−80°, and according to its chemical behavior the arsine must be appreciably ionized.[12]

We wish to acknowledge the aid of a grant from the National Research Council for the liquid nitrogen used in this study.

Summary

Arsine has been prepared in good yields by the action of ammonium bromide on sodium arsenides in liquid ammonia. Arsine was found to be the only arsenic containing gas liberated in the reaction. No solid arsenic hydrogen compounds are formed.

The vapor tension of solid and liquid arsine has been determined over a considerable range of temperature. From the measurements the boiling point has been found to be −62.4°; the melting point, −116.3°; the heat of vaporization, 416_5 cal./mole; the heat of sublimation, 484_0 cal./mole; and the heat of fusion, 67_5 cal./mole.

The density of liquid arsine has been determined at temperatures ranging from the melting point to the boiling point.

Liquid arsine is only slightly soluble in liquid ammonia.

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[12] In connection with this problem a rapid method of separation and determination of arsine in an arsine–ammonia gas mixture was found. Ammonia may be removed quantitatively from a mixture of the two gases without loss of arsine by liquefying the mixed gases on anhydrous calcium chloride which has been previously heated in a vacuum to 400°. The ammonia combines with the calcium chloride to form a solid ammonate but the arsine does not produce a similar combination possessing any appreciable stability at temperatures as low as −78°. If the calcium chloride and its ammonate are kept at this temperature, the arsine may be distilled into a suitable container and condensed at the temperature of liquid nitrogen. Two such treatments were found to remove the ammonia quantitatively from 200 cc. of a mixture of the gases containing 90% ammonia by volume, without loss of arsine.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrogen Compounds of Arsenic. II. Sodium and Potassium Dihydrogen Arsenides

BY WARREN C. JOHNSON AND ALPHONSE PECHUKAS

Ammonia is known to exhibit some acidic properties since it conducts electricity to an appreciable extent and reacts with strongly electropositive metals to form dihydrogen nitrides (amides). Joannis[1] has shown that phosphine reacts with the common alkali metals in liquid ammonia to produce dihydrogen phosphides (phosphamides). In the case of potassium the reaction may be expressed as

$$K + PH_3 = KPH_2 + 0.5H_2$$

Since arsenic shows a greater tendency than phosphorus to become electropositive one would expect the arsenic–hydrogen bonds of arsine to be weaker than the phosphorus–hydrogen bonds of phosphine. If the reaction between the alkali and alkaline earth metals and the hydrogen compounds of the fifth group elements is dependent upon the lability of the hydrogen atoms, arsine would be expected to react with these metals more readily than does phosphine and, in turn, ammonia. Gay-Lussac and Thenard[2] observed that hydrogen is liberated from arsine when the latter is treated with sodium or potassium and that the arsenic probably enters into combination with the metal. Lebeau[3] investigated this reaction further, both with the pure alkali or alkaline earth metals and their liquid ammonia solutions. He prepared calcium arsenide (Ca_3As_2) by the action of liquid arsine on solid calcium; in liquid ammonia solution arsine was found to react with calcium rapidly to give a yellow compound which decomposes at 150° to produce a brown arsenide of calcium. Using sodium instead of calcium, he obtained a bright yellow solution when arsine was passed into a liquid ammonia solution of the metal. Evaporation of this solution produced a red solid to which Lebeau ascribed the composition $Na_3As(NH_3)_x$.

Since arsine is appreciably soluble in liquid ammonia[4] and appears to be somewhat ionized in this medium, it appeared advisable to prepare some of the alkali metal salts and study the chemistry of these substances.

The Reaction of Arsine with Sodium and Potassium.—Gaseous arsine, of known purity,[4] was passed into a solution containing a weighed amount of sodium or potassium in liquid ammonia at −78°. The type of apparatus used has been described elsewhere.[5] The arsine was found to react very rapidly with the ammonia solution of the metal, changing the color of the latter from

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(1) Joannis, *Compt. rend.*, **119**, 557 (1894).

(2) Gay-Lussac and Thenard, *Ann. chim. phys.*, [1] **73**, 229 (1810).

(3) Lebeau, *Bull. soc. chim.*, [3] **23**, 251, 340 (1900); *Ann. chim. phys.*, [7] **25**, 470 (1902).

(4) Johnson and Pechukas, THIS JOURNAL, **59**, 2065 (1937).

(5) Kraus and Brown, *ibid.*, **52**, 4031 (1930).

the characteristic blue to green and finally to a brilliant yellow. The disappearance of the blue color was used as an indicator for the completion of the reaction. Hydrogen was liberated in the reaction and was separated from the unreacted arsine and identified by its vapor density and failure to condense at liquid nitrogen temperatures (mol. wt. found, 4.8, 4.5). The metal dihydrogen arsenide appeared to be appreciably soluble in liquid ammonia, producing a bright yellow color.

