

CCA - 111

544.12:546.19

Reactions of Cations of the II Analytical Group with Iodide-ion and Ether in Presence of Hydrochloric Acid. III. Reaction of Arsenic

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Received June 28, 1957

Besides antimony and bismuth, arsenic (III) ion also gives with iodide ion and ether in presence of hydrochloric acid a liquid reaction product, yet a greater concentration of iodide and of hydrochloric acid is needed than for the reaction of antimony and of bismuth respectively.

The product is likely to be an etherate of a hydrate of the arsenious hydroiodic acid. If a drop of the product is cautiously introduced into water, hydrolysis occurs at the interface of the two liquid phases (water-reaction product), and the surface of the droplet becomes covered by a white firm film of arsenic trioxide.

The reaction can serve as an identification test for arsenic, being specific and unusual in type.

The reactions of antimony and of bismuth with potassium iodide and ether in presence of hydrochloric acid^{1,2} represent a special type of reactions not reported as yet.

The reaction product is liquid and forms a third phase in the primary two-phase system ether-water. Among the cations of the II analytical group arsenic (III) ion also gives a reaction of that type, but under other conditions than antimony and bismuth.

For the preparation of the liquid product of antimony and of bismuth, respectively, small quantities of potassium iodide and of hydrochloric acid suffice. The reaction of bismuth is inhibited by the excess of the reagents, while the reaction of antimony is not influenced. Under conditions that favour the formation of the liquid reaction product of antimony as well as that of bismuth, the three-phase system could not be obtained in the solution of arsenic; moreover, a white precipitate of arsenic trioxide was formed. For a positive reaction with arsenic, greater concentrations of potassium iodide and of hydrochloric acid are needed.

In order to find out the optimum reaction conditions, the concentration and volume of the solution of arsenic and of the reagents were varied.

The investigation of the composition of the liquid product of arsenic indicates that the compound is an etherate of a hydrate of the arsenious hydroiodic acid as are the products of antimony and of bismuth, respectively.³

If a drop of the product is introduced into water, a white firm film of arsenic trioxide forms at the interface of the two liquids.

EXPERIMENTAL

Various solutions of arsenic trioxide in hydrochloric acid were used.

Reagents: Freshly prepared at room temperature saturated solution of potassium iodide in water, 25% hydrochloric acid and diethyl ether.

The conditions of the reaction were examined on varying the volume of the solutions of arsenic as well as of the added solution of potassium iodide and of ether.

Degradation of the reaction product in air and in water. Few drops of the product were transferred to a watch-glass. Soon a firm opaque residue — orange in colour (AsI_3) — and a small quantity of a liquid, acid to litmus ($\text{HI} - \text{H}_2\text{O}$), remained.

A drop of the product was cautiously introduced by means of a pipette to the bottom of a Petri-dish filled with water. The surface of the droplet becomes covered by a white firm zone of arsenic trioxide.

A too low concentration of hydrochloric acid and a too small quantity of potassium iodide caused a negative reaction, and hydrolysis to arsenic trioxide occurred, that appeared in form of a white turbidity or a precipitate. By increasing the concentrations of hydrochloric acid and of potassium iodide a more intense precipitation of arsenic triiodide was obtained and its hydrolysis was inhibited.

To obtain a three-phase reaction a corresponding quantity of ether is needed. When the added quantity of ether was not sufficient, only two layers were obtained i. e. liquid product — water-layer or water-layer — liquid product. On addition of larger quantities of ether, the liquid product collected at the ether-water interface and gradually formed drops, that one by one, even thirty and more (if the solution is concentrated), fell to the bottom of the test tube or remained in the water-layer (if the concentration of potassium iodide was high). On adding more and more of ether, less and less of the product was obtained and finally a limit above which the liquid product does not separate as a third phase was reached.

The course of the reaction could be followed on further addition of 25% hydrochloric acid. In that way a direct contact of the hydrochloric acid with the ether-layer as well as with the adjoining liquid was established and the formation of a brown cloudiness in the ether layer and precipitation of arsenic triiodide (orange in colour) at the ether-water interface resulted. Meanwhile between the ether-water phases a third phase of the system i. e. the liquid reaction product of arsenic (dark red) appeared.

While performing the experiments with solutions of arsenic in 10% hydrochloric acid, almost always the reaction was negative. If the concentration of hydrochloric acid was too high and the quantity of ether too low, only one phase resulted.

The colour of the liquid product of arsenic almost equals that of the liquid products of antimony and of bismuth. The three liquid compounds differ in their degradation and hydrolysis products.

The investigated reaction with the subsequent hydrolysis of the obtained liquid product is specific for arsenic (III) ion. For that reason the above described interaction between arsenic (III) ion, iodide ion and ether in presence of hydrochloric acid can serve as an identification test for arsenic. For that purpose the following procedure is suggested: A 1–3% solution in arsenic (III) ion in 25% hydrochloric acid (1–2 ml.) is agitated with a saturated solution

of potassium iodide in water (0.5—1 ml.) and ether (1—2 ml.). One drop of the obtained liquid product is cautiously transferred by means of a pipette to the bottom of a Petri-dish full of water.

REFERENCES

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IZVOD

Reakcije kationa II. analitičke skupine s jodid-ionom i eterom u nazočnosti klorovodične kiseline. III. Reakcija arsena

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Arsen(III)-ion daje tekući reakcijski produkt s kalijevim jodidom i eterom u nazočnosti klorovodične kiseline. Za pozitivan ishod reakcije u otopini arsena potrebna je veća koncentracija kalijeva jodida odnosno klorovodične kiseline nego kod antimona¹ i biznuta². Produkt je vjerojatno eterat hidrata arseno-jodovodične kiseline. Stavi li se kap produkta u vodu, dolazi na graničnoj zoni do hidrolize, pa se površina kapi prevuče bijelim krutim slojem arsenova trioksida. Reakcija se može iskoristiti za dokazivanje arsen(III)-iona. Postupak: 1—2 ml 1—3% otopine s obzirom na arsen(III)-ion u 25% klorovodičnoj kiselini promućka se s 0.5—1 ml zasićene vodene otopine kalijeva jodida i 1—2 ml etera. Pritom se dobiva trofazni sistem: eter-crveno bojen tekući produkt-vodeni sloj. Kapljica produkta stavi se zatim u vodu: na dodirnoj zoni izluči se bijeli čvrsti sloj (As_2O_3).

ZAVOD ZA FARMACEUTSKU KEMIJU
FARMACEUTSKI FAKULTET
ZAGREB

Primljeno 28. lipnja 1957.