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New reactions involving the oxidative *O*-, *N*-, and *C*-phosphorylation of organic compounds by phosphorus and phosphides in the presence of metal complexes

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Abstract. The mechanisms of new catalytic reactions leading to the formation of di- and tri-alkyl phosphates, di- and tri-alkyl phosphites, phosphoramidites, phosphazenes, phosphines, and phosphine oxides from hydrogen, copper, and zinc phosphides and white and red phosphorus are analysed. The mechanisms of the activation of the reactants by metal complexes and of the reactions involving the oxidative P–O, P–N, and P–C coupling of organic compounds to phosphorus and phosphides are considered. The bibliography includes 124 references.

I. Introduction

The products of the P–C, P–N, and P–O coupling, namely di- and tri-alkyl phosphates, di- and tri-alkyl phosphites, phosphazenes, phosphorinanes, phosphines, and phosphine oxides, are stable organic compounds[1,2] and are widely used as extractants for the lanthanides, the actinides, and other heavy metals from mineral raw materials and the waste from atomic power plants,[3,4] as monomers for the synthesis of organophosphorus fire- and heat-resistant polymers,[5,6] as additives to fuels and lubricating materials, as corrosion inhibitors, etc.

The available methods for the synthesis of the above compounds are based on the P–C, P–N, and P–O coupling of organic substances to the high-valence phosphorus compounds $POCl_3$, and PCl_5, which are synthesised using the expensive and extremely toxic chlorine.[1–7] Dorfman et al[8] discovered the reactions involving the P–C, P–N, and P–O coupling of organic compounds to low-valence inorganic phosphorus compounds, which lead to the formation of some of the substances listed above. Low-valence phosphorus compounds, namely phosphine, transition metal phosphides, hypophosphite, tetraphosphorus, and polyphosphorus are highly toxic waste from modern phosphorus and hypophosphite manufacturing plants produced on a large scale.[9–11] White phosphorus is present in weak phosphorus sludge, which is not utilised nowadays and is stored in sludge accumulators.

Important advantages of the new reaction involving the oxidative P–C, P–N, and P–O phosphorylation of organic substances by low-valence inorganic compounds are mild conditions, a high rate, and a high selectivity, which facilitates the isolation technology of the pure product.[8] This makes it possible to use the waste from phosphorus undertakings in which phosphorus-containing compounds are present in small amounts.

The wide variety of the products formed in P–C, P–N, and P–O oxidative coupling to aliphatic and aromatic compounds (phosphine, transition metal phosphides, tetraphosphorus and polyphosphorus, and hypophosphite) and reaction conditions do not rule out the existence of a series of common features of interest in the organic chemistry of low-valence phosphorus compounds, which have been extremely little investigated, and in the metal complex catalysis of homogeneous and topochemical processes.

II. Oxidative P–O coupling of tetraphosphorus to alcohols

Despite the evident usefulness of tetraphosphorus in organic synthesis, there are as yet no data concerning the processes based on it.[12–40] Homolytic reactions are characteristic of tetraphosphorus, whereas heterolytic reactions proceed with

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difficulty.[10] It has been observed[41-43] that, when tetraphosphorus is placed in an arene–alcohol solution of divalent copper salts under a O_2 atmosphere at 50–150 °C, reactions involving the oxidative P–O coupling of P_4 to ROH proceed very rapidly and with a high selectivity.

Reactions (1) and (3) predominate in the arene–alcohol solutions of $CuHal_2$ (Hal = Cl, Br), while reaction (2) predominates in $CuSO_4$, and $Cu(CO_2R)_2$ solutions (R = CH_3, C_3H_7, $C_{17}H_{35}$; arene = benzene, toluene, xylene).[8] Copper(II) sulfate and carboxylate complexes stimulate also the formation of dialkyl phosphite, in contrast to the halide complexes. The product ratio $(RO)_3PO/(RO)_3P$ depends not only on the nature of the ligands but also on the ROH concentration. If the amount of ROH diminishes, the ratio $(RO)_3PO/(RO)_3P$ also falls. Dialkyl phosphate is obtained at elevated temperatures.

$$P_4 + 5O_2 + 12ROH \longrightarrow 4(RO)_3PO + 6H_2O; \quad (1)$$

$$P_4 + 3O_2 + 12ROH \longrightarrow 4(RO)_3P + 6H_2O; \quad (2)$$

R = CH_3, C_2H_5, C_3H_7, C_4H_9, *iso*-C_4H_9, C_5H_{11}, *iso*-C_5H_{11}, C_8H_{17}, C_6H_5.

$$P_4 + 3O_2 + 8R'OH \longrightarrow 4(R'O)_2HPO + 2H_2O; \quad (3)$$

R′ = *iso*-C_3H_7.

The catalytic activity of copper(II) complexes also depends on the nature of the anions and increases when the halides are replaced by the sulfates, acetates, and especially butyrates and stearates. Both the rate of reduction of copper(II) by tetraphosphorus and the rate of oxidation of copper(I) by oxygen increase in this series of ligands. In contrast to the sulfate and acetate complexes, the butyrate and stearate complexes are readily soluble in benzene–alcohol solutions and in their presence the oxidative P–O coupling of P_4 to ROH proceeds selectively and at a high rate. The acidopyridinecopper(II) complexes have a higher activity.[41] The addition of pyridine to arene–alcohol solutions of $CuHal_2$, $CuSO_4$, and $Cu(CO_2R)_2$ leads to a sharp increase in the rate of reaction and in the $(RO)_3PO/(RO)_3P$ ratio and to a decrease in the yield of $(RO)_2(HO)PO$.

$$P_4 + 5O_2 + 8ROH \longrightarrow 4(RO)_2(HO)PO + 4H_2O. \quad (4)$$

Under an argon atmosphere, tetraphosphorus reacts almost instantaneously with arene–alcohol solutions of copper(II) complexes.

Reactions (5)–(8) take place over a period of 30–50 s.[41-43] The univalent and metallic copper formed is readily reoxidised by air to the divalent state. During the regeneration period, the alkyl halides and sulfates are hydrolysed to the alcohol by the water formed in this process, while alkyl carboxylates accumulate in the system. In the presence of acids, trialkyl phosphites are dealkylated to dialkyl phosphites. The rate of dealkylation increases with increase in the acidity of the medium (on passing from the sulfate and carboxylates to the halides) and also with decrease in the molecular mass of the group R. The dealkylation of trialkyl phosphites ends in the stage involving the formation of dialkyl phosphites, which are dealkylated very slowly. The

$$P_4 + 16ROH + 20CuX_2 \longrightarrow 4(RO)_3PO + 20CuX + 4RX + 16HX; \quad (5)$$

$$P_4 + 16ROH + 20CuX_2 \longrightarrow 4(RO)_2(HO)PO + 20CuX + 8RX + 12HX; \quad (6)$$

X = Cl, Br.

$$P_4 + 12ROH + 6CuY_2 \longrightarrow 4(RO)_3P + 6Cu + 12HY; \quad (7)$$

$$P_4 + 12R'OH + 6CuY_2 \longrightarrow 4(R'O)_2HPO + 6Cu + 4R'Y + 8HY; \quad (8)$$

Y = SO_4^{2-}, RCO_2^-.

oxygen-containing acido-ions (OH^-, SO_4^{2-}, RCO_2^-) are relatively unreactive in these reactions. Trialkyl phosphites form[44] stable complexes with copper(I) halides of the type $CuX \cdot P(OR)_3$ and $CuX \cdot 2P(OR)_3$. Copper(I) trialkyl phosphite complexes are greasy substances with melting points from 90 to 180 °C depending on the nature of the alkoxy-group. They are soluble in ether, benzene, acetone, and alcohols, can be readily detected by ^{31}P NMR spectroscopy in the range –6 to –10 ppm,[44,45] and are readily decomposed by chlorine with formation of trialkyl phosphates and copper(II) complexes.

Reactions (3) and (4) have been investigated in detail by kinetic and potentiometric methods.[41-43] The introduction of an arene solution of P_4 into an alcoholic solution of CuX_2 or CuY_2 under a O_2–Ar atmosphere is accompanied by a sharp shift of the redox potential of the Cu(II)/Cu(I) couple in the cathodic direction. At the same time, the pressure falls in a closed system and the absorption of O_2 begins. As O_2 is absorbed, the redox potential gradually returns to the anodic region. Analysis of the reaction mixture during the experiment by gas chromatography and ^{31}P NMR spectroscopy showed that the sharp shift of the redox potential in the cathodic direction is caused by the rapid reduction of Cu(II) to Cu(0) by tetraphosphorus in conformity with reactions (5)–(8). At the end of the process, when P_4 has been consumed, the redox potential shifts in the anodic direction as a result of the oxidation of Cu(0) to Cu(I) by oxygen. The rate constant for the reduction of Cu(II) by tetraphosphorus to Cu(0) was calculated from the magnitude and time of the cathodic shift of the redox potential at the beginning of the experiment:

$$k_{red} = \frac{W}{[Cu(II)][P_4]} \text{ litre mol}^{-1}\text{ s}^{-1} \quad (9)$$

(in C_2H_5OH, k_{red} = 1–5 litre mol^{-1} s^{-1}), while the rate constant for the oxidation of CuX and CuY by oxygen was found from the magnitude and time of the anodic shift of the redox potential:

$$k_{ox} = \frac{W}{[Cu(I)][O_2]} \text{ litre mol}^{-1}\text{ s}^{-1} \quad (10)$$

(in C_2H_5OH, k_{ox} = 0.1–0.9 litre mol^{-1} s^{-1}). Tetraphosphorus is sparingly soluble in polar solvents and readily soluble in weakly polar and non-polar solvents. Thus the solubility of P_4 is 10^4 g $litre^{-1}$ s^{-1} in carbon disulfide, 10^2 g $litre^{-1}$ in arenes, 50 g $litre^{-1}$ in alkanes, 40 g $litre^{-1}$ in carbon tetrachloride, 30 g $litre^{-1}$ in alcohol, and 10^{-3} g $litre^{-1}$ in water. Owing to the sparing solubility of P_4 in alcohol, benzene–alcohol and toluene–alcohol mixtures, which readily dissolve P_4 and copper(II) complexes, which only sparingly dissolve in H_2O, were used. Without the arene (in alcohol) and without alcohol (in the arene), the oxidation of P_4 by oxygen with formation of P_4O_{10} is slow.

The water formed by reactions (1)–(4) inhibits the reaction of P_4 with ROH and stimulates the P–O coupling to H_2O, affording phosphoric acid. Water is coordinated to copper(II) compounds more readily than ROH. According to UV spectroscopic data for water–alcohol solutions of copper(II) compounds, the alcohol complexes of copper(II) are formed at a H_2O concentration less than 10%.[46] In arene–alcohol solutions of copper(II) compounds, water exerts the least influence on the composition of the complexes. Owing to the presence of the arene, the water generated during reactions (1)–(4) does not affect the course of the oxidative *O*-phosphorylation of alcohols by tetraphosphorus. As a result of its sparing solubility in the arene–alcohol mixture (0.6 g $litre^{-1}$), water forms a separate phase. The arene can function as a phase transfer catalyst. It dissolves selectively ROH, P_4, and the copper(II) complexes, ensures the occurrence of the reaction between P_4 and ROH, and prevents the reaction between P_4 and H_2O.

An excess of acido-anions interferes with the coordination of P_4 to copper(II) complexes and has a negative influence on the rates of reactions (5)–(8). At a high concentration of

acido-ligands, P_4 does not reduce copper(II) complexes. In non-aqueous solvents, acido-ligands form stable complexes with copper(II) anions. On passing from aqueous to non-aqueous solutions, the stability constants of these acido-complexes increase by several orders of magnitude in opposition to the change in the dielectric constant [relative permittivity] and in the donor number (DN) of the solvent. Table 1 lists the formation constants (β_j) of the copper(II) chloride complexes in various solvents.

Table 1. The equilibrium constants (β_j) of the reaction $Cu^{2+}_{sol} + jCl^- \rightleftarrows CuCl_j^{2-j} + sol.$

Solvent (DN)	$CuCl^+_{sol}$	$CuCl_{2\,sol}$	$CuCl^-_{3\,sol}$	$CuCl^{2-}_{4\,sol}$
H_2O (18)	0.4	0.6	0.1	−0.8
DMF (24)	4.4	3.0	12.0	12.9
TMF (23)	7.3	12.4	16.8	19.4
$(CH_3)_2CO$ (17)	8.4	14.5	19.9	21.5
THF (20)	10.7	20.3	23.9	25.7
$(CH_3)_2SO$ (30)	3.4	5.2	7.3	7.9
PC (15)	12.0	22.7	29.0	34.0

Complexes saturated by acido-ligands are already obtained[47] at a ratio ligand/Cu(II) > 6. The maximum rates of reactions (1)–(4) are attained when coordinatively unsaturated copper(II) complexes predominate in the arene–alcohol solution. Coordinatively saturated copper(II) complexes do not react with tetraphosphorus.[41–43] The ligand effect observed is due to the fact that the η^1-tetraphosphorus complexes are characterised by a lower reactivity than the η^2-tetraphosphorus complexes. Since two free coordination sites in the equatorial plane are necessary for the η^2-coordination of P_4, an excess of acido-ligands interferes with the addition of P_4 to copper(II) ions. Only electron-donating ligands (Cl^-, Br^-, NH_3, SO_4^{2-}, RCO_2^-) interfere with the η^2-coordination of P_4, whilst electron-accepting ligands (CH_3CN, ROH, H_2O, Py) stimulate the incorporation of P_4 into the coordination sphere of Cu(II).[41–43] An important feature of reactions (1)–(4) is the fact that the O_2/P_4 ratio is equal to the stoichiometric coefficient and is independent of the O_2 concentration, temperature, and the composition of the system. Oxygen is consumed only in the oxidation of P_4 and does not participate in the alcohol oxidation reaction.[41–43]

The rate constants for the reduction of copper(II) salts by tetraphosphorus increase [k_{red} = 2.24 (CH_3OH) and 1.47 (C_4H_9OH) litre mol^{-1} s^{-1}], while the rate constants for the oxidation by oxygen change little [k_{ox} = 0.12 (CH_3OH) and 0.17 (C_4H_9OH) litre $mol^{-1}s^{-1}$], in parallel with increasing acidity of the alcohols. Such variation indicates the participation in the reaction of acidoalkoxophosphorus complexes of copper(II).

A decrease in the concentration of ROH in the system as a result of its replacement by $(C_4H_9O)_3PO$ leads to a fall in the yield of trialkyl phosphates [from 66% to 20% for tetrahydrofuran (THF)], to an increase in the yield of trialkyl phosphites, and to a slight change in the rate constants for reactions (5)–(7). After the addition of $(C_4H_9O)_3PO$ (c = 1.83 mol $litre^{-1}$), k_{red} changes from 2.35 to 2.63 litre mol^{-1} s^{-1} and k_{ox} changes from 0.1 to 0.09 litre mol^{-1} s^{-1}.

