A rubber stopper, covered with tin foil and equipped with a gas inlet tube (extending to the bottom of the flask) and a gas outlet tube, was then introduced into the neck of the flask. Oxygen was passed through the solution for three hours before exposing to the mercury arc.[7]

After the exposure was completed the reaction mixture was transferred to an ordinary flask and the required quantity of solid sodium bicarbonate was added. The solution was then distilled to small volume. Acetol tests were made on the distillate and pyruvic acid, and urea tests on the residue.

The author wishes to acknowledge his indebtedness to Professor Oskar Baudisch for many helpful suggestions and criticisms.

Summary

1. When aqueous solutions of thymine in an atmosphere of oxygen are illuminated by a quartz mercury arc, the pyrimidine is split to some extent into urea and pyruvic acid; no acetol is formed.

2. The reaction is catalyzed by ferrous sulfate and by potassium ferrocyanide, the former being the more active catalyst. The products obtained are the same as those in the absence of catalysts.

3. No split occurs in an atmosphere of nitrogen, even in the presence of ferrous sulfate or potassium ferrocyanide.

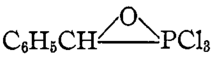
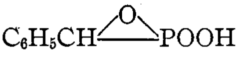
New Haven, Connecticut

[Contribution from the Chemical Laboratory of Harvard University]

ADDITION REACTIONS OF THE PHOSPHORUS HALIDES. VIII. KINETIC EVIDENCE IN REGARD TO THE MECHANISM OF THE REACTION

By J. B. Conant and V. H. Wallingford

Received October 17, 1923

In one of the earlier papers of this series[1] the mechanism of the reaction between phosphorus trichloride and benzaldehyde was investigated. It was shown that the halide and aldehyde combined in the absence of any other substance to form an addition product to which we ascribed the formula  $C_6H_5CH\overset{O}{\longleftrightarrow}PCl_3$ (I), because on decomposition with water (or acetic acid) a "phostonic" acid,  $C_6H_5CH\overset{O}{\longleftrightarrow}POOH$ (II), was formed. This monobasic acid was transformed into the hydroxy dibasic acid, C_6H_5-$CHOHPO_3H_2$, on boiling with water. Since the phostonic acid was found in the product of the reaction of benzaldehyde, phosphorus trichloride and acetic acid (or acetic anhydride), it was concluded that the compound I was intermediate in the reaction which took place in these solvents. Ac-

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[7] In experiments with nitrogen, the gas was freed from traces of oxygen by passing it through a strong alkaline solution of pyrogallol and through an aqueous suspension of ferrous hydroxide.

[1] This Journal, 42, 2337 (1920).

cording to the mechanism at that time suggested, the primary addition reaction which had been shown to be reversible went to completion in the presence of acetic acid (or anhydride) because the reagent employed reacted with the compound I and removed it from the equilibrium. This mechanism thus explained why good yields of organic phosphorus compounds were obtained only when some reagent such as acetic acid or acetic anhydride was employed. It was equally convenient in explaining the results with unsaturated ketones[2] (1,4 addition) and the addition reactions of a variety of substituted phosphorus halides.[3]

We have now made a more thorough investigation of the reaction between benzaldehyde and the trichloride from a kinetic standpoint and find that the mechanism in the simple form as first proposed will not suffice. We have verified the fact that the reversible reaction, $C_6H_5CHO + PCl_3 \rightleftharpoons C_6H_5CH\overset{\diagup O \diagdown}{\rule{2em}{0.4pt}}PCl_3$, does take place, but have found that the reaction is much slower than our early work indicated; the speed of this reaction is, indeed, much too slow to make it a conceivable step in the process which takes place in the presence of acetic acid or acetic anhydride.

