

THE HYDROLYSIS PRODUCTS OF DIPHOSPHORUS TETRACHLORIDE AND DIPHOSPHORUS TETRAIODIDE*

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(Received April 26th, 1965)

It has been reported¹ that the alkaline hydrolysis of phosphorus halides and pseudohalides leads to the formation of compounds containing phosphorus-phosphorus bonds. This report led us to the investigation of the hydrolysis of diphosphorus tetrachloride and diphosphorus tetraiodide in both acidic and basic solutions. We have separated the hydrolysis products by anion exchange chromatography. The results of this study are described in this paper.

EXPERIMENTAL

Preparation of diphosphorus tetrachloride and diphosphorus tetraiodide

Diphosphorus tetrachloride (P_2Cl_4) was prepared from phosphorus trichloride by the method of SANDOVAL AND MOSER². The procedure described by FINCH³ was used for the purification of P_2Cl_4 . The melting point (-28°) served as a check of the purity of each sample. Immediately after purification 0.5 to 0.6 g of P_2Cl_4 was vacuum distilled into each pyrex capsule which had been previously heated under vacuum to remove absorbed surface water. The capsules were sealed and stored in darkness at -78° until needed for hydrolysis.

Diphosphorus tetraiodide (P_2I_4) was prepared in an inert atmosphere box by direct combination of white phosphorus and resublimed iodine in benzene⁴. After recrystallization from benzene the P_2I_4 (m.p. 125°) was dried. Pyrex capsules were then filled with 2-4 g of the P_2I_4 and stored in darkness under a nitrogen atmosphere until needed for hydrolysis.

Biphosphine was prepared by the reaction of calcium phosphide with water according to the method of EVERS AND STREET⁵. Water was not removed from the biphosphine preparations.

Apparatus and procedure for hydrolysis

The reaction vessel was a heavy walled suction flask fitted with a rubber stopper containing a nitrogen inlet tube and a glass sleeve. A glass rod to which the P_2Cl_4 capsules were sealed was inserted in the sleeve. By pushing on the glass rod the capsules were crushed against the bottom of the reaction vessel. In the case of P_2I_4 the capsules were not sealed to the glass rod, but placed in the reaction vessel and broken with the rod.

* Taken in part from a thesis submitted by JAMES H. WIERSMA in partial fulfillment of the requirements for the degree of Master of Science, June 1965.

Nitrogen gas was continuously bubbled through the hydrolysis apparatus. The nitrogen flow was initiated 15 to 30 min before the capsules were opened and continued for 3 h in alkaline hydrolysis and for 5 h in the acidic hydrolysis. The nitrogen gas was purified and water saturated by passing through two traps containing Oxysorbent (Burrell Corp., Pittsburgh, Pa.), and two traps containing solution of the same composition as that in the reaction flask. The nitrogen was bubbled through the hydrolysis solution to remove volatile products, and then through two traps containing 5% $HgCl_2$ solution. These two traps remove phosphine which precipitates as the mercury chlorophosphide complex⁶, $P(HgCl)_3$. Only the reaction vessel and the saturating traps were kept in a constant temperature bath maintained at 24.9°.

All alkaline hydrolysis experiments were carried out using 100 ml of stock solution of 4.78 *N* sodium hydroxide. The acidic hydrolysis experiments used 100 ml of distilled water.

Analysis

The soluble phosphorus-containing hydrolysis products were separated by anion exchange chromatography by the method of POLLARD, NICKLESS AND ROTHWELL⁷. Anions with a retention volume greater than 450 ml were eluted with 4 *N* HCl. Biphosphine and the lower oxyanions of phosphorus were converted to orthophosphoric acid by addition of 15 ml of a 2:1 solution of concentrated nitric acid and bromine water to each fraction followed by heating at 100° until colorless. The phosphate was analyzed spectrophotometrically as the phosphomolybdovanadate complex⁸.

The acidic hydrolysis gave a yellow precipitate which was separated by centrifugation. The supernatant was adjusted to pH 10 with sodium hydroxide, separated and analyzed by the procedure described above.

The yellow precipitate in the acidic hydrolysis of P_2I_4 is described by KOLITOWSKA⁹ as a subhydride of phosphorus with a formula $(P_2H)_x$. A dry sample of the yellow precipitate formed in the hydrolysis of P_2Cl_4 was heated in an evacuated tube to 500°. A measure of the gas evolved was consistent with the formula $(P_2H)_x$ reported by KOLITOWSKA. Thereafter, the yellow precipitate was oxidized and analyzed for phosphorus only.

Since the mercuric ion does not interfere with the formation of the phosphomolybdovanadate complex, the $P(HgCl)_3$ formed by the PH_3 and mercuric chloride was oxidized with nitric acid-bromine water solution and analyzed for phosphorus.

RESULTS

The relative percentages of phosphorus found in various chemical species in the hydrolysis of P_2Cl_4 and P_2I_4 in both acidic and alkaline solution are given in Table I.

