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# On Phospho-hydrocyanic Acid [Preliminary Paper]

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**Contribution from the Chemical Laboratory of Lehigh University.**

# ON PHOSPHO-HYDROCYANIC ACID.

BY W. B. SHOBER AND F. W. SPANUTIUS.

## PRELIMINARY PAPER.

One of us, several years ago, working under the direction of Dr. Launcelot Andrews, attempted to prepare the phosphorus analogue of hydrocyanic acid—an acid the composition of which would be represented by the formula HCP—by heating chloroform and zinc phosphide together in a sealed tube. The reaction was expected to take place in this way:

$$2CHCl_3 + Zn_3P_2 = 2HCP + 3ZnCl_2.$$

The results obtained were not satisfactory. Recently the work

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[1] I have been unable to trace the paper alluded to, and I therefore cannot communicate where it was published.

has been taken up again, in this laboratory Other methods have been tried and we have succeeded in preparing the sodium salt of phospho-hydrocyanic acid.

When dry ammonia is passed over heated sodium the reaction expressed by the following equation takes place:

$2Na + 2NH_3 = 2NH_2Na + H_2$.[1]

When sodium amide is treated with carbon monoxide, under the proper conditions, sodium cyanide is formed:

$$NH_2Na + CO = NaCN + H_2O.$$

We repeated these experiments, substituting phosphine for ammonia, when the following reactions took place:

$2Na + 2PH_3 = 2PH_2Na$[2] $+ H_2$; or, possibly,
$2Na + PH_3 = Na_2HP + H_2$; or
$3Na_2 + 2PH_3 = 2Na_3P + 3H_2$. And then,
$PH_2Na + CO = NaCP + H_2O$.

The method of procedure was as follows: A clean, thoroughly dry piece of hard-glass tubing about 75 cm. long and 1.5 cm. in diameter was placed in a combustion-furnace. To the front end was attached a calcium-chloride tube, then a Woulff bottle containing concentrated sulphuric acid, the inlet and outlet tubes reaching *almost* to the surface of the acid; finally, two Woulff bottles containing a saturated solution of copper sulphate. The object of these last was to decompose any phosphine which had escaped the action of the sodium. The last bottle was connected with a hood. To the rear end of the glass tube was attached a long (35 cm.) drying tube containing soda-lime; to this, another tube of the same length filled with small pieces of potassium hydroxide; to this two wash-bottles containing sulphuric acid, and finally a wash-bottle containing potassium-permanganate solution. Hydrogen was passed through the entire apparatus until all air was expelled.

While a rapid current of hydrogen was still passing through, a small quantity (1.5 grams) of sodium, free from oxide and

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[1] Beilstein and Geuther: Ann. Chem. (Liebig) **108**, 88.

[2] It is not known certainly that $NaNH_2$ is the correct formula for the compound formed by the action of sodium upon ammonia. Assuming that $NaNH_2$ is the correct expression, the composition of the phosphorus compound formed under similar conditions is probably to be expressed by $NaPH_2$, although it may be $Na_2PH$ or $Na_3P$. In any case it is probably similar in its composition to the sodium compound, which, whatever it may be, yields sodium cyanide when treated with carbon monoxide. So this compound of phosphorus, whatever its composition, yields, when treated with carbon monoxide, *sodium phosphocyanide*.

hydroxide, was transferred to the glass tube. In order to prevent the action of the air and moisture and to keep the surfaces as bright as possible, the outside coating of the metal was removed under benzene. Without removing the benzene which adhered to it, the metal was quickly placed in the tube. The benzene was expelled by the aid of heat and the rapid current of hydrogen. When the benzene was completely removed, the hydrogen generator was replaced by a phosphine generator, from which all air had previously been expelled, and the permanganate and sulphuric-acid wash-bottles removed.[1] The phosphine was obtained by treating zinc phosphide with sulphuric acid. Heat was applied to the sodium until it melted. Phosphine was then generated slowly and passed through the apparatus. The bright silvery surface of the sodium began to blacken and show evidence of some action. Small black particles floated around on the surface of the metal, until finally the whole mass became covered with a thick black crust. The phosphine was passed until all of the sodium was converted into this black substance, then, without allowing the apparatus to cool, dry carbon monoxide, free from air and carbon dioxide, was passed over this black substance for an hour. After the furnace was cool the glass tube was removed. On exposure to the air small particles of the substance ignited spontaneously. The tube was at once closed, when these small explosions ceased. It was then filled with absolute alcohol which had been standing over anhydrous copper sulphate for three months, corked up and allowed to stand for 12 hours. The alcohol became darker in color until it was a deep red. A sediment was deposited. Since the compound of sodium and phosphine is extremely unstable—decomposing upon exposure to the air—and since the difficulties in the way of establishing its composition are very great—in fact, even greater than those that are encountered when an attempt is made to determine the composition of the compound which is usually represented by the formula $NaNH_2$;—further, since sodium phosphocyanide is also extremely unstable; we have found it impossible up to the present to analyze these compounds. Nevertheless, satisfactory evidence of the composition of sodium phosphocyanide is obtained by a study of its decomposition-products.

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[1] Phosphine decomposes on passing through concentrated sulphuric acid. It deposits a reddish-yellow substance, presumably phosphorus, which on standing in contact with the acid explodes violently.

The alcohol and residue were transferred to a beaker and a small quantity of water added. Phosphine was immediately evolved in large quantites. This may have been due to the decomposition of sodium phosphocyanide, monosodium phosphine, disodium phosphine, trisodium phosphine, or to several of these compounds. The black substance above referred to probably consists of a mixture of at least two of these compounds. Since sodium cyanide is decomposed by alkalies into formic acid and ammonia, sodium phosphocyanide should be decomposed into formic acid and phosphine. The possible reactions giving rise to phosphine are these:

$$NaH_2P + H_2O = NaOH + PH_3.$$
$$Na_2HP + 2H_2O = 2NaOH + PH_3.$$
$$Na_3P + 3H_2O = 3NaOH + PH_3.$$
$$NaCP + H_2O = H.COONa + PH_3.$$

Each of these compounds would yield phosphine, but there is only one that could yield formic acid.

Water was added until phosphine ceased to be evolved. The solution was then evaporated, a fluffy black substance was formed and filtered off. Upon drying it, the quantity obtained was too small to investigate. The filtrate, which was strongly alkaline, was neutralized with phosphoric acid and subjected to distillation. A portion of the distillate was heated to 60°–70° and a solution of mercuric chloride was added. A heavy precipitate of mercurous chloride gave unmistakable evidence of the presence of formic acid. The presence of formic acid shows conclusively that the reaction referred to above had taken place, thus showing that the sodium salt of phosphohydrocyanic acid is capable of existence.

With the advent of this compound a new field is opened. If a class of phosphorus compounds analogous to the cyanides, both organic and inorganic, can be prepared, they will form a remarkable series of compounds, each one of which will be an additional link in the chain of analogy between the related elements, nitrogen and phosphorus.

This also foreshadows the existence of a compound the composition of which will probably be represented by CP or $C_2P_2$, analogous to cyanogen.

We have been obliged to discontinue this investigation for the present, but in the near future we shall take it up again.

SOUTH BETHLEHEM, PA., *February*, 1894.