5.2	6.4	7.3	7.5	—
5	3.9	4.6	5.4	7.5	—

Table VI. Quantity of sulfuric acid separated in terms of per cent.

H ₂ SO ₄ \ Time.	1 hr.	2	4	6	8
Contrast	55.7	70.0	81.0	86.7	88.5
2.5g.	40.6	51.8	60.4	62.2	—
5	28.3	35.0	42.4	43.4	—

D: Effect of the quantity of water, or concentration of hydroarsonic acid.

When water was added or diluted

hydroarsonic acid was employed, poor results were obtained. The results are shown in the following table, and Fig. II

Table VII. Quantity of Barium sulfonate precipitated.

Conc. \ Time.	1 hr.	2	4	6	8
95%	6.8	8.3	9.5	10.1	10.3
80	6.0	7.3	8.5	8.9	9.1

Fig II

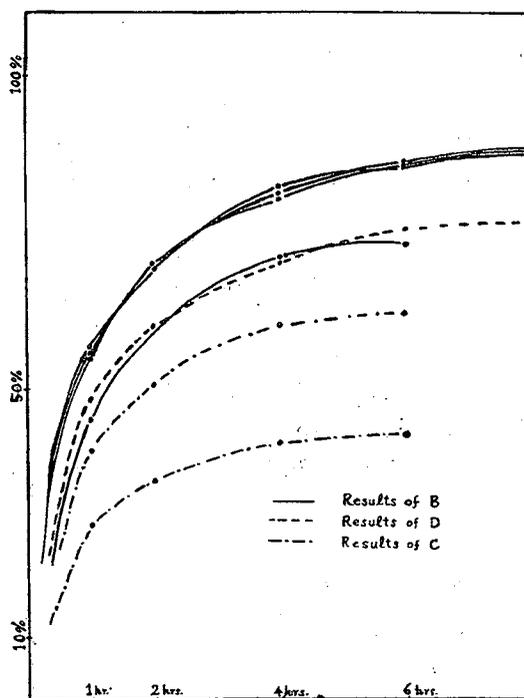


Table VIII. Quantity of sulfuric acid separated in terms of per cent.

Conc. \ Time.	1 hr.	2	4	6	8
95%	55.7	70.0	81.0	86.5	88.5
80	48.1	60.4	71.7	75.5	77.5

Reaction solution was kept at room temperature for a week, but no sulfuric acid was separated.

Results C. showed that sulfuric acid separated during the reaction, influenced the reaction give to a poor results. Therefore, a satisfactory result may be expected if sulfuric acid is removed as it separates.

Thus the following experiment was done to confirm the expectation.

E: Barium phenolsulfonate was used as starting material and half of the sulfuric acid which separated was precipitated with Barium sulfonate.

The mixture of 12.8g, of barium phenolsulfonate and 16g. of 95% hydroarsonic acid was heated at 135°C.. Then the mixture solidified after ten minutes. 80% Hydroarsonic acid was added to dissolve the salt, and a similar result was obtained. Unreacted barium salt was determined in the form of bariumsulfonate by addition of sulfuric acid. The reaction proceeded very slowly, because barium phenolsulfonate might be sparingly soluble in the reaction mixture.

This results are shown in the following table, and Fig. III.

Fig III

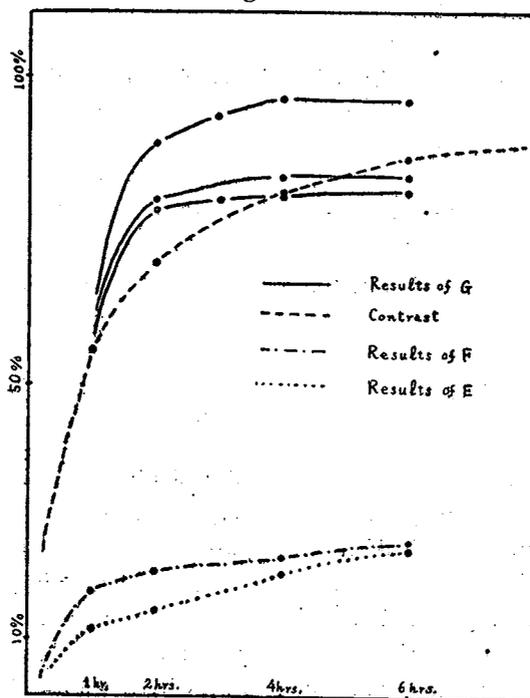


Table IX. Quantity of Barium sulfonate precipitated.

Conc. \ Time.	1 hr.	2	4	6	8
Contrast	6.8	8.8	9.5	10.1	10.3
95%	4.9	4.5	3.6	3.1	—
80	6.1	6.1	6.0	6.0	—

Table X. Quantity of sulfuric acid separated in terms of per cent.

Conc. \ Time.	1 hr.	2	4	6	8
Contrast	55.7	70.2	81.0	86.7	88.5
95%	11.0	14.2	20.9	24.6	—
80%	0.01	0.01	0.01	0.01	—

F: Barium arsonate was used to remove half of the separated sulfuric acid as barium sulfonate.