After the ammonia had been removed from the reaction mixture by evaporation, a very pale yellow, almost white, solid was left crystallized on the walls of the reaction vessel. The solid salt does not contain any ammonia of crystallization at room temperature since in every experiment the weight of the product was found to correspond to the sum of the weights of the alkali metal and arsine used. In one instance the solid was allowed to stand for sixty hours *in vacuo* at room temperature and was found to remain unchanged. No change in weight was observed and when redissolved in ammonia at −33° the solution of the salt behaved chemically as though freshly prepared. Evidently, the salt is not ammonolyzed in solution at temperatures as high as −33°. When the salt is exposed to air a vigorous reaction takes place with the liberation of considerable heat and the deposition of a brown solid, presumably arsenic and solid arsenic-hydrogen compounds. Data for the preparation of the sodium and potassium dihydrogen arsenides are given in Table I. The following equation expresses the course of the reaction

$$\mathrm{M + AsH_3 = MAsH_2 + 0.5H_2}$$

where M represents either sodium or potassium.

The Action of Ammonium Bromide on Potassium Dihydrogen Arsenide.—Additional evidence for the composition of potassium dihydrogen arsenide was obtained by treating an ammonia solution of the salt with ammonium bromide, which behaves as an acid in this medium. A condensable gas was liberated in the reaction and was found to be arsine. It was separated from ammonia by treatment with calcium chloride[4] and identified by its vapor density. The results are recorded in Table II and conform to a reaction which may be expressed by the equation

$$\mathrm{KAsH_2 + NH_4Br = KBr + NH_3 + AsH_3}$$

Column 1, Table II, refers to the weight of potassium used in the preparation of $KAsH_2$. The amount of arsine liberated in the reaction and subsequently collected was found to be about 90–95% of the theoretical amount. This difference is probably due in part to a loss involved in the collection of the arsine over water; in addition, it is difficult to recover small amounts of the gas quantitatively.

TABLE I

THE PREPARATION OF SODIUM AND POTASSIUM DIHYDROGEN ARSENIDES[6]

Metal used, g.	Arsine used, cc.	H_2 obtained, cc.	Molar ratio $M: AsH_3: H_2$
	Sodium		
0.139	144.0		1:1.00
.357	346.7		1:1.00
.216	214.0	112.8	1:1.00:0.54
	Potassium		
0.0482	24.1	11.9	1:0.87:0.43
.0873	47.3	24.2	1:0.95:0.48
.133	74.7	36.7	1:0.98:0.49
.160	93.0	47.0	1:0.99:0.50
.175	102.7	49.7	1:1.00:0.49
.188	107.8	54.5	1:0.99:0.50
.224	127.2	65.2	1:1.00:0.51
.237	138.1	68.9	1:1.02:0.51

TABLE II

ACTION OF NH_4Br ON $KAsH_2$ IN LIQUID AMMONIA

Wt. K, g.	Mol. wt. of gas	AsH_3 (found), cc.	AsH_3 (calcd.) cc.
0.174	78.6	75.8	79.3
.0742		34.9	38.8
.0482	78.4	20.7	24.1
.0873		43.1	47.3

The Action of Potassium Amide on Arsine.—An amount, 0.118 g., of metallic potassium was dissolved in liquid ammonia containing a few mg. of ferric nitrate as a catalyst for the formation of potassium amide. The solution of the latter at −78° was treated with an excess of arsine gas with the formation of a yellow solution characteristic of potassium dihydrogen arsenide. An amount, 66.9 cc., of arsine was consumed in the reaction; thus 3.05 millimoles of potassium converted to the amide required 2.95 millimoles of arsine. Evidently, the reaction is

$$\mathrm{KNH_2 + AsH_3 = KAsH_2 + NH_3}$$

The Action of Methyl Chloride on Potassium Dihydrogen Arsenide.—To further substantiate the composition of potassium dihydrogen arsenide and to obtain some information relative to its chemistry, the salt was treated with methyl chloride in liquid ammonia at −78°. As an illustrative experiment, 0.1083 g. (2.69 millimoles) of potassium was treated with 66.4 cc. (2.96 millimoles) of arsine and the excess arsine was removed by fractional distillation. The yellow solution of the salt so obtained was treated with 62.4 cc. (2.79 millimoles) of methyl chloride and a white precipitate appeared in the liquid ammonia as its yellow color faded. After the volatile products of the reaction had been removed by evaporation, the residue left in the reaction flask was analyzed for chloride ion, which was found to be present. The residue was dissolved in water, with the formation of a clear solution, and after the hydrogen ion concentration had been adjusted with dilute nitric acid, standard silver nitrate solution was added

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[6] Experiments with sodium and arsine were performed by Dr. A. E. Sidwell of this Laboratory.