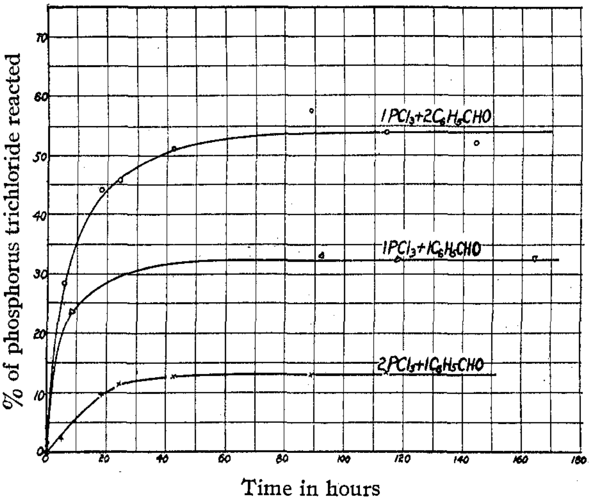

Fig. 1.—The reaction between phosphorus trichloride and benzaldehyde with no solvent

We have carefully studied the kinetics of the reaction between benzaldehyde and the trichloride both in the absence of any other material and in benzene as a solvent. The experimental difficulties of measuring the speed of this reaction are great and the accuracy of the work therefore leaves much to be desired but, as the summary in Table I shows, the results

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[2] This Journal, **42**, 830 (1920).

[3] *Ibid.*, **43**, 1665 (1921); **45**, 165 (1923); **45**, 762 (1923).

are sufficiently concordant to enable us to draw significant conclusions in regard to the point at issue. The experimental details of the measurements are described in the experimental portion of the paper. The course of the reaction was followed by removing samples from the reaction mixture from time to time and rapidly decomposing them with a large excess

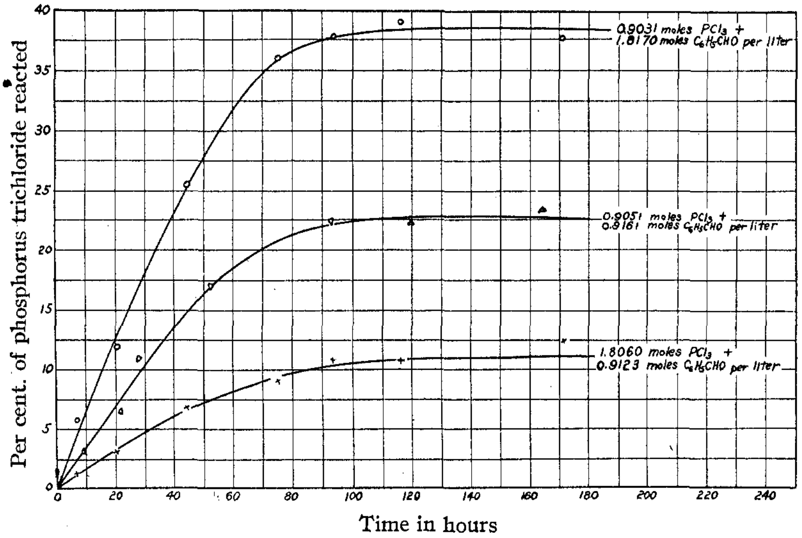


Fig. 2.—The reaction between phosphorus trichloride and benzaldehyde in benzene

TABLE I

SUMMARY OF KINETIC MEASUREMENTS

Volume of solvent Cc.	Moles PCl_3	Moles C_6H_5CHO	$k_1 \times 10^3$	Average $k_1 \times 10^3$	K
None	0.0573	0.0573	(0.56)		0.126
None	.0573	.1146	(4.60)		.216
None	.1146	.0573	(0.71)		.533
25	.0226	.0226	4.3	5.1	.416
			3.9		
			5.9		
			6.1		
25	.0226	.0452	5.0	4.8	.424
			3.9		
			5.4		
25	.0452	.0226	2.3	2.5	.182
			2.6		
			2.7		
25	.0452	.0452	2.7	4.0	.266
			3.6		
			4.5		
			4.2		
			5.2		
				Av. 4.1	.309

of cold water; the amount of phosphorus acid formed was then determined and from this the amount of trichloride which had not reacted. Figs. 1 and 2 show the course of the reaction graphically; it is obvious that it comes to a definite equilibrium after many hours. The composition of the equilibrium mixture varies according to the law of mass action with the relative amounts of benzaldehyde and trichloride and the volume. Very similar curves were obtained by noting the change in volume of a mixture of the trichloride and benzaldehyde, the diminution in volume corresponding to the addition reaction. This indirect method gives satisfactory confirmation of our analytical study of the kinetics of the reaction.