6.1g. Of barium arsonate was added to the reaction mixture and was heated at 135°C.. Barium arsonate that remained unreacted was determined quantitatively

by sulfuric acid. The reaction took place very slowly and this shows that bariumphenolsulfonate was formed from phenolsulfonic acid and barium arsonate. These results are shown in the following table, and Fig. III.

Table XI. Quantity of bariumsulfonate precipitated.

Time.	1 hr.	2	4	6	8
	4.0g.	3.6	3.3	3.0	—

Table XII. Quantity of sulfuric acid separated in terms of per cent.

Time.	1 hr.	2	4	6	8
	16.8	20.0	22.4	24.9	—

Results of experiments were comparatively poor. The result may be due to the fact that barium phenolsulfonate was barely soluble in the reaction mixture. Then after 1 hr. 9.3g. of barium arsonate were added to the reaction mixture respectively in order that barium

phenolsulfonate might not formed. The reaction took place very quickly in this case.

The remaining part of sulfuric acid was determined by the magnesium chloride. The results are shown in the following table and Fig. III.

Table XIII. Quantity of Barium sulfonate precipitated.

H_7AsO_4	$Ba_3(AsO_4)_2$	+ 1 hr.	+ 2	+ 3	+ 5
Contrast		8.3	—	9.5	10.1
10g.	9.3g.	0.5	—	0.9	1.0
10	6.1	4.8	5.5	5.8	5.7
8.5	6.1	3.5	3.6	3.8	4.0

Table XIV. Quantity of sulfuric acid separated in terms of per cent.

H_2SO_4	$Ba_3(AsO_4)_2$	+ 1 hr.	+ 2	+ 3	+ 5
Contrast		70.0	—	81.0	86.7
10g.	9.3g.	80.3	—	83.6	84.3
10	6.1	88.6	94.4	96.7	96.0
8.5	6.1	78.8	78.8	80.0	82.1

Though, apparent in results were very excellent, for some unknown reason no p-hydroxylphenyl arsonic acid was obtained, but instead insoluble anorganic material was obtained in abundant quantity. This may show that p-hydroxyl phenylarsonic acid might have been decomposed by the catalytic action of barium ion.

From results obtained in the present

work it may be concluded that in synthesis of p-hydroxyl phenylarsonic acid, when phenolsulfonic acid and hydroarsonic acid are heated at 130°-135°C. for 4-6 hrs., the best result is obtained. But at higher temperature and in longer time p-hydroxyl phenyl arsonic acid may be decomposed, and therefore the yield is poor in this case.

Experimental

(1) 26.4g. of pure p-hydroxylphenyl-sulfonic acid was mixed with 30g. of 95% hydroarsonic acid, heated at 130°C. for 4 hrs., poured into 200cc. of water and filtrated. In this filtrate, sulfuric acid separated and hydroarsonic acid consumed to replace may be determined quantitatively by barium chloride. 35g. of barium chloride was consumed to precipitate barium sulfonate. (Theoretical amount is 37g., and this shows that 94.5% of sulfon radical was separated.) Barium sulfonate weighed 33g., and it is

equivalent to 35g. of barium chloride.

Next, after barium sulfonate was removed, the filtrate was alkalized by ammoniac. 15.5g. of barium chloride was consumed to precipitate barium arsenate. (Theoretical amount is 16g.)

(2) 50g. of phenol was mixed with 50g. of 95% sulfuric acid and warmed on the water bath for 24 hrs. And in this reaction mixture was added 100g. of 95% hydroarsonic acid, and heated at 135°C. for 6 hrs..

The stirrer was run to insure through

mixing. After the content of the flask was partially cooled, they are poured into 660cc. of water and mechanically stirred. Finely ground barium hydroxide was added gradually to the well-stirred water solution until the material was slightly alkaline to litmus. After removal of the barium arsonate by filtration, the mother liquor and washings are treated with sulfuric acid until the solution contains neither barium nor sulfate ions. When the barium sulfonate has been separated and thoroughly washed, neutralized to litmus with sodium hydroxide, evaporated until the solution becomes coated with crystals, and then treated with 2.5 volumes of

alcohol. After the mixture had cooled in ice-box, the sodium p-hydroxyphenylarsonic acid was separated, washed with alcohol, and dried in an oven at 80°C.

Yield is 70g. (65% of the theoretical amount.)

$C_6H_5O_4AsNa$	Calculated As: 30.93
	Found As: 31.25

(3) 3.0g. of sodium p-hydroxyphenylarsonate was dissolved in 18cc. of water, added 5.2g. of potassium iodide and 100cc. of diluted sulfuric acid (1:5), heated to boiling, cooled and precipitated p-iodophenol. Yield of raw substance is 2.2g. (80% of the theoretical amount) m. p. 92°C. (Recrystallisation from water)

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