XXXI.—*Contributions to the Chemistry of Oxygen Compounds. I. The Compounds of Tertiary Phosphine Oxides with Acids and Salts.*

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MANY new conceptions of valency have been described during recent years. That the valencies commonly ascribed to the elements do not serve to explain all experimental results is readily recognised from a consideration of many of the so-called molecular compounds. It is obvious that the affinities to which the formation of molecular compounds is due are weaker than those by reason of which atomic compounds exist, and many names have been given to these weaker valencies: for example, krypto, complex, neutral, partial, residual, supplementary. That these subsidiary valencies differ from the main valencies only in degree has been expressed by Werner (*Annalen*, 1902, 322, 261) in his theory of principal ("Haupt") and supplementary ("Neben") valencies, according to which the constitution of a compound is determined by the principal and supplementary valencies of the elements along with the co-ordination constant.

The discovery of the basic properties of oxygen compounds (Collie and Tickle, *Trans.*, 1899, 75, 710; Baeyer and Villiger, *inter alia*, *Ber.*, 1901, 34, 2679) gave a stimulus to the speculations as to valency, and many attempts have been made to determine the constitution of these "oxonium" compounds. We are making a detailed study of the "molecular" compounds formed by substances containing oxygen and some other element in columns 4—8 of the periodic table. In the present communication are described a number of such compounds formed by the tertiary phosphine oxides with acids and metallic salts. These are all well-defined compounds which have been recrystallised from water or alcohol, and have the general formula

Thus the compounds which tri-methyl-, -ethyl-, -propyl-, -phenyl-, and -benzyl-phosphine oxides form with the following acids: ferrocyanic, cobalticyanic, dichromic, chlorauric, camphoric, iodobismuthic, and iodomeric, and the following salts: zinc chloride and iodide, cadmium iodide, and mercuric and cobalt chlorides, conform to these general formulæ, whilst those with hydrochloric, trichloroacetic, pyruvic, and chloroplatinic acids and with cupric and ferric chlorides are exceptions.

The constitution of one of these compounds, namely, triphenyl-

phosphine oxide hydrochloride, $(C_6H_5)_3PO \cdot HCl$, could be represented by either of the following formulæ:

The former formula is very improbable for the following reasons: (i) there is no evidence that a phosphine oxide behaves in solution as a basic hydroxide; an aqueous solution of triethylphosphine oxide, for example, has no effect on the birotation of dextrose, and may therefore be regarded as free from hydroxyl ions, and (ii) it offers no explanation (among other things) of the analogy between the compounds formed by the oxides with acids and those with metallic salts.

The second formula is based on the assumption of the quadrivalency of oxygen. This assumption, whilst it may explain the constitution of this hydrochloride, does not satisfactorily explain the constitution of such compounds as $2(CH_3)_3PO \cdot H_4Fe(CN)_6$, $4(CH_3)_3PO \cdot H_2PtCl_6$, and so on. For the addition of R_3PO to HX is assumed to form a saturated compound, and therefore the addition of a second molecule of R_3PO to HX seems improbable. A formula such as

appears highly improbable, as it is opposed to the known constitution of chloroplatinic acid. This assumption of the quadrivalency of oxygen is rendered less likely by the close analogy existing between the compounds of the oxides with acids and those with metallic salts, thus, $2(CH_3)_3PO \cdot ZnI_2$, $(C_2H_5)_2PO \cdot CuCl_2$, and the series of compounds of the type of $3(C_7H_7)_3PO \cdot Fe_2Cl_6$, prepared by Fleissner (*Ber.*, 1880, 13, 1665).