In the first three experiments recorded in Table I no solvent was employed, but the proportions of the reactants were varied; the volumes necessary for the calculation of the equilibrium constant were known from the volumetric experiments mentioned above. In the last four experiments benzene was used as the solvent and the volume and proportion of the reactants were varied. The value of k_1 the true reaction velocity to the right was calculated from Equation 3, which is the integrated form of Equation 2, which in turn follows from Equation 1 by substituting the value $k_2 = k_1/K$, where $K = \frac{[\text{Addition product}]}{[C_6H_5CHO]\ [PCl_3]}$. Equation 1 is the usual equation for the apparent speed of a reversible reaction of the type $A + B \rightleftarrows AB$. The values for k_1 calculated in the first three experiments are not included in the final averages, since the nature of the solvents is not comparable. It should be noted that in spite of this fact the constants are of the same order of magnitude.

$$\frac{dx}{dt} = k_1(a - x)\ (b - x) - k_2x \qquad (1)$$

$$\frac{dx}{dt} = k_1(a - x)\ (b - x) - \frac{k_1x}{K} \qquad (2)$$

$$k_1 = \frac{2.303\,K}{t\sqrt{q}} \log \left[\left(\frac{2Kx + m - \sqrt{q}}{2Kx + m + \sqrt{q}}\right)\left(\frac{m + \sqrt{q}}{m - \sqrt{q}}\right)\right] \qquad (3)$$

where $a = [PCl_3]$, $b = [C_6H_5CHO]$ (moles per liter), $m = -(Ka + Kb + 1)$, and $q = (Ka + Kb + 1)^2 - 4K^2ab$.

In the procedure usually employed for the preparation of the hydroxyphosphonic acid, the aldehyde, trichloride and acetic acid are mixed together and kept at 25–30°; in less than half an hour the reaction is practically complete as can be shown by pouring a sample into water and observing the absence of benzaldehyde. If this reaction proceeds through the intermediate addition reaction whose speed we have measured, the speed should be no faster than that of this slow addition reaction. We can easily calculate this from the value of k_1 in Table I (4×10^{-3}), the concentrations of the reactants and the usual formula (4) for a bimolecular reaction where equal amounts of reactants are employed. The volume

$$t = \frac{1}{k}\left(\frac{x}{a(a - x)}\right) \tag{4}$$

in the usual procedure is such that $a = 2$ moles per liter; solving now for t when $x = 0.5$ (50% reacted) and 0.9 (90% reacted) we find 100 and 800 hours, respectively. Yet the actual reaction is practically complete in less than 30 minutes. This enormous discrepancy between the calculated and observed times might be due to some catalytic influence of the solvent; acetic acid and benzene are very different substances. To test this point we have devised a method of causing the reaction to go to completion in benzene by gradually adding water in very small amounts. If the water is added in very small drops over a period of a half an hour (the solution of the trichloride and aldehyde in benzene being agitated) a considerable quantity of hydroxyphosphonic acid is formed. It can be isolated by extracting the benzene with water and evaporating the aqueous layer. Table II summarizes several such experiments; in the last column are given the times necessary to form the amount of phosphonic acid actually isolated calculated from Equation 5 and $k_1 = 4 \times 10^{-3}$.

$$t = \frac{2.303}{(a - b)k_1} \log \frac{b(a - x)}{a(b - x)} \tag{5}$$

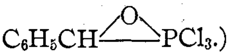
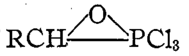
Table II

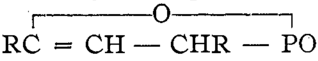
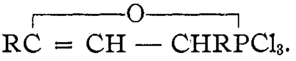
Comparison of Actual and Calculated Times for Forming Phosphonic Acid

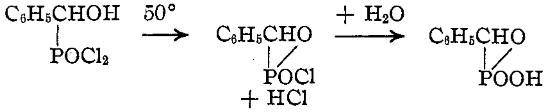
C_6H_5CHO G.	PCl_3 G.	Solvent Cc.	Temp. °C.	Yield of $C_6H_5CHOHPO_3H_2$ G.	Actual time Hours	Calc. time from Eq. 5; Hours
5	3.2	30	25	1.8	0.5	96
3.9	5	40	25	1.1	.5	53
10	13	none	0	10.0	.25	59

