CLVIII.—*The Interaction of Metallic Oxides and Phosphoryl Chloride, Alone and in the Presence of Certain Organic Compounds.*

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Apatite, $(Ca_3P_2O_8)_3,CaF_2$, and wagnerite, $Mg_3P_2O_8,MgF_2$, are two important minerals, the formulæ of which are usually written as indicated, suggesting that the compounds are to be regarded as complex derivatives of the metallic fluoride (or, in some cases, chloride), in which the halogen is directly attached to the metal.

There is, however, little experimental foundation for such an assumption, and in some ways it is perhaps more probable that the halogen is more closely associated with the phosphorus.

The following investigation was commenced in the hope that by preparing simple chlorophosphates and determining their constitution, it would be possible to throw light on the nature of more complex halogen compounds such as the above.

We found that when freshly ignited lime and freshly distilled phosphoryl chloride were mixed and allowed to remain at the ordinary temperature or gently boiled, a well crystallised compound was gradually formed, which analysis showed to have the formula $CaO,2POCl_3$.

This behaviour is not restricted to lime, and magnesia gives either $MgO,2POCl_3$ or $MgO,3POCl_3$, according to the conditions of the experiment. We have also obtained well crystallised compounds, $MnO,3POCl_3$ and $ZnO,3POCl_3$, but not in an absolutely pure state, owing to various difficulties which will be referred to shortly. Lime also yields a compound with three molecules of phosphoryl chloride in certain circumstances.

All the other metallic oxides which we have investigated (CdO, CoO, CuO, Cu_2O, HgO, Al_2O_3, Fe_2O_3) react with phosphoryl chloride, but apparently not in such a simple manner as do lime and magnesia, and the chloride of the metal appears to be the chief product.

As was to be expected, these compounds of phosphoryl chloride are extremely sensitive to moisture, and in consequence of this the analyses often show low values for the chlorine, and a deficit, sometimes of several per cent., which it is almost impossible to prevent entirely.

In such cases, if the deficit is taken to be due to the replacement of a certain amount of chlorine by hydroxyl, it is found that the atomic ratio of the total chlorine to phosphorus is almost exactly as three to one, as it should be, of course, for a compound of phosphoryl chloride.

Having found that phosphoryl chloride and certain oxides readily combined to give the compounds above mentioned, the effect of solvents on the course of the reaction was investigated.

It was found that when lime was added to a solution of phosphoryl chloride in acetone, ethyl acetate, methyl benzoate, or ethyl benzoate, which had been dried over calcium chloride and redistilled, a vigorous reaction occurred, which in the first two cases was sufficient to cause the solvent to boil. Some hydrogen chloride is evolved during this process, and the lime passes into solution. The solution on cooling deposits beautiful prismatic crystals, the analyses of which correspond very closely with the formulæ:

$CaO,P_2O_3Cl_4,2C_3H_6O$; $CaO,P_2O_3Cl_4,2C_4H_8O_2$; $CaOP_2O_3Cl_4,2C_8H_8O_2$; and $CaO,P_2O_3Cl_4,2C_9H_{10}O_2$.

These compounds are clearly the compound $CaO,P_2O_3Cl_4$ crystallised with two molecules of ketone or ester. In agreement with this view is the fact that the organic part of the molecule can be changed by simple recrystallisation from another solvent. Thus by recrystallising the ethyl acetate compound from acetone, the acetone compound is obtained and vice versa.

Exactly similar organic derivatives have been obtained, using magnesium oxide and manganous oxide.

The formation of these organic compounds is brought about by traces of moisture present in the organic solvents, or which are absorbed during the course of the experiment, and there is some reason for thinking that the moisture acts preferably on the previously formed compound $CaO,2POCl_3$, rather than on the phosphoryl chloride. In any case, the organic compounds can be obtained equally well by treating the previously prepared compound $CaO,2POCl_3$ with the organic solvent in which it dissolves, yielding a solution from which the organic derivative of the compound $CaO,P_2O_3Cl_4$ crystallises.