DISCUSSION

We have found a volatile phosphorus-containing compound in the basic hydrolysis of both P_2Cl_4 and P_2I_4 . The fact that this compound was found in the third fraction removed from the anion exchange column meant that it was not retained

TABLE I

RELATIVE PERCENTAGES OF PHOSPHORUS FOUND AS VARIOUS SPECIES DURING ACIDIC AND ALKALINE HYDROLYSIS OF P_2Cl_4 AND P_2I_4

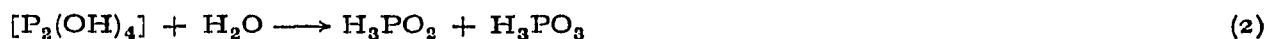
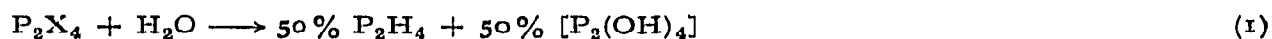
Species	P_2Cl_4 Basic	P_2I_4 Basic	P_2Cl_4 Acidic	P_2I_4 Acidic
Phosphorus p^1	23.7	17.2	19.5	7.5
Oxyanions p^3	14.3	14.8	52.1	73.7
Formed* p^5	6.5	7.7	13.2	14.9
Anions with two or more phosphorus atoms	1.4	2.2		
P_2H_4	50.4	53.2		
PH_3	3.7	4.9	10.3	3.1
Subhydride			4.9	0.8

* Nomenclature according to BLASER AND WORMS¹⁰.

by the resin, and therefore could not be anionic. When the third fraction from the basic hydrolysis was boiled and the gases were passed into 5 % mercuric chloride solution a white precipitate formed, presumably $P(HgCl)_3$, the complex of phosphine and mercuric chloride. On this basis we assumed that the volatile phosphorus compound in the third fraction must be phosphine or biphosphine, since biphosphine undergoes thermal decomposition into phosphine. We have excluded phosphine as a possibility because its solubility¹¹ in sodium hydroxide is not high enough to account for the phosphorus content found. In addition, since the nitrogen carrier was bubbled through the reaction mixture for three hours it seems unlikely that phosphine gas would not have been totally removed. As a final check, biphosphine was prepared from calcium phosphide. A sample of this biphosphine in sodium hydroxide was chromatographed using the same column used for analysis of the hydrolysis products, and found also in the third fraction eluted.

Other investigators^{9,12} have postulated that the hydrolysis of P_2I_4 proceeds by the formation of $P_2(OH)_4$. If $P_2(OH)_4$ were the sole initial product and P_2H_4 formed by the disproportionation of this compound, the maximum amount of phosphorus resulting as P_2H_4 would be 20 %. Since in the basic hydrolysis of P_2Cl_4 and P_2I_4 we find 50 % of the phosphorus as P_2H_4 there remain but two possibilities. Either all or part of the phosphorus initially exists as P_2H_4 . If all the phosphorus initially exists as P_2H_4 then we must assume that the phosphorus oxyanions result from the slow oxidation of biphosphine by the hypohalite ion. However, we have found that the amount of biphosphine remains constant whether the samples are analyzed 2 h or several days after hydrolysis.

In the basic hydrolysis of P_2Cl_4 and P_2I_4 our results fit the following scheme within the limits of experimental error:



The phosphate ion appears to form by the disproportionation of some of the H_3PO_3 :



It is not unreasonable that $P_2(OH)_4$ be an unstable intermediate in the hydrolysis of P_2X_4 . This compound has been reported as being unstable in basic solutions¹²; however, it is also possible that P_2H_4 , H_3PO_2 and H_3PO_3 have a common precursor other than $P_2(OH)_4$.

The hydrolysis of P_2Cl_4 and P_2I_4 in acidic solutions probably proceeds by the same mechanism as in basic solutions. The difference in hydrolysis products may be due to the fact that under acidic conditions the hypohalous acids are strong oxidizing agents capable of reacting with P_2H_4 . The presence of the phosphorus subhydride (P_2H)_x is evidence of the existence of P_2H_4 at some step in the hydrolysis⁵.

It is interesting to note that more phosphine is evolved from the acidic hydrolysis of P_2Cl_4 than from the acidic hydrolysis of P_2I_4 . This may be due to the formation of phosphonium iodide which would remain in solution until oxidized by the hypoiodous acid. A similar explanation cannot be given in the hydrolysis of P_2Cl_4 due to the instability of phosphonium chloride¹³.

The formation of diphosphine indicates that P_2Cl_4 and P_2I_4 hydrolyze *via* water attacking both the phosphorus and the halogen. Halogen attack, as is the case in the hydrolysis of NCl_3 , may be more favorable in the hydrolysis of P_2I_4 in view of the lower difference in the electronegativities between phosphorus and iodine. Steric hinderance of the phosphorus may also play a role in the hydrolysis of these two compounds.

ACKNOWLEDGEMENTS

The authors wish to thank Miss E. A. ANDREWS for her assistance, and the U.M.K.C. School of Pharmacy for the use of some equipment.

SUMMARY

Anion exchange chromatography has been used to determine the hydrolysis products of diphosphorus tetrachloride and diphosphorus tetraiodide in both acidic and basic solutions.

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