In fact we regard the results described in this communication as a confirmation of the theory of "oxonium" compounds put forward by Werner (*Annalen*, 1902, 322, 296), and therefore prefer to formulate these compounds on the assumption of supplementary valencies on the part of the oxygen atom in the oxide, as $(R_3PO) \dots HX$ and $(R_3PO) \dots MeX$. Thus the combination in the first case is supposed to occur through the agency of the supplementary valencies of the oxygen of the oxide and the hydrogen of the respective acids, and in the second case through the agency of the supplementary valencies of the oxygen of the oxide and of the metallic radicles of the salts. The platinichlorides then would have a co-ordination formula,

What influence (if any) the phosphorus has on the constitution of these molecular compounds can be only brought out by further studies on other oxygen compounds, the results of which we hope shortly to communicate to the Society. In the present communication we have been able to show that the relative mass of R in compounds R_3PO has no effect within the limits tried, namely, methyl, ethyl, propyl, phenyl, to benzyl, on the constitution of these molecular compounds.

The constitution of "Grignard" reagents has often been represented by formulæ of the type $\begin{array}{c} \text{CH}_3 \\ \text{IMg} \end{array} > \text{O} < \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array}$ (compare Baeyer and Villiger, *loc. cit.*), but can be better represented, according to Werner's theory, by $(\text{C}_2\text{H}_5)_2\text{O} \dots \text{CH}_3\text{MgI}$. We have discovered that the ether may be replaced in these reagents by compounds containing oxygen other than ethers; thus, magnesium dissolves in benzene containing methyl iodide and tribenzylphosphine oxide giving a compound of the probable formula $\{(\text{C}_7\text{H}_7)_3\text{PO}\}_2 \dots \text{CH}_3\text{MgI}$, assuming its formation to be due to the agency of supplementary valencies of the oxygen atoms and the carbon of the organo-magnesium iodide.

These phosphine oxides are only weak bases. Thus, trimethylphosphine oxide hydrogen trichloroacetate is hydrolysed in $N/6$ aqueous solution at 30° to the extent of about 89 per cent. as measured by the inversion of cane sugar method.

Preparation of Tertiary Phosphine Oxides.—The old method of preparing the tertiary phosphine oxides by treating with potassium hydroxide the mixture of iodides obtained when phosphorus is heated with an alkyl iodide in a sealed tube is a very tedious and unpleasant operation. It is far easier to prepare them from the mixture obtained by treating a "Grignard" reagent with phosphorus oxychloride. During the course of our experiments, in a paper by Sauvage (*Compt. rend.*, 1904, 139, 674) it was briefly shown that phosphorus oxychloride reacts with aromatic organo-magnesium compounds to form the substances R_3PO and $R_2PO\cdot OH$. As the method of preparation in the case of the aromatic series presents no difficulty, it will be sufficient to give the details of the preparation by the latter method of tripropylphosphine oxide, a trialkyl phosphine oxide, which has not previously been described.

Tri-n-propylphosphine Oxide.—A dilute ethereal solution of magnesium *n*-propyl bromide is placed in a large flask, provided with a reflux condenser, and well cooled with a mixture of ice and salt. This solution is then very slowly, with constant shaking, mixed with a dry ethereal solution of the calculated quantity of phosphorus oxychloride. After the very vigorous reaction is over, water is added, along with sufficient hydrochloric acid to dissolve any excess of magnesium, and the ether distilled off. The solution is then mixed with a large excess

of sodium hydroxide and the resulting paste slowly distilled from a copper flask. When the aqueous distillate is fractionated, the oxide is obtained in the fraction boiling at $260\text{--}265^\circ/759\text{ mm}$. *Tri-n-propylphosphine oxide*, when freshly distilled, solidifies in colourless, lustrous, silky needles, which melt at 38° , have no smell, and are very hygroscopic.

Compounds with Ferrocyanic Acid.

These compounds may be prepared by mixing aqueous solutions of the acid and the phosphine oxide. Small, colourless needles separate and soon turn green on exposure to light or moist air. Owing to the solubility of these compounds in water, they are more conveniently prepared from alcoholic solutions of the acid and oxide. These solutions, when mixed, deposit white or pale green, microcrystalline precipitates, which after washing with alcohol are sufficiently pure for analysis.