The compounds of pyrophosphoryl chloride, $P_2O_3Cl_4$, obtained by us seem of especial interest as confirming the results obtained by Besson (*Compt. rend.*, 1897, **124**, 1099), who showed that this compound is the first product of the action of moisture on phosphoryl chloride which can be isolated. He was, however, never able to obtain more than a very small amount of pyrophosphoryl chloride in this way. It is therefore of interest to obtain derivatives of this compound which indicate quantitative conversion of phosphoryl chloride into pyrophosphoryl chloride, derivatives, moreover, which are well crystallised and well defined. On solution of these in water, orthophosphoric acid is formed immediately, and this is in agreement with the behaviour of pyrophosphoryl chloride itself, as stated by Geuther and Michaelis (*Ber.*, 1871, **4**, 766).

No compounds of phosphoryl chloride with oxides have been obtained by previous workers, and from what has been said it will be seen that the statement found sometimes (Dammer "Handbuch," 1894, II., **1**, 134; Casselmann, *Annalen*, 1856, **98**, 228) that phosphoryl chloride reacts with metallic oxides to form chloride and phosphate of the metal requires qualifying. Gustavson (*J. Russ. Phys. Chem. Soc.*, 1871, **3**, 225) showed that boron trioxide and phosphoryl chloride react with formation of a double compound, $BCl_3,POCl_3$.

The oxidic compounds described in the present paper seem of especial interest from the fact that any salt-like character is only very feebly developed, their behaviour being more typical of that of "molecular compounds." This is unusual in the case of metallic oxides which usually give rise to salts. We consider, however, that there is no fundamental structural difference between, for example, $CaO,2POCl_3$ and $CaO,2PO(OH)_3$ [$CaH_4P_2O_8,H_2O$], and that from some points of view the first compound may be regarded as derived from the second by replacement of the hydroxyl groups by chlorine. It seems to us also that the existence of such compounds as $CaO,2POCl_3$ lends some support to the view that even in compounds like apatite and wagnerite the halogen is directly attached to phosphorus. We are seeking further evidence in favour of this view.

We hope to discuss the precise nature of the compounds of phosphoryl chloride and pyrophosphoryl chloride in another paper, as well as the mechanism of the reaction between phosphoryl chloride and metallic oxide which leads to the formation of metallic chloride in certain cases.

EXPERIMENTAL.

Reactions between Oxides and Phosphoryl Chloride.

In the following experiments the freshly ignited oxide was added to excess of freshly distilled phosphoryl chloride. The mixture enclosed in a sealed tube was, except when otherwise stated, heated to 110° in an oil-bath until examination showed that the oxide had reacted completely. The crystalline solid was then collected, and drained on porous plate in a desiccator containing potassium hydroxide and sulphuric acid until dry and powdery. In all these operations precautions were taken to exclude moisture as far as possible.

$CaO,2POCl_3$.—The quantities of lime and phosphoryl chloride employed averaged about 0·56 gram and 10 c.c. respectively. The lime was gradually converted into a crystalline powder consisting of small, rectangular prisms. The length of time required for this transformation varied considerably, but was never less than two days at 110°. The following analyses refer to different preparations:

Found: CaO = 16·16, 16·22, 15·15; P_2O_5 = 38·62, 39·33, 39·92; Cl = 58·58, 56·16, 57·89.

$CaO,2POCl_3$ requires CaO = 15·43; P_2O_5 = 39·1; Cl = 58·64 per cent.

From the appearance of the crystals formed, it is clear that the compound $CaO,2POCl_3$ is also formed when lime and phosphoryl chloride interact at 25° or at the room temperature, but the change taking place very slowly under these conditions has not time for completion before a further change sets in. This causes the contents of the tube to become pasty, owing to the formation of a very fine solid. We have not been able to obtain satisfactory analyses of this solid owing to the difficulty of separating it from the excess of phosphoryl chloride, but those we have made point to the formation of a compound $CaO,3POCl_3$.

