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Oxidation of Phosphorus with Water at High Temperature and Pressure in the Presence of Alkali. The Production of Phosphorous Acid

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In a previous work[1] it was shown that phosphorus with water at high temperature and pressure gives phosphoric acid and hydrogen and simultaneously there appear as intermediate products phosphorous acid and phosphine. Both intermediate products react with water at high temperature and pressure to form also hydrogen and phosphoric acid

$P_4 + (3 + n)H_2O = P_2O_3{\cdot}nH_2O + 2PH_3$ Primary reaction

$P_2O_3{\cdot}nH_2O + 2H_2O = P_2O_5{\cdot}nH_2O + 2H_2$ Secondary reaction (1)

$2PH_3 + (5 + n)H_2O = P_2O_5{\cdot}nH_2O + 8H_2$ Secondary reaction (2)

In the present work the oxidation of phosphorus with water under pressure in the presence of sodium hydroxide was investigated. As a result, conditions were worked out whereby it is possible to obtain only one salt of phosphorous acid.

Dulong, even in 1816, showed that by boiling phosphorus with an aqueous alkaline solution, hypophosphorous acid and phosphine are formed. But the reaction proceeds extremely slowly and several days are required for the phosphorus to dissolve entirely. Thomsen improved the method of obtaining hypophosphorous acid by using for this purpose barium oxide.[2]

It seemed of interest to investigate the reaction of alkali upon phosphorus at higher temperatures and pressures. The first experiments made by V. V. Ipatieff and the senior author gave interesting results. The oxidation reaction of phosphorus under pressure at 100° proceeds also very slowly and is limited to the formation of salts of hypophosphorous acid. At 200–300° the reaction proceeds very rapidly, sometimes continuing for several minutes, whereby as a result phosphorous acid is obtained; sometimes the oxidation goes so far as to form phosphoric acid. It was also observed that the amount of alkali employed has a great effect upon the yield of phosphorous acid, and under certain conditions it is possible to obtain only one salt of that acid.

In view of the fact that V. V. Ipatieff was unable to continue this study, it was carried further by the present authors. It was ascertained that *phosphorous acid* in the form of the disodium salt is obtained in a short time (about one hour) by heating phosphorus at not higher than 300° with the quantity of sodium hydroxide (in the form of a 30% aqueous solution) calculated necessary for the formation of the dimetallic salt. At a higher temperature and with less concentrated alkali solution phosphoric acid is obtained because the reaction is greatly catalyzed by the alkali.

Furthermore, it was possible to prove that in the presence of sodium hydroxide the oxidation reaction goes through hypophosphorous acid.

Method of Investigation

The experiments were carried out in a silver tube inclosed within a high-pressure apparatus as previously described.[1]

The phosphine was determined either by the volumetric method, or, in case of a small content, by the gravimetric method by means of silver nitrate. The analysis of the acids of phosphorus was carried out according to the method of Wingler,[3] except that the oxidation with bromine was extended by us to several hours instead of ten minutes as recommended by the author.[4]

Consideration of the Experiments.—The tests listed in Table I were made in order to ascertain the effect of concentration of the alkali.

Comparing the data of experiments 5, 6 and 8, we see that by using the same concentration of sodium hydroxide at almost the same temperature and time of heating the amounts of phosphorous acid formed are different. At the reaction temperature of 225° there was always obtained approximately the same yield of phosphorous acid, although the concentration of alkali was varied from N to 9 N. The significance of the data obtained in experiments 32, 35 and 36 is

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(1) V. N. Ipatieff and C. Freitag, *Z. anorg. allgem. Chem.*, **215**, 388 (1933).

(2) Thomsen, *Ber.*, **7**, 934 (1874).

(3) Wingler, *Z. anal. Chem.*, **62**, 335 (1925).

(4) It should be pointed out that the success of the analysis of the acids by this method depends largely on observing correctly the change in color of the indicators at the beginning and end of neutralization in the titration. It is of some assistance to establish the method of change previously in corresponding concentrations by titrating beforehand known solutions of salts of acids of phosphorus. In doubtful cases, the oxidation with bromine was verified by titration by means of a manganese salt.