TABLE III

VAPOR TENSION OF METHYLARSINE

Temp., °C.	−74.0	−71.7	−69.3	−66.8	−64.8	−62.8	−60.2	−58.0	−56.0	−54.2	−51.5
Press., mm.	18.2	21.1	24.1	28.5	33.0	37.1	43.7	49.9	55.3	63.0	71.7
Temp., °C.	−49.6	−46.5	−44.4	−42.2	−40.6	−38.4	−36.1	−33.3	−31.6	−29.2	−27.1
Press., mm.	80.0	94.7	105	119	127	143	158	182	198	220	242
Temp., °C.	−24.8	−22.5	−21.0	−19.0	−17.1	−16.1	−15.2	−13.6	−12.3	−11.0	− 9.8
Press., mm.	268	294	313	338	364	381	397	418	442	468	496
Temp., °C.	− 8.6	− 6.9	− 5.8	− 4.2	− 2.3	− 1.0	0.0	1.8	3.0		
Press., mm.	520	544	578	606	657	687	709	753	781		

until the dichlorofluorescein indicator end-point was reached. The solution so prepared required 26.36 cc. of 0.0990 *N* silver nitrate solution, corresponding to 2.61 millimoles of potassium chloride in the original solution. Evidently, a reaction occurs between potassium dihydrogen arsenide and methyl chloride leading to the formation of an almost quantitative amount of potassium chloride. The yield of methylarsine was found to range from 70 to 80% based on the equation

$$KAsH_2 + CH_3Cl = KCl + CH_3AsH_2$$

Evaporation of the liquid ammonia solution liberated large quantities of ammonia, a small amount of methylarsine and the unreacted methyl chloride. Most of the ammonia was removed by passing the mixture through water. The residual gases were dried in the vacuum system with phosphorus pentoxide and were then subjected to fractional distillation. Methylarsine was identified by its molecular weight determined by the vapor density method (found: 91.0, 93.0, 93.9, 93.1, 93.2; calcd. for CH_3AsH_2, 92.0).

Vapor Tension of Methylarsine.—The vapor tension of liquid methylarsine was determined over a range of temperature, −74 to +3°. Standardized ammonia and pentane vapor tension thermometers were used for the temperature measurements. The normal boiling point of the substance was found to be 2.0°, which value corresponds very closely to that reported by Dehn[7] (2° at 755 mm.). The heat of vaporization was calculated from the vapor tension data and found to be 539_0 cal./mole. The melting point was found to be −143° by the method of Stock.[8] The vapor tension data are given in Table III.

Methylarsine and Potassium.—A small amount of metallic potassium, 0.1372 g. (3.5 millimoles), was dissolved in liquid ammonia at −78° and methylarsine was passed into the solution until the blue color was discharged. For this process 77.4 cc. or 3.45 millimoles of methylarsine was required. Hydrogen gas, 39.4 cc. (1.75 millimoles), was liberated in the reaction. It was collected by means of a Toepler pump and its vapor density was determined (mol. wt. found, 3.8). The resulting ammonia solution appeared orange in color. Evidently methylarsine reacts with metallic potassium in liquid ammonia as follows

$$CH_3AsH_2 + K = CH_3AsHK + 0.5H_2$$

Addition of ammonium bromide regenerates methylarsine from the potassium salt.

$$CH_3AsHK + NH_4Br = KBr + CH_3AsH_2 + NH_3$$

The molecular weight of the methylarsine formed in the reaction was determined by the vapor density method (found, 92.3; calcd. for CH_3AsH_2, 92.0). The physical and chemical properties of the potassium salt of methylarsine will be described in a later communication.

Thermal Decomposition of Potassium Dihydrogen Arsenide.—Potassium dihydrogen arsenide is thermally stable at room temperature. When heated it shows no evidence of decomposition below 115°. At this temperature it begins to darken, becoming brown in color, with the liberation of a gas. This gas was forced over mercury with a Toepler pump, its volume was measured and it was identified as hydrogen by its molecular weight (found, 2.5, 2.3, 2.2). Decomposition of the solid may be completed by heating to 175°. The residue appears blue-black in color. Data for the decomposition of the arsenide are given in Table IV. Column one represents the amount of potassium used in the preparation of $KAsH_2$. The calculated volume of hydrogen given in the third column is taken as twice the volume of hydrogen liberated in the preparation of $KAsH_2$. The results show that one mole of hydrogen gas is liberated for every mole of $KAsH_2$ subjected to decomposition. The reaction may be expressed by the equation

$$KAsH_2 = KAs + H_2$$

TABLE IV

THERMAL DECOMPOSITION OF POTASSIUM DIHYDROGEN ARSENIDE

Wt. K, g.	H_2 (found), cc.	H_2 (calcd.), cc.
0.1032	55.6	56.4
.1858	101.0	103.0
.1884	104.0	109.0
.1186	64.6	66.8
.1142	61.7	63.4
.0869	47.2	49.8
.2244	121.5	130.4
.1069	61.1	63.8
.1810	97.2	105.0
.1795	95.1	102.0
.1216	65.7	68.8