The discrepancy shown in Table II between the actual time of the experiments and the calculated time can hardly be accounted for by any catalytic effect of the solvent. Except for the small increments of water the solvents were the same. The presence of the water is, of course, necessary to cause the reaction to go to completion and form the hydroxyphosphonic acid; no direct experimental test of its catalytic effect on the addition reaction is possible. If the addition reaction is not to be discarded as the intermediate step in the rapid formation of the hydroxyphosphonic acid it would be necessary to suppose that the presence of small amounts of water, of large amounts of acetic acid or of acetic anhydride all had about the same enormous catalytic influence on the speed of the addition reaction. The effect of hydrogen chloride is ruled out, as experiments in which we saturated the reactants with this gas showed the usual rate of reaction (measured volumetrically). There seems to be no escape from the conclusion that *the reversible combination of benzaldehyde and phos-*

phorus trichloride which forms the compound I is not intermediate in the reaction when carried out in acetic acid, acetic anhydride or by slowly adding water.

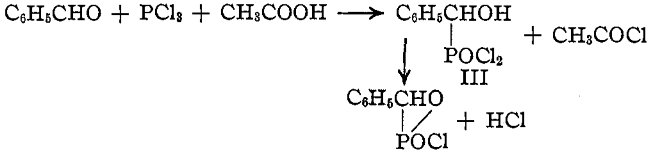
Further evidence of an entirely different sort leads to the same conclusion. If an equilibrium mixture of phosphorus trichloride and benzaldehyde is decomposed with water a considerable amount of the phostonic acid II is formed as shown by the formation of a characteristic white precipitate with a concentrated solution of ammonium molybdate. (The formation of the phostonic acid on the hydrolysis of the equilibrium mixture is, indeed, the evidence for writing the formula of the addition compound I as  $C_6H_5\overbrace{CH\text{———}PCl_3}^{O}$.) If, instead of waiting many hours for the slow addition reaction to proceed to equilibrium, we gradually add one molecular equivalent of water to a freshly prepared mixture of aldehyde and trichloride at a low temperature, we obtain different results. An oil is formed (hydrogen chloride being evolved towards the end of the reaction) which is completely soluble in water, and yet the aqueous solution gives no test for the phostonic acid. On evaporation *at room temperature* a good yield of the hydroxyphosphonic acid, $C_6H_5CHOHPO_3H_2$, is obtained. Obviously, in this experiment, water, the trichloride and benzaldehyde have reacted to form the hydroxyphosphonic acid. Thus, the assumption of the intermediate formation of  $R\overbrace{CH\text{———}PCl_3}^{O}$ and the phostonic acid is contradicted by direct chemical as well as kinetic evidence.

There remains to be explained the formation of the phostonic acid (or related substances) when acetic acid or acetic anhydride is used. The isolation of the phostonic acid from such reaction mixtures seemed in our earlier work to be good evidence for the mechanism then proposed. Similarly, the proof of the existence of compounds of the type  $\overbrace{RC = CH - CHR - POCl}^{O}$ as the chief product of the action of the trichloride and acetic anhydride on unsaturated ketones was taken as evidence that the reaction proceeded through the compound  $\overbrace{RC = CH - CHRPCl_3}^{O}$. The following experiment together with the kinetic evidence just discussed destroys this evidence, at least in the case of benzaldehyde and by analogy in the case of the unsaturated ketones as well. If the oil obtained at a low temperature by the gradual addition of one molecular equivalent of water to benzaldehyde and the trichloride is warmed to 50–60°, hydrogen chloride is evolved, and a resin is formed. This resin on dissolving in water gives a solution which contains a large amount of the phostonic acid, whereas the oil before losing hydrogen chloride gave a solution containing only the phosphonic acid. The reactions must be as follows.