Trimethylphosphine oxide hydrogen ferrocyanide is very soluble in water, but insoluble in cold alcohol; it crystallises from either of these media in small, colourless needles. Analysis gave $N=21.03$; $H_4Fe(CN)_6=53.39$; $2(CH_3)_3PO, H_4Fe(CN)_6$ requires $N=21.00$; $H_4Fe(CN)_6=54.00$ per cent.

Triethylphosphine oxide hydrogen ferrocyanide was only obtained from the mixed aqueous solutions of the acid and oxide after the addition of concentrated hydrochloric acid, which precipitates it in the form of a microcrystalline powder. This quickly turns green in moist air. Analysis gave $C=44.65$; $H=7.38$; $Fe=11.55$; $H_4Fe(CN)_6=44.53$; $2(C_2H_5)_3PO, H_4Fe(CN)_6$ requires $C=44.62$; $H=7.02$; $Fe=11.60$; $H_4Fe(CN)_6=44.62$ per cent.

Tripropylphosphine oxide hydrogen ferrocyanide is much less soluble than the analogous methyl compound. Analysis gave $C=50.37$; $H=8.27$; $H_4Fe(CN)_6=38.41$; $2(C_3H_7)_3PO, H_4Fe(CN)_6$ requires $C=50.70$; $H=8.10$; $H_4Fe(CN)_6=38.03$ per cent.

Triphenylphosphine oxide hydrogen ferrocyanide is insoluble in water and only slightly soluble in warm alcohol. Analysis gave $C=65.08$; $H=4.63$; $N=11.38$; $H_4Fe(CN)_6=28.33$;

$2(C_6H_5)_3PO, H_4Fe(CN)_6$
requires $C=65.28$; $H=4.40$; $N=10.88$; $H_4Fe(CN)_6=27.98$ per cent.

Compounds with Cobalticyanic Acid.

These can all be prepared by mixing hot alcoholic solutions of the acid and the tertiary phosphine oxide. On cooling the mixture, the compounds separate out in a crystalline condition.

Trimethylphosphine oxide hydrogen cobalticyanide is very soluble in warm water or alcohol, from both of which it crystallises in colourless,

glistening needles. When heated, it changes to a light green colour at about 200° . Analysis gave $C=33.05$; $H=5.88$; $N=19.61$; $H_3Co(CN)_6=50.35$; $2(C_2H_5)_3PO, H_3Co(CN)_6, 1\frac{1}{2}H_2O$ requires $C=33.59$; $H=5.83$; $N=19.59$; $H_3Co(CN)_6=50.77$ per cent.

The water of crystallisation cannot be accurately determined as the compound does not lose this below 115° , and prolonged heating above this temperature partially decomposes the substance.

Triethylphosphine oxide hydrogen cobalticyanide was obtained in the form of white, prismatic crystals which, when recrystallised from water, melted at 174° . Analysis gave $C=38.66$; $H=7.37$; $H_3Co(CN)_6=38.85$; $2(C_2H_5)_3PO, H_3Co(CN)_6, 4H_2O$ requires $C=38.69$; $H=7.34$ and $H_3Co(CN)_6=39.06$ per cent.

Tripropylphosphine Oxide Hydrogen Cobalticyanide.—When concentrated aqueous solutions of tripropylphosphine oxide and cobalticyanic acid are mixed, pale yellow, cubical crystals separate out quite readily. These, when recrystallised from water, still retain a faint yellow colour and melt at 119° . Analysis gave $C=42.27$; $H=8.10$; $N=12.40$; $H_3Co(CN)_6=32.33$; $2(C_3H_7)_3PO, H_3Co(CN)_6, 6H_2O$ requires $C=42.48$; $H=8.41$; $N=12.39$; $H_3Co(CN)_6=32.15$ per cent.

Triphenylphosphine oxide hydrogen cobalticyanide is a very pale yellow substance soluble in water and alcohol. From the latter it separates out in transparent, indefinite, prismatic crystals, which melt at 172° . Analysis gave $C=60.57$; $H=5.05$; $N=10.11$; $H_3Co(CN)_6=25.71$; $2(C_6H_5)_3PO, H_3Co(CN)_6, 3H_2O$ requires $C=60.87$; $H=4.71$; $N=10.14$; $H_3Co(CN)_6=26.33$ per cent.