TABLE I

EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON OXIDATION OF PHOSPHORUS

	Reactants						Products, % by wt. of original phosphorus converted into				P unreacted, % of original
		NaOH						Sodium salts of			
Expt.	P, g.	G.	Concn.	Calcd. for salt	Temp., °C.	Heating, hrs.	PH_3	H_3PO_2	H_3PO_3	H_3PO_4	
6	6.0	7.9	N	Mono-	175–298	9.5	0.07	...	..	90.1	..
					298[a]	1.0[a]					
5	4.32	11.26	N	Di-	170–300	8.5	.04	...	19.92	73.16	..
					295–300[a]	2.0[a]					
8	3.04	11.85	N	Tri-	195–296	10	.25	...	57.5	40.0	..
					296[a]	1.5[a]					
32	7.05	8.75	N	Mono-	225	2	8.08	7.0	48.22	..	32.7[b]
35	12.63	16.6	4 N	Mono-	225	2	13.45	4.4	46.9	..	36.2
36	12.20	15.15	9 N	Mono-	230	2	15.56	...	47.1	..	38.2
46	12.6	32.15	9.75 N	Di-	230	0.5	21.0	...	76.7	..	..
48	12.05	31.1	9.75 N	Di-	185	2.25	20.75	...	75.97	..	..
31	3,2	12.4	N	Tri-	223	2	10.94	...	84.4	..	..
33	10.45	40.4	4 N	Tri-	225	1.5	18.75	...	78.5	..	..

[a] The second lines show the temperature and time of highest heating. [b] A complete balance is not obtained because part of the phosphorus combines with the copper part of the apparatus.

that by using phosphorus in the proportion to form the monometallic salt, only 50% of the phosphorus is oxidized at 225°; hypophosphorous acid is also obtained under these conditions. In experiments 46, 48, 31 and 33 at 225° the amount of alkali used was that calculated for formation of di- and trisodium salts and the phosphorus was oxidized to phosphorous acid. Analysis showed that in all cases the dimetallic salt was obtained.

These experiments explain the effect of sodium hydroxide on the course of the reaction. When an insufficient amount of alkali is used, *i. e.*, only enough for the formation of the mono salt, the reaction ceases when one-half of the phosphorus is oxidized and the disodium salt is formed; the surplus phosphorus remains in the form of the red modification and does not oxidize at 225°.

Besides the indicated factor, the temperature has a great effect on the oxidation reaction of phosphorus. In the presence of a double amount of alkali the temperature of 230° may be considered the optimum with regard to the reaction velocity (see experiment 46); also, under these conditions the formation of phosphoric acid does not take place. It should be noted that a more intensive oxidation is brought about not only by raising the temperature, but also by the duration of heating even at the low temperature of 200°. However, raising the temperature gives a rather greater yield of phosphoric acid than does increasing the time of heating at a lower temperature. The formation of phosphoric acid occurs mainly on account of the oxidation of phosphine and this oxidation is accomplished very slowly at 230°, but very rapidly at 300°.

The experiments reported in Table II give an understanding about the nature of a more intensive oxidation of phosphorus occurring at 300°.

TABLE II

EFFECT OF TEMPERATURE ON THE OXIDATION OF PHOSPHORUS BY WATER IN THE PRESENCE OF SODIUM HYDROXIDE

	Reactants						Products, % by wt. of original P converted into		
		NaOH						Sodium salts of	
Expt.	P, g.	G.	Concn.	Calcd. for salt	Temp., °C.	Heating, hrs.	PH_3	H_3PO_3	H_3PO_4
21	10.6	27.5	4 N	Di-	205–208	24	4.24	79.86	9.18
20	10.64	27.5	4 N	Di-	199–208	48	0.4	85.05	10.25
19	10.51	26.51	4 N	Di-	250–300	81	.5	...	96.0
24	12.32	32.0	9 N	Di-	300–311	12	.4	7.5	89.0
27	10.95	42.4	4 N	Tri-	251–310	16	.1	39.33	56.43

An excess of alkali, as seen from experiments 24 and 27, retards the oxidation of phosphorous acid (compare also experiments 6, 5 and 8 in Table I).

Therefore, for a successful oxidation of phosphorus to phosphoric acid it is necessary to avoid an excess of alkali. On the other hand, we have to consider the fact that an insufficient amount of alkali affects adversely the quantity of phosphorus reacted, and for complete oxidation it is necessary to raise the temperature above 300°. These propositions were corroborated by additional experiments.

Formation of Hypophosphorous Acid

Experiments 32 and 35 in Table I show that hypophosphorous acid is obtained along with phosphorous acid. On the basis of these data it could be assumed that hypophosphorous acid is formed at a temperature not higher than 225° and in the absence of free alkali. On the basis of these assumptions additional experiments were carried out where alkali was used in an amount calculated for formation of the mono salt.