The compound $CaO,2POCl_3$ is exceedingly sensitive to moisture, and dissolves at once in water, yielding a strongly acid solution.

$MgO,2POCl_3$ *and* $MgO,3POCl_3$.—Magnesium oxide reacts far more readily with phosphoryl chloride than does lime, which is probably chiefly due to the fact that the magnesium compound is markedly soluble in phosphoryl chloride, whereas the calcium compound is insoluble.

On heating magnesium oxide and phosphoryl chloride in a sealed tube to 110°, one of two things may happen: either the oxide is slowly converted into a crystalline compound without any marked evidence of solution, or else practically all the oxide may dissolve. The solution obtained in the latter case deposits large (5 mm.) and well defined crystals on cooling, although it may remain supersaturated for a considerable time.

The compound obtained in the first case consists of $MgO,2POCl_3$, and in the second case of $MgO,3POCl_3$.

Which course the reaction takes seems to be more or less a matter of accident:

Found: MgO = 11·14; P_2O_5 = 42·38; Cl = 62·95.

$MgO,2POCl_3$ requires MgO = 11·60; P_2O_5 = 40·88; Cl = 61·33 per cent.

Found: MgO = 7·8; P_2O_5 = 43·2; Cl = 63·2.

$MgO,3POCl_3$ requires MgO = 8·07; P_2O_5 = 42·52; Cl = 63·79 per cent.

The phosphoryl chloride in these compounds is relatively loosely held. It can be slowly removed by simply washing with light petroleum or by the action of heat. Then again the chemical behaviour of the compounds described is very similar to that of phosphoryl chloride itself. Thus, when the compound $CaO,2POCl_3$ is treated with moist air or alcohol, all the chlorine is removed as hydrogen chloride; whilst one molecule of $CaO,2POCl_3$ reacts with 8 molecules of aniline or 12 molecules of ammonia just as two molecules of phosphoryl chloride would.

From this behaviour it is to be concluded that the compounds described in this paper belong to that large group of compounds called, somewhat vaguely, "molecular compounds."

$MnO,3POCl_3$.—Manganous oxide is slowly converted into a very pale pink substance when heated to 110° with phosphoryl chloride. This seems to consist chiefly of manganous chloride with a considerable amount of the compound $MnO,3POCl_3$. The latter is sparingly soluble in phosphoryl chloride, which renders its separation from the manganous chloride possible. The mixture of manganous oxide and phosphoryl chloride is sealed up in a fairly long, stout tube bent at an angle of about 90°. The materials are heated in one limb to 110° until the liquid is saturated, when it is carefully decanted into the other limb, where, on cooling, crystals of the compound $MnO,3POCl_3$ are deposited. The liquid is then poured back into the other limb and again saturated, and these processes continued until sufficient crystals have accumulated. The tube is then opened, and the solid products separated for analysis. It is not easy to obtain more than a small quantity of the compound in this way, and owing to the smallness of the crystals the difficulty of separating and handling it is intensified. The result is that a considerable amount of moisture is almost inevitably absorbed, so that the analyses are not very satisfactory:

Found: $MnO = 13{\cdot}14$; $P_2O_5 = 41{\cdot}3$; $Cl = 53{\cdot}52$.

$MnO,3POCl_3$ requires $MnO = 13{\cdot}35$; $P_2O_5 = 40{\cdot}08$; $Cl = 60{\cdot}12$ per cent.

After allowing for the oxygen-equivalent of the chlorine there is a deficit of 4·44 per cent. due to moisture absorbed during the handling and in the desiccator, this moisture being partly present as such, and having partly reacted with the chlorine to evolve hydrogen chloride.

During one experiment the formation of large, pink crystals was observed at one stage. These were not, however, separated, and could not be obtained again. They very possibly consisted of the compound $MnO,2POCl_3$, for we have obtained a beautiful ethyl acetate derivative of this compound, $MnO,P_2O_3Cl_4,2C_4H_8O_2$, which will be described presently.