Compounds with Chloroauric Acid.

These compounds are prepared by mixing hot concentrated aqueous or alcoholic solutions of the phosphine oxide and chloroauric acid. On cooling, the solution deposits beautiful, yellow, flat, hexagonal plates, which after washing with cold water are sufficiently pure for analysis.

Trimethylphosphine oxide hydrogen aurichloride is very soluble in hot water, from which it readily crystallises; it melts at 94.5° . Analysis gave $C=13.52$; $H=3.58$; $Au=37.8$; $2(CH_3)_3PO, HAuCl_4$ requires $C=13.74$; $H=3.63$; $Au=37.6$ per cent.

Triethylphosphine oxide hydrogen aurichloride is less soluble in water than the corresponding methyl compound and melts at $54-56^{\circ}$. Analysis gave $Au=32.8$; $2(C_2H_5)_3PO, HAuCl_4$ requires $Au=32.3$ per cent.

Tripropylphosphine oxide hydrogen aurichloride crystallises from hot water and melts at $67-69^{\circ}$. Analysis gave $C=30.90$; $H=6.35$;

Au = 28.51; $2(\text{C}_3\text{H}_7)_3\text{PO}, \text{HAuCl}_4$ requires C = 31.20; H = 6.22; Au = 28.47 per cent.

Triphenylphosphine oxide hydrogen aurichloride melts at 179°. Analysis gave Au = 22.09; $2(\text{C}_6\text{H}_5)_3\text{PO}, \text{HAuCl}_4$ requires Au = 21.99 per cent.

Tribenzylphosphine oxide hydrogen aurichloride melts at 222.5°. Analysis gave Au = 20.3; $2(\text{C}_7\text{H}_7)_3\text{PO}, \text{HAuCl}_4$ requires Au = 20.1 per cent.

Compounds with Dichromic Acid.

Solutions of the phosphine oxides when mixed with saturated solutions of chromic anhydride in dilute sulphuric or nitric acid readily deposit crystals of these molecular compounds, which are very similar in appearance to potassium dichromate. On exposure to light, they turn black and then become insoluble in water.

Trimethylphosphine oxide hydrogen dichromate crystallises from water or dilute nitric acid in bright red, hard, glistening prisms which darken at 200° and begin to melt at 204°. Analysis gave $\text{H}_2\text{Cr}_2\text{O}_7 = 54.5$; $\text{CrO}_3 = 49.8$; $2(\text{CH}_3)_3\text{PO}, \text{H}_2\text{Cr}_2\text{O}_7$ requires $\text{H}_2\text{Cr}_2\text{O}_7 = 54.2$; $\text{CrO}_3 = 49.7$ per cent.

Triethylphosphine oxide hydrogen dichromate crystallises in hair-like needles and melts at 100–102°. Analysis gave C = 29.64; H = 6.20; $\text{H}_2\text{Cr}_2\text{O}_7 = 45.14$; $2(\text{C}_2\text{H}_5)_3\text{PO}, \text{H}_2\text{Cr}_2\text{O}_7$ requires C = 29.63; H = 6.59; $\text{H}_2\text{Cr}_2\text{O}_7 = 44.86$ per cent.

Tripropylphosphine oxide hydrogen dichromate melts and decomposes at 164°. It is only slightly soluble in water. Analysis gave C = 38.09; H = 7.38; $\text{H}_2\text{Cr}_2\text{O}_7 = 44.53$; $2(\text{C}_3\text{H}_7)_3\text{PO}, \text{H}_2\text{Cr}_2\text{O}_7$ requires C = 37.89; H = 7.72; $\text{H}_2\text{Cr}_2\text{O}_7 = 44.86$ per cent.

Compounds with Iodobismuthic Acid.