Acido-complexes of copper(II) not containing ROH react with P_4 to form acyl phosphates, which can be readily detected by ^{31}P NMR spectroscopy:[45] Cl_3PO (5 ppm), $(RCO_2)_3PO$ (−20 ppm), $(RCO_2)_2HPO$ (7 ppm), $(RCO_2)_2(OH)PO$ (−6 ppm), and $(RCO)_2(OH)_2PO$ (−3 ppm).

In an arene–acetic acid solution and other systems of the type arene–carboxylic acid, the previously unknown oxidative P–O coupling of P_4 to carboxylic acids takes place.

$$P_4 + 20Cu(RCO_2)_2 \longrightarrow 4(RCO_2)_3PO + 20Cu(RCO_2) + 4(RCO_2)O. \quad (11)$$

Triacyl phosphates partly decompose with formation of diacyl and monoacyl phosphates.

$$(RCO_2)_3PO + RCO_2H \longrightarrow (RCO_2)_2(HO)PO + (RCO_2)O; \quad (12)$$

$$(RCO_2)_2(HO)PO + RCO_2H \longrightarrow (RCO_2)(HO)_2PO + (RCO_2)O. \quad (13)$$

In the absence of copper(II) complexes, tetraphosphorus in an arene–alcohol solution is slowly oxidised by oxygen to the phosphorus oxide P_4O_{10}, the esterification of which proceeds extremely slowly and only as far as primary and secondary phosphoric acid esters.

$$P_4O_{10} + 6ROH \longrightarrow 2(RO)(HO)_2PO + 2(RO)_2(HO)PO. \quad (14)$$

The chain oxidation of P_4 by oxygen does not occur owing to the low O_2 and P_4 concentrations in the liquid phase.[48]

The influence of the acidity of the medium has been investigated by the method involving the addition of pyridine and by varying the HCl/LiCl ratio in the reaction system. With increase in the acidity of the medium, the rate of reactions (5)–(7) falls (k_{red} diminishes from 4.53 to 0 litre mol^{-1} s^{-1} in C_2H_5OH) and the yield of dialkyl phosphates increases (from 3.3% to 53.3% for diethyl phosphate). The addition of pyridine increases significantly the rates of reactions (5)–(7) and the yields of trialkyl phosphates.[41–43]

It follows from the data presented that P_4 reacts better with acidoalkoxocopper(II) complexes than with the acidoalcohol-copper(II) complexes. Iron(II) and iron(III) halides, sulfates, and carboxylates are an order of magnitude less reactive then the analogous copper(II) complexes.

The experimental data enumerated above indicate a coordination mechanism of the reduction of copper(II) complexes by tetraphosphorus.

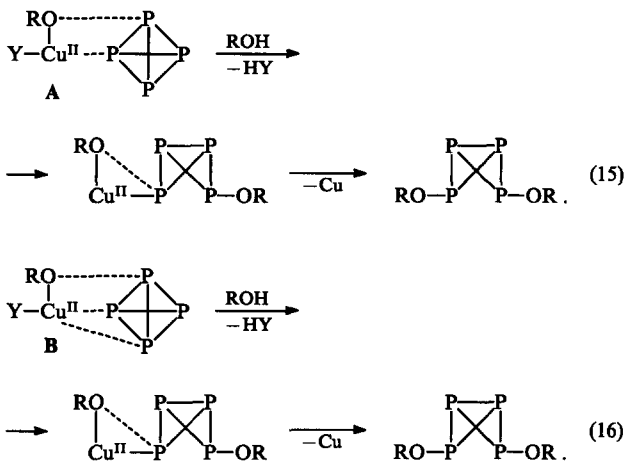
The reduction of acidoalkoxocopper(II) complexes by tetraphosphorus to Cu(0) consists of two stages: the insertion of P_4 in the Cu–OR bond with formation of the monoalkoxytetraphosphine anion $P_4(OR)^-$ and the reductive coupling of the RO^- and $P_4(OR)^-$ ligands with formation of dialkoxytetraphosphine.

The coordination mechanism is supported by the low activation energies (50–60 kJ mol^{-1}) compared with the dissociation energies of the bonds P–P (230 kJ mol^{-1}) and Cu–OR (260 kJ mol^{-1}) as well as the negative entropies of activation ($\Delta S^{\neq}_{red} = -82$ J mol^{-1} K^{-1} and $\Delta S^{\neq}_{ox} = -80$ J mol^{-1} K^{-1} in C_2H_5OH). The driving forces of the reaction involving the insertion of P_4 in the Cu–OR bond and the reductive dimerisation of the hydroxo- and polyalkoxyphosphine anions are the high energy of the P–O bond (340 kJ mol^{-1}) and the high redox potential of the Cu(II)/Cu(0) couple (0.34 V).

The subsequent stages of the oxidative alkoxylation of cyclic and linear dialkoxy- and tetraalkoxy-phosphides and dialkoxy- and tetraalkoxy-diphosphines by acidocopper(II) complexes are faster.

According to recent data,[29–33] P_4 can function both as a η^1- and η^2-ligand. On η^1-coordination (**A**) [(15)], the tetrahedral P_4 molecule is activated, being converted into a trigonal pyramid the vertex of which is directed towards the metal atom. The $P_{base}-P_{apex}$ distance (2.20 Å) is longer than the $P_{base}-P_{base}$ distance (2.09 Å). As a result of η^2-coordination (**B**), the edge linked to the metal is lengthened by 0.25 Å compared with the P–P bond in the free molecule (2.21 Å). Bidentate coordination of P_4 promotes a greater activation of the molecule than monodentate coordination. On bidentate binding of P_4, the P–P distance increases to an extent greater by 0.14 Å than on monodentate binding,[29–33] ensuring a greater loosening of P_4. The coordinatively saturated copper(II) complexes, incapable

of effecting the η^2-coordination of tetraphosphorus, are therefore characterised by a lower catalytic activity than the coordinatively unsaturated complexes, which are capable both of η^1- and η^2-coordination.[41-43]



(15)

(16)

The stages involving the insertion of P_4 in the Cu—OR bond and the reductive coupling of the OR^- and $P_4(OR)^-$ ligands have been investigated in detail by the CNDO method (complete neglect of differential overlap).[43] Calculations have been carried out for anionic acidoalkoxotetraphosphorus and acidomonoalkoxytetraphosphine complexes and cationic pyridinehydroxoaminoalkoxotetraphosphorus, aminoalkoxomonoalkoxytetraphosphine, aquoalkoxotetraphosphorus, and aquoalkoxomonoalkoxytetraphosphine complexes of copper(II).

The nature of the P_4 activation depends on the denticity of the ligands and the overall charge of the copper complex. The non-polar P_4 molecule is activated as a result of coordination: the energies of the P—P bonds diminish non-uniformly and effective charges appear on the P atoms, where they were absent before complex formation. In contrast to free P_4, the coordinated tetraphosphorus becomes an electron acceptor and interacts vigorously with ligands having an unshared electron pair (RO^-, HO^-, Hal^-). The HO^- ion models the behaviour of sulfate and carboxylate ligands. The ligands having no free unshared electron pair after coordination with copper(II) (H_2O, ROH, NH_3, Py) interact only weakly with P_4.[43]

The effective charges on the P atoms and the total, covalent, and ionic energies of the bonds between the ligands (between the chemically non-bonded atoms) were used to determine the composition of the many-centre transition state. The ligands in the copper(II) complex interact most strongly with the P atoms of the P_4 molecule which are not linked to the central copper atom. The energies of the bonds between the atoms and the ligands increase significantly with increase in the total positive charge on the complexes: in the anionic copper(II) complexes, the ligands interact much more weakly with P_4 than in the cationic complexes.[43]

The reductive coupling of the RO^- and $P_4(RO)^-$ ligands takes place with participation of the P atom bound covalently to the Cu(II) ion. If P_4 is inserted in the Cu—OR bond via a four-centre cyclic transition state (**A**) or (**B**), then the reductive elimination of the ligands RO^- and $P_4(RO)^-$ takes place via a three-membered cyclic intermediate. On the other hand, according to CNDO calculations, a covenient situation for the stage involving the reductive dimerisation of the alkoxo- and monoalkoxotetraphosphine ligands occurs in anionic complexes in the presence of electron-donating ligands. In such complexes the Cu—P bond, ruptured during the reductive coupling of the RO^- and $P_4(RO)^-$ ligands, is weakest.

$$P_4(OR)_2 \xrightarrow[-Cu]{Cu(OR)_2} P_4(OR)_4 \xrightarrow[-Cu]{2Cu(OR)_2} \longrightarrow 2P_2(OR)_4 \xrightarrow[-Cu]{2Cu(OR)_2} 4(RO)_3P. \quad (17)$$

Since cationic and anionic complexes are respectively more suitable for the stage involving the insertion of P_4 in the Cu—OR bond and the reductive coupling stage, optimum conditions are attained when uncharged copper(II) complexes are used. The rate of reaction therefore passes through a maximum when the number of acido-ligands is varied.[43]

III. Oxidative P—N coupling of tetraphosphorus to amines

Copper(II) complexes exhibit a high catalytic activity in oxidative P—N coupling of P_4 to primary and secondary amines.[49] Tetraphosphorus reacts with amines in the presence of oxygen with formation of phosphazo-compounds.

$$P_4 + 16RH_2N + 5O_2 \longrightarrow 4(RHN)_3P{=}NR + 10H_2O. \quad (18)$$

$$P_4 + 16R_2HN + 5O_2 \longrightarrow \longrightarrow 4(R_2N)_3P{=}NR + 6H_2O + 4ROH; \quad (19)$$

R = C_2H_5, C_6H_{11}, $C_6H_5CH_2$.

Under argon, tetraphosphorus reduces Cu(II) to Cu(0).

The zerovalent copper formed by reactions (20) and (21) is instantly regenerated by air. The new reactions (18)–(21) are very rapid. When primary ($C_6H_5CH_2NH_2$, $C_6H_{11}NH_2$) and secondary ($C_5H_{10}NH$) amines are used, we have the ratio $O_2/P_4 \simeq 5$. The formation of phosphazo-compounds by reactions (18)–(21) is of preparative value.[50,51] The new method of synthesis of triaminophosphazoalkyls is much simpler than that already available,[50] which is based on the P—N coupling of primary amines to trichlorophosphazohydrocarbons and the oxidative imination of phosphorus(III) compounds by *N*-chloroamines.[50-52]

$$P_4 + 10CuX_2 + 16RH_2N \longrightarrow \longrightarrow 4(RHN)_3P{=}NR + 10Cu + 20HX. \quad (20)$$

$$P_4 + 10CuX_2 + 16R_2HN \longrightarrow \longrightarrow 4(R_2N)_3P{=}NR + 10Cu + 4RX + 16HX. \quad (21)$$

Amines react with P_4 faster by one to two orders of magnitude than alcohols. In solutions in amines, the rate constants for the reduction of copper(II) by tetraphosphorus and for the oxidation of copper (I) by oxygen, calculated by Eqns (9) and (10), are higher than in alcoholic media. According to ^{31}P NMR spectroscopic data, reactions (18)–(21) proceed selectively. The ^{31}P NMR spectra contain only peaks characteristic of phosphazenes (10–20 ppm) and phosphorous triamide complexes of copper(I): $CuX[P(NR_2)_3]$ (10 ppm).[45]

The behaviour of amine systems under an oxygen atmosphere is similar to that of the alcohol systems. The kinetic ($W-\tau$) and conversion ($W-Q$) curves [τ is the time (s), W the rate of reaction (mol g^{-1} s^{-1}), and Q the degree of conversion of P_4] pass through an extremum for the ratio $Cu/P_4 < 10$ and have a descending form for $Cu/P_4 > 10$. When solutions of P_4 in an arene and of CuX_2 in an amine are mixed, the potential undergoes a sharp shift in the cathodic direction. As O_2 is absorbed, the redox potential of the Cu(II)/Cu(I) couple returns to the initial value. The rates of reactions (18)–(21) increase with increase in the concentrations of copper(II), NR_2H (or NRH_2), and O_2 and in temperature, whereas the addition of pyridine causes their increase by two orders of magnitude. It has been established by IR spectroscopy that the amine complexes of copper(II) in pyridine form acidoamino-complexes;[53] the reaction is accelerated in an excess of the amine and particularly after the addition of pyridine.[54]

The many-electron synthesis of phosphazo-compounds consists of stages involving the oxidative amination of tetraphosphorus and the oxidative imination of phosphorous triamide. In the rate-limiting stage, P_4 is inserted in the Cu–NRH or Cu–NR_2 bond. The diaminotetraphosphine is then rapidly oxidised by acidocopper(II) complexes in the presence of an amine to phosphorous triamide.

$$Cu(NRH)_2P_4 \longrightarrow Cu + P_4(NRH)_2. \quad (22)$$

$$P_4(NRH)_2 + 5CuX_2 + 10NRH_2 \longrightarrow$$
$$\longrightarrow 5Cu + 4P(NRH)_3 + 10HX. \quad (23)$$

In the presence of acids HX, phosphorous amides undergo acidolysis via a stage involving the formation of acyl phosphites, which acylate the amine produced. In order to prevent the acidolysis of phosphorous triamides, an excess of the amine was added to the reaction medium. The HX molecules generated as a result of reaction (23) are hydrolysed to the alcohol. The phosphorous triamides are oxidised further by the acidocopper(II) complexes to alkylaminophosphonium halides.

$$(R_2N)_3P + CuX_2 \longrightarrow Cu + (R_2N)_3PX_2. \quad (24)$$

The alkylaminophosphonium halides formed split off the alkyl halide by the Arbuzov reaction[55] with formation of dialkylaminohalophosphazoalkyl.

$$(R_2N)_3PX_2 \rightleftharpoons (R_2N)_2XP{=}NR + RX. \quad (25)$$

The dealkylation of alkylaminophosphonium halide takes place because of the considerable difference between the P–N (65–70 kcal mol^{-1}) and P=N (100–125 kcal mol^{-1}) bond energies. In contrast to the irreversible reactions of alkoxyphosphonium halides, leading to the conversion of P–O bonds into P=O, i.e. reaction (25) is reversible.

$$(RO)_3PX_2 \longrightarrow (RO)_2XP{=}O + RX.$$

The extent of reaction (25) depends on the reactivity of the reaction products—phosphazo-compounds and alkyl halides. Since dialkylaminohalophosphazoalkyls are highly basic,[51] the equilibrium constant of reaction (25) is small at the normal temperature. Aminophosphonium chlorides, containing only amino-groups, decompose fully at temperatures above 150 °.