Action of Phosphoryl Chloride on Zinc Oxide.—Large amounts of zinc oxide will dissolve in phosphoryl chloride at the ordinary temperature with considerable ease. If the phosphoryl chloride be in moderate excess, about ten days are required for complete solution; the less the excess of phosphoryl chloride the longer is the time required, and the more viscous is the resulting clear solution. When the reagents were mixed in the proportion of one molecule of zinc oxide to two of phosphoryl chloride, and the tube left on its side so as to bring a large surface of the oxide in contact with the liquid, a homogeneous solution which was so viscous as almost to constitute a glass was obtained after six months.

A mixture in the proportion of one molecule of zinc oxide to three of phosphoryl chloride had, after three months, deposited crystals consisting chiefly of small, rhombic plates, possibly mixed with some of another kind. The solution, originally viscous, was now quite mobile.

Analysis of the crystals gave:

Found: $ZnO = 22{\cdot}40$; $P_2O_5 = 32{\cdot}86$; $Cl = 56{\cdot}81$.

Allowing for the oxygen equivalent of the chlorine, we have $112{\cdot}07 - 12{\cdot}80 = 99{\cdot}27$, showing a deficit (moisture) of 0·73 per cent.

This corresponds very closely with a mixture of 76·93 per cent. of the compound $ZnO,3POCl_3$ and 23·07 per cent. of zinc chloride.

The action of heat on the clear solutions of zinc oxide in phosphoryl chloride is somewhat peculiar. On raising the temperature they become turbid, and gradually separate into two liquid layers, the lower of which is more viscous than the other. The temperature at which this separation begins depends on the concentration of the zinc oxide. The greater the concentration the lower is the temperature required. If too little zinc oxide is present, no separation may occur, even at 100°. With one gram of zinc oxide in about 15 grams of phosphoryl chloride, separation into two layers began at 56°. On gradually raising the temperature, while more and more of the lower viscous layer separated, it at the same time gave off bubbles of the more mobile liquid, and became in consequence still more viscous. The mutual solubility of the two liquids clearly diminishes with rise of temperature; on cooling, the two again mix completely.

An experiment was performed in which a solution of zinc oxide in phosphoryl chloride was heated to 100° in a wide tube sealed at one end to a narrow one. The tube was held vertically, so that the viscous liquid collected in the narrow part. When separation was complete, the tube was removed from the bath, and inverted to separate the mobile from the viscous liquid. The latter on cooling became almost a glass, and the portion of the tube containing it was cut off. It was weighed, and the contents analysed:

Found: $ZnO = 21 \cdot 24$; $P_2O_5 = 36 \cdot 45$; $Cl = 54 \cdot 61$.
$ZnO,2POCl_3$ requires $ZnO = 20 \cdot 96$; $P_2O_5 = 36 \cdot 60$; $Cl = 54 \cdot 81$ per cent.

It is doubtful whether such a product can be regarded as a definite compound.

Action of Phosphoryl Chloride on Other Oxides.—Cadmium, cobaltous, cupric, cuprous, mercuric, ferric, and aluminium oxides all react with phosphoryl chloride, both at the ordinary temperature and when heated to 100°, but the rate of reaction is in most cases slow, and varies considerably. In all cases the colour of the product formed is that of the anhydrous chloride, of which it seems chiefly composed. We have only actually separated and analysed the solid in the case of cadmium and cupric oxides. In the case of ferric oxide a large amount dissolves in the phosphoryl chloride, which becomes dark reddish-brown.

Owing to the difficulty of separation, the analysis of the cadmium product was not satisfactory, but was sufficient to show that one was dealing with a mixture containing a large percentage of cadmium chloride.

The product obtained from cupric oxide could be more easily handled, and two experiments gave the following analytical results:

Found: $CuO = 46 \cdot 96, 55 \cdot 51$; $P_2O_5 = 14 \cdot 31, 16 \cdot 36$; $Cl = 46 \cdot 54, 37 \cdot 51$.