Trimethylphosphine oxide hydrogen bismuthic iodide was prepared by mixing concentrated aqueous solutions of the oxide and potassium bismuthic iodide. On adding hydriodic acid, brilliant red crystals separated out, which crystallised from warm dilute hydriodic acid in clusters of bright red, prismatic needles. It is decomposed by excess of water, giving a dirty brown powder (probably of BiI_3) which dissolves in hydriodic acid. When heated, it blackens and evolves dark vapours, chiefly iodine. Analysis gave C = 8.10; H = 2.34; Bi = 22.93; $2(\text{CH}_3)_3\text{PO}, \text{HBiI}_4$ requires C = 7.99; H = 2.11; Bi = 23.08 per cent.

Triethylphosphine oxide hydrogen bismuthic iodide was prepared in a similar manner to the methyl compound, which it closely resembles in properties. When heated, it blackens and decomposes at 130°.

Analysis gave $C = 14.45$; $H = 3.12$; $Bi = 21.33$; $2(C_2H_5)_3PO, HBiI_4$ requires $C = 14.62$; $H = 3.14$; $Bi = 21.21$ per cent.

Compounds with Iodomercuric Acid.

Triethylphosphine oxide hydrogen mercuric iodide was prepared by mixing concentrated aqueous solutions of the oxide and potassium mercuric iodide. To this solution, cooled in a freezing mixture, was added hydriodic acid, the reddish-brown oil which separated was treated with a dilute solution of sodium thiosulphate and desiccated. After a short time, the oil solidified to a mass of beautiful, yellow, crystalline needles, which were pressed and dried on a porous plate. On heating, the crystals soften at 31° and melt at $32-33^\circ$. Analysis gave $C = 16.81$; $H = 3.66$; $HI = 16.2$; $2(C_2H_5)_3PO, HHgI_2$ requires $C = 16.94$; $H = 3.65$; $HI = 15.1$ per cent.

Triparylphosphine oxide hydrogen mercuric iodide was prepared in a similar manner to the corresponding ethyl compound, which it closely resembles in properties; it melts at $52-54^\circ$. Analysis gave $C = 22.51$; $H = 4.70$; $HI = 12.6$; $2(C_3H_7)_3PO, HHgI_2$ requires $C = 23.12$; $H = 4.60$; $HI = 13.7$ per cent.

Compounds with Chloroplatinic Acid.

Compounds of the oxides and chloroplatinic acid are readily obtained by mixing warm concentrated aqueous solutions of the two components. When the solutions cool they separate out in beautiful, large, flaky crystals, which seem to vary in colour with the amount of acid in the molecule.

Trimethylphosphine oxide hydrogen platinichloride is insoluble in alcohol, but very soluble in warm water, from which it crystallises in beautiful, deep red, pyramidal crystals which melt at 126° . Analysis gave $C = 18.49$; $H = 5.21$; $H_2PtCl_6 = 52.73$; $4(CH_3)_3PO, H_2PtCl_6$ requires $C = 18.51$; $H = 4.88$; $H_2PtCl_6 = 52.67$ per cent.

A similar compound has been described by Hofmann and Collie (Trans., 1888, 53, 636), but they give the formula

Triethylphosphine oxide hydrogen platinichloride was recrystallised from dilute hydrochloric acid and melts at 150° . Analysis gave $C = 30.34$; $H = 6.44$; $H_2PtCl_6 = 43.53$; $4(C_2H_5)_3PO, H_2PtCl_6$ requires $C = 30.44$; $H = 6.55$; $H_2PtCl_6 = 43.34$ per cent.

Triparylphosphine oxide hydrogen platinichloride crystallises in light brown flakes, which are soft and are quite different in appearance from the methyl and ethyl compounds; it is very soluble in water and melts at $92-93^\circ$. Analysis gave $C = 44.18$; $H = 9.19$; $6(C_7H_7)_3PO, H_2PtCl_6$ requires $C = 44.17$; $H = 8.73$ per cent.