In the catalytic process, the equilibrium in reaction (25) shifts to the right, since dialkylaminochlorophosphazoalkyl forms complexes with the copper(II) ion and reacts with the excess of dialkylamine, affording triaminophosphazoalkyl.

$$(R_2N)_2XP{=}NR + R_2HN \longrightarrow (R_2N)_3P{=}NR + HX. \quad (26)$$

Thus triaminophosphazoalkyls can be obtained from tetraphosphorus and primary and secondary amines in a high yield and at a high rate. Methods of synthesis of specific substances are being developed at the present time.

The phosphorus–nitrogen bond in triaminophosphazoalkyls is very stable and is not ruptured even after prolonged refluxing with water. According to ^{31}P NMR spectroscopic data,[51] triaminophosphazoalkyls react with water to form only phosphonium bases.

$$(R_2N)_3P{=}NR + H_2O \rightleftharpoons (R_2N)_3P(NHR)OH.$$

The hydrolytic stability of triaminophosphazo-compounds permits their extensive use for preparative purposes.[51]

IV. Oxidative P–O coupling of red phosphorus to alcohols

Despite the expansion in recent years of the scale of its manufacture, red phosphorus (P_n), is hardly used in organic synthesis because of its low reactivity.[12–40] It is inert in both homolytic and heterolytic reactions.[39,40]

In alcoholic solutions of CuX_2 and 80–200 °C, the topochemical oxidation of polyphosphorus by oxygen to trialkyl and dialkyl phosphates takes place at a high rate and with a high selectivity. This process was first described by Dorfman and coworkers.[56–59]

$$P_n + 3n\,ROH + 1.25n\,O_2 \longrightarrow n(RO)_3PO + 1.5n\,H_2O. \quad (27)$$

$$P_n + 2n\,ROH + 1.25n\,O_2 \longrightarrow$$
$$\longrightarrow n(RO)_2(HO)PO + 0.5n\,H_2O; \quad (28)$$

R = CH_3, C_2H_5, C_3H_7, C_4H_9, *iso*-C_4H_9, C_5H_{11}, *iso*-C_5H_{11}, C_8H_{17}.

In the absence of O_2 (and Ar), red phosphorus reacts with an alcoholic solution of CuX_2.

$$P_n + 5n\,CuX_2 + 4n\,ROH \longrightarrow$$
$$\longrightarrow n(RO)_3PO + 5n\,CuX + 4n\,HX + n\,RX. \quad (29)$$

$$P_n + 4n\,ROH + 5n\,CuX_2 \longrightarrow$$
$$\longrightarrow n(RO)_2(HO)PO + 5n\,CuX + 2n\,RX + 3n\,HX. \quad (30)$$

The ratio $(RO)_3PO/(RO)_2(HO)PO$ diminishes from 20.0 to 0.7 with decrease in the amount of ROH.

Oxygen and red phosphorus are consumed only in the formation of organic phosphates, the yields of which relative to P_n and O_2 are always equal and amount to ~100%. The reaction products—trialkyl and dialkyl phosphates—are good solvents for reactions (27) and (28), so that the organic phosphates can be synthesised virtually until the complete consumption of the alcohol. The organic phosphates are separated from the catalyst by extraction with heptane and subsequent vacuum distillation: at 4–5 Torr, trialkylphosphate is distilled away, whilst dialkyl phosphate remains in the still residue. The copper(I) ions formed by reactions (29) and (30) are rapidly oxidised by oxygen. During regeneration, copper(I) is oxidised to copper(II) and alkyl halides are hydrolysed by water to the alcohols.

The oxidative P–O coupling of P_n to glycols (glycerol, ethylene and diethylene glycols, butanediol) in dioxane leads to the formation of linear and cyclic alkyl phosphates.

In isopropyl alcohol, dialkyl phosphites are formed.

$$P_n + 0.75O_2 + 2n\,R'OH \longrightarrow n(R'O)_2HPO + 0.5n\,H_2O; \quad (31)$$

$$P_n + 3n\,CuX_2 + 3n\,R'OH \longrightarrow$$
$$\longrightarrow n(R'O)_2HPO + 3n\,CuX + 2n\,HX + n\,RX; \quad (32)$$

R' = *iso*-C_3H_7.

The organic phosphates obtained in reactions (27) and (28) were investigated by IR and ^{31}P NMR spectroscopy and gas chromatography. Their boiling points, densities, and refractive indices were also measured.

Red phosphorus purified with a hot NaOH solution was used for the investigations [according to spectroscopic emission analysis, the amount of the impurity (Si) did not exceed 0.1%–1.0%]. The existence of long-range order in P_n was established by X-ray powder diffraction, but the state of the substance is nearly amorphous.The surface of P_n is made up of chains of interlinked P_4 molecules.

The kinetic ($W-\tau$) and conversion ($W-\alpha$) curves (α is the degree of conversion of red phosphorus), having the shape typical of topochemical reactions,[60] pass through a maximum. With increase in temperature and the concentrations of CuX_2, O_2, ROH, and other reaction components, the maximum on the ($W-\tau$) curves becomes more distinct and is attained at lower values of τ. On the other hand, the position of the maximum on the ($W-\alpha$) curves, manifested at lower degrees of conversion (α = 0.01–0.1), changes little when the reaction temperature and the solution components are varied.

For alcohols ranging from CH_3OH to *iso*-C_5H_{11}, the activation energies for reactions (27) and (28) in the kinetic regime

(in the region of the maximum rate) are 50–140 kJ mol^{-1}, while the activation entropies are −145 to −75 J mol^{-1}K^{-1}. The kinetic and activation parameters depend on the composition of the solution. Studies with the aid of the Coulter counter and X-ray photoelectron spectroscopy showed that the specific surface and particle size of P_n do not change during the experiment and are 1200 cm^3 g^{-1} and 24 μm respectively. During the reaction, the P_n surface is oxidised and is 90% covered by phosphorus(V) compounds. Intermediates in the phosphorus oxidation reaction were not detected.[56–59]

The maximum rate of reaction was used to calculate the specific surface by the formula

$$W_{sp} = \frac{2W_{max}}{\pi g S}, \text{ mol m}^{-2}\text{s}^{-1}, \quad (33)$$

where g is the sample weight, S is the specific surface of P_4, and W_{max} the maximum reaction rate.

The specific rates of reactions (27) and (28) are independent of the mass of P_n and increase with increase in the concentrations of O_2, ROH, and CuX_2 in the liquid phase. Furthermore, the rate of the reaction is influenced by the nature of the solvent. Thus reactions (27) and (28) are faster in benzonitrile than in $(RO)_3PO$, and the topochemical process is appreciably affected by pyridine, H_2O, HCl, LiCl, P_2O_5, H_2SO_4, and $C_6H_5CH_2N$ [$C_6H_5CH_2NH_2$?Ed. of Translation]. When the HCl concentration is varied, the specific rate curve passes through a sharp maximum (i.e. the promoting and inhibiting effects are manifested mainly by H^+ions), while variation of the LiCl concentration results in a broad maximum on the reaction rate curve. The amine inhibits reactions (27) and (28), whilst pyridine slightly reduces their rates. A small amount of added H_2SO_4 (up to a concentration of 1 mol litre^{-1}) leads to the formation of alkyl and dialkyl sulfates. However, large amounts of P_2O_5 (in excess of 1 mol litre^{-1}) induce the conversion of alcohols into olefins. The specific rates of reactions (27) and (28) and the yields of products change only slightly after the addition into an alcoholic solution of $CuCl_2$ of even large amounts of Br^- and I^- ions. However after the replacement of $CuHal_2$ by $CuSO_4$, $Cu(RCH_2CO_2)$, $MnCl_2$, $CoCl_2$, $Mn(AcO)_2$, $Co(AcO)_2$, $Fe(AcO)_3$, oxygen ceases to be absorbed.[56–59]

The data presented indicate the activation of the surface of red phosphorus by HX as a result of the rupture of the P–P bonds between the molecules of tetraphosphorus.

$$P_n + HX \rightleftharpoons P_n(HX). \quad (34)$$

Subsequently HX-activated red phosphorus adsorbs the heterovalent dimer $Cu_2X_3(ROH)$, which predominates, according to UV spectroscopic data,[47] in alcoholic solutions of the CuX_2–CuX mixture.

$$P_n(HX) + Cu_2X_3(ROH) \rightleftharpoons Cu_2X_3(ROH)P_n(HX). \quad (35)$$

The two-electron redox decomposition of the surface complex formed in stage (35) leads to the formation of polyphosphonite and metallic copper on the surface.

$$Cu_2X_3(ROH)P_n(HX) \longrightarrow \longrightarrow Cu + CuX + P_n(OR)_2HX + 2HX. \quad (36)$$

In the presence of CuX_2, copper dissolves rapidly[49] and is oxidised by O_2 via reaction (37).

$$4CuCl + O_2 + 4HCl \longrightarrow 4CuCl_2 + 2H_2O. \quad (37)$$

According to ^{31}P NMR spectra,[45] reactions (27) and (28) proceed relatively selectively. Mainly trialkyl and dialkyl phosphates are obtained (chemical shifts of −1 and −2 ppm respectively), while in *iso*-C_3H_7OH peaks corresponding to derivatives of tetracoordinate phosphorus, i.e. $(RO)_2HPO$ (1 ppm), are observed. On the basis of these data, one can postulate that trialkyl phosphate is formed from dialkyl phosphite produced on dealkylation of trialkyl phosphite.

$$(RO)_3P + HCl \longrightarrow (RO)_2HPO + RCl. \quad (38)$$

According to the results of Okamoto et al.,[61,62] dialkyl phosphite is readily oxidised by $CuCl_2$ in alcohol to trialkyl phosphate.

$$(RO)_2HPO + 2CuCl_2 + ROH \longrightarrow \longrightarrow (RO)_3PO + 2CuCl + 2HCl. \quad (39)$$

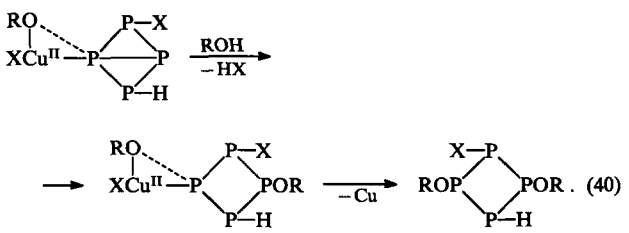
Thus reactions (29)–(37) include acid–base and oxidation-reduction stages. Copper(II) ions oxidise fairly rapidly the surface atoms of red phosphorus by virtue of the high potential of the two-electron Cu(II)/Cu(0) transition, which is 0.34 V. Iron(II), cobalt(II), and manganese(II) carboxylates, for which the potentials of such transitions are low (approximately −0.3 V), do not catalyse the reaction. Iron(III) ions, which tend to undergo only a one-electron transfer, do not exhibit an activity either. A distinctive characteristic of all the oxidants, under the influence of which the oxidative P–O and P–N coupling of low-valence phosphorus compounds to ROH, NRH_2, and H_2O,takes place, is the ability to transfer an even number of electrons.[63]

The acid–base stage is accelerated with increase in the acidity of the medium and of the alcohols (*iso*-$C_5H_{11}OH$ < *iso*-C_4H_9OH < C_4H_9OH ≪ C_3H_7OH < C_2H_5OH < CH_3OH), the pK values for which vary from 19 to 15. However, the oxidation-reduction stage is retarded with increase in the acidity of the medium, which hinders the formation of haloalkoxocopper(II) complexes. In the presence of an excess of Cl^- ions, the penta- and hexa-halo-complexes predominate. These are inactive in reactions (29) and (30) as a consequence of the absence of ROH in the coordination sphere.

On the one hand, water accelerates the acid–base stage owing to the increased acidity (pK_a = 14) and, on the other, it displaces the ROH molecules from the copper(II) complexes. Therefore, on raising the concentrations of HX, H_2O, and LiCl, the rate of formation of organic phosphates passes through a maximum.

The results obtained provide grounds for the assumption that the oxidation-reduction stage (36) takes place in two substages: the insertion of P_n(HX) in the Cu–OR bond and the reductive coupling of the RO^- and $P_n(HX)(OR)^-$ ions with formation of the dialkoxypolyphosphine $P_n(HX)(OR)_2$ and metallic copper. The transition states in both substages have a cyclic structure. This is indicated by the low activation energies (~50 kJ mol^{-1}), negative activation entropies (~ −100 J mol^{-1} K^{-1}), and the nature of the dependence of the rates of reactions (29) and (30) and of the yields of products on the composition of the coordination sphere of copper(II). The subsequent stages in the oxidative alkoxylation of cyclic and linear di- and tetraalkoxypolyphosphines by haloalkoxocopper(II) complexes are fast.

The coordination mechanism (40) of reaction (41) has been investigated quantum-chemically by the CNDO method using the cluster model of adsorption.[59] The organic fragment of the solid (cluster) was used in the cluster models. The rupture of bonds in



(40)

$$P_4(OR)_2(HX) \xrightarrow[-Cu,\ HX]{Cu(OR)_2} P_4(OR)_4 \xrightarrow[-2Cu]{2Cu(OR)_2} \longrightarrow 2P_2(OR)_4 \xrightarrow[-2Cu]{2Cu(OR)_2} 4(RO)_3P. \quad (41)$$

the tetraphosphorus clusters was compensated by the formation of bonds between the valence-unsaturated phosphorus atoms via a hydrogen atom (P_4H_2). This is the usual way of taking into account the boundary conditions in small clusters and of eliminating the influence of the bond dissociation between the atom clusters and the solid which is employed in cluster models.[64] It was assumed that the atoms of the tetraphosphorus clusters on the surface have the same structure as in the bulk phase.

In order to select the structure of the cyclic transition intermediate of the inner-sphere reaction (40), use was made of the method proposed by Dorfman et al.,[59] based on the comparison of the energies of the total, covalent, and ionic bonds between the ligands (between the chemically non-bonded atoms of the complex). Calculations were performed for both anionic and cationic clusters with different numbers of anions and molecules in the coordination sphere of copper(II).