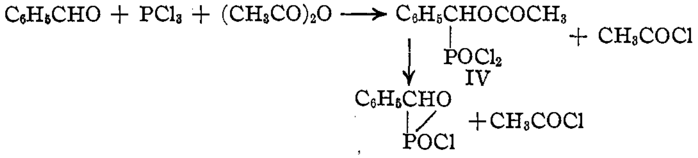


$$\underset{\mathrm{POCl_2}}{\mathrm{C_6H_5CHOH}} \xrightarrow{50^\circ} \underset{\substack{\mathrm{POCl}\\ +\,\mathrm{HCl}}}{\mathrm{C_6H_5CHO}} \xrightarrow{+\,\mathrm{H_2O}} \underset{\mathrm{POOH}}{\mathrm{C_6H_5CHO}}$$

The loss in weight during the change from oil to resin corresponds closely to the loss of one molecular equivalent of hydrogen chloride. If this process takes place so readily (hydrogen chloride begins to be evolved at 20–30°) it is evident that unless special precautions are taken a phostonic acid derivative will be formed *from an open chain compound by loss of hydrogen chloride* or in the case of acetic anhydride by loss of acetyl chloride. Thus it now seems probable that the first products of the action of acetic acid or acetic anhydride are III and IV, which then decompose at least partially as follows.

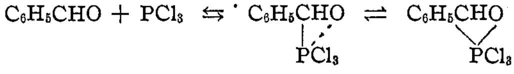


$$\mathrm{C_6H_5CHO + PCl_3 + CH_3COOH} \longrightarrow \underset{\substack{\mathrm{POCl_2}\\ \mathrm{III}}}{\mathrm{C_6H_5CHOH}} + \mathrm{CH_3COCl}$$
$$\downarrow$$
$$\underset{\mathrm{POCl}}{\mathrm{C_6H_5CHO}} + \mathrm{HCl}$$



$$\mathrm{C_6H_5CHO + PCl_3 + (CH_3CO)_2O} \longrightarrow \underset{\substack{\mathrm{POCl_2}\\ \mathrm{IV}}}{\mathrm{C_6H_5CHOCOCH_3}} + \mathrm{CH_3COCl}$$
$$\downarrow$$
$$\underset{\mathrm{POCl}}{\mathrm{C_6H_5CHO}} + \mathrm{CH_3COCl}$$

In the above equations the aldehyde, trichloride and reagent are represented as interacting directly to give an open-chain organic phosphorus compound. This may be the best way of representing this reaction; certainly our previous mechanism involving the compound, $\mathrm{RCH}\overset{\mathrm{O}}{\triangle}\mathrm{PCl_3}$, as an intermediate must be discarded. There is every reason to believe that there is no intermediate compound such as phosphorous acid or phosphorous oxychloride involved, as repeated attempts to allow the trichloride to react with the reagent first and then to add the benzaldehyde have failed to yield any product. Two possible ways are now left of representing the reaction; either it is a simultaneous interaction of the three molecules, or else some addition compound other than $\mathrm{RCH}\overset{\mathrm{O}}{\triangle}\mathrm{PCl_3}$ is involved. It was suggested[4] on purely theoretical grounds that the first step in all such reactions of the carbonyl group (or of conjugated carbonyl compounds) might be the attraction of the unsaturated carbon atom for the unsaturated phosphorus atom; the resulting addition compound would be V.



V

$$\mathrm{C_6H_5CHO + PCl_3} \leftrightarrows \underset{\mathrm{PCl_3}}{\mathrm{C_6H_5CHO}} \rightleftharpoons \underset{\mathrm{PCl_3}}{\mathrm{C_6H_5CHO}}$$

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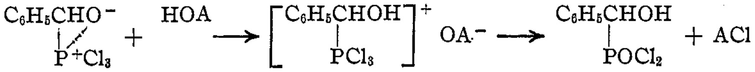
[4] This Journal, **43**, 1705 (1921).

