THE ACTION OF PHOSPHORUS TRICHLORIDE ON ORGANIC ACIDS; MONOACETYL PHOSPHOROUS ACID.

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Received January 22, 1912.

It is a striking fact that the course of one of the most important type reactions in organic chemistry is not definitely known. Two different reactions for the action of phosphorus trichloride on organic acids are given in the latest editions of standard text books of organic chemistry. Thus, for the preparation of acetyl chloride Beilstein,[1] Meyer and Jacobson[2] and Gatterman[3] give the equation

(1) $3CH_3CO_2H + 2PCl_3 \longrightarrow 3CH_3COCl + P_2O_3 + 3HCl.$

Richter[4] and Holleman[5] give the equation

(2) $3CH_3CO_2H + PCl_3 \longrightarrow 3CH_3COCl + P(OH)_3.$

As indicated above, one equation represents the formation of the acid chloride and *phosphorous acid* while the other gives the acid chloride, *phosphorous oxide* and hydrochloric acid as the products of the reaction.[6] As a matter of fact, the evolution of hydrochloric acid in considerable quantities is always observed in carrying out this reaction and to explain this fact it has been assumed that the phosphorous acid, which is first formed, reacts with a second molecule of the trichloride to give free HCl and P_4O_6, which result is expressed in equation (1). This latter assumption is directly contradictory to the results of Thorpe and Tutton,[7] who showed that in the first place hydrogen chloride reacts very readily with P_2O_3 or P_4O_6, according to the following equation:

$$P_4O_6 + 6HCl \longrightarrow 2PCl_3 + 2H_3PO_3$$

They also showed that phosphorous acid and phosphorus trichloride react together only *very slowly* and probably in accordance with the following equation, confirming the work of Geuther[8] on this subject:

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[1] "Handbuch d. Org. Chem.," Ed. **1893**, Bd. I, 458.

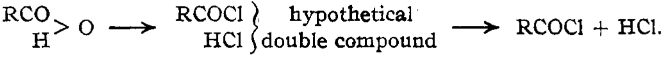
[2] "Lehrbuch d. Org. Chem.," 2nd Ed., **1907**, Bd. I, 561.

[3] "Practical Methods of Organic Chemistry." Translation of 4th German edition by W. B. Schober, **1905**, p. 122.

[4] "Organische Chemie." Eleventh Edition, Bonn, 1909. To prepare acetyl chloride the author recommends the proportions required by equation [1].

[5] "Organic Chemistry." A. F. Holleman. Translation of 2nd Dutch edition by A. J. Walker, New York (**1904**), p. 114.

[6] Delacre (*Chem. Zentr.*, **1902**, I, 1197) agrees with equation (1) and advances the theory that the mechanism of the reaction is probably



$$\begin{matrix}RCO\\H\end{matrix}\!\!>O \longrightarrow \left.\begin{matrix}RCOCl\\HCl\end{matrix}\right\}\begin{matrix}\text{hypothetical}\\\text{double compound}\end{matrix} \longrightarrow RCOCl + HCl.$$

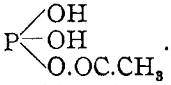
There is no experimental evidence of the existence of such a double compound and in view of the data brought forward in the present paper such an assumption is not in accord with the facts. Tissier (*Ann. chim. phys.*, [6] **29**, 384) advanced the equation $6RCO_2H + 3PCl_3 \longrightarrow 6RCOCl + H_3P_3O_6 + 3HCl.$

[7] *J. Chem. Soc.*, **59**, 1019 (1891).

[8] *J. prakt. Chem.*, [2] **8**, 359 (1874).

$$PCl_3 + 4P(OH)_3 \longrightarrow 3H_3PO_4 + P_2 + 3HCl$$

Thus Thorpe and Tutton obtained 4.0 g. PCl_3, 1.5 g. H_3PO_4, 2.7 g. H_3PO_3 and 0.4 g. phosphorus from 5.0 g. P_4O_6 and an excess of hydrogen chloride in an experiment which lasted one week. Therefore, if this work of Thorpe and Tutton and of Geuther is correct, and there appears to be no reason to doubt it, the liberation of the large quantities of hydrochloric acid in the preparation of the chlorides of organic acids by phosphorus trichloride cannot result from the action of the chloride on phosphorous acid. However, the work of Thorpe and Tutton[1] and of Thorpe[2] is contradictory since in the latter publication the author considers that the yields[3] point definitely to equation (1).

