THE ACTION OF HYDROGEN PHOSPHIDE ON FORMALDEHYDE. II[1]

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As a preface to the second communication on this subject, it may be of interest to state briefly why this investigation was undertaken. As the result of investigations in various branches of science, a number of authors have expressed the opinion in recent years that the original atmosphere of the earth contained little free oxygen. It has seemed not unreasonable, to the present writer, to go a step further and to consider some of the reactions that might have taken place if free oxygen were absent altogether. Under those conditions complex compounds might have been formed, which would constitute a starting-point for further organic evolution. Without going into the various cosmogonic theories, it may be said that such an atmosphere, similar to the sun's, would contain free hydrogen and carbon monoxide and dioxide, which react to give formaldehyde under certain conditions,[2] and hydrogen chloride, which would generate hydrogen phosphide from phosphides present in the original crust (meteorites usually contain phosphides). On the other hand, compounds of phosphorus with formaldehyde (which has a genetic relation to the sugars) would seem to be of interest in view of the groupings occurring in the nucleic acids, the distinctive components of the most vital part of the cell.

In the first article the primary condensation product $(CH_2OH)_4PCl$ was described and referred to as tetrahydroxymethylene-phosphonium chloride in analogy to the term tetrahydroxyethylidene-phosphine for $(CH_3CHOH)_3P(C(OH)CH_3)$ as used in Beilstein.[3] As the constitution of the compound is now fully established, it will conform better to modern nomenclature to call it tetrakis(hydroxymethyl)phosphonium chloride.

Continuing the former work, a more detailed investigation of the action of alkalies and of carbonates on the mother substance was undertaken. This action was found to take place in two steps. Using sodium hydroxide at room temperature or with gentle heating not above 80°, one molecule of hydrogen is evolved and the action stops with the formation of tris(hydroxymethyl)phosphine oxide. On boiling, a second molecule of hydrogen is given off. An alkaline carbonate, such as sodium carbonate, gives the same results, but the action is slower. A neutral carbonate, like calcium or barium carbonate, produces but one molecule of hydrogen, even on long boiling. Subsequent addition of sodium hydroxide to the boiling solution frees the second molecule of hydrogen.

The intermediate compound, tris(hydroxymethyl)phosphine oxide, may

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[1] Alfred Hoffman, THIS JOURNAL, **43,** 1684 (1921).

[2] Beilstein, 4th ed., Vol. I, p. 559.

[3] Beilstein, 3d ed., Vol. I, p. 921.

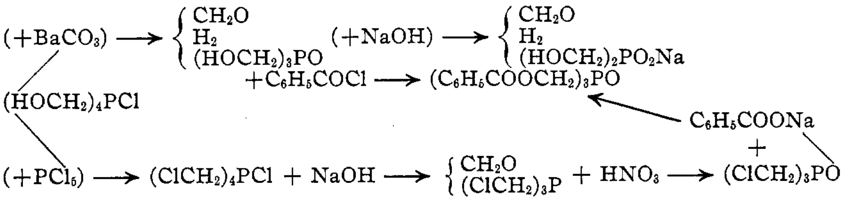
be isolated as a sirup or as its crystalline tribenzoate. Either of these compounds evolves a molecule of hydrogen on boiling with sodium hydroxide. The final product of the reaction is bis(hydroxymethyl)phosphinic acid, $(HOCH_2)_2PO_2H$, which was isolated as a crystalline barium salt.

As a test for the presence of hydroxyl groups, the action of phosphorus pentachloride on the mother substance was investigated. A well-crystallizing substance, tetrakis(chloromethyl)phosphonium chloride, $(CH_2Cl)_4PCl$, was obtained. The solution of the chloride reacts with alkalies, ammonia or even sodium bicarbonate to give the oily tris(chloromethyl)phosphine, according to the reaction

$$(ClCH_2)_4PCl + 2NaOH = (ClCH_2)_3P + CH_2O + 2NaCl + H_2O$$

The ready hydrolyzation of the tetrakis(chloromethyl)phosphonium chloride seems to indicate that the corresponding hydroxide is a feeble base. Tris(chloromethyl)phosphine also has but slight basic properties. It is soluble in strong mineral acids, but the solution hydrolyzes completely on evaporation. Dry hydrogen chloride passed into the .carbon bisulfide solution of the phosphine did not seem to react. Unlike trimethylphosphine,[4] the trichloroderivative shows no tendency to oxidize to the corresponding oxide by exposure to the air, but by boiling with nitric acid the crystalline tris(chloromethyl)phosphine oxide was obtained. On heating the trichloro oxide with dry sodium benzoate to 200°, the tribenzoate of tris(hydroxymethyl)phosphine oxide was formed, identical with the product of the action of benzoyl chloride on the latter. An attempt was made to prepare the oxide by the action of phosphorus pentachloride on tris(hydroxymethyl)phosphine oxide, but only black, tarry products were obtained.

