[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

A BASIC ARSENATE OF CALCIUM

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Considerable attention has been given in recent years to the preparation and properties of calcium arsenate because of its commercial use as an insecticide for certain crops. Coad[1] claims that this product is the best material yet found in combating the cotton boll weevil. In this country, 1360 metric tons (3 million pounds) were manufactured in 1919, 4540 metric tons (10 million pounds) in 1920,[2] and 7270 metric tons (16 million pounds) in 1922.[3] The increase in the demand for calcium arsenate for boll weevil control has even raised the question as to whether the supply of commercial white arsenic which is now available in this country is sufficient to meet that demand. In fact, the supply, quality and cost of calcium arsenate for agricultural use has suddenly become a question of national importance.

Practically all of the literature dealing with the preparation and properties of commercial calcium arsenate either states or implies that the material consists of tricalcium arsenate together with varying amounts of other calcium compounds such as calcium hydroxide and calcium carbonate. The present method of manufacture is to add arsenic acid to a heated suspension of calcium hydroxide, using the latter substance in considerable excess over the amount theoretically required for the formation of tricalcium arsenate. These conditions are such that if a basic calcium arsenate is capable of existence it might be formed in more or less quantity.

For some time one of the writers has believed that tricalcium arsenate may slowly hydrolyze to form a more insoluble basic arsenate quite analogous to the basic arsenate of lead first prepared by Tartar and Robinson,[4] and later studied by McDonnell and Smith,[5] and by Smith.[6] Experimental results in this Laboratory have confirmed this belief, and it is the purpose of this paper to give the preparation, composition and some of the properties of the basic compound obtained, together with such comments as may be advisable concerning the commercial applications.

Experimental Part

Tricalcium arsenate was prepared in a manner similar to that used by Robinson[7] by adding a solution of disodium hydrogen arsenate in slight

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[1] Coad, *U. S. Dept. Agr. Bull.*, 875, **1920**.

[2] Ambruster, *Chem. Met. Eng.*, **26,** 1155 (1922).

[3] *Ind. Eng. Chem.*, **15,** 208 (1923).

[4] Tartar and Robinson, THIS JOURNAL, **36,** 1843 (1914).

[5] McDonnell and Smith, *ibid.*, **38,** 2027 (1916).

[6] Smith, *ibid.*, **38,** 2014 (1916).

[7] Robinson, *J. Agr. Research,* **13,** 281 (1918).

excess to a solution of calcium chloride. The resulting mixture was then made distinctly alkaline with sodium hydroxide. After some hours the amorphous, flocculent precipitate was washed, first by decantation and then by suction on a Büchner funnel. The analysis of the dried precipitate showed it to be tricalcium arsenate.

Calcium ammonium arsenate was prepared in an analogous manner using ammonium hydroxide instead of sodium hydroxide. On standing, the crystalline calcium ammonium arsenate separates rather quickly from concentrated salt solutions, and more slowly from dilute ones.

Both the tricalcium arsenate and the calcium ammonium arsenate were hydrolyzed by the following procedure.

Approximately 8 g. of the washed material (undried) was placed in a Pyrex flask of 2 liters' capacity, with about 1.75 liters of freshly distilled water. The flask was then connected to a reflux condenser and the contents heated to gentle boiling. The boiling was continued for days, the water being siphoned off from the solid material each morning and replaced with fresh distilled water. Qualitative tests on the liquid removed showed from day to day a steadily decreasing content of arsenate ion until about the twelfth day when it apparently became constant. The solid material was white, amorphous and almost gelatinous. After being filtered off by suction, it was dried to constant weight at 100° and analyzed.

The calcium was determined by precipitating it as calcium oxalate from acetic acid solution, dissolving the precipitate in dil. sulfuric acid and titrating the solution in the usual manner with standard potassium permanganate solution. The concentration of the acetic acid solution was kept as low as possible in the precipitation of the calcium oxalate to eliminate any appreciable error due to the solubility of this substance in the acid.

The arsenic was determined in the manner outlined for the analysis of lead arsenate by the Association of Official Agricultural Chemists.

The analyses of the materials obtained from the different hydrolyses are given in Table I. Sample 2 was divided into two portions, one portion being subjected to the action of boiling water for three weeks longer than the other portion, to ascertain whether there would be any further change in composition. Samples 3 and 4 were obtained from the hydrolysis of calcium ammonium arsenate.

A portion each of Sample 1 and Sample 4 as obtained from the hydrolysis was placed in a paraffin bottle with a 100cc. portion of a solution made by diluting 75 cc. of a saturated solution of calcium hydroxide with 25 cc. of carbon dioxide-free distilled water. The bottles were sealed and allowed to stand at room temperature with occasional shaking for two months to permit any change in the solid phase when in contact with an alkaline solution. The solid material was then filtered from the solution, washed thoroughly, first by decantation and finally by suction, dried and analyzed. The data from these analyses are also included in Table I.