The dotted line in Formula V was used to represent an "inner polar bond" such as exists in the betaines and certain amino acids. If Compound V in the above scheme were rapidly formed in small amounts relative to the other factors in the equilibria, the kinetics of the reaction would be identical with that of the simple addition reaction. An addition compound of this type may be the true intermediate in the course of the usual rapid reaction with acetic acid, acetic anhydride or water (under the special conditions mentioned above). It would be expected to give derivatives of the hydroxyphosphonic acid rather than of the phostonic acid if it reacted with the reagent to produce true salts which decomposed thus,



$$\begin{array}{c}C_6H_5CHO^-\\ |\diagup\\ P^+Cl_3\end{array} + HOA \longrightarrow \left[\begin{array}{c}C_6H_5CHOH\\ |\\ PCl_3\end{array}\right]^+ OA^- \longrightarrow \begin{array}{c}C_6H_5CHOH\\ |\\ POCl_2\end{array} + ACl$$

For the reasons given in the paper referred to, we believe that there is much to recommend the assumption that the first step in the reaction of carbonyl compounds with phosphorus halides and derivatives of ammonia is the formation of "inner salt" addition compounds. We favor, therefore, this mechanism for the reaction of phosphorus trichloride and benzaldehyde. There is, however, at present no evidence in favor of this view rather than that of representing the process as a simple trimolecular reaction.

Experimental Part

Kinetic Measurements

Materials and Reagents.—The benzaldehyde used was purified by distilling it twice at atmospheric pressure and then in a stream of dry carbon dioxide at 20 mm., the first and last portions of the distillate being discarded. It was used immediately except in a few instances in which it was kept for 24 hours in a sealed bottle. The phosphorus trichloride was distilled thrice through a fractionating column; it boiled constantly at 76°. The benzene was dried over metallic sodium before it was used.

General Procedure.—The method employed in following the course of the reaction consisted in mixing the two reactants alone or with benzene in a small flask suspended in a thermostat at 25°, removing samples from time to time and determining the amount of unchanged phosphorus trichloride by decomposing it with water and analyzing the solution for phosphorous acid by oxidizing it to phosphoric acid with bromine and determining the latter by the usual molybdic acid method. When no solvent was employed the volume change during the reaction was measured in a special apparatus.

The benzaldehyde was carefully weighed in a small glass-stoppered flask and the phosphorus trichloride added by means of a pipet which had been previously calibrated at 25° in terms of the weight of trichloride that it would deliver. The components were thoroughly mixed at 25° and a portion transferred by means of a pipet to a very small flask with a long graduated neck; the portion transferred was of such amount that it filled this flask nearly to the top of the graduations. The contents of the flasks were protected from atmospheric moisture not only by the glass stoppers but by a section of rubber tubing clamped over the tops of the flasks. Both flasks were placed in the thermostat and the readings of the meniscus in the graduated flask noted when samples were withdrawn for analysis from the larger flask. Before these readings were taken the stopper was loosened for a moment to equalize the internal and atmospheric pressures. Such change of volume plotted against time gave curves parallel to those showing the course of the reaction as determined by analysis.

When benzene was used as a solvent, an aliquot sample of a mixture of phosphorus trichloride and benzene was shaken with water and the phosphorous acid determined as described below. A known amount of this analyzed mixture was then placed in the flask containing the weighed amount of benzaldehyde. There was no appreciable volume change during the reaction when a solvent was employed.

Samples were removed from the flask containing the reaction mixture by means of a calibrated pipet of special construction and decomposed by shaking with 50 cc. of distilled water in a separatory funnel. Great difficulty was at first encountered in obtaining consistent results (particularly in the experiments without a solvent) as during the decomposition the reaction continued to a certain extent. A great deal of experimentation convinced us that it was impossible to decompose the reaction mixture directly with water without causing the formation of considerable amounts of phosphonic acid. By diluting the reaction mixture with benzene, however, fairly significant results could be obtained as shown by the fact that the analysis of the reaction mixture five minutes after it was mixed corresponded to only a slight reaction. This is the point in the procedure at which the greatest errors are introduced; even under the most favorable circumstances we were able to devise, some reaction seems to have taken place during the decomposition. The variations in the values of k_1 and K are to be attributed to this source of error. The best procedure was to add the sample to a mixture of 50 cc. of water and 30 cc. of benzene in a separatory funnel, which was then stoppered and shaken vigorously for 5 minutes. The water solution was drawn off and extracted with 25 cc. of benzene to remove unchanged benzaldehyde, and warmed on the steam-bath for a few minutes to remove any benzene. It was then diluted to a definite volume (100 cc.) and an aliquot portion taken for analysis.