The second experiment was carried out in a sealed tube, and several weeks were required for all the oxide to react. The analysis corresponds closely with a mixture of 25·48 per cent. of copper metaphosphate* and 74·52 per cent. of cupric chloride, although there is slightly too much copper, probably present as unaltered oxide.

In the first experiment, which was carried out in a flask fitted with ground-in air condenser and calcium chloride drying tube, the reaction only required twenty-four hours, but the analysis shows a deficit of 2·77 per cent. If this is regarded as moisture which has replaced chlorine by hydroxyl, the analytical figures would indicate a mixture of 38·97 per cent. of the compound $CuO,2POCl_3$ and 61·03 per cent. of cupric chloride.

Compounds of the Type $MO,P_2O_3Cl_4,2X$ (where X = the organic

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* On treating the product with water a slate-coloured solid (probably the metaphosphate) separated, which only dissolved slowly after the addition of nitric acid.

solvent).—These were all obtained by adding the freshly ignited oxide to a solution of phosphoryl chloride in the organic liquid, which had been dried over calcium chloride and freshly distilled. It is best to only use a little more than two molecules of phosphoryl chloride to one of oxide. Solution was assisted when necessary by gentle heating, the mixture being contained in a flask with ground-in air condenser closed by a calcium chloride tube. The solution was then allowed to crystallise in a desiccator containing solid potassium hydroxide and concentrated sulphuric acid. The crystals separating were washed with a small quantity of the solvent, drained on porous plate in the desiccator, and analysed. Under these conditions sufficient moisture was present in the solvent or absorbed during the experiment to effect the displacement of the two atoms of chlorine. The hydrogen chloride thus formed can be absorbed and estimated, as was actually done in one or two cases. On solution in water these compounds are completely decomposed with separation of the organic portion of the molecule—which in a few cases was directly estimated. As a rule, however, it was obtained by difference.

$CaO,P_2O_3Cl_4,2(CH_3{\cdot}CO{\cdot}CH_3)$.—This forms beautiful transparent crystals several mm. long, which are sparingly soluble in cold acetone. During the preparation of this compound the solution becomes brown owing to the condensing action of the liberated hydrogen chloride on the acetone. By carefully washing the crystals they can be obtained colourless, and then keep fairly well in a sealed tube. If not properly washed they soon become brown:

Found: $CaO = 13{\cdot}73, 13{\cdot}48$; $P_2O_5 = 33{\cdot}23, 34{\cdot}20$; $Cl = 33{\cdot}13, 34{\cdot}08$; C_3H_6O (by diff.) $= 27{\cdot}37, 25{\cdot}92$.

$CaO,P_2O_3Cl_4,2C_3H_6O$ requires $CaO = 13{\cdot}21$; $P_2O_5 = 33{\cdot}49$; $Cl = 33{\cdot}45$; $C_3H_6O = 27{\cdot}39$ per cent.

In the second experiment the crystals had been left for forty-eight hours in an evacuated desiccator containing sulphuric acid, and had evidently lost a little acetone.

$MnO,P_2O_3Cl_4,2(CH_3{\cdot}CO{\cdot}CH_3)$.—In this case a considerable amount of manganous chloride is formed, from which the acetone solution must be decanted. On crystallisation, small prisms of a pale pink colour are obtained. The analysis is not very satisfactory, probably owing to the presence of a certain amount of manganous chloride:

Found: $MnO = 16{\cdot}44$; $P_2O_5 = 31{\cdot}66$; $Cl = 33{\cdot}14$; C_3H_6O (by diff.) $= 26{\cdot}24$.

$MnO,P_2O_3Cl_4,2C_3H_6O$ requires $MnO = 16{\cdot}78$; $P_2O_5 = 33{\cdot}59$; $Cl = 33{\cdot}55$; $C_3H_6O = 23{\cdot}65$ per cent.