Tribenzylphosphine oxide hydrogen platinichloride has been described by Fleissner (*loc. cit.*) and also by Letts and Collie (*Trans. Roy. Soc. Edin.*, 1888, **30**, Pt. I, 181). We have repeated their experiments and confirmed the formula $4(C_7H_7)_3PO, H_2PtCl_6$ given by the latter. We could not obtain a compound having the formula $3(C_7H_7)_3PO, PtCl_4$, as described by Fleissner. The compound melts and decomposes at $240-241^\circ$.

Compounds with Organic Acids.

Trimethylphosphine oxide hydrogen camphorate was prepared by mixing concentrated alcoholic solutions of the oxide and the acid. On standing in a vacuum, beautiful, clear, hard crystals were formed, which, after recrystallisation from alcohol, melted at $91-93^\circ$. Analysis gave $C = 50.06$; $H = 9.50$; $C_8H_{14}(CO_2H)_2 = 52.58$;

requires $C = 50.00$; $H = 8.86$; $C_8H_{14}(CO_2H)_2 = 52.09$ per cent.

Triethylphosphine oxide hydrogen pyruvate was prepared by mixing concentrated alcoholic solutions of the oxide and the acid. On standing, small, colourless, prismatic needles separated out. After recrystallisation from alcohol, they melted at $75-77^\circ$. Analysis gave $C = 46.88$; $H = 6.96$; $CH_3 \cdot CO \cdot CO_2H = 57.7$;

requires $C = 46.45$; $H = 7.42$; $CH_3 \cdot CO \cdot CO_2H = 58.8$ per cent.

Trimethylphosphine oxide hydrogen trichloroacetate was prepared by mixing concentrated aqueous solutions of the oxide and the acid. On standing, small, colourless crystals separated out. They are quite odourless, are not deliquescent, and melt at 67° . Analysis gave $C = 23.29$; $H = 4.10$; $CCl_3 \cdot CO_2H = 64.2$; $(CH_3)_3PO, CCl_3 \cdot CO_2H$ requires $C = 23.48$; $H = 3.91$; $CCl_3 \cdot CO_2H = 64.0$ per cent.

Triphenylphosphine oxide hydrogen trichloroacetate was prepared by mixing concentrated alcoholic solutions of the oxide and the acid. On standing for some time, small crystals separated out, which melted at $95-97^\circ$; it was recrystallised from alcohol, from which it separates in colourless rhombs which melt at $97-99^\circ$. Analysis gave $C = 54.17$; $H = 3.80$; $CCl_3 \cdot CO_2H = 37.09$; $(C_6H_5)_3PO, CCl_3 \cdot CO_2H$ requires $C = 54.35$; $H = 3.62$; $CCl_3 \cdot CO_2H = 37.03$ per cent.

Compounds with Hydrochloric Acid.

These derivatives, of which we have only succeeded in preparing the phenyl and benzyl compounds, are obtained by dissolving the phosphine oxide in a warm alcoholic solution of hydrochloric acid. On standing, white, cubical crystals separate out.

Triphenylphosphine oxide hydrogen chloride melts at $183-185^\circ$.

Analysis gave $\text{HCl} = 11.56$; $(\text{C}_6\text{H}_5)_3\text{PO}, \text{HCl}$ requires $\text{HCl} = 11.61$ per cent.

Tribenzylphosphine oxide hydrogen chloride separates from alcoholic hydrochloric acid in clusters of small, white crystals, which, on heating, melt at 169° and evolve bubbles of gas; then they solidify and remelt at $208\text{--}210^\circ$ (the free oxide melts at 214°). On adding an aqueous solution of sodium carbonate to a warm alcoholic solution of the hydrochloride, a faint effervescence is seen, and on cooling crystals of the oxide separate. On analysis, the crystals gave $\text{HCl} = 10.43$ (by acidimetry) and 10.25 by titration with silver nitrate; $(\text{C}_7\text{H}_7)_3\text{PO}, \text{HCl}$ requires $\text{HCl} = 10.24$ per cent.