It was necessary to oxidize the phosphorous acid to phosphoric acid under definite conditions because the hydroxyphosphonic acid was immediately oxidized by bromine in weakly alkaline solution. In strongly acid solution, on the other hand, the phosphorous acid was oxidized very slowly. In the procedure adopted after much experimentation, the aliquot sample (25 cc.) was gradually treated with bromine water (at room temperature) until the color was that produced by 2 cc. of saturated bromine water diluted to 25 cc.; 15 to 30 minutes was required for the oxidation. The excess of bromine was then removed by the addition of sodium sulfite solution. The solution was then diluted to 150 cc. with 5% nitric acid, warmed to 60°, treated with an excess of molybdic acid solution[5] and allowed to stand for 18 hours. The precipitate was separated on a Gooch crucible, washed with 1% potassium nitrate solution and then dissolved in standard sodium hydroxide solution. The solution was then diluted to 150 cc. and titrated with nitric acid using phenolphthalein as the indicator. The analytical procedure was tested by repeatedly analyzing a dilute solution of phosphorous acid (made by decomposing phosphorus trichloride with water) with and without the addition of hydroxyphosphonic acid; the results all agreed within 0.8%. Several determinations of phosphoric acid gravimetrically and by reducing the molybdenum compound checked the standard procedure satisfactorily.

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[5] Scott, "Methods of Analysis," D. Van Nostrand Co., p. 316–317.

Two typical series of data are given in Table III; Table I is a summary of all results. The method of calculation and the significance of the symbols are described in the theoretical portion of this paper.

TABLE III

TYPICAL DATA

A. Phosphorus trichloride and benzaldehyde with no solvent

PCl_3 = 7.87 g. C_6H_5CHO = 6.07 g. Original density of mixture = 1.296. 1 cc. NaOH = 0.00699 g. PCl_3. Volume of pipet = 1.638 cc. Aliquot analyzed = 0.1 in each case.

Time from start hrs.	Volume decrease %	Net NaOH used Cc.	PCl_3 found for whole sample	Total PCl_3 in sample if unreacted	% PCl_3 reacted = 100 y	a	b	$x = ya$	$k_1 \times 10^3$	K
$^1/_{12}$	0.0	16.86	1.180	1.200	1.7	5.32	5.32	..	..	...
8	4.4	13.71	0.960	1.256	23.6	5.55	5.55	1.32	0.55	...
92	7.7	12.44	.870	1.300	33.1	5.78	5.78	1.89	..	0.126
118	7.7	12.54	.878	1.300	32.5					
164	7.7	12.48	.873	1.300	32.8					

B. Phosphorus trichloride and benzaldehyde in benzene

PCl_3 = 3.109 g. a = 0.9051 mole per liter. C_6H_5CHO = 2.43 g. b = 0.9161 mole per liter. Volume = 25 cc. 1 cc. NaOH = 0.00699 g. PCl_3. Volume of pipet = 1.638 cc. Aliquot analyzed = 0.25 in each case. Total PCl_3 in sample if unreacted = 0.2037 g.

Time from start hrs.	Volume decrease %	Net NaOH used Cc.	PCl_3 found for whole sample	Total PCl_3 in sample if unreacted	% PCl_3 reacted = 100 y	a	b	$x = ya$	$k_1 \times 10^3$	K
$^1/_{12}$	...	7.32	0.2048	...	−0.5	..	...	..	..	...
8.8	...	7.05	.1972	...	3.2	..	..	0.029	4.31	...
21.5	...	6.78	.1904	...	6.5	..	..	.058	3.91	...
28.0	...	6.48	.1816	...	10.9	..	..	.098	5.90	...
52.0	...	6.02	.1688	...	17.1	..	..	.154	6.09	...
93.0	...	5.64	.1580	...	22.5	..	..	.206	..	0.416
120.0	...	5.66	.1584	...	22.3					
164.5	...	5.56	.1556	...	23.6	Av. k_1 = 5.05 × 10^{-3}				

The Use of Water as a Condensing Agent

A mixture of 5 g. of benzaldehyde and 3.2 g. of phosphorus trichloride in 30 cc. of dry benzene was kept at 25°. Water was added drop by drop during half an hour, at the end of which time the benzene layer was extracted with water. The aqueous layer on evaporation yielded 1.8 g. of a solid which was identified by conversion into the aniline salt of α-hydroxybenzyl-phosphonic acid (m. p., 201–202°). In another experiment, 3.9 g. of benzaldehyde and 5 g. of phosphorus trichloride in 40 cc. of benzene yielded by the same procedure 1.1 g. of solid phosphonic acid, a yield of 16%.