$CaO,P_2O_3Cl_4,2(C_2H_5·O·CO·CH_3)$. — This compound crystallises readily in long prisms, only sparingly soluble in cold ethyl acetate:

Found: CaO = 11·69; P_2O_5 = 29·57; Cl = 29·14; $C_4H_8O_2$ (by diff.) = 36·27.

$CaO,P_2O_3Cl_4,2C_4H_8O_2$ requires CaO = 11·57; P_2O_5 = 29·34; Cl = 29·31; $C_4H_8O_2$ = 36·39 per cent.

$MgO,P_2O_3Cl_4,2(C_2H_5·O·CO·CH_3)$.—This was prepared in just the same way as the calcium compound. The ethyl acetate solution has, however, a marked tendency to remain supersaturated. Fine crystals can be obtained, very similar to, but larger than, those of the calcium compound. The prisms are fairly broad, and may be from 0·5 to 1·0 cm. long:

Found: MgO = 8·55, 8·56; P_2O_5 = 30·57, 28·84; Cl = 30·70, 30·48; $C_4H_8O_2$ (by diff.) = 37·10, 39·00.

$MgO,P_2O_3Cl_4,2C_4H_8O_2$ requires MgO = 8·74; P_2O_5 = 30·32; Cl = 30·28; $C_4H_8O_2$ = 37·59 per cent.

The second analysis refers to a preparation obtained from the action of ethyl acetate on previously prepared $MgO,3POCl_3$.

$MnO,P_2O_3Cl_4,2(C_2H_5·O·CO·CH_3)$.—A small quantity of manganous chloride is commonly formed in this preparation, from which the solution is decanted into the crystallising dish. The compound forms magnificent pink prisms, somewhat resembling cubes, and several mm. long:

Found: MnO = 14·25; P_2O_5 = 28·34; Cl = 28·76; $C_4H_8O_2$ (by diff.) = 35·11.

$MnO,P_2O_3Cl_4,2C_4H_8O_2$ requires MnO = 14·22; P_2O_5 = 28·48; Cl = 28·44; $C_4H_8O_2$ = 35·27 per cent.

This compound is clearly derived from the compound $MnO,2POCl_3$, although we have not actually obtained that compound itself.

$CaO,P_2O_3Cl_4,2(C_2H_5·O·CO·C_6H_5)$.—This is a white compound, crystallising in small prisms, moderately soluble in hot ethyl benzoate. On solution of the solid in water, the ester, being insoluble, separates out. It was collected, dissolved in ether, the ethereal solution washed and dried, the ether driven off, and the residual ester weighed:

Found: CaO = 8·50; P_2O_5 = 22·21; Cl = 20·88; $C_9H_{10}O_2$ = 50·0 (by diff. = 55·46).

$CaO,P_2O_3Cl_4,2C_9H_{10}O_2$ requires CaO = 9·21; P_2O_5 = 23·35; Cl = 23·32; $C_9H_{10}O_2$ = 49·34 per cent.

The solid analysed contained a small quantity of adhering ester, which it is impossible to remove completely on porous plate. On this account, in the following preparation of the methyl derivative the free ester was removed by distillation at 100° in a Töpler vacuum.

$CaO,P_2O_3Cl_4,2(CH_3{\cdot}O{\cdot}CO{\cdot}C_6H_5)$:

Found: $CaO = 9{\cdot}75$; $P_2O_5 = 24{\cdot}97$; $Cl = 23{\cdot}25$; $C_8H_8O_2$ (by diff.) $= 47{\cdot}27$.

$CaO,P_2O_3Cl_4,2C_8H_8O_2$ requires $CaO = 9{\cdot}66$; $P_2O_5 = 24{\cdot}48$; $Cl = 24{\cdot}45$; $C_8H_8O_2 = 46{\cdot}90$ per cent.