The composition of the residue, which has been represented as KAs, is open to question. It might be considered as K_3As_3,[9] a mixture of K_3As and metallic arsenic or a mixture of several polyarsenides of potassium. Some information regarding this question might be obtained by treating the KAs residue with ammonium bromide and also with methyl chloride in liquid ammonia solution. Such a study is now being undertaken.

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(7) Dehn, *Am. Chem. J.*, **33**, 107 (1905).

(8) Stock, *Ber.*, **50**, 156 (1917).

(9) Zintl, Goubeau and Dullenkopf, *Z. physik. Chem.*, **154**, 1 (1931).

Summary

Arsine reacts with sodium, potassium and potassium amide in liquid ammonia to form the corresponding alkali metal dihydrogen arsenide.

Arsine is regenerated from the dihydrogen arsenide salt by ammonium bromide in liquid ammonia.

Methyl chloride reacts with potassium dihydrogen arsenide in liquid ammonia to produce methylarsine. Some of the physical properties of methylarsine have been determined.

Potassium dihydrogen arsenide decomposes at temperatures in excess of 115° to produce hydrogen and a polyarsenide of potassium.

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NOTES

Oxidation-Reduction Potentials of Hydroxynaphthoquinones in Alkaline Solutions

BY ERIC G. BALL

Studies by Hill[1] on the oxidation-reduction potential of phthiocol (2-methyl-3-hydroxy-1,4-naphthoquinone) have shown that this compound gives titration curves in strongly alkaline solutions that indicate the formation of a semiquinone. In agreement with these findings I am able to report that phthiocol in 1.0 *M* sodium hydroxide gives a titration curve which is much steeper than that predictable on the basis of the two equivalent change reported previously at lower *p*H values.[2] Titrations performed by reduction with sodium hydrosulfite or by oxidation with potassium ferricyanide of phthiocol previously reduced with hydrogen and palladium black gave identical results. At *p*H 13.50 the midpoint potential (E_0') of the symmetrical titration curve is −0.555 volt. The slope of the curve may be defined by the usual equation if *n* is assigned the unorthodox value of 1.21. Procedures and standards employed were the same as described previously.[2] Modification of the Clark type shaking apparatus for *p*H determinations so as to exclude oxygen rigorously permitted consistent values to be obtained for 1 *M* sodium hydroxide solutions.

Lapachol was found to behave in a manner similar to phthiocol. At *p*H 13.50 the value of E_0' for this compound is −0.568 volt. The slope of the curve is, however, not as steep as that for phthiocol at this same *p*H value. In this connection it is of interest to note that the first and second dissociation constants of the reductant of phthiocol are larger than those for reduced lapachol.[3] Whether or not a relationship exists between these properties is not determinable without further data. An extension into more alkaline solutions of the studies previously reported[3] on similar hydroxynaphthoquinones might be enlightening since these compounds would probably behave in a manner similar to phthiocol and lapachol, and yet their reductants possess dissociation constants sufficiently different to test this hypothesis.

It was reported by Hill[1] that the change in slope of titration curves of phthiocol began at about *p*H 9.0. In view of this fact the data previously reported[2] for the titration of phthiocol at *p*H 10.50 and there interpreted as a two equivalence change have been reanalyzed carefully. When treated by the method of Reed and Berkson[4] the data fit the theoretical two equivalence curve within ± 0.1 mv. over the range 15-85% oxidation. It is true then, however, that the extremes of the curve deviate more than is normal in this unpoised region. If the end-point is chosen arbitrarily, a better fit can be obtained between the extremes of the curve and the theoretical, but then a deviation of ± 1.0 mv. is encountered over the range 15-85% oxidation. It is thus apparent that the interpretation of the data in this *p*H range is dependent upon slight variations in the investigator's choice of the end-point and the reliability of the potentials observed in the unpoised regions of the titration. In this connection it must be emphasized that unless the potentials recorded are corrected for those changes of *p*H which are caused by the

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(1) Hill, *Proc. Soc. Exptl. Biol. Med.*, **35**, 363 (1936).

(2) Ball, *J. Biol. Chem.*, **106**, 515 (1934).

(3) Ball, *ibid.*, **114**, 649 (1936).

(4) Reed and Berkson, *J. Phys. Chem.*, **33**, 760 (1929); see also Clark and Perkins, THIS JOURNAL, **54**, 1228 (1932).