I have found that one source of the hydrogen chloride evolved in the reaction in question is the reaction of acetyl chloride on phosphorous acid yielding an acetyl derivative, probably a mixed acid anhydride of the formula  $P\left\langle\begin{matrix}OH\\OH\\O.OC.CH_3\end{matrix}\right.$. On adding pure acetyl chloride to crystallin phosphorous acid hydrogen chloride is evolved, slowly at 20° but quite rapidly on warming to 50°. One and possibly two hydroxyl groups enter into the reaction, depending upon the duration of the reaction and the removal of the hydrochloric acid.

The well known use of acid chlorides in testing for hydroxyl groups appears not to be strictly limited to alcohols since, as is well known, the chlorides of organic acids may also react with the hydroxyl in the carboxyl group, forming anhydrides, the degree of completion of the reaction depending upon the removal of hydrogen chloride. According to Anschütz,[4] the reaction between acetyl chloride and acetic acid is slow and incomplete, but Wedekind[5] has stated that the addition of a tertiary amine serves to remove hydrochloric acid and good yields of anhydride may be obtained in this manner. In phosphorous acid there are two and possibly three hydroxyl groups[6] and it is therefore to be expected that the chlorides of organic acids will react with it, giving a mixed acid anhydride. I have found that warming to the boiling point of acetyl

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[1] *Loc. cit.*

[2] *J. Chem. Soc.*, 37, 186 (1880).

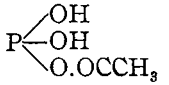
[3] Thorpe does not describe the methods employed by him to determin the yields of hydrochloric acid and acetyl chloride. As ordinarily carried out, both phosphorus trichloride and acetyl chloride are carried over by the hydrochloric acid in considerable quantities, and furthermore the acetyl chloride obtained, when the amounts of the reacting substances required by equation (1) are taken, contains much phosphorus trichloride and hydrochloric acid. It is obviously impossible to arrive at quantitative data, with respect to these products, by fractional distillation.

[4] *Ann.*, 226, 5 (1884).

[5] *Ber.*, 34, 2070 (1901). Compare Tschitschibabin, *Chem. Zentr.*, 1901, II, 543.

[6] Compare Vorländer, *Ann.*, 320, 114 (1902).

chloride under a return condenser removes the hydrogen chloride completely enough for the reaction to proceed smoothly.

The compound  $P\begin{cases}OH\\OH\\O.OCCH_3\end{cases}$ is analogous with the so-called mixed acid anhydrides recently prepared by Fry, Francis, and Pictet and his students. Acetic anhydride and nitric anhydride give the nitrate CH_3COONO_2,[1] benzoyl chloride and silver nitrate give benzoyl nitrate[2] and chromyl chloride and potassium acetate yield the diacetyl derivative of chromic acid.[3] Acetyl compounds of boric and arsenious acids are also known, the former being easily prepared by the action of acetyl chloride on boric acid. A mixed anhydride of phosphoric and acetic acids of doubtful composition was made by Carius and Kämmerer[4] to which they assigned the formula $P_2H_3O_5(C_2H_3O)_2$ and stated that it was decomposed by water to acetic and phosphoric acids. Menschutkin[5] attempted to prepare an acetyl derivative of phosphorous acid by heating with acetyl chloride to 120° in a bomb tube. The reaction product was *poured into water* and a lead salt prepared which contained organic matter and which the author regarded as probably $P_2H_3O_3(C_2H_3O)$.

In addition to the isolation of monoacetylphosphorous acid I have proven that when acetyl chloride is prepared according to equation (1) no phosphorous oxide is formed, the residue consisting of phosphorous acid and a small amount of the acetyl derivative. The phosphorus trichloride in excess of that required by equation (2) was recovered unchanged. Furthermore the evolution of hydrochloric acid from the action of acetyl chloride on pure crystallin phosphorous acid has been determined quantitatively and although a diacetyl derivative has not been isolated the amount of hydrochloric acid given off under certain conditions seems to indicate that a diacetyl derivative may be formed.