Table III

	Reactants						Products, % by wt. of original P converted into			
		NaOH						Na salts of		
Expt.	P, g.	G.	Concn.	Calcd. for salt	Temp., °C.	Heating, hrs.	PH_3	H_3PO_2	H_3PO_3	P, unreacted
61	7.12	9.2	*N*	Mono-	223	2	6.0	9.5	58.9	Present
62	4.82	6.2	*N*/2	Mono-	225	2	5.0	4.0	51.8	Present

Phosphoric acid was not formed at all and hypophosphorous acid was obtained in a quantity not exceeding 9 to 10% of the amount of phosphorus employed. We did not succeed in improving the yield of hypophosphorous acid in spite of a whole series of experiments with varying conditions relative to heating, concentration and quantity of alkali used in the reaction.

In order to study the effect of alkali concentration on oxidizability of hypophosphorous acid, experiments listed in Table IV were carried out. In all the tests 20 cc. of a hypophosphorous acid solution (approximately 50% concentration) containing 4.47 g. of phosphorus was used.

Table IV

Effect of Temperature on the Oxidation of Hypophosphorous Acid in the Presence of Sodium Hydroxide

	NaOH solution				Products, % by wt. of original P in H_3PO_2 obtained as Sodium salts of			
Expt.	Cc.	Concn. *N*	Temp., °C.	Heating, hrs.	PH_3	H_3PO_2	H_3PO_3	H_3PO_4
79	25	9.75	170	3.5	..	99.0	..	..
80	25	9.75	193–208	1.75	..	100.0	..	..
83	25	9.75	258–278	1.75	..	9.0	..	90.5
84	25	9.75	258–300	2.0	..	Trace	..	98.5
81	29	17	160	0.50	..	...	99.5	..
89	50	9.75	170	.16	..	...	99.0	..

Experiments 79 and 80 show that the sodium salt of hypophosphorous acid is distinguished by its stability and does not undergo oxidation at 200°; above 250°, its oxidation proceeds very rapidly and completely to phosphoric acid (experiments 83 and 84). On account of the acid medium in the final product, there remains some unchanged hypophosphorous acid and traces of it may be detected even at 300°.

Quite a different picture is obtained when the salt of hypophosphorous acid is heated in an alkaline medium. If to one mole of the acid is added two moles of alkali, as is seen in experiments 81 and 89, hypophosphorous acid is oxidized completely in the course of several minutes, but now into phosphorous acid. The oxidation proceeds so rapidly that when the temperature reaches 160° it is possible to observe the movement of the needle on the manometer on account of the evolution of hydrogen.

$$NaH_2PO_2 + (NaOH, H_2O) \longrightarrow Na_2HPO_3 + H_2O + H_2$$

Oxidation of salts of hypophosphorous acid proceeds without evolution of phosphine.[5] The reaction may be explained by the assumption that under the influence of alkali one atom of hydrogen becomes, at a certain temperature, capable of being replaced by a metal and the mono-salt thus formed is easily oxidized into the more stable dimetallic salt of phosphorous acid.

These experiments upon oxidation of a salt of hypophosphorous acid in the presence of alkali completely explain its absence in the products of oxidation of phosphorus, when the alkali is used in an amount necessary for the formation of a dimetallic salt, since it is oxidized even at a low temperature to the salt of phosphorous acid.

Summary

1. Oxidation of phosphorus by water vapor under pressure in the presence of sodium hydroxide yields various products of oxidation depending on the amount of alkali used and the temperature.

2. In the presence of sodium hydroxide used in an amount sufficient for the formation of the disodium salt of phosphorous acid, only phosphorous acid is obtained at a temperature not higher than 225°. At a temperature higher than 250° phosphoric acid is also obtained.

3. In the presence of sodium hydroxide used in the proportion required for formation of the mono-salt there is obtained, at a temperature not higher than 225°, a mixture of hypophosphorous and phosphorous acids, with the former acid not exceeding 9 to 10% of the phosphorus used.

4. The oxidation of the sodium salt of hypophosphorous acid may be carried out completely to phosphorous acid or phosphoric acid (without evolution of phosphine) depending upon the amount of sodium hydroxide used and the temperature.

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[5] Passage of large amounts of gas after oxidation reactions through a solution of silver nitrate did not bring about any change in the latter, whereas this test is sensitive to even traces of phosphine.