Compounds of the Phosphine Oxides with Metallic Salts.

These compounds, which are prepared by mixing a concentrated aqueous or alcoholic solution of the phosphine oxide with an aqueous or alcoholic solution of the particular salt, generally separate quite readily, and were recrystallised and analysed.

Trimethylphosphine oxide zinc iodide was obtained in small, white prisms which are not deliquescent; they are very soluble in water and in hot alcohol, and on recrystallisation from the latter solvent melt at 168° . Analysis gave $\text{C} = 14.40$; $\text{H} = 3.78$; $2(\text{CH}_3)_3\text{PO}, \text{ZnI}_2$ requires $\text{C} = 14.31$; $\text{H} = 3.58$ per cent.

Triethylphosphine oxide cupric chloride separates from alcohol in light brown prisms which melt at 233° to a dark liquid; it is decomposed by water. Analysis gave $\text{C} = 26.92$; $\text{H} = 5.48$; $(\text{C}_2\text{H}_5)_3\text{PO}, \text{CuCl}_2$ requires $\text{C} = 26.87$; $\text{H} = 5.60$ per cent.

Hofmann (*Annalen*, 1861, Suppl. I, 2) described the compound $2(\text{C}_2\text{H}_5)_3\text{PO}, \text{ZnI}_2$, and Pebal (*Annalen*, 1862, 120, 194) the compound $2(\text{C}_2\text{H}_5)_3\text{PO}, \text{CuSO}_4$.

Triphenylphosphine oxide cadmium iodide crystallises from hot alcohol in white, stout prisms which melt at 192.5° and are insoluble in water. The analysis of this compound gave $\text{C} = 46.80$; $\text{H} = 3.64$, whereas $2(\text{C}_6\text{H}_5)_3\text{PO}, \text{CdI}_2$ requires $\text{C} = 46.85$; $\text{H} = 3.25$ per cent.

Triphenylphosphine oxide zinc chloride crystallises from alcohol in hard, colourless, small prisms, which are insoluble in water and melt at $229\text{--}230^\circ$. Analysis gave $\text{C} = 62.82$; $\text{H} = 4.43$; $2(\text{C}_6\text{H}_5)_3\text{PO}, \text{ZnCl}_2$ requires $\text{C} = 62.43$; $\text{H} = 4.34$ per cent.

Triphenylphosphine oxide mercuric chloride crystallises from alcohol in white prisms which melt at $120\text{--}122^\circ$. Analysis gave $\text{C} = 52.37$; $\text{H} = 3.79$; $2(\text{C}_6\text{H}_5)_3\text{PO}, \text{HgCl}_2$ requires $\text{C} = 52.24$; $\text{H} = 3.63$ per cent.

Triphenylphosphine oxide cobalt chloride separates from warm alcohol in deep blue, cubical crystals which melt at 233° . Analysis gave $\text{C} = 62.92$; $\text{H} = 4.61$; $2(\text{C}_6\text{H}_5)_3\text{PO}, \text{CoCl}_2$ requires $\text{C} = 62.98$; $\text{H} = 4.38$ per cent.

Triphenylphosphine oxide zinc iodide crystallises from alcohol in small, colourless rhombs and melts at 223—226°. Analysis gave C=49·28; H=3·44; $2(\text{C}_6\text{H}_5)_3\text{PO}, \text{ZnI}_2$ requires C=49·37; H=3·43 per cent.

Compound of Methyl Magnesium Iodide and Tribenzylphosphine Oxide.