Discussion of the Reaction.

Since chlorides of organic acids may be prepared by treating the acid with hydrogen chloride and a dehydrating agent, it is not unreasonable to assume that the reaction under discussion is catalyzed by a trace of water and that the phosphorus trichloride serves both as a source of hydrochloric acid and as a dehydrating agent. However, in view of the results of Autenrieth and Geyer[6] on the reaction between phosphorus pentachloride and phenols it seems probable that the chlorides of phosphorus are able to react directly with hydroxyl in any compound. More-

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[1] Pictet and Khotinsky, *Ber.*, 40, 1163 (1907).

[2] Francis, *Ibid.*, 39, 3798 (1906).

[3] Fry, THIS JOURNAL, 33, 690 (1911).

[4] *Ann.*, 131, 170 (1864).

[5] *Ibid.*, 133, 317 (1865).

[6] *Ber.*, 41, 146 (1908).

over, it is shown in the present communication that the chloride of the acetyl group, which radical possesses only a small negative polarity,[1] reacts with phosphorous acid, which is a comparatively strong acid. The known data concerning the reactivity of other acid chlorides upon hydroxyl derivatives are extremely meager, but it appears reasonable to assume that the point of equilibrium in such reactions will depend upon the relative polarity of the atoms or radicles bound to the hydroxyl group or chlorine atoms. A very similar reaction is that of benzene sulfochloride on alcohol, the velocity of which is accelerated by the substitution of chlorine, bromine or iodine in the phenyl group.[2] It is almost impossible to prepare trichloracetyl chloride by the action of phosphorus trichloride on trichloracetic acid, the yield being extremely small. The ease with which such weak acid-forming substances as $AsCl_3$, $SbCl_3$, $SiCl_4$, $AlCl_3$, $FeCl_3$ and $COCl_2$ hydrolyze with water suggests that our knowledge of the behavior of these substances toward hydroxyl derivatives could be very greatly extended.

Experimental Part.

Action of Acetyl Chloride on Phosphorous Acid.—The liberation of hydrogen chloride by the action of acetyl chloride on pure, crystallin phosphorous acid was quantitatively measured in the following manner: The reaction mixture was warmed to 50° under a return condenser and the hydrochloric acid liberated was absorbed in water. An aliquot part of the aqueous acid solution was titrated for total acidity and then for total chlorine as chloride. The hydrochloric acid set free and acetyl chloride carried over may readily be calculated from these results. Thirty-five grams of acetyl chloride were added to 10 g. crystallin phosphorous acid. The liberation of hydrochloric acid began at room temperature and at 50° was quite rapid. At the end of two hours the aqueous solution in which the gases were absorbed was titrated and the results found may be stated as follows:

	Grams.
Hydrogen chloride liberated	6.734
Hydrogen chloride calculated for mono-acetyl derivative	4.44
Acetyl chloride carried over	3.214

A repetition of the above experiment, using 15.6 g. phosphorous acid and 35.0 g. acetyl chloride, gave, in $1^1/_2$ hours:

	Grams.
Hydrogen chloride liberated	7.677
Hydrogen chloride calculated for mono-acetyl derivative	6.65
Acetyl chloride carried over	2.115

A third experiment was made with the hope of isolating an acetyl

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[1] Derick, THIS JOURNAL, 33, 1156 (1911).

[2] Goubeau, *Chem. Zentr.*, 1911, II, 18.

compound of phosphorous acid. In this experiment 75 g. acetyl chloride set free 28.61 g. of hydrochloric acid from 65 g. phosphorous acid during 4 hours on the water bath. A white crystallin crust formed on the surface of the phosphorous acid, but it was found to be impossible to isolate this substance in a pure condition.

The mono-acetyl derivative of phosphorous acid was prepared in a state of purity in the following way: Five grams of phosphorous acid were diluted in 40 cc. acetic anhydride at room temperature. To this solution 10 cc. acetyl chloride were added and the mixture warmed to 50°, at which temperature a white crystallin substance was deposited. After standing for 20 minutes at this temperature the supernatant liquid was decanted, the crystals washed five times with dry ether and the remaining ether removed at ordinary temperature by exhausting to 10 mm.