The solubility of the basic compound obtained by hydrolysis was determined. Some of the material was placed in a thermostat at 25° with freshly distilled water in 2-liter Pyrex flasks and then stirred by means of a stream of air which had been passed successively through a cotton plug, dil. sulfuric acid, dil. sodium hydroxide solution and distilled water to remove dust, ammonia, carbon dioxide and other impurities. Aliquot portions of 500 cc. were taken at different intervals and evaporated to dryness in platinum evaporating dishes, dried at 105°, and weighed. After 9 days' stirring, Flask 1 contained 0.0043 g. of basic calcium arsenate in 100 g. of water and Flask 2, 0.0045 g.; after 14 days' stirring, Flask 1 contained 0.0049 g. and Flask 2, 0.0046 g.; and after 18 days' stirring, Flask 1 contained 0.0049 g. and Flask 2, 0.0048 g.

Table I

Analysis of the Products Secured from the Hydrolysis of Tricalcium Arsenate and of Calcium Ammonium Arsenate

Sample number	Calcium as CaO %	Arsenic as As_2O_5 %	Ratio As_2O_5/CaO
1	42.85	53.85	1.25
2	43.38	54.2	1.25
2 (after 3 weeks' further boiling with water)	42.3	53.2	1.25
3	43.08	54.2	1.26
4	42.1	52.1	1.24
1 (after 2 months' contact with calcium hydroxide solution)	43.05	53.41	1.24
2 (after 2 months' contact with calcium hydroxide solution)	43.40	53.81	1.24
Calcd. for $Ca_3(AsO_4)_2$	42.25	57.75	1.37
Calcd. for $3Ca_3(AsO_4)_2.Ca(OH)_2$	43.9	54.16	1.23

Discussion of Results

The data of Table I show that a product is obtained from the hydrolysis in which the ratio of calcium to arsenic is quite constant and corresponds within experimental error to a basic compound represented by the formula, $3Ca_3(AsO_4)_2.Ca(OH)_2$. Evidently, the hydrolytic reaction may be represented by the equation, $10Ca_3(AsO_4)_2 + 6H_2O \longrightarrow 3\ [3Ca_3(AsO_4)_2.Ca(OH)_2] + 2H_3AsO_4$.

The product obtained from the hydrolysis does not change in composition upon standing in contact with calcium hydroxide solution. This result affords further evidence that the material is a definite compound and not a mixture of two solid phases of a three-component system giving a constant solubility at a quadruple point. In this connection it may be well to add that tricalcium arsenate has been found to undergo very slow chemical change when in contact with dilute, carbonate-free solutions of sodium and ammonium hydroxides. The basic material from the hydrolysis, however, did not show any appreciable change under these conditions.

This basic calcium arsenate belongs to the group of basic salts of which the mineral apatite is the most common naturally occurring representative. Further, it is quite analogous to the "hydroxyapatite," $3Ca_3(PO_4)_2.Ca(OH)_2$, reported by Bassett.[8]

While the analyses show the *ratio* of calcium to arsenic to be that corresponding to the compound, $3Ca_3(AsO_4)_2.Ca(OH)_2$, the actual content of these constituents is less than that calculated on the basis of the formula. The authors have made very sure that no impurities other than water were present. Drying at 180° did not result in any further loss of water and some preliminary drying tests at even higher temperatures did not show any appreciable loss in weight. Apparently the compound is not a hydrate of definite composition but because of its colloidal nature retains moisture very tenaciously. Bassett[8] used different means and temperatures for drying "hydroxyapatite," yet he obtained analogous results. He states: "The analytical deficit is unaccounted for and the only explanation appears to be that it is due to water held so firmly that it is not driven off by very strong ignition."

The solubility of tricalcium arsenate was determined by Robinson[7] who found that 0.0140 g. (dried at 100°) was soluble in 100 g. of water. There must have been a slight amount of hydrolysis occurring in this determination, and the material obtained upon evaporation of the solution was not wholly tricalcium arsenate. The results of the solubility determinations show that the basic arsenate is approximately one-third as soluble as the tricalcium arsenate. The writers wish to point out here that the above data on the solubility of the basic calcium arsenate were secured from experiments using a single sample of material; they have not had opportunity to make further determinations.

The results here reported indicate that the basic arsenate would be superior to the tricalcium arsenate for use as an insecticide. The former is less soluble, is not hydrolyzed and consequently is less liable to cause injury to foliage. The physical properties of the basic compound are not widely different from those of tricalcium arsenate and from this point of view should be as well adapted for use.

In the preparation of commercial calcium arsenate by adding arsenic acid to a suspension of calcium hydroxide in considerable excess, tricalcium arsenate is first formed which then probably hydrolyzes more or less completely to the basic compound. This change to the basic salt is favored by the excess of calcium hydroxide, which combines with the acid formed from the hydrolysis, and by keeping the reacting materials well stirred and hot. Further experimental work will be necessary to determine the time required to make this change complete.