The flow sheet illustrates the relation of the compounds described.



Experimental Part

Analysis of the Tribenzoate of Tris(hydroxymethyl)phosphine Oxide.—In the first article the composition of this substance was given tentatively as $C_{24}H_{21}O_8P$, as based on the phosphorus content. The carbon determination by combustion gives widely varying results due to the occlusion of carbon by phosphoric acid or phosphates. It has now been found possible to obtain good results by wet oxidation using chromic acid.[5] This showed that the true composition is $C_{24}H_{21}O_7P$. The hydrogen was determined by the usual combustion.

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[4] Cahours and A. W. Hofmann, *Ann.*, **104,** 30 (1857).

[5] Messinger, *Ber.*, **23,** 2757 (1892).

Anal. Calcd. for $C_{24}H_{21}O_7P$: C, 63.72; H, 4.6; P, 6.8. Calcd. for $C_{24}H_{21}O_8P$: C, 61.5; H, 4.4; P, 6.6. Found: C, 63.48, 63.61; H, 4.8; P, 6.9.

Action of Barium Carbonate and of Sodium Hydroxide on Tetrakis(hydroxymethyl)-phosphonium Chloride.—0.2148 g. of the chloride in 5 cc. of water was boiled with barium carbonate for eight hours; 24.9 cc. of hydrogen was given off, when all action ceased. Calcd. for $1H_2$: 29.6 cc. Then a solution of sodium hydroxide was added and on boiling an additional 29 cc. of hydrogen was obtained.

Action of Sodium Hydroxide on Tri(hydroxymethyl)phosphine Oxide Tribenzoate.—1.0338 g. of tribenzoate boiled with 1 g. of sodium hydroxide in 8 cc. of water gave 54.5 cc. of hydrogen; calcd. for $1H_2$ under the same conditions: 55.4 cc.

Preparation of Tetrakis(chloromethyl)phosphonium Chloride.—Six and six-tenths grams of tetrakis(hydroxymethyl)phosphonium chloride and 30 g. of phosphorus pentachloride in 100 cc. of carbon tetrachloride were boiled gently for four hours. Hydrogen chloride was evolved and the product separated in crusts. These were filtered with suction, washed with a little carbon tetrachloride and recrystallized from a mixture of 80 cc. of ethyl acetate and 15 cc. of methyl alcohol; yield 7.7 g.; calcd., 9.2. g. The product consists of white crystals, easily soluble in water, but not hygroscopic. It is easily soluble in methyl and ethyl alcohols, difficultly in ethyl acetate, chloroform and carbon tetrachloride. The dry compound is odorless, but its aqueous solution has a distinct odor due to hydrolysis and the breaking up of the phosphonium hydroxide into the phosphine. It melts at 192–193°.

Anal. Calcd. for $C_4H_8Cl_5P$: Cl, 67.1; P, 11.7. Found: Cl, 66.7; P, 11.2.

If the substance is dissolved in water, acidified with nitric acid and silver nitrate added, one molecule of silver chloride is precipitated; calcd. for 1 Cl, 13.4; found, 13.3. If, however, the aqueous solution is treated with sodium bicarbonate and, after removing the phosphine with carbon bisulfide, treated with nitric acid and silver nitrate, two molecules of silver chloride are formed: calcd. for 2 Cl, 26.8; found, 26.34. If the solution is treated with sodium hydroxide and let stand for a week or more, the phosphine again dissolves and the chlorine is practically all in the ionized form: calcd. for 4 Cl, 53.6; for 5 Cl, 67.1; found, Cl, 56.2.

Preparation of Tris(chloromethyl)phosphine.—Five grams of tetrakis(chloromethyl)-phosphonium chloride in 20 cc. of water was treated with 8 g. of sodium bicarbonate. The solution became milky and gave a strong formaldehyde reaction with fuchsin reagent. The phosphine was shaken out with carbon bisulfide, dried over sodium sulfate and distilled under diminished pressure; b. p. 100° (7 mm.). Heated at atmospheric pressure it decomposes. It is a colorless, mobile liquid of a powerful, benumbing odor; sp. gr. 20°, 1.414. It appears to be stable indefinitely in contact with air, showing no signs of oxidation. It is slightly soluble in water and easily in organic solvents.