The coordination of the tetraphosphorus cluster to the copper(II) ion results in a non-uniform weakening of the P–P bonds of the $P_4(H)_2$ cluster. The coordinated $P_4(H)_2$ cluster becomes an electron acceptor and forms bonds with the inner-sphere ligands (HO, RO, X) having an unshared electron pair after coordination. The ligands, which lose a free electron pair as a result of coordination to copper(II) (H_2O, ROH), react weakly with $P_4(H)_2$.[59] For this reason, the rate of the P–O coupling of P_n to alcohols passes through a maximum as the acidity of the medium is varied (as the HCl concentration in CH_3OH is varied from 0 to 5.6 mol litre^{-1}, the maximum rate is attained at c_{HCl} = 0.6 mol litre^{-1}) and increases with increase in the acidity of ROH. The ligands form the strongest bonds with the P atoms of $P_4(H)_2$ which are not linked to the central atom. In the cationic complexes, the bonds between $P_4(H)_2$ and the ligands are stronger than in the anionic complexes.[59] Therefore the catalytic activity of copper(II) halides passes through a maximum as the number of halide ions in the coordination sphere is varied.[56–59]

V. Oxidative P–O coupling of phosphine to alcohols

Since phosphine reacts poorly with organic substances,[9,10] a considerable amount of the highly toxic PH_3 in phosphorus and hypochlorite factories is burnt in order to achieve detoxification.[11]

As early as 1972, it was observed[46] that PH_3 is absorbed very rapidly by an alcoholic solution of copper(II) chloride. It was later established that PH_3 reacts with alcohol to form the products of oxidative phosphorylation, the nature of which depends on temperature and the nature of the ligand.[8,63,65–79] Under a O_2 atmosphere at 25–70 ° in halide systems ($CuHal_2$), the main reaction product is trialkyl phosphate (yield up to 100%).

$$PH_3 + 2O_2 + 3ROH \longrightarrow (RO)_3PO + 3H_2O; \quad (42)$$

R = CH_3, C_2H_5, C_3H_7, C_4H_9, *iso*-C_4H_9, C_5H_{11}, *iso*-C_5H_{11}, C_8H_{17}, $NH(C_2H_4OH)(C_2H_4)$.

Dialkyl phosphites are obtained from secondary alcohols—for example:

$$PH_3 + 1.5O_2 + 2iso\text{-}C_3H_7OH \longrightarrow (iso\text{-}C_3H_7O)_2HPO + 2H_2O. \quad (43)$$

In carboxylate and sulfate systems [alcoholic solutions of $Cu(RCO_2)_2$ and $CuSO_4$] at 25–70 °, trialkyl phosphites are formed preferentially:

$$PH_3 + 1.5O_2 + 3ROH \longrightarrow (RO)_3P + 3H_2O. \quad (44)$$

In contrast to tetraphosphorus, phosphine forms at 100–150 °C a considerable amount of dialkyl phosphate (up to 98%) in both halide and carboxylate systems.[8]

$$PH_3 + 2O_2 + 2ROH \longrightarrow (RO)_2(HO)PO + 2H_2O. \quad (45)$$

Reactions (42)–(45) can be achieved both by a continuous method involving the supply of a dilute PH_3–O_2–Ar mixture into the reactor and by a periodic method in which a mixture of PH_3 and Ar is initially introduced into the reactor and then O_2 is added.[8,63–70] Under an argon atmosphere at 25–75 ° in halide systems, the absorption of PH_3 is accompanied by the formation of univalent copper and trialkyl phosphate.

$$PH_3 + 8CuX_2 + 2ROH \longrightarrow (RO)_3PO + 8CuX + RX + 7HX; \quad (46)$$

X = Cl, Br.

In the carboxylate and sulfate systems at a low temperature (25–70 °C), trialkyl phosphite and metallic copper are obtained.

$$PH_3 + 2CuY_2 + 3ROH \longrightarrow (RO)_3P + 3Cu + 6HY; \quad (47)$$

Y = SO_4^{2-}, $R'CO_2^-$; R′ = CH_3, C_3H_7, $C_{17}H_{35}$.

At a high temperature (100–150 °C), dialkyl phosphate is formed in both cases.

$$PH_3 + 8CuX_2 + 4ROH \longrightarrow (RO)_2(HO)PO + 8CuX + 2RX + 6HX. \quad (48)$$

$$PH_3 + 4CuY_2 + 4ROH \longrightarrow (RO)_2(HO)PO + 4Cu + 2RY + 6HY; \quad (49)$$

X = Cl, Br; Y = RCO_2, $0.5\,SO_4$.

In the presence of H_2O, reactions involving the oxidative phosphorylation of the alcohol and water take place.

$$PH_3 + 8CuX_2 + ROH + 3H_2O \longrightarrow (RO)(HO)_2PO + 8CuX + 8HX. \quad (50)$$

$$PH_3 + 8CuY_2 + ROH + 3H_2O \longrightarrow (RO)(HO)_2PO + 4Cu + 8HY. \quad (51)$$

The addition of acid (HCl) stimulates the formation of dialkyl phosphate (up to 86%), while the addition of a base (pyridine) stimulates the formation of trialkyl phosphite (at 25–70 °C) and trialkyl phosphate (at 100–150 °C), the yield of the latter increasing to 88 % – 100%.[8,63,65–70]

The univalent or metallic copper formed by reactions (46)–(51) is oxidised by oxygen or air via reactions (37) and (52).

$$2Cu + 4HY + O_2 \longrightarrow 2CuY_2 + 2H_2O. \quad (52)$$

Simultaneously with the regeneration of copper(II), alkyl halides and sulfates are hydrolysed to the initial alcohols.

$$RX + 2H_2O \longrightarrow ROH + HX. \quad (53)$$

Alkyl carboxylates do not decompose, accumulating in the system. In the presence of pyridine, the mode of reaction is independent of the nature of the acido-ligand but does depend on temperature. At low temperatures, a reaction of type (47) takes place, whilst at high temperatures the following reaction occurs;

$$PH_3 + 4CuY_2 + 4ROH \longrightarrow (RO)_3PO + 4Cu + RY + 7HY. \quad (54)$$

On dilution of the alcohol with another organic solvent, mainly a dialkyl phosphate is formed. Copper salts are separated from other reaction products by vacuum distillation and can be reused.[8,63–70]

The rate of the oxidative P–O coupling of PH_3 to alcohols also depends on temperature, the nature of the acido-ions, and the concentrations of ROH, CuX, H_2O, HX, and pyridine. Reactions (46)–(51) are autocatalytic and begin only after the accumulation of a certain amount of CuX or CuY. When the initial copper(I) concentration is appreciably lower than the copper(II) concentration, the initial rate is close to zero. With increase in the amount of the absorbed PH_3 and time, the rate of reaction also increases,

reaching a maximum and then falling to zero. The conversion ($W-Q$) and kinetic ($W-\tau$) curves pass through an extremum.[8,63-70] The maximum rate is attained when the current copper(II) and copper(I) concentrations are equal. The conversion curves are described by the equation

$$W = k_1[Cu(II)]^{0.5}[Cu(I)]^{0.5}[PH_3]^{0.5}[ROH]^{0.5}, \quad (55)$$

where k_1 is the rate constant (litre mol^{-1} s^{-1}); k_1 = (0.2–2.7) × 10^{-2} in the presence of $CuCl_2$, $Cu(C_3H_7CO_2)_2$, and $Cu(C_{17}H_{35}CO_2)_2$ and k_1 = (0.2–20) × 10^{-3} when the process is catalysed by $CuSO_4$. The rates of reactions (46)–(51) were determined from the consumption of PH_3, copper(II) and from the accumulation of $(RO)_3PO$, $(RO)_2HPO$, $(RO)_2(OH)PO$ and RY.

In a mixed aqueous alcoholic solution of acido-complexes of copper(II), reactions (50) and (51) take place. The rates of these reactions in the $ROH-H_2O-CuY_2-NH_4OH-HX$ system are minimal at pH 2–5. They increase with increase in the concentrations of both NH_4OH and HX.[49] A high yield of trialkyl phosphate (up to 100%) is achieved only in anhydrous systems.[8,63-70] According to UV spectroscopic data, copper(II) complexes of alcohols exist only for a H_2O content less than 10%. As in other organic solvents, in alcohol the stability constants of the copper(II) compounds increase.

On the basis of UV and EPR spectroscopic, magnetic susceptibility, and potentiometric data, one can assume that phosphine is oxidised by acidoalcoholcopper(II) complexes in the halide, sulfate, and carboxylate systems and by acidoammine- and acidopyridinecopper(II) complexes in the ammonia and pyridine systems.[63]

According to ^{31}P NMR spectroscopic data, the products of the incomplete substitution of the H atoms in PH_3 by alkoxy- or hydroxy-groups [the phosphinite $(RO)H_2P$ and the phosphonite $(RO)_2HP$], characterised by chemical shifts in the region of 100 and180 ppm, do not accumulate. Hence it follows that in the rate limiting stage one H atom of PH_3 is substituted by an alkoxy- or hydroxy-group as a result of the two-electron reduction of copper(II) to the zerovalent state.[8,63-70] The subsequent substitution of the remaining H atoms by an alkoxy- or hydroxy-group is rapid. The metallic copper formed is oxidised by copper(II) ions via a reaction of the type:

$$Cu + CuCl_2 \rightleftharpoons 2CuCl; \qquad K_c = 8 \times 10^6.$$

Since the products of the incomplete substitution of the H atoms of PH_3 by a functional group, which are characterised by a higher oxidation–reduction potential and in which the ligand properties are more pronounced,[44] are oxidised faster then phosphine, a coordination mechanism of the rate-limiting stage must be postulated.[8,63-70] This is indicated by the low activation energy, the negative entropy, and fractional exponents in Eqn (55).

It follows from the UV spectra and kinetic data that copper(I) ions catalyse the reduction of copper(II) by phosphine as a result of the formation of the dimer Cu_2^{3+}.

Copper(II) and copper(I) ions form the dimeric complexes $Cu_2L_6Y_3$ by virtue of the presence in the coordination sphere of copper of the acido-ions (X^-, Y^-) having an unshared electron pair and capable of functioning as bridges between the two copper atoms. Such complexes, which increase the solubility of copper(I), are formed in both aqueous and non-aqueous media.[44,47] Phosphine, water, pyridine, and ammonia, which have no free unshared electron pair after coordination to copper, cannot serve as bridging ligands and cannot participate in the formation of dimers. Therefore the heteronuclear Cu_2^{3+} dimers predominate in mixed Cu(II)–Cu(I) solutions in the absence of PH_3.[47]

$$CuL_4Y_2 + CuL_2Y \rightleftharpoons Cu_2L_6Y_3; \quad (56)$$

L = ROH, H_2O, NH_3, Py.

The catalytic effect of copper(I) is due to its unusual tendency to form complexes with phosphine.[44] Together with other low-valence ions of d^{10} metals [Ag(I), Hg(II), Au(I), Pd(II)], copper(I) ions form stable complexes with PH_3.[44,63] The ions of metals having a different electronic configuration, such as those of copper(II), do not form complexes with PH_3.[44] Apparently copper(II) oxidises the phosphine coordinated to copper(I) via the formation of a dimer.

The oxidative hydroxylation of PH_3 in acid aqueous alcoholic and alcoholic solutions of CuX_2 proceeds via the following key stages:

$$\left[\begin{array}{c} X \\ | \\ Cu_2X_2 \cdots PH_3 \end{array}\right]^{\neq} \longrightarrow Cu_2X_2(PH_3X) \xrightarrow[-HX]{}$$

$$\longrightarrow Cu + CuX + XPH_2. \quad (57)$$

$$XPH_2 + ROH \longrightarrow (RO)PH_2 + HX. \quad (58)$$

The low activation energy (10–40 kJ mol^{-1}) and the negative activation entropy (−140 to −300 J mol^{-1} K^{-1}) show that PH_3 reacts with the X^- ion in the coordination sphere of the copper atom, forming a three-membered transition state.

In the rate-limiting stage (57), PH_3 is inserted in the Cu–X bond with formation of a phosphorane (or a quasi-phosphonium salt), which decomposes with formation of a halophosphine (XPH_2), Cu(0), and HX. This mechanism agrees with the properties of derivatives of trivalent phosphorus.[48,71-73] A characteristic feature of the latter [PH_3, PR_3, $P(C_6H_6)_3$, $P(OR)_3$, $(RO)H_2P$, $(RO)_2HP$, etc.] is reactions involving the formation of pentacovalent products, in which the phosphorus atom forms with the substrate simultaneously either two σ-bonds or a σ- and a π-bond.[48] An analogous stage in which PR_3 undergoes inner-sphere insertion in the M–O bond is rate-limiting in the reaction where trialkylphosphines are oxidised by oxygen in the presence of platinum, ruthenium, cobalt, iron, rhenium, and copper complexes.[71]

In the synthesis of vinylarenes from alkenes and aryl halides in the presence of $Pd(CH_3CO_2)_2-P(C_6H_5)_3$, the reductive elimination of the aryltriphenyl phosphonium salt is a side reaction,[73] which is accelerated when the aryl halide contains strong electron-donating substituents (a hydroxy- or amino-group).

Since the stability of the phosphonium salt increases with decrease in the number of P–H bonds, the rate of the stage of type (57) increases as the H atoms of PH_3 are replaced by alkoxy- or hydroxy-groups. The alcoholysis of the halophosphine [reaction (58)] is rapid.[48]

In neutral alcoholic and aqueous alcoholic media, the reduction of copper(II) involves a different mechanism. In the key stage of reaction (59), phosphine is inserted in the Cu–OR bond, as a result of which the tricoordinate phosphorus atom is converted into a pentacoordinate atom. The resulting phosphorane decomposes with formation of a phosphinite, zerovalent copper, and HY.[8,63-70]

$$Y_3Cu(ROH)PH_3 \xrightarrow[-HY]{} \left[\begin{array}{c} OR \\ | \\ Y_2Cu_2 \cdots PH_3 \end{array}\right]^{\neq} \longrightarrow$$

$$\longrightarrow Y_2Cu_2(PH_3OR) \xrightarrow[-HY]{} Cu + CuY + (RO)PH_2. \quad (59)$$

The valence of copper ions does not change on formation of the intermediate phosphorane $Cu_2Y_2(ROPH_3)$. Since the acidity of the phosphorane is appreciably higher than that of PH_3, the redox decomposition is accompanied by the dissociation of a P–H bond. The subsequent oxidation of the phosphinite $ROPH_2$ to trialkyl phosphite is faster than for PH_3.

$$ROPH_2 + 2Cu_2Y_3 + 2ROH \longrightarrow$$

$$\longrightarrow (RO)_3P + 2Cu + 2CuY + 4HY. \quad (60)$$

In alkaline alcoholic media, the phosphine is oxidised by copper(II) ions in a different way. Whereas in neutral media

[reaction (59)] only the coordinated ROH molecule is deprotonated, in alkaline media not only ROH but also the phosphine is ionised [reaction (61)]. In the rate-limiting stage of reaction (61), the reductive elimination of the phosphinite takes place on interaction of the phosphide with the alkoxide ion.

$$Y_3Cu_2(ROH)PH_3 \xrightarrow[-2HY]{} \left[\begin{array}{c} RO \\ | \\ YCu_2 \cdots PH_2 \end{array}\right]^{\neq} \longrightarrow$$

$$\longrightarrow (RO)PH_2 + CuY + Cu. \qquad (61)$$

This mechanism also agrees with the coordination properties of metal phosphides.[71] The acidity of the HZ molecules [Z = OH, OR, NH_2, NR_2, Hal, RCO_2, SH, CN, SR, PH_2, PRH, PR_2, $PO(OR)_2$, $P(OR)_2$, PH(OR), OPH(OR), etc.] increases by several orders of magnitude on complex formation.[74] According to Kukushkina[71] and Dohle et al.,[72] the phosphide ligand bound to osmium, chromium, molybdenum, and tungsten ions and formed on deprotonation of secondary and primary phosphines is alkylated by methyl iodide (an electrophile) or is alkoxylated by an alkoxide ion (a nucleophile).