Recrystallisation of $CaO,P_2O_3Cl_4,2(CH_3{\cdot}CO{\cdot}CH_3)$ *from Ethyl Acetate.*—One gram of freshly prepared

$$CaO,P_2O_3Cl_4,2(CH_3{\cdot}CO{\cdot}CH_3)$$

was dissolved by the aid of heat in about 15 c.c. of freshly distilled ethyl acetate. On cooling, there was an abundant separation of crystals, which on analysis gave the following figures, showing that they consisted of the ethyl acetate compound:

Found: $CaO = 12{\cdot}02$; $P_2O_5 = 29{\cdot}97$; $Cl = 29{\cdot}33$; $C_4H_8O_2$ (by diff.) $= 35{\cdot}29$.

$CaO,P_2O_3Cl_4,2C_4H_8O_2$ requires $CaO = 11{\cdot}57$; $P_2O_5 = 29{\cdot}34$; $Cl = 29{\cdot}31$; $C_4H_8O_2 = 36{\cdot}39$ per cent.

A similar experiment to the above was carried out, starting with the ethyl acetate compound, and recrystallising it from acetone. Crystals of the acetone compound resulted.

Experiments with Diethyl Oxalate and Ethyl Trichloroacetate.

It has already been mentioned (p. 1405) that from the behaviour of mixtures of lime and phosphoryl chloride at 25° it is probable that a compound, $CaO,3POCl_3$, is finally formed at that temperature by continued action of an excess of phosphoryl chloride on the compound $CaO,2POCl_3$ formed first of all.

The existence of the compound $CaO,3POCl_3$ has been confirmed by experiments carried out in presence of diethyl oxalate or ethyl trichloroacetate.

Lime dissolves fairly readily in a mixture of phosphoryl chloride and either of these esters when heated to 110°. It is advisable to use about ten parts by weight of phosphoryl chloride and thirty parts of ester to one part of lime. Solution of the lime is complete in about twenty-four hours, and on cooling well formed crystals slowly separate. About a week was required for complete separation from the oxalate solution, which yielded brilliant, rhombohedral prisms about 2 mm. long. Unfortunately, in spite of their appearance, these crystals did not consist of one compound only. It seems clear that what happens is as follows: First of all, either the compound $CaO,2POCl_3$ or $CaO,3POCl_3$ or a mixture of both is formed, according to the concentrations employed. Under the influence of any traces of moisture present the oxalic ester derivative of the compound $CaO,P_2O_3Cl_4$ is formed from the compound $CaO,2POCl_3$. Moisture also acts on the compound $CaO,3POCl_3$, replacing chlorine by hydroxyl, with formation of compounds incapable of combining with organic esters, etc. It seems certain that the power of adding on these organic molecules is confined to the compounds of the general formula $MO,P_2O_3Cl_4$.

The results obtained in presence of oxalic and trichloroacetic esters can be explained in this way, but, owing to the complicated nature of the problem, it is unnecessary to give more than one analysis, and that mainly to show that the compound $CaO,3POCl_3$ is formed. The analysis refers to a well crystallised preparation from an oxalic ester experiment:

Found: $CaO=10{\cdot}00$; $P_2O_5=37{\cdot}10$; $Cl=52{\cdot}25$; $C_6H_{10}O_4$ (by titration with $KMnO_4$) $=5{\cdot}19$; H_2O (by diff.) $=7{\cdot}23$.

$Ca:P=1:2{\cdot}92$.

Reaction between Lime and Phosphoryl Chloride in Presence of Ether.

In absolute ether lime reacts slowly with phosphoryl chloride to give the compound $CaO,2POCl_3$. This conversion can be effected in a sealed tube at 25° in somewhat longer than three weeks. A tube sealed up for that length of time gave a solid, which on analysis gave the following analytical figures:

Found: $CaO=17{\cdot}42$; $P_2O_5=37{\cdot}15$; $Cl=52{\cdot}11$. Deficit (ether) $=5{\cdot}08$.

Ratio: $Ca:P:Cl:Ether=1{\cdot}24:2{\cdot}08:5{\cdot}88:0{\cdot}28$.

Even with the above precautions a small quantity of the compound $CaO,P_2O_3Cl_4,2C_4H_{10}O$ appears to have been formed. The lime, moreover, is not completely converted.