To a mixture of 10 g. of benzaldehyde and 13 g. of phosphorus trichloride in a flask immersed in a freezing mixture, 1.7 g. of water (1 mole) was added drop by drop during 15 minutes, the mixture being violently agitated. Hydrogen chloride began to be evolved when about half of the water had been added. The flask was immersed in a water-bath at 10–15° until evolution of hydrogen chloride almost ceased. The loss in weight of the mixture corresponded to the evolution of one molecular equivalent of hydrogen chloride.' The resulting oil was light yellow; portions of it were used in the following experiments.

1. Five g. was treated with an excess of cold water in which it completely dissolved. A portion of this solution gave no precipitate with molybdic acid showing the absence of phostonic acid (see below). The aqueous solution was evaporated at room temperature by means of a current of air. The resulting oil was converted into an aniline salt by treatment with aniline in ethereal solution; 3.5 g. of aniline salt, m. p., 194–197°, was obtained, equivalent to 10 g. of phosphonic acid in the original mixture,

or a 57% yield. The salt after recrystallization from alcohol melted at 201–202° and was identified as the salt of hydroxybenzyl-phosphonic acid.

2. When 11.4 g. of the oil was gradually warmed to 50–60°, hydrogen chloride began to be evolved rapidly at room temperature. The resulting gum was heated for a few moments at 120° to expel the last of the hydrogen chloride. On cooling, the material was a reddish resin weighing 8.2 g. The loss in weight from the oil corresponded to one molecular equivalent of hydrogen chloride. The resin dissolved in water and the solution gave a voluminous precipitate with molybdic acid solution characteristic of the phostonic acid. Five g. of the resin was evaporated to dryness several times with dil. hydrochloric acid and an aniline salt prepared in the usual way; 3.5 g. (m. p., 190–195°) was obtained which after recrystallization melted at 201–202°.

A sample of the barium salt of anhydro α-hydroxy-benzylphosphonic acid (the phostonic acid) prepared and purified according to our early work[6] was dissolved in dil. nitric acid and when an excess of molybdic acid solution was added a voluminous white precipitate was formed; neither phosphorous acid nor the hydroxyphosphonic acid produced a precipitate under the same conditions. The test was delicate enough to detect 0.2 g. of phostonic acid in 150 cc. of solution. This test gave positive indications of large amounts of the phostonic acid in an aqueous solution obtained by decomposing an equilibrium mixture of benzaldehyde and phosphorus trichloride and also from reaction mixtures in which acetic acid or acetic anhydride had been used.

Summary

1. The kinetics of the reaction between benzaldehyde and phosphorus trichloride have been investigated. The combination of these two substances has been found to proceed to a definite equilibrium both in the absence of a solvent and in benzene solution. The composition of the equilibrium mixture is in accord with the law of mass action.

2. Our earlier explanation of the mechanism for the reaction between carbonyl compounds, phosphorus trichloride and acetic acid or anhydride assumed that this addition reaction was an intermediate step. This explanation must now be abandoned because the speed of this addition reaction has been found to be much too low to account for the experimental results obtained in acetic acid solution.

3. The gradual addition of small amounts of water to a mixture of benzaldehyde and the trichloride causes an irreversible reaction to take place. The product appears to be an open-chain phosphorus compound which easily loses hydrogen chloride forming a ring compound (a phostonic acid derivative). This fact vitiates our earlier conclusions that such compounds were formed from a primary cyclic addition product.

4. The reaction between the trichloride, an aldehyde and acetic acid must be either a direct interaction of the three molecules or a reaction in which some open-chain addition product of unstable nature is an intermediate. We incline to the latter alternative and favor an "inner salt" formula put forward previously on purely theoretical grounds.

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[6] Ref. 1, p. 2344.