Pyridine promotes the formation of copper(II) alkoxide and phosphide complexes because it increases the acidity of the coordinated HZ molecules.[54] Pyridine not only influences the mechanism of the inner-sphere reactions of the phosphine–alcohol complexes of copper(II) but also the behaviour of the intermediate organophosphorus compounds. Together with the bands corresponding to the chemical shifts characteristic of trialkyl phosphates, dialkyl phosphates, and trialkyl phosphate complexes of copper(I) (−1, −2, and 15 ppm respectively), the ^{31}P NMR spectra of the reaction products always contain bands typical for dialkyl phosphites (8 ppm).[45] When a secondary alcohol is used, for example *iso*-C_3H_7OH, a dialkyl phosphite becomes the main product. The yield of dialkyl phosphite in the sulfate and carboxylate systems is always higher than in the halide systems.[8,63–70]

It follows from the data presented that trialkyl and dialkyl phosphates are obtained when dialkyl and monoalkyl phosphites, formed on the dealkylation of trialkyl phosphite, are oxidised by copper(II) complexes.

The derivatives of tricoordinate phosphorus $(RO)_3P$ are dealkylated much more readily than the derivatives of tetracoordinated phosphorus $(RO)_2HPO$, (RO)(HO)HPO, $(RO)_2(HO)PO$, and $(RO)_3PO$.[48] The rate of dealkylation falls with increase in the pH of the medium and the length of the hydrocarbon group and on transition from the halide to the carboxylate and sulfate systems. Pyridine and an excess of the alcohol bind HX and HY, forming oxonium and pyridinium salts, and reduce the degree of decarboxylation of trialkyl phosphates.[48]

$$(RO)_3P + HY \longrightarrow (RO)_2HPO + RY. \qquad (62)$$

$$(RO)_2HPO + CuY_2 + ROH \longrightarrow$$
$$\longrightarrow (RO)_3PO + Cu + 2HY. \qquad (63)$$

$$(RO)_2HPO + HY \longrightarrow (RO)(HO)HPO + RY. \qquad (64)$$

$$(RO)(HO)HPO + CuY_2 + ROH \longrightarrow$$
$$\longrightarrow (RO)_2(HO)PO + Cu + 2HY. \qquad (65)$$

It has been shown by kinetic and physicochemical methods that the mechanism of the P–O coupling of PH_3 to the alcohol in the coordination sphere of copper(II) depends on the pH of the medium. In neutral and acid media, phosphine is inserted in the Cu–ligand (X^-, RO^-) bond in the rate-limiting stage with formation of a phosphorane, which decomposes with formation of a phosphinite, acid, and zerovalent copper. In ammonia and pyridine media, which promote the deprotonation of phosphine and the alcohol, the phophinite undergoes reductive elimination in the key stage as a result of the coupling of the phosphide and the alkoxide. In an alkaline medium, the rate of reduction of copper(II) by phosphine increases with increase in the positive charge of the complex, i. e. with increase in the number of NH_3 or pyridine molecules in the inner sphere of copper(II). In acid and neutral media, the rate of reaction increases with increase in the number of acido-ligands, i. e. with increase in the negative charge of the copper(II) complex.[8,63–70]

In order to elucidate the causes of the dependence of the mechanism of the P–O coupling of PH_3 to ROH in the composition of the copper(II) complex, the hypothetical intermediates in reactions (46)–(51), formed in acid, neutral, and alkaline media, and the free PH_3 and ROH molecules were subjected to a detailed quantum-chemical study.

The complexes were investigated by the CNDO [65] and Mulliken–Wolfsberg–Helmholtz (MWH) [75–77] methods. The CNDO method yields a total energy of the complex, from which it is possible to estimate the probability of the formation of the postulated intermediate, the charges on all the atoms (permitting a comparison of the electrophilic and nucleophilic properties of the coordinated molecules), and the total, covalent, and ionic energies of the bonds between all the atoms of the adduct.[78] A program, employing a semiempirical version of the parametrisation of the CNDO method and modified for the investigation of the structures of transition metal complexes, was developed for the calculations.[78] The 3*d*, 4*s*, and 4*p* orbitals of copper(II) and the valence *s* and *p* orbitals of the coordinated molecules were employed as the basis set. A distorted octahedral structure of the copper(II) complexes, in which the reacting molecules (ROH, PH_3) and ions (RO^-, PH_2^-, X^-) are located in the equatorial plane in the *cis*-positions relative to one another, was adopted. The standard geometry of the ligands was assumed.[65]

Alcohols and phosphines are extremely weak OH and PH acids ($pK_a \simeq 15–32$). They are activated by very weak bases in anhydrous solvents[79] and by metal complexes.[71,74] High-valence and low-valence metal cations are required respectively for the activation of alcohols and phosphines. Under the influence of metal complexes, the acid dissociation constants of the PH and OH acids increase by several orders of magnitude.[74] In selecting the intermediates, account was taken of the fact that the composition of the coordination sphere of copper(II) changes as a function of the pH of the medium. Cationic and anionic complexes predominate in ammonia and halide solutions respectively.[54] With increase in the basicity of the medium, there is an increase in the probability of alkoxo- and phosphido-reactions, i. e. reactions that result in the formation of alkoxo- and phosphido-ligands.[54]

In order to investigate the behaviour of the intermediates, the energies of the bonds between the atoms within the coordinated molecules (P–H, O–H), and between the copper atoms and the electron-donating atoms of the ligands (Cu–P, Cu–O, Cu–X), which are ruptured in the reactions involving the oxidative P–O coupling of PH_3 to ROH, were calculated. In addition, the P–O, P–X, H_P–X, H_P–O, H_O–X, H_O–P, H_O–O bond energies in the initial reactants before the formation of chemical bonds in the reactions involving the oxidative P–O coupling of PH_3 to ROH were evaluated (H_O and H_P are hydrogen atoms linked to O and P atoms).[67]

The key stages in the reactions involving the inner-sphere P–O coupling of PH_3 to ROH — insertion and reductive elimination of ligands — proceed via the intermediate formation of a polar many-centre metallacycle in which bonds are dissociated and new ones are formed simultaneously [reactions (57), (59), (61)].

By comparing the energies of the bonds between atoms which are and are not linked chemically, it is possible to find the probable structure of the cyclic many-centre transition state and the direction of the concerted redox decomposition of the intermediate complex and to estimate the influence of the solvent. The energy of the bonds between atoms separated by a distance greater than the sum of the covalent radii is low and is much lower than the energies of chemical bonds.[65]

The behaviour of intermediates in an acid medium was investigated with the aid of copper(II) complexes containing

different numbers of alcohol, phosphine and water molecules and halide ions. The properties of the neutral medium were inferred from the results of calculations for hydroxo- and alkoxo-phosphinecopper(II) complexes. The hydroxo-ligands in these complexes were modelled by sulfate, phosphate, and carboxylate anions. The copper–ammonia and copper–pyridine systems were investigated by means of calculations for the hydroxo- and alkoxo-pyridinephosphinecopper(II) and hydroxo- and alkoxo-aminephosphinecopper(II) complexes. The number of neutral molecules (PH_3, NH_3, Py, H_2O) and anions (PH_2^-, Cl^-, HO^-, RO^-) was varied in such a way that the charge on the complexes changed from +2 to −4.[65]

In the coordination sphere, the weakly polar PH_3 molecule is activated and becomes polar. Whereas in the free PH_3 molecules the effective charges on the P and H atoms are zero, coordination results in the appearance on these atoms of charges which depend on the composition and the overall charge of the complex. In the anionic complexes, the charge on the phosphorus atom is positive, while in the cationic complexes it is negative. The ionic character of the P–H in the coordinated PH_3 molecule is enhanced. On complex formation, the alcohol molecule is activated to a much greater extent. The ionic character of the O–H bond increases significantly as a result of coordination, the effective negative charge on the oxygen atom increases, and there is also an increase in the positive charge on the H atom, which varies as a function of the composition and overall charge of the complex.[65]

The nature of the activation of PH_3 depends to a greater extent on the composition and charge of the complex than in the case of alcohols. Judging from the charge on the phosphorus atom, phosphine acquires nucleophilic and electrophilic reactivity in the cationic and anionic complexes respectively. Judging from the charges on the oxygen atom, the alcohol and water exhibit a nucleophilic activity in both positively and negatively charged complexes. Owing to the relatively weak ionic character of the P–H bond in phosphine compared with the O–H bond in the alcohol, the activity of phosphine depends more on the dielectric constant of the medium.[80] It follows from the comparison of the ionic characters of the P–H and O–H bonds and the charges on the P, O, and H atoms that the hydroxo-reaction is preferable to the alkoxo-reaction and especially the phosphide-reaction. The formation of hydroxide ions in the coordination sphere of copper(II) is more probable than the formation of alkoxide and phosphide ions. The Cu–P, Cu–O and Cu–X bond energies increase sharply on passing from the phosphine and alcohol complexes to the phosphide, alkoxide, and hydroxide complexes. As a result of the deprotonation of phosphine, there is a sharp increase in the ionic character of the Cu–P bonds. Since in polar media ionic bonds are more reactive than covalent bonds,[80] an increase in the amount of ionic character of the bond entails an increase in its reactivity.

In the haloaquophosphinealcohol complexes, which predominate in acid media, the Cu–X bond is most ionic. For this reason, oxidative halogenation of phosphine and alcoholysis of the halophosphine formed take place in acid media [reactions (57) and (58)].[46]

The coordination character of the reaction is stimulated by the bond arising between the ligands. According to quantum-chemical calculations,[65] the coordinated phosphine forms fairly strong bonds with the ligands in anionic copper(II) complexes. Presumably the redox decomposition of the haloaquophosphine-alcohol- and alkoxophosphine-copper(II) complexes takes place as a result of the insertion of PH_3 in the Cu–X and Cu–OR bonds [reactions (57)–(61)].[65]

Cationic copper(II) complexes predominate in ammoniacal and pyridine media.[54] According to the results of a quantum-chemical study,[65] phosphine does not form bonds with the ligands in such complexes. Furthermore in alkaline media, phosphide and alkoxide ligands are produced.[79] Ammine- and pyridine–copper complexes undergo redox decomposition as a result of the interaction between the phosphide and alkoxide ions. The phosphinite formed as a result of the reductive coupling of the phosphide and alkoxide ligands is more readily deprotonated ($pK_a = 15$) than PH_3 ($pK_a = -14$). Phosphinite and phosphonite are therefore more rapidly oxidised by copper(II) ions than phosphine.

The inner-sphere reactions (65) are also promoted by ligands which do not participate directly in the redox decomposition of the intermediate complex.[65] According to quantum-chemical calculations, these ligands form fairly strong bonds with the hydrogen atoms of PH_3 and ROH, offering nucleophilic support to the phosphido- and alkoxo-reactions leading to the formation of phosphide and alkoxide ions in the coordination sphere. Particularly strong bonds are formed between the H atoms of phosphine and the alcohol in the cationic copper complexes.

Thus the mechanism of the activation of phosphine and the alcohol in the coordination sphere of copper(II) has been investigated by the CNDO method. It was shown that the probability of the insertion of PH_3 in the metal–ligand bond and of the reductive coupling of the phosphide and alkoxide ligands can be estimated from the energy of the bond between the reacting ligands. In acid and neutral media, which promote the formation of anionic copper(II) complexes, phosphine is inserted in the metal–ligand bond in the key stage: in ammonia and pyridine solutions, which ensure the formation of cationic complexes, the reductive coupling of the phosphide and alkoxide ligands takes place in the rate-limiting stage.

VI. Oxidative P–C coupling of phosphine to alcohols

A whole series of new organic reactions with participation of platinum(II) and platinum(IV) halides, e.g. the oxidation of alkanes, arenes, olefins, alcohols, carbon monoxide, etc., have been observed in recent years.[81–86] The oxidising activity of platinum(II) and platinum(IV) halides as a rule varies in parallel with the kinetic constants for the exchange of ligands and the thermodynamic stability constants and antiparallel to the redox potentials and Pt–X bond energies.[81–87] Platinum(II) halides usually catalyse the reduction of platinum(IV) by various substrates via the formation of dimers containing platinum(II) and platinum(IV). New reactions involving the oxidative alkoxylation and hydroxyalkylation of phosphine have been described.[63,88–90]

$$PH_3 + 3Na_2PtCl_6 + 3ROH \longrightarrow \longrightarrow 3Na_2PtCl_4 + (RO)_3P + 6HCl; \quad (66)$$

R = CH_3, C_2H_5, C_3H_7, C_4H_9, *iso*-C_4H_9, C_5H_{11}, *iso*-C_5H_{11}, C_8H_{17}.

$$PH_3 + 3RCH_2OH + 1.5Na_2PtCl_6 \longrightarrow \longrightarrow (RCH_2)(RCHOH)_2PO + 1.5Pt + 3NaCl + 6HCl. \quad (67)$$

$$PH_3 + 4RCH_2OH + 2Na_2PtCl_6 \longrightarrow \longrightarrow (RCH_2O)_3PO + 2Pt + 4NaCl + RCH_2Cl + 7HCl; \quad (68)$$

R = C_3H_7, C_4H_9, *iso*-C_4H_9.

When a PH_3–Ar gas mixture, even one containing only traces of phosphine, is passed at 25–150 ° through an alcoholic solution of the Na_2PtCl_6 complex, known to be very inert and stable,[87] trialkyl phosphites (at 25–70 °) as well as trialkyl phosphates and tertiary phosphine oxides (at 90–150 °C) are formed.[88,89]

The new reactions are very rapid. Reaction (66) terminates after the reduction of platinum(IV) to platinum(II), whilst reactions (67) and (68) terminate after the reduction of platinum(IV) to zerovalent platinum, which is precipitated as a black fine-grained deposit on the bottom of the reactor. During the absorption of PH_3 by an alcoholic solution of Na_2PtCl_6, the redox potential (φ) of the Pt(IV)/Pt(II) couple shifts in the cathodic direction.[88,89]

The changes in the PH_3–Na_2PtCl_6–ROH system are analysed in terms of the nature of the conversion ($W-Q$), kinetic ($W-\tau$), and potentiometric ($\varphi-Q$, and $\varphi-\tau$) curves. The conversion and kinetic curves pass through a maximum in all cases.