A mixture of 250 c.c. of dry benzene (free from thiophen), methyl iodide (1·5 grams), and magnesium powder (0·3 gram) was boiled for several hours; the solution remained quite clear and no magnesium dissolved. Then to this mixture was added tribenzylphosphine oxide (3·0 grams) dissolved in benzene. After a short time, the clear liquid became cloudy and the magnesium began to dissolve. The mixture was boiled for seven hours and then filtered hot. On cooling, small, colourless, prismatic needles separated; these were collected, washed with the mother liquor, and dried in a desiccator. When heated, they shrivel up and melt at 163—166°. When treated with dilute hydrochloric acid, they are decomposed, a colourless, inflammable gas is evolved, the free oxide is formed, and the solution contains magnesium chloride and iodide. The compound undergoes partial decomposition when recrystallised from benzene. An estimation of the metallic constituent gave $\text{Mg}=2·41$; $2(\text{C}_7\text{H}_7)_3\text{PO}, \text{CH}_3\text{MgI}$ requires $\text{Mg}=2·98$ per cent.

Experiments to show that Triethylphosphine Oxide is a very weak base.

The birotation of a 5 per cent. solution of dextrose was compared with that of a similar solution containing also 1 per cent. of triethylphosphine oxide. The rate of change in the rotation of the dextrose was found to be the same in both solutions, showing that the oxide is a very weak base and that its aqueous solution contains no hydroxyl ions.

TABLE I.—*Dextrose alone at 25°.*

Time in minutes.	Rotation.	$1/t \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$
0	11·53°	—
8	10·89	0·0107
18	10·23	0·0108
38	9·32	0·0109
45	9·16	0·0104
57	8·84	0·0105
62	8·64	0·0114
∞	7·94	—

Mean $K=0·0107$.

TABLE II.—*Dextrose with the Oxide at 25°.*

Time in minutes.	Rotation.	$1/t \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$
0	11·00°	—
5	10·66	0·0108
18	10·00	0·0108
30	9·47	0·0108
46	9·06	0·0105
54	8·86	0·0108
71	8·65	0·0103
∞	8·10	—

Mean $K=0·0107$.

Experiments to determine the amount of Hydrolysis of the Compounds of Trimethylphosphine Oxide with Trichloroacetic and Cobalticyanic Acids.

A 25 per cent. solution of cane sugar was inverted with the acids and the rate of inversion compared with that of a similar solution containing the compound of the oxide and the acid. The experiments were performed at 30° and the strength of the solutions taken so that they each contained the same amount ($N=0.158$) of acid, free or combined.

TABLE III.—*Cane Sugar and Trichloroacetic Acid.*

Time in minutes.	Rotation.	$1/t \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$
0	+15.93°	—
112	13.16	0.000573
155	12.20	0.000573
205	11.10	0.000579
243	10.30	0.000585
307	8.98	0.000597
437	6.65	0.000612
2840	-1.11	0.000577
∞	-4.24	—

Mean $K=0.000585$.

TABLE IV.—*Cane Sugar and the Compound of Oxide and Cobalticyanic Acid.*

Time in minutes.	Rotation.	$1/t \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$
0	+16.01°	—
77	14.25	0.000510
103	13.67	0.000515
123	13.20	0.000525
144	12.82	0.000514
232	11.08	0.000519
298	9.96	0.000514
328	9.36	0.000524
∞	-4.23	—

Mean $K=0.000517$.

Whence the approximate hydrolysis $\frac{517}{585} \times 100 = 88.3$ per cent.

TABLE V.—*Cane Sugar and Cobalticyanic Acid.*

Time in minutes.	Rotation.	$1/t \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$
0	+15.71°	—
100	13.11	0.000596
165	11.46	0.000621
285	8.67	0.000652
340	7.80	0.000635
348	7.76	0.000622
441	6.52	0.000641
1810	-2.89	0.000607
∞	-4.50	—

Mean $K=0.000625$.

TABLE VI.—*Cane Sugar and the Compound of Oxide and Cobalticyanic Acid.*

Time in minutes.	Rotation.	$1/t \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$
0	+15.87°	—
55	14.52	0.000544
88	13.71	0.000555
152	12.23	0.000565
330	8.93	0.000551
402	7.77	0.000551
1515	-1.52	0.000558
1900	-2.55	0.000545
∞	-4.52	—

Mean $K=0.000553$.

Whence the approximate hydrolysis $\frac{553}{625} \times 100 = 88.5$ per cent.

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