While no definite quantitative data are available to show the exact

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[8] Bassett, *J. Chem. Soc.*, **111**, 620 (1917).

amount of basic calcium arsenate present in commerical samples, there are statements in the literature which indicate that it may be present in considerable quantity. Haywood and Smith[9] concluded from a study of the water soluble arsenic in samples of calcium arsenate prepared by using calcium hydroxide and arsenic acid in varying amounts, that "all commercial calcium arsenates should be at least as basic as $4CaO.As_2O_5$." These investigators also state that this material "consists of tri-calcium arsenate, probably with some water of crystallization together with an excess of calcium hydroxide and calcium carbonate." The work reported in this paper would indicate that under the method of preparation and examination used a considerable amount of the basic compound may have been present.

McDonnell, Smith and Coad[10] in their study of the chemical changes in commercial calcium arsenate during storage have obtained results indicating the presence of a basic arsenate. They determined the amount of carbon dioxide absorbed in samples stored in containers sufficiently open to permit contact with air and found the carbon dioxide to reach a limiting value in from six to nine months. In discussing their data, they make this very significant comment: "It might naturally be assumed that this corresponds to the complete carbonation of the free lime in the samples, the final mixture being essentially tricalcium arsenate and calcium carbonate. Calculating the limiting carbon dioxide values to their equivalent calcium oxide values and subtracting these from the total calcium oxide, however, leaves calcium oxide remaining in amounts from 0.2 to 4.8 per cent. in excess of the quantity necessary to form tricalcium arsenate with the total arsenic oxide of the sample. Pure tricalcium arsenate octahydrate $Ca_3(AsO_4)_2.8H_2O$, containing 42 per cent. total arsenic oxide, gave about 3 per cent. water-soluble arsenic oxide, while the completely carbonated commercial samples exceeded 1 per cent. in only one case, which seems to argue against this being the only calcium arsenate in commercial samples. Further work will be necessary before the question of the presence of basic arsenates can be definitely settled."

The writers hope that the study of this basic arsenate of calcium will lead to the production of a more uniform commercial product and the formulation of better standards for judging it.

Summary

1. A basic calcium arsenate, $3Ca_3(AsO_4)_2.Ca(OH)_2$, has been prepared by the hydrolysis of tricalcium arsenate.

2. The solubility of this basic arsenate in water at 25° has been determined and found to be 0.0048 g. in 100 g. of water.

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[9] Haywood and Smith, *U. S. Dept. Agr. Bull.*, 750, **1918.**

[10] McDonnell, Smith and Coad, *U. S. Dept. Agr. Bull.*, 1115, **1922.**

3. Comments on the possible commercial application of the results obtained have been made.

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[Contribution from the Kent Chemical Laboratory of the University of Chicago]

THE ABSENCE OF HELIUM FROM THE GASES LEFT AFTER THE PASSAGE OF ELECTRICAL DISCHARGES: I, BETWEEN FINE WIRES IN A VACUUM; II, THROUGH HYDROGEN; AND III, THROUGH MERCURY VAPOR

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Introduction

The Whole Number Rule and Nuclear Stability

The "Whole Number Rule"[1] has an important bearing upon the question of atomic stability. This rule states that the atomic weight of any pure atomic species, other than hydrogen, is very close to a whole number on the basis of oxygen as 16. Thus the packing effect in the formation of helium from hydrogen is large and amounts to 0.77%, but the further packing when complex atoms are formed from helium is so small that its effects have not been observed thus far in the atomic weights. According to the special relativity theory of Einstein, a loss of mass of 0.77% indicates an energy output of 6.7×10^{11} calories per mole of helium formed, as was pointed out[2] in 1915. This indicates the great probability that the helium nucleus is exceedingly stable; so stable that it seems entirely improbable that it can be disintegrated into hydrogen by the use of any source of energy now known. While it is easy to obtain sufficient energy to effect such a disintegration, the difficulty comes in obtaining the energy in a sufficiently concentrated form to enable its application to such a minute particle. However, it is possible that later discoveries may reveal alpha particles of a speed so high that the kinetic energy per particle will be as high as the energy of formation of the particle from hydrogen.

The smallness of the packing effect between helium and the heavier atoms gives some evidence in favor of the idea that the alpha particles in a complex nucleus preserve their individuality to a considerable extent.[3]

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[1] Harkins and Wilson, This Journal, **37,** 1367 (1915).

[2] Harkins and Wilson, *Phil. Mag.*, **30,** 723 (1915). Tolman, This Journal, **44,** 1902 (1922).

[3] There is the possibility, however, that the alpha particles lose their individuality to a considerable extent, and that the constancy of the packing effect is due to some characteristic of the positive and negative electrons, or to a compensation due to some unknown factor.