The rate of reaction (66) is described by the equation

$$W = k_1[Pt(IV)]^{0.5}[Pt(II)]^{0.5}[PH_3]^{0.5}[ROH]^{0.5} \quad (69)$$

After the reduction of platinum(IV) to platinum(II), the spent solution is readily regenerated with a dilute Cl_2–Ar gas mixture.

$$NaPtCl_4 + Cl_2 \longrightarrow Na_2PtCl_6. \quad (70)$$

During the regeneration of platinum, trialkyl phosphites are oxidised to the phosphates.

$$(RO)_3P + Cl_2 + ROH \longrightarrow (RO)_3PO + RCl + HCl. \quad (71)$$

The kinetic parameters of reactions (67) and (68) are characterised by a more complex formula:

$$W = k_1[PH_3]^{0.5}[ROH]^{0.5}([Pt(IV)]^{0.5}[Pt(II)]^{0.5}) + k_2[Pt(II)], \quad (72)$$

where k_1 and k_2 are the rate constants (litre mol^{-1} s^{-1}).

It follows from Eqns (69) and (72) that reactions (66)–(68) proceed in the coordination spheres of dimeric and mixed haloalkoxophosphineplatinum(IV) and the corresponding platinum(II) complexes. As platinum(IV) is reduced to platinum(II), the colour of the solution changes from bright orange to dark brown, which indicates the formation of heterovalent platinum complexes.[80] The coordination mechanism of reactions (66)–(68) is indicated by the low activation energies ($E^{\neq}$ = 28–56 kJ mol^{-1}) and entropies ($\Delta S^{\neq}$ = −140 to −20 J mol^{-1} K^{-1}), the fractional order with respect to the reactants [Pt(IV), PH_3, ROH)], the negative influence of H_2O, HCl, and NaCl, and the positive influence of NaBr, NaI, and platinum(II). Platinum(II) iodides and bromides catalyse the insertion of PH_3 and ROH in the coordination spheres of platinum(IV) chlorides.[87]

At a low temperature, the products [$(RO)_3P$ and Pt(II)] form the stable complexes [$Pt(P(OR)_3]/PtCl_4$, which are insoluble in alcohols. The composition of the complexes was established by X-ray [powder? PCMA in Russian (Ed. of Translation)] diffraction and X-ray photoelectron and IR spectroscopic methods.[88,89] The intermediate organophosphorus compounds, formed at a high temperature, were investigated by ^{31}P NMR spectroscopy.[45] Analysis of the reaction medium during the experiment demonstrated the occurrence of chemical shifts characteristic of $(RCH_2O)_3P$ (95–100 ppm), $(RCHOH)_3P$ (−40 to −30 ppm), $(RCH_2)(RCHOH)_2PO$ (40–50 ppm), $(RCH_2O)_2HPO$ (4–8 ppm), and $(RCH_2O)_3PO$ (−3 ppm).[45] Hence it follows that trialkyl phosphates are formed in the following way:

$$Pt_2X_5(PH_3)(RO)^- \longrightarrow 2PtX_2 + (RO)PH_2 + HX. \quad (73)$$

$$Pt_2X_5(ROPH_2)(RO) \longrightarrow 2PtX_2 + (RO)PH + HX. \quad (74)$$

$$Pt_2X_5[(RO)_2PH](RO) \longrightarrow 2PtX_2 + (RO)_3P + HX. \quad (75)$$

$$PtX_2[(RO)_3P] + HX \longrightarrow PtX_2[(RO)_2HPO] + RX. \quad (76)$$

$$Pt_2X_5[(RO)_2HPO](RO) \longrightarrow 2PtX_2 + (RO)_3PO + HX. \quad (77)$$

According to Eqns (73)–(77), the alcohol is activated as a result of deprotonation and the formation of the covalent Pt–O bond.[91] Reactions (74)–(77) are faster than reaction (73), since, in contrast to phosphine, phosphinite, phosphonite, and phosphite readily form complexes with platinum(IV) and platinum(II).[92,93] Platinum(II) promotes not only the insertion of PH_3 and ROH into the coordination sphere of platinum(IV) [87] but also the dealkylation of trialkyl phosphites.[92,93] Thus the hydrolysis of $(CH_3O)_3P$ in water at 25 °C takes more than 40 h, whilst in the presence of K_2PtCl_6 it reaches completion instantaneously.[92] Whereas the conversion of trialkyl phosphite into dialkyl phosphite [reaction (76)] is rapid, the subsequent hydrolysis of dialkyl phosphite is slow even in the presence of platinum(II).[92]

Since the phosphine chlorination products (PCl_3 and PCl_5), characterised by chemical shifts of 220 and −80 ppm respectively,[45] were not detected, presumably trialkyl phosphites are formed under the influence of platinum(IV) via the successive substitution of the hydrogen atoms of phosphine by alkoxy-groups, dealkylation of trialkyl phosphite to dialkyl phosphite, and the substitution of the hydrogen atoms in dialkyl phosphites by alkoxy-groups. Phosphine, phosphinite phosphonite, and dialkyl phosphite are inserted in the Pt–O bond, forming a phosphorane.

Phosphine, phosphinite, phosphonite and dialkyl phosphite behave similarly to unsaturated compounds (olefins, carbon monoxide), which typically undergo insertion in the metal–ligand bond.[74,81,82,94,95] Since the stability of the phosphorane increases as the hydrogen atoms of phosphine are replaced by a functional group,[48] the reactions involving the oxidation of phosphinite, phosphonite, and dialkyl phosphite by platinum(IV) are faster than the oxidation of phosphine.[88,89] The driving forces of reactions (78) are the appreciable Pt(IV)/Pt(II) redox potential and the high P–O bond energy. Similarly, trialkyl phosphates are formed from phosphine on treatment with platinum(II), but the reaction is faster, since platinum(II) halides enter relatively easily into ligand exchange, in contrast to platinum (IV) halides.[87]

$$\left[\begin{array}{l} RO \\ X_5Pt_2{-}PH_3 \end{array}\right]^{\neq} \longrightarrow X_5Pt_2(PH_3OR) \longrightarrow$$

$$\longrightarrow 2PtX_2 + (RO)PH_2 + HX. \quad (78)$$

According to ^{31}P NMR spectroscopic data, alkyl(dihydroxyalkyl)phosphine oxide is obtained from tri(hydroxyalkyl)-phosphine.

$$(RCHOH)_3P \longrightarrow (RCHOH)_2(RCH_2O)P \longrightarrow$$

$$\longrightarrow (RCHOH)_2(RCH_2)PO.$$

Tri(hydroxyalkyl)phosphines with electron-donating substituents isomerise to tertiary phosphine oxides, in contrast to tri(hydroxyalkyl)phosphines with electron-accepting substituents, which are converted into phosphites.[9]

Tri(hydroxyalkyl)phosphine can be obtained from phosphine and the alcohol on treatment with platinum(IV) and platinum(II) halides. In the rate-limiting stage, a hydrogen atom of phosphine is replaced by a hydroxyalkyl group. The subsequent substitution of the hydrogen atoms of primary and secondary phosphines by a hydroxyalkyl group proceeds similarly but faster, since, in contrast to phosphine, alkylphosphines are readily coordinated to platinum(IV).[93] There are no chemical shifts characteristic of primary (−60 ppm) and secondary (−140 ppm) phosphines in the ^{31}P NMR spectra.[45]

$$Pt_2X_6(PH_3)(RCH_2OH) \rightleftharpoons Pt_2X_4(PH_2)(RCHOH) + 2HX. \quad (79)$$

$$Pt_2X_4(PH_2)(RCHOH) \longrightarrow 2PtX_2 + PH_2(RCHOH). \quad (80)$$

$$Pt_2X_4(PH_2)(RCHOH) \rightleftharpoons Pt_2X_3(PH_2)(\eta^2\text{-}RCHO) + HX. \quad (81)$$

$$Pt_2X_3(PH_2)(\eta^2\text{-}RCHO) \xrightarrow[-PtX_2]{HX}$$

$$\longrightarrow PtX(PH_2)(RCHO) \longrightarrow PH_2(RCHOH). \quad (82)$$

The alcohol is activated by the β-elimination of hydrogen, the formation of a bidentate (η^2-type) aldehyde bound to the metal,[94,95] and the formation of the organometallic Pt–C bond.[81,82] The β-elimination reactions are typical for transition metal compounds.

The β-hydrogen atoms are eliminated on treatment with either the metal, or nucleophiles, or electrophiles. The stabilisation of the transition state by the π-bond formed renders the β-position extremely reactive.[95]

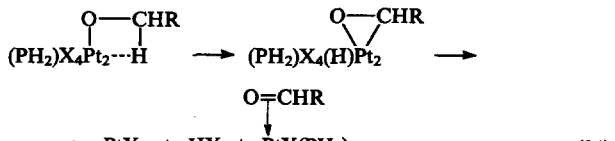
$$\begin{array}{l} HOHRC{-}H \\ (PH_2)X_5Pt_2 \end{array} \xrightarrow[-HX]{} X_4(PH_2)Pt_2(RCHOH) \longrightarrow$$

$$\longrightarrow PH_2(RCROH) + 2PtX_2. \quad (83)$$

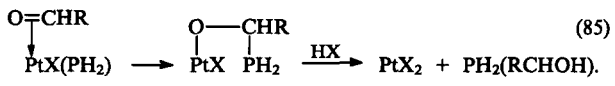
Mono(hydroxyalkyl)phosphine is formed as a result of the insertion of PH_3 in the Pt–C bond. Platinum(II) behaves similarly to platinum(IV), but all the stages involving platinum(II) are faster.[88,89]

The hydroxyalkylation of phopshine takes place as a result of the oxidation of the alcohol by platinum(IV) to the aldehyde and subsequent addition of phosphine to the carbonyl compound.

Studies have shown that reaction (84) without PH_3 proceeds very slowly,[85,86] whilst reaction (85) in the presence of platinum(IV) and platinum(II) occurs only when concentrated phosphine is employed.[9]



(84)



(85)

Reactions (66)–(68) take place not only in alcoholic but also in alcohol–pyridine solutions of Na_2PtCl_6. The pyridine complexes of platinum(IV) and platinum(II) activate PH_3 and ROH via deprotonation.

Phosphinite is formed as a result of the inner-sphere coupling of the ligands (the phosphide and alkoxide), the reaction being promoted by pyridine, which is a powerful π-acceptor.[54]

$$Pt_2X_4Py_2(PH_2)(RO) \longrightarrow 2PtX_2 + PH_2OR. \quad (86)$$

In a quantum-chemical study of the mechanism of the interaction of phosphine with the alcohol, the energies (total, covalent, and ionic) of the bonds between all the atoms of the platinum(IV) and platinum(II), containing different numbers of molecules (H_2O, ROH, NH_3, Py, PH_3) and ions (PH_2^-, RO^-, HO^-, X^-), were calculated by the CNDO method.[90] The total, covalent, and ionic bond energies were evaluated using the method described by Fischer and Kollmar.[78] Phosphine, the alcohol, and water in the coordination sphere of platinum(IV) and especially platinum(II) are appreciably activated as a result of the increase in the amount of ionic character of the P–H and O–H bonds, which increase the reactivity of molecules in polar media.[80] The energy of the bond between the alkoxide ion and phosphine increases on passing from platinum(IV) to platinum(II).[90] Platinum(II) activates the P–H dissociation process via the formation of the $Pt-H_P$ single bond. The deprotonation of the alcohol activates the halide ions, promoting the formation of the $X-H_O$.[90]

The mechanism of the reduction of platinum(IV) to platinum(II) by phosphine, including the stage in which PH_3 is inserted in the Pt–OR bond, operates only in alcoholic media, which promote the formation of ionic complexes distinguished by a high energy of the bond between the phosphorus atom of phosphine and the oxygen atom of the alkoxide ion. The mechanism of the oxidation of phosphine by platinum(IV) and platinum(II), including the stage in which the phosphide and alkoxide ions are coupled, operates only in alcohol–pyridine systems, where cationic complexes predominate. These are distinguished by the appreciable energy of the bond between the phosphorus and oxygen atoms of the phosphide and alkoxide ions.[90]

In order to elucidate the mechanism of the catalysis by platinum(II) complexes of the reduction of platinum(IV) by phosphine [reactions (66)–(68)], the quantum-chemical molecular orbital perturbation (MOP) method was used. The bond energy between atoms separated by a distance greater than the sum of the covalent radii was calculated by the MOP method, which had been first applied in the estimation of the reactivities of ligands.[75–77] The bond energy proved to be appreciably lower than the energies of chemical bonds.[96–98] By comparing the energies between the atoms of the intermediate complex which are not linked chemically, it was possible to find the probable structure of the multi-centre cyclic transition state.[96] The higher the bond energy between atoms not linked chemically (the more negative the stabilisation energy), the greater the probability of the chemical bond between them in the transition state.[97,98]

The stabilisation energies have been calculated by the MOP method for reactions in which the coordinated phosphine is the electron acceptor, while the alcohol (or the alkoxide ion) is the electron donor, and also for reactions where phosphine is the electron donor and the alcohol (alkoxide or chloride ion) is the electron acceptor.[67] On coordination to platinum(IV), phosphine is activated. The negative charge on the oxygen atom and the positive charge on the phosphorus atom increase. As a result of coordination, phosphine acquires electron-accepting properties, while the electron-donating properties of the alcohol are enhanced. In the case where PH_3 is the acceptor and the alcohol is the donor, the stabilisation energy is more negative than in the case where the above ligands act in the opposite directions. It becomes more negative when ROH is replaced by RO^- and Cl^- is replaced by Br^- and I^- ions.[67]

The stabilisation energies have been calculated by the MOP method for the reactions of phosphine coordinated to platinum(II) with the alcohol bound to platinum(IV) and of phosphine bound to platinum(IV) with the alcohol coordinated to platinum(II). It was found that the perturbation energies for the inner-sphere reactions are appreciably higher than for the outer-sphere reactions. Hence it follows that the reaction between phosphine and the alcohol occurs in the coordination sphere of platinum(IV), while platinum(II) catalyses the formation reactions of the platinum(IV) complexes of haloalkoxyphosphines by accelerating the ligand exchange processes.[87]

VII. Oxidative P–O coupling of phosphine to alcohols in the presence of chlorine

The reactions of chlorine with the halogens in aqueous media and in the gas phase have been investigated in fair detail.[99–102] It has been observed[49] that, on chlorination of PH_3 in an alcohol at 50–70 °C, trialkyl phosphate is formed rapidly and in a high yield.

$$PH_3 + 4Cl_2 + 4ROH \longrightarrow (RO)_3PO + RCl + 7HCl; \quad (87)$$

R = C_4H_9, *iso*-C_4H_9, C_5H_{11}, *iso*-C_5H_{11}.