If the reaction is carried out in a flask fitted with air condenser, and no special precautions are taken to ensure that the ether is absolutely free from moisture, the reaction occurring is much more energetic, the ether being sometimes caused to boil. Under these conditions larger proportions of the pyrophosphoryl chloride derivative are obtained; some of the compound $CaO,2POCl_3$ is, however, always present, and owing, moreover, to the fact that the ether compound begins to separate before all the lime has passed into solution it is difficult to obtain a pure product. The best preparation of the ether compound which we have obtained was got by the continued action of ether on an oxalic ester preparation. The final product of the action of ether consisted of small, brilliant rhombohedra. On solution in water it was evident that the crystals contained considerable quantities of ether, although titration with permanganate showed that about 10 per cent. of the organic portion of the molecule was oxalic ester and not ether:

Found: $CaO = 12{\cdot}57$; $P_2O_5 = 31{\cdot}20$; $Cl = 29{\cdot}51$; $C_6H_{10}O_4 = 2{\cdot}66$; $C_4H_{10}O$ (by diff.) $= 30{\cdot}71$.

$CaO,P_2O_3Cl_4,2C_4H_{10}O$ requires $CaO = 12{\cdot}28$; $P_2O_5 = 31{\cdot}14$; $Cl = 31{\cdot}11$; $C_4H_{10}O = 32{\cdot}45$ per cent.

Reactions of Zinc, Cadmium, Cobaltous, and Cupric Oxides with Phosphoryl Chloride in Presence of Ethyl Acetate.

We have been unable to obtain any crystalline organic derivatives from the interaction of zinc oxide, phosphoryl chloride, and ethyl acetate.

In the case of cadmium oxide a white powder, seen to be crystalline under the microscope, was formed. It was quite insoluble in ethyl acetate, and the analysis gave the following figures:

	CdO.	P_2O_5.	Cl.	Ethyl acetate (by diff.).
Expt. I.	57·20	5·48	33·35	11·49
Expt. II.	49·11	7·25	31·96	18·88

The white solid is evidently a mixture of the compound

$$CdO,P_2O_3Cl_4,2(C_4H_8O_2)$$

and cadmium chloride (the latter apparently being combined with a variable amount of ethyl acetate of crystallisation). Experiment I, for example, can be apportioned as follows:

As $CdO,P_2O_3Cl_4,2(C_4H_8O_2)$ ... $CdO = 4{\cdot}94$; $P_2O_5 = 5{\cdot}48$; $Cl = 5{\cdot}48$; $C_4H_8O_2 = 6{\cdot}78$, leaving (by difference) as $CdCl_2$ . . . $CdO = 52{\cdot}26$; $Cl = 27{\cdot}87$; $C_4H_8O_2 = 4{\cdot}71$ per cent.

Atomic ratio: Cd : Cl in the latter $= 1 : 1{\cdot}93$.

The reaction between cobaltous oxide, phosphoryl chloride, and ethyl acetate leads to the formation of a blue solution, from which nothing could be crystallised suitable for analysis, and of a blue solid which was simply cobalt chloride combined with some ethyl acetate.

With cupric oxide the course of the reaction is somewhat similar to that followed in the case of cadmium oxide. If large quantities of cupric oxide and phosphoryl chloride, in proportion to the ethyl acetate, are used, the reaction may be very vigorous. No copper passes into solution. The solid product appears to be more complex than in other cases, and is probably a mixture of the compounds CuP_2O_6, $CuO,P_2O_3Cl_4,2(C_4H_8O_2)$, and cupric chloride (combined with some ethyl acetate), as evidenced by the following analytical figures:

	CuO.	P_2O_5.	Cl.	Ethyl acetate (by diff.).
Expt. I.	38·88	24·58	33·59	10·52
Expt. II, ...	39·33	14·58	35·51	18·58

In conclusion, we wish to thank Messrs. R. Kingan, F. O. Rice, and E. T. Williams for assistance in preparing some of the compounds described above.

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