The substance was analyzed by heating with fuming nitric acid to 160° in a bomb tube. The phosphoric acid thus obtained was determined gravimetrically.

0.2403 g. substance gave 0.2210 g. $Mg_2P_2O_7$ corresponding to 25.30% phosphorus; calculated for $CH_3CO.PO_3H_2$, 25.00% P.

Attempts to prepare this substance by employing acetic anhydride alone gave brown, tarry smears which were not further investigated. It was also observed that phosphoric anhydride reacts energetically with acetic anhydride with charring and evolution of considerable heat.

Action of Phosphorus Trichloride on Acetic Acid.—In the first experiment of this series 40 g. phosphorus trichloride (1 molecule) and 52.5 g. acetic acid (3 molecules) were employed. The two substances were simply poured together and warmed on the water bath for half an hour under a return condenser, in the usual manner. The gases were absorbed in water as in the previous experiments. It was assumed that both phosphorus trichloride and acetyl chloride would be carried over in considerable quantities with the hydrogen chloride. These substances were quantitatively determined in the following manner: Phosphorus trichloride was calculated from a determination of phosphorous acid, the latter substance being determined by boiling an aliquot part of the solution with bromine water and determining the phosphoric acid thus formed. Acetyl chloride was calculated from the acetic acid formed. The acetic acid was determined from the total acidity minus the phosphorous and hydrochloric acids. (It was found to be possible to titrate phosphorous acid with sodium hydroxide against phenolphthalein within about 1.0% of the correct value, since the hydrolysis of Na_2HPO_3 in concentrated solutions is very slight.) The total chlorine was determined by titration with silver nitrate. The experiment may be summarized as follows:

	Grams.
Gases:	
Hydrogen chloride liberated	10.67
Hydrogen chloride calculated for [1] Thorpe's equation	15.91
Acetyl chloride carried over	7.347
Phosphorus trichloride carried over	0.452
Distillate:	
Weight of crude distillate (acetyl chloride and acetic anhydride)	43.0
Weight of distillate boiling from 50–55°	20.2
Total acetyl chloride formed approximately	27.5
Residue:	
Weight	28.4
Weight of residue calculated for P_4O_6	15.8
Weight of residue calculated for H_3PO_3	24.2
Weight of residue minus acetic acid removed by distillation with steam	23.6

The residues evidently consisted of phosphorous acid and a small proportion of the acetyl derivative. The residue was heated to 100°–105° and a vacuum of 14 mm. applied but nothing distilled over. It is therefore conclusively shown that no phosphorous oxide is formed under these conditions, since this substance is a liquid distilling in a vacuum of 18 mm. at 64.4°. The residue completely freed from acetyl chloride and acetic anhydride by this treatment was subjected to steam distillation and 5.07 g. acetic acid obtained. From the above facts it is probable that in the formation of the acetyl derivative present in the residue, phosphorous acid itself is first formed.

Action of Phosphorus Trichloride on Acetic Acid According to Thorpe's Equation.—In the following experiment 35 g. of phosphorus trichloride (2 mol.) were added to 22.8 g. glacial acetic acid. The experimental procedure and methods of calculation were the same as in the previous experiments, the reaction mixture being warmed on the water bath for one-half hour. The results obtained may be summarized as follows:

	Grams.
Gases:	
Hydrogen chloride liberated	3.808
Acetyl chloride carried over	5.250
PCl_3 carried over	1.203
Distillate:	
Acetyl chloride	23.44
PCl_3	11.15
Hydrogen chloride	0.94
Residue:	
Weight	13.1

The distillate was analyzed by pouring into water and determining the phosphorous acid, hydrochloric acid and acetic acid as described above. The large amount of phosphorus trichloride recovered is particularly worthy of note. The residue could not be distilled at 100°

and 14 mm. Analysis showed it to contain 36.02% phosphorus; calculated for H_3PO_3, 37.80%.

These facts show conclusively that also under these conditions no phosphorous oxide is formed. Equation (1) is therefore wrong.

The low per cent of phosphorus in the residue and the hydrochloric acid liberated are probably due to the formation of a small amount of the mixed anhydride.