At a low temperature (8–25 °C), reaction (87) takes place in the presence of pyridine.[49]

The development of the reaction via a branched-chain mechanism was suppressed by using dilute gaseous PH_3–Ar and Cl_2–Ar mixtures, which were mixed separately with the alcohol in a preliminary step. Phosphine and chlorine entered the reactor in a countercurrent, so that there was a high PH_3 concentration and a low Cl_2 concentration at the inlet to the reactor, while at the outlet the opposite situation obtained — a high Cl_2 concentration and a low PH_3 concentration. The rate of supply of Cl_2 and PH_3 was regulated by means of the Cl_2/Cl^- chlorine electrode potential.[103] For this purpose, the reactor was fitted with a potentiometric device consisting of platinum and calomel half-cells. The latter contained only Hg, Hg_2Cl_2, and a ground joint as the electrolytic bridge. Such a calomel electrode, without the traditional agar–agar bridge, did not break at high temperatures and did not affect the composition of the liquid phase.

The introduction of PH_3 into an alcoholic solution of Cl_2 is accompanied by a sharp shift of the potential in the cathodic direction up to a value which depends on the ratio Cl_2/PH_3 in the gas phase. On reducing the rate of supply of PH_3 or on increasing that of Cl_2, the potential shifted synchronously in the anodic direction, whilst on raising the rate of supply of PH_3 or reducing that of Cl_2 the shift was in the cathodic direction. Therefore the potentiometric method made it possible to follow continuously, during the experiment, the PH_3/Cl_2 ratio in the liquid phase and the reactivity of the system.[46]

The yield of alkyl phosphates in reactions involving different alcohols remained high up to high degrees of conversion of the alcohol. Chlorine reacted preferentially with phosphine and hardly reacted with the alcohol, since the rate constant for the chlorination of an alcohol is relatively low.[103]

The mechanism of reaction (87) was investigated by ^{31}P NMR spectroscopy.[45] Only trialkyl phosphate with a chemical shift of -2 ppm was formed in an excess of the alcohol. In the presence of a deficiency of the alcohol, small peaks due to the pentacoordinate phosphorus derivatives PCl_5, Cl_3PO, $(RO)_2ClPO$, $(RO)_4PCl$, $(RO)_3PCl_2$ (-40, 5, 4, -8, and -27 ppm respectively) appeared apart from the high $(RO)_3PO$ peak (-2 ppm). The tricoordinate phosphorus derivatives PCl_3, $(RO)_2PCl$, $(RO)_3P$ (219, 170, and 140 ppm) and pentaalkoxyphosphorus $(RO)_5P$ (-80 ppm) were not detected. Hence it follows that reaction (87) takes place with the rapid formation and subsequent reactions of phosphorus pentachloride.

The most important feature of the reactions of PCl_5 with alcohols as well as other hydroxylated compounds is the preliminary formation of phosphoryl chloride [reaction (89)]. The rate of the subsequent alcoholysis of Cl_3PO increases with increase in the pH of the medium.[48] This sequence of the reactions of PCl_5 with ROH and H_2O is caused by the formation of the stable phosphoryl group $P=O$.[48] The reactions of phosphoryl chlorides with H_2O and ROH take place as stepwise elimination of HCl [reactions (90) and (91)][104] and are accelerated in the presence of HCl binding agents (an excess of ROH and pyridine).[48] In the presence of a deficiency of the alcohol, reaction (92), leading to the formation of dialkyl phosphates, predominates.[104]

$$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl. \quad (88)$$

$$PCl_5 + ROH \longrightarrow Cl_3PO + RCl + HCl. \quad (89)$$

$$Cl_3PO + 2ROH \longrightarrow (RO)_2ClPO + HCl. \quad (90)$$

$$(RO)_2ClPO + ROH \longrightarrow (RO)_3PO + HCl. \quad (91)$$

$$(RO)_2ClPO + ROH \longrightarrow (RO)_2(HO)PO + RCl. \quad (92)$$

By virtue of the very high rate and selectivity, reaction (87) can be applied to utilise even trace amounts of PH_3 and Cl_2.

VIII. Oxidative P–N coupling of phosphine to primary and secondary amines

The P–N coupling of primary and secondary phosphines to primary and secondary amines proceeds under severe conditions (only in the presence of formaldehyde) with formation of aminomethylation products.[9] The reaction involving oxidative P–N coupling of phosphine to primary and secondary amines, discovered by Dorfman et al.,[53] yields triaminophosphazoalkyls.

$$PH_3 + 4RH_2N + 4CuY_2 \longrightarrow (RHN)_3P{=}NR + 4Cu + 8HY. \quad (93)$$

$$PH_3 + 4R_2HN + 4CuY_2 \longrightarrow (R_2N)_3P{=}NR + 4Cu + 7HY + RY; \quad (94)$$

R = C_2H_5, $C_6H_5CH_2$, C_6H_{11}, .

A solution of CuY_2 in a primary or secondary amine at 15–30 °C rapidly absorbs even traces of PH_3 from the PH_3–Ar gas mixture.[53] When the reaction takes place in argon, phosphine is selectively converted into triaminophosphazoalkyl and copper(II) ions are reduced to zerovalent copper. The zerovalent copper formed by reactions (93) and (94) is almost instantaneously oxidiised by air. The following reactions take place in the presence of O_2:

$$PH_3 + 4RH_2N + 2O_2 \longrightarrow (RHN)_3P{=}NR + 4H_2O. \quad (95)$$

$$PH_3 + 4R_2HN + 2O_2 \longrightarrow (R_2N)_3P{=}NR + 3H_2O + ROH. \quad (96)$$

The rates of reactions (93) and (94) depend significantly on temperature and the concentrations of the reactants (CuY_2, RH_2N, R_2HN, PH_3) and reaction products [H_2O, CuX, $(RHN)_3P{=}NR$, $(R_2N)_3P{=}NR$]. The influence of the concentrations of the above substances on the reaction rate is described by the equation

$$W = k[Cu(II)]^{0.5}[Cu(I)]^{0.5}[PH_3]^{0.5}[RNH]^{0.5}, \quad (97)$$

where k is the rate constant (litre $mol^{-1}\,s^{-1}$). Pyridine is an effective solvent for reactions (93)–(96), which are two orders of magnitude faster in it.[53]

The fractional orders with respect to the reactants, the low activation energy ($E^{\neq}$ = 34 kJ mol^{-1}) and entropy ($\Delta S^{\neq}$ = -7160 J $mol^{-1}\,K^{-1}$), and the negative influence of H_2O indicate a coordination mechanism for the rate-limiting stage. Only the products of the interaction of PH_3 with the components forming part of the composition of the coordination sphere of copper(II) are formed.

The composition of the copper(II) complexes in amines has been investigated by UV and IR spectroscopy.[80] The electronic spectra of solutions CuY_2 (Y = Cl, Br, OAc, RCO_2, etc.) in $C_6H_5CH_2NH_2$ contain an absorption band at 670 nm, indicating the identity of their structures regardless of the nature of the ligands. According to IR spectroscopic data, $Cu(OAc)_2$ induces a shift of the N–H absorption band from 1600 to 1550 cm^{-1} and the appearance in the stretching region of a new set of bands at 3210, 3290, 3320 and 3360 cm^{-1}. The decrease in the stretching vibration frequency of the carboxylate ion from 1405 to 1570 cm^{-1} indicates a decrease in the Cu–O bond order as a result of the formation of bridges in the dimeric copper(II) complexes. An additional absorption band at 660 cm^{-1}, due to the formation of the amide bond following the addition of benzylamine to the copper(II) ion, arises in the IR spectra of the complexes.

The nature of the intermediate organophosphorus compounds was investigated by ^{31}P NMR spectroscopy.[45] After the reduction of copper(II) with phosphine to copper(I), the regeneration of copper(II) with air, and the precipitation of copper ions with KI, the spectra of solutions of $Cu(OAc)_2$ and $CuCl_2$ in $C_6H_5CH_2NH_2$ and $C_2H_5NH_2$ contain only the bands at 30 and 20 ppm characteristic of phosphorous triamides. The products of the incomplete substitution of the hydrogen atoms of phosphine by amino-groups (phosphinamidite and phosphonamidite) do not accumulate. Characteristic narrow bands at 1000–1100 cm^{-1} (P–N); 1600, 1490, and 1450 cm^{-1} (C–H in C_6H_5); 3215, 3245 and 3230 cm^{-1} (N–H), and 695 and 740 cm^{-1} (H–C) were observed in the IR spectra of the product obtained in $C_6H_5CH_2NH_2$. The accumulation of HCl was inferred from the 2500–2700 cm^{-1} band and that of H_2O was inferred from the intense broad band at 3400, 1640 cm^{-1} (O–H). Hydrogen chloride appears as a result of reactions (93) and (94) and water is formed during the regeneration of the spent copper(II) solution with oxygen. According to IR spectroscopic data, amines are hardly oxidised by copper(II) chlorides and acetates. Amines are also not chlorinated by copper(II) chlorides.[53]

In solutions in primary and secondary amines, the reduction of copper(II) by phosphine includes the stage involving the deprotonation of the substrates.

Ammonia, amines, and phosphine are very weak NH and PH acids ($pK_a \simeq 31-35$) and are activated by strong bases in anhydrous solvents[79] and by metal complexes.[74] The activation of amines requires the high-valence Ti(IV), Pt(IV), Au(III), Rh(III), and Ir(III) metal cations,[74] while that of phosphines requires the low-valence Cu(I), Ag(I), Au(I), Hg(II), and Pd(II)metal cations.[63] The tendency of amines to enter into reactions involving the formation of amino- and phosphino-ligands on treatment with metal complexes becomes enhanced with increase in basicity on passing from ammonia to primary and secondary amines[54] and from phosphine to primary and secondary phosphines. Under the influence of metal complexes, the acid

dissociation constants of the PH and NH acids increase by several orders of magnitude.[74]

$$Cu_2X_3(R_2HN)_6PH_3 \longrightarrow Cu_2X(R_2HN)_5(PH_2)(R_2N) + 2HX. \quad (98)$$

The acid properties of coordinated amines and apparently phosphines increase by several orders of magnitude with increase in their number in the inner sphere or after the introduction of pyridine into the latter.[54] Pyridine therefore proved to be a convenient solvent for the oxidative P–N coupling of amines to phosphine.[53] The stepwise formation constants of the amine complexes of copper(II) and copper(I) are independent of the nature of the amines, but they are two orders of magnitude higher than the values of the constants of the pyridine complexes of copper(II) and copper(I) and for this reason the copper(II) and copper(I) ions contain the amine over a wide range of amine/pyridine ratios. This is indicated also by potentiometric data. The addition of amines to a pyridine solution of CuX_2 shifts the potential of the Cu(II)/Cu(I) couple in the cathodic direction. An amine does not inhibit reactions (93) and (94), whereas pyridine accelerates them, since it stimulates the amido- and phosphido[proton-loss]-reactions. The aminophosphino-copper(II) complexes undergo redox decomposition with formation of phosphinous amide.

Reaction (99), involving the reductive coupling of the phosphino- and amino-ligands, is consistent with the known tendency of the P–N bonds in organophosphorus compounds to dissociate under the influence of metal complexes with formation of oxidative addition products.[71] The mechanism of the reductive P–N coupling of phosphine to amine has been investigated by the CNDO method.[78]

$$Cu_2X(R_2HN)_5(PH_2)(R_2N) \longrightarrow$$
$$\longrightarrow Cu + CuX(R_2HN)_2 + 3R_2NH + R_2NPH_2. \quad (99)$$

The configurations of the PH_3 and NH_3 molecular orbitals are as follows: PH_3 $(a_1^2e^42a_1^22e^03a_1^0)$, NH_3 $(a_1^2e^42a_1^23a_1^02e^0)$.[98,105] In contrast to NH_3, the $2e$ orbital of PH_3 has a lower energy than $3a_1$, which indicates the inclusion of the $3d$ orbitals of phosphorus in the basis set, since the $2e$ molecular orbital has in the main $3d$ character. According to Pearson,[98] inversion in amines takes place readily, in contrast to phosphines, the barriers for NH_3 and PH_3 being respectively 5.2 and 37.2 kcal mol^{-1}. In the NH_3, PH_3, AsH_3, SbH_3 series, the ionisation potentials of the molecules change very little,[98] despite the fact that the energies of the atomic orbitals of the heteroatoms increase monotonically. In the above series of hydrides, the mixing of the s and p orbitals of the heteroatoms diminishes, which leads to an increase in the $2a_1 \rightarrow 3a_1$ energy difference, the stabilisation of the pyramidal form, the narrowing of the bond angle NH_3 (108°), PH_3 (93°)], a decrease in basicity [NH_3 (pK_a = 9.2), PH_3 (pK_a = −14)], and an increase in the total bond energy and in the positive charge on the heteroatom. For this reason, PH_3 differs from NH_3 by an appreciably lower reactivity.[63]

The weakly polar PH_3 molecule is activated in the coordination sphere and becomes polar. Whereas the effective charge on the phosphorus and hydrogen atoms in the free PH_3 molecule is zero, after coordination a charge, which depends on the composition and the total charge of the complex, arises on these atoms. In the anionic complexes, the charge on the phosphorus atom is positive, whilst in the cationic complexes it is negative. The ionic character of the P–H bond in the coordinated PH_3 molecule becomes more pronounced.

On complex formation, the amine molecule is activated to a much greater extent than the PH_3 molecule. As a result of coordination, there is a significant increase in the amount of ionic character of the N–H bond and negative and positive charges increase on the nitrogen and hydrogen atoms respectively, varying as a function of their composition and the overall charge of the complex.

The nature of the activation of PH_3 depends more on the composition and charge of the complexes than that of the activation of amines. Judging from the effective charge on the phosphorus atom, in the cationic and ionic complexes phosphine acquires nucleophilic and electrophilic reactivity respectively. Judging from the charges on the nitrogen atom, amines exhibit a nucleophilic reactivity in both positively and negatively charged complexes. Since the N–H bond is more polar than the P–H bond, the formation of amide ions in the coordination sphere of copper(II) is more realistic than the formation of phosphide ions.

The Cu–P and Cu–N bond energies increase sharply on passing from phosphine and amine complexes to phosphide and amide complexes. As a result of the deprotonation of the substrates, the amount of the ionic character of the metal–ligand bonds, especially the Cu–P bond, increases.