Anal. Calcd. for $C_3H_6Cl_3P$: Cl, 59.3. Found: Cl, 59.4.

Preparation of Tris(chloromethyl)phosphine Oxide.—0.75 g. of the phosphine was boiled for one hour with 4 cc. of nitric acid (sp. gr. 1.2). After evaporating on the water-bath until the odor of nitric acid had disappeared, a sirup remained which crystallized on cooling; m. p. 88–89°; easily soluble in water and alcohol. For analysis it was dried *in vacuo* at 78°.

Anal. Calcd. for $C_3H_6OCl_3P\cdot{}^1/_2HO$: Cl, 52.1. Found: Cl, 52.2, 52.23.

Mixed with sodium benzoate and heated at 200° for one hour, a waxy material resulted. After removing the excess sodium benzoate with boiling water, an oil remained which solidified on cooling. Recrystallized from methyl alcohol, it melted at 110°, showing no depression when mixed with the benzoylation product of tris(hydroxymethyl)phosphine oxide.

Preparation of the Barium Salt of Bis(hydroxymethyl)phosphinic Acid.—Three and eight-tenths grams of tetrakis(hydroxymethyl)phosphonium chloride dissolved in 100 cc. of water was boiled with 19 g. of barium hydroxide for several hours until the evolution of hydrogen ceased. The barium was then removed with a slight excess of sulfuric acid and the hydrochloric acid with silver carbonate. From the filtrate, dissolved silver was precipitated with hydrogen sulfide. The filtrate was then evaporated on the water-bath to a sirup and the heating continued for some time to drive off any formic acid which might have resulted from the action of barium hydroxide on formaldehyde. The acid was then converted into the barium salt by boiling with water and barium carbonate, the filtrate evaporated to small bulk and allowed to crystallize. The crystals were washed with a little water. The mother liquor seemed to contain caramel-like substances formed by the action of barium hydroxide on formaldehyde. The product consisted of well-developed crystals, moderately soluble in water, insoluble in alcohol.

Anal. Calcd. for $C_4H_{12}O_8P_2Ba$: Ba, 35.4; P, 16.02. Found: Ba, 35.2; P, 15.68.

Summary

The action of alkali on tetrakis(hydroxymethyl)phosphonium chloride has been shown to take place in two stages, giving first tris(hydroxymethyl)phosphonium oxide and finally bis(hydroxymethyl)phosphinic acid and liberating one molecule of hydrogen at each stage. With a neutral carbonate the action stops at the oxide stage.

Tetrakis(chloromethyl)phosphonium chloride was prepared from the corresponding hydroxy derivative by treating with phosphorus pentachloride. This was converted into tris(chloromethyl)phosphine and the latter to tris(chloromethyl)phosphine oxide.

A crystalline barium salt of bis(hydroxymethyl)phosphinic acid was obtained.

The work is being continued.

KEW GARDENS, NEW YORK

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TRIORGANO THALLIUM COMPOUNDS. THALLIUM TRIETHYL AND THALLIUM DIETHYL TRIPHENYLMETHYL

BY H. P. A. GROLL

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The only organo thallium compounds known are of the type R_2TlX,[1] *i. e.*, salts of the bases R_2TlOH first isolated by R. J. Meyer and A. Bertheim.[2] Many alkyl and aryl compounds of this type have been prepared by D. and A. E. Goddard,[3] E. Krause and A. v. Grosse.[4] F. Hein and E. Markert[5] and A. E. Goddard[3] attempted without success to prepare TlR_3 or $(Tl(C_2H_5)_2)_2$.

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[1] Hansen, *Ber.*, **3**, 3 (1870); Hartwig, *ibid.*, **7**, 298 (1874).

[2] Meyer and Bertheim, *ibid.*, **37**, 2051 (1904).

[3] Goddard and Goddard, *J. Chem. Soc.*, **119**, 672, 1310 (1921); **121**, 36, 256, 482 (1922).

[4] Krause and Grosse, *Ber.*, **58**, 272, 1933 (1925).

[5] Hein and Markert, *ibid.*, **61**, 2255 (1928).