The Formation of Acetic Anhydride.—Thorpe suggested that the formation of acetic anhydride in his experiments might have been due to the dehydrating action of the phosphorous oxide on acetic acid or to the action of acetyl chloride on acetic acid. According to my results the latter view is the correct one.

As the preparation of acetyl chloride is ordinarily carried out the yield is considerably diminished by the formation of acetic anhydride, unless a large excess of PCl_3 is taken. It is commonly observed that if the quantities required by equation (1) are taken, little or no acetic anhydride is formed. The reason for this becomes readily apparent if one considers the equilibrium

$$CH_3COOH + CH_3COCl \leftrightarrows (CH_3CO)_2O + HCl,$$

and the effect which the addition of PCl_3 would have upon such a mixture in equilibrium. Obviously, the result would, by the removal of acetic acid with the formation of more acetyl chloride, lead to the conversion of more anhydride into chloride, *provided* that the hydrogen chloride had not been removed by the return condenser route. If this is the function of the excess of phosphorus trichloride it should be possible to obtain acetyl chloride by passing hydrochloric acid into a mixture of acetic anhydride and phosphorus trichloride. This is corroborated by the following experiment:

Dry hydrogen chloride was passed into a mixture of 25 g. acetic anhydride (3 molecules) and 15 g. phosphorus trichloride ($1^1/_4$ molecules). Hydrogen chloride was rapidly absorbed, the solution becoming warm and depositing phosphorous acid. Distillation gave 36.5 g. acetyl chloride boiling between 50–57°, the theoretical yield being 38.4 g. Doubtless a small quantity of acetylphosphorous acid was also formed.

The results of the above experiment indicated that on the preparation of acetyl chloride according to equation (2), as ordinarily done in the laboratory, *i. e.*, under a return condenser, the hydrochloric acid necessary for the conversion of the acetic anhydride into the chloride is removed from the reaction mixture. This view is supported by the following experiment: Twenty-five grams of glacial acetic acid (3 molecules) were treated with 24 g. phosphorus trichloride ($1^1/_4$ molecules) and the reaction mixture allowed to stand at 18° for six hours under a slight pressure (equal to 10 cm. concentrated sulfuric acid). A small amount of hydrochloric acid was slowly and regularly given off. On distillation 31.0 g. acetyl chloride boiling from 50° to 55° were obtained; theoretical yield, 32.5 g. It is therefore evident that the formation of acetic anhydride can be reduced to almost nil by a simple modification of the experimental conditions. So far as reduction of the yield of chloride is concerned the formation of acetic anhydride is usually a more serious factor than the formation of acetylphosphorous acid.

In conclusion, it might be stated that the yellow or brown color of the phosphorous acid residue, which is often assumed to be due to phosphorus, is probably due to the decomposition of acetylphosphorous acid since it has been observed that at approximately 100° this substance melts with slight decomposition turning yellow to brown in color.

Summary.

It has been proven that the action of phosphorus trichloride on acetic acid may be represented by the following equations:

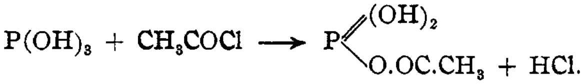
(*a*) $$3CH_3COOH + PCl_3 \longrightarrow CH_3COCl + H_3PO_3$$

Two secondary reactions take place, the most important of which is expressed by the reaction

(*b*) $$CH_3COOH + CH_3COCl \leftrightarrows (CH_3CO)_2O + HCl.$$

This reaction may be minimized by a simple modification of the conditions of the experiment. The secondary reaction next in importance is the formation of a mixed anhydride of phosphorous and acetic acids expressed by the equation

(*c*)



$$P(OH)_3 + CH_3COCl \longrightarrow P\begin{cases}(OH)_2 \\ O.OC.CH_3\end{cases} + HCl.$$

The equation, given in many standard books, expressing the reaction of phosphorus trichloride on acetic acid with the formation of phosphorous oxide is unqualifiedly wrong.

It is obviously possible to extend and amplify this investigation in many directions, and the author regrets that the press of other work prevents further experiments along these lines.

The author desires to express his indebtedness to Professor William McPherson, of Ohio State University, for first calling his attention to our unsatisfactory knowledge of the reaction discussed above.

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