Since cationic copper(II) complexes, in which phosphine does not form bonds with the ligands, predominate in amine media, the mechanism which rules out the formation of phosphide and amide ions and their reductive coupling with formation of phosphinous amide predominates in the reactions. A three-centre transition state, characterised by a low activation energy and a negative activation entropy, is formed in the rate-limiting stage.

$$(R_2HN)_4Cu(R_2N)(PH_2) \longrightarrow \left[(R_2HN)_4Cu \begin{matrix} NR_2 \\ \diagdown \\ \diagup \\ PH_2 \end{matrix} \right]^{\neq} \longrightarrow$$
$$\longrightarrow Cu + R_2NPH_2 + 4R_2HN. \quad (100)$$

Similarly phosphinous amide is oxidised by copper(II) ions to phosphonous diamide and the latter is oxidised to phosphorous triamide, but the reaction is faster since phosphinous amide and phosphonous diamide have a higher acidity ($pK_a \simeq 15$) than phosphine ($pK_a = -14$).[48]

Ligands which do not participate directly in the redox decomposition of the intermediate complex render considerable assistance in activating the substrates. According to CNDO data, these ligands form fairly strong bonds with the hydrogen atoms of PH_3, R_2HN, and RH_2N and are involved in nucleophilic cooperation with the amido- and phosphido-reactions, which lead to the appearance of amide and phosphide ions in the coordination sphere. Specially strong bonds are formed between the hydrogen atoms of phosphine and the amine in cationic complexes.

The driving forces of reactions (93)–(96), in which phosphine undergoes oxidative amination and oxidative imination, are the difference between the P–N and P=N bond energies as well as the high Cu(II)/Cu(0) redox potential, which increases after the addition of pyridine.[54] In contrast to trialkyl phosphites, phosphorous triamides are readily oxidised by oxygen and sulfur. They form stable pseudophosphonium salts because the P=N bond energy is appreciably lower than the P=O bond energy.[48] The state of the P=N bond depends on the electronegativity of the substituents at the nitrogen and phosphorus atoms. The multiplicity of the P=N bond increases with increase in the electronegativity of the substituents at the phosphorus atom and with decrease in the electronegativity of those at the nitrogen atom.[50,51]

IX. P–C coupling of phosphine to aldehydes

Reactions involving the P–C coupling of phosphine to carbonyl compounds lead to phosphines with functional group substituents.[9,106,107] It has been shown[108–110] that, when concentrated phosphine is passed through an aqueous solution of aldehydes and ethylenediaminenickel(II) complexes, reactions involving the hydroxymethylation of phosphine take place with a high selectivity and at a high rate. ($E^{\neq}$ = 10 kJ mol^{-1}, $\Delta S^{\neq} = -150$ J mol^{-1} K^{-1}).

$$PH_3 + 3CH_2O \longrightarrow P(CH_2OH)_3. \quad (101)$$

$$PH_3 + 4CH_2O + H_2O \longrightarrow (HO)P(CH_2OH)_4. \quad (102)$$

In $NiCl_2$ solution, the main product is tri(hydroxymethyl)-phosphine [reaction (101)], whilst in the presence of acidoamine-nickel complexes the main product is hydroxytetra(hydroxy-methyl)phosphine [reaction (102)]. Under optimum conditions, $(HO)P(CH_2OH)_4$ and $P(CH_2OH)_3$ are obtained in approximately 100% yields. The reaction products were isolated by distilling away the unreacted CH_2O and were analysed by ^{31}P, ^{13}C, and ^1H NMR and IR spectroscopic methods.

In the presence of $NiCl_2$, the rate of reaction (101) is given by the formula

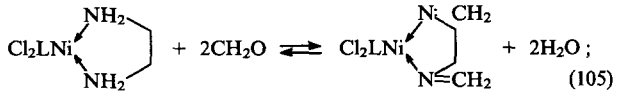
$$W = k[CH_2O]^{0.5}[NiCl_2]^{0.5}[PH_3]^{0.5}[P(CH_2OH)_3]^{0.5}. \quad (103)$$

The addition of primary and secondary amines to an aqueous formaldehyde solution of $NiCl_2$ leads to a significant increase in the rate of reaction (102), while the addition of tertiary amines inhibits this reaction.

In order to investigate the influence of the nature and concentration of the amine on the rate of reaction (102), primary monoamines (NH_2CH_3, $NH_2C_2H_5$) secondary monoamines [$NH(CH_3)_2$, $NH(C_2H_5)_2$], and tertiary monoamines [$N(CH_3)_3$, $N(C_2H_5)_3$] as well as the diamine $C_2H_4(NH_2)_2$ were used. The intermediate tri(hydroxymethyl)phosphine, aldehyde, amine, and mixed aminoaldehyde complexes of nickel(II) were investigated by ^{31}P NMR and UV spectroscopy. Ethylenediamine (En) complexes of nickel(II) showed the highest catalytic activity. The catalytic properties of this system are described by the formula

$$W = k[CH_2O]^{0.5}[NiCl_2]^{0.5}[PH_3]^{1.5}[En]^{0.5}[P(CH_2OH)_3]^{0.5}. \quad (104)$$

Investigations made it possible to put forward the following mechanism for the catalytic effects of ethylenediaminenickel(II) complexes in reaction (102):

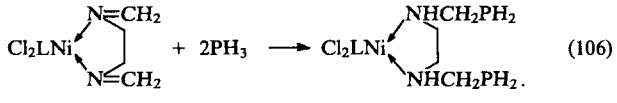


(105)

L = $P(CH_2OH)_3$.

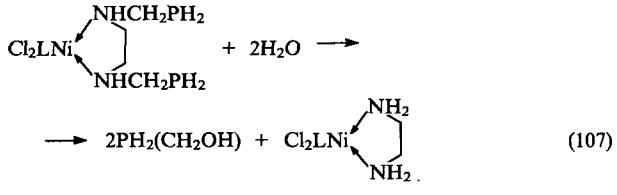
The outer-sphere condensation of coordinated ethylene-diamine with CH_2O [reaction (105)] leads to the formation of ethylenediaminenickel(II) complexes.[71]

Phosphine also reacts with the ethylenediamine complexes via an outer-sphere mechanism:



(106)

Ethylenebis(aminomethylphosphine) formed by reaction (106) decomposes subsequently with formation of the initial ethylenediaminenickel(II) complex and the reaction inter-mediate — mono(hydroxymethyl)phosphine.



(107)

Hydrolysis of ethylenebis(aminomethylphosphine) at the C–N bond occurs only in the presence of one methyl group. With increase in the number of these groups, the resistance of aminoalkylphosphines to hydrolysis at the C–N bond also increases.[9] The successive substitution of the hydrogen atoms in PH_3 by the hydroxymethyl group takes place in conformity with stages (105)–(107). The second and third hydrogen atoms are substituted faster since mono- and di-(hydroxymethyl)phosphines are appreciably more reactive than PH_3.

Tertiary amines deactivate nickel(II) complexes, since they do not contain a mobile hydrogen atom and do not form imines on interaction with CH_2O.

Thus the mechanism of the P–C coupling of phosphine to formaldehyde differs fundamentally from the mechanism of P–O and P–N coupling of phosphine to alcohols and amines. Whereas oxidative P–O and P–N coupling takes place via an inner-sphere mechanism, P–C coupling involves an outer-sphere mechanism. The catalytic cycle includes three key stages. In the first stage, ethylenediiminenickel(II) complexes are formed from the ethylenediamine complexes and formaldehyde, while in the second stage ethylenebis(aminomethylphosphine)nickel(II) complexes are produced from ethylenediiminenickel(II) complexes and PH_3. In the concluding stage, the ethylenebis(aminomethyl-phosphine)nickel(II) complexes are hydrolysed at the C–N bond with formation of mono(hydroxymethyl)phosphine and the regeneration of the initial ethylenediaminenickel(II) complex.

The effluent gas from hypophosphite factories, containing 70% of PH_3 and 30% of H_2, is an extremely suitable source of phosphine for reaction (102). The reaction product — hydroxy-tetra(hydroxymethyl)phosphine — is used as the monomer for the synthesis of fire-resistant and thermostable organophosphorus polymers. The reaction proceeds in aqueous media and the reaction product is a solid and can be readily separated from the reaction mixture after distilling away water.

X. Oxidative P–C coupling of phosphine and tetraphosphorus to nitriles

Copper(II) carboxylates and halides exhibit a high catalytic activity in the oxidative P–C coupling of phosphine and tetraphosphorus to acetonitrile.[49,63]

$$PH_3 + 3CuY_2 + 3CH_3CN \longrightarrow \longrightarrow (CNCH_2)_3P + 4Cu + 6HY. \quad (108)$$

$$P_4 + 20CuX_2 + 16CH_3CN \longrightarrow \longrightarrow 4(CNCH_2)_3P{=}NCX_2CH_3 + 20CuX + 12HX. \quad (109)$$

The Cu(0) and Cu(I) formed as a result of reactions (108) and (109) are oxidised by oxygen. Since acetonitrile coordinates more effectively to Cu(I) than to Cu(II), the redox potential of the copper couple in CH_3CN is much higher than in pyridine.[54] The rate of the Cu(II) → Cu(I) reduction stage therefore increases in CH_3CN but the Cu(I) → Cu(II) oxidation stage is retarded.

The nature of the products of the reaction of phosphine and tetraphosphorus with the nitrile depends on the nature of the ligand. Carboxylate ligands promote the formation of tri(cyano-methyl)phosphine, while halide ligands promote the formation of tri(cyanomethyl)phosphazoalkyl. In the former case, the ^{31}P NMR spectra contain only peaks in the region of −6 ppm, which are characteristic of phosphines, while in the latter case they contain peaks in the region of −6 and 14 ppm, which are typical for phosphines and phosphazo-compounds.[45]

Nitriles effectively activate transition[111] and non-transition[112] metal complexes. Complexes of the high-valence metals Ta(V), Nb(V), W(VI), U(IV), and Sn(IV), on the one hand, and the metals Pd, Pt, Rh, Cu, Ag, and Au,[74] on the other, induce respectively electrophilic and nucleophilic activities in the C≡N group. The low-valence metal complexes catalyse the dissociation of the C–C_α and C_α–H bonds in nitriles.[74] The α-cyano-carbanions (CH_2CN^-) formed under the influence of low-valence metal complexes are highly reactive and react rapidly with the coordinated electrophile.[71] When there are no hydrogen atoms in the α position and no coordinated electrophiles, low-valence metal complexes catalyse oxidative coupling of nitriles (C_6H_5CN) to phosphine with a break of the C–C_x bond.[74]

In the presence of high-valence non-transition metals, nitriles interact with a hydrogen halide and are converted into imines and amines.

$$RCN + HX \longrightarrow RCX{=}NH \xrightarrow{HX} RCX_2{-}NH_2. \quad (110)$$

The IR spectra of the products of the interaction of the nitrile with HX at 25 °C contain no bands due to the stretching vibrations of the C≡N bond of the nitrile, but the absorption bands due to the C–Cl, C=N and N–H bonds are observed.[112] Under the influence of high-valence metal ions, nitriles react at 70–90 °C with carboxylic acids to form primary and secondary amides.[112]

$$RCN + 2RCO_2H \longrightarrow RCONH_2 + (RCO)_2O. \quad (111)$$

$$RCN + RCO_2H \longrightarrow (RCO)_2NH. \quad (112)$$

Copper(I) ions effectively stimulate the hydration of nitriles.[113]

$$RCN + H_2O \longrightarrow RCONH_2. \quad (113)$$

In the presence of low-valence transition metals, reactions (111) and (112) are slow even at high temperatures (110–180 °C).[112]

The properties of the coordinated nitriles described above justified the assumption that copper(I) and copper(II) carboxylates stimulate the dissociation of the C_α–H bonds and the oxidative cyanoalkylation of phosphine, while copper(I) and copper(II) halides promote the dissociation of the C_α–H bonds, the oxidative cyanoalkylation of phosphine, and the oxidative imination of tri(cyanoalkyl)phosphine.

The new methods of synthesis of phosphines and phosphazo-compounds are simpler than the methods based on reactions of metallated alkyls with halophosphines or of alkali metal phosphides with alkyl halides.[1–6]

XI. Oxidative P–O coupling of zinc and copper phosphides to alcohols

The phosphides of *d* metals are not used in organophosphorus synthesis owing to their low reactivity.[114] Only alkali and alkaline earth metal phosphides are used in the chemistry of organophosphorus compounds because of their relatively high reactivity.[9] Bearing in mind that considerable amounts of waste containing transition metal phosphides (ferrophosphorus, copper and zinc phosphides, slags) are formed in the undertakings of the phosphorus industry, studies in the field of the organic chemistry of phosphides are of practical interest.

Dorfman and coworkers[115–122] established for the first time that zinc and copper phosphides can be used to obtain trialkyl and dialkyl phosphates. In an alcoholic solution of copper(II) chloride, Zn_3P_2 and Cu_3P are readily oxidised by oxygen to $(RO)_3PO$ and $(RO)_2(HO)PO$.

$$Zn_3P_2 + 6ROH + 4O_2 \longrightarrow 2(RO)_3PO + 3Zn(OH)_2. \quad (114)$$

$$Cu_3P + 3ROH + 2O_2 \longrightarrow (RO)_3PO + 3Cu(OH). \quad (115)$$

$$Zn_3P_2 + 8ROH + 4O_2 \longrightarrow 2(RO)_2(HO)PO + 3Zn(OH)_2 + 2R_2O. \quad (116)$$

$$Cu_3P + 4ROH + 2O_2 \longrightarrow (RO)_2(HO)PO + 3Cu(OH) + R_2O. \quad (117)$$

In the absence of O_2 (in argon) in alcoholic $CuCl_2$ solution, zinc and copper phosphides decompose rapidly with formation of $(RO)_3PO$ and $(RO)_2(HO)PO$.

Cyclic phosphates are formed from glycols, for example from butanediol. When a secondary alcohol (*iso*-C_3H_7OH) is used, dialkyl phosphites are obtained.

The copper(I) ions formed as a result of reactions (118)–(123) are oxidised by oxygen.

Alkyl halides, formed in reactions (118), (119), (122), and (123), hydrolyse [reaction (53)] during the regeneration of copper(II), while the alcohol is not oxidised by oxygen.

$$Zn_3P_2 + 16CuCl_2 + 8ROH \longrightarrow 2(RO)_3PO + 3ZnCl_2 + 16CuCl + 8HCl + 2RCl. \quad (118)$$

$$Cu_3P + 4ROH + 8CuCl_2 \longrightarrow (RO)_3PO + RCl + 11CuCl + 4HCl. \quad (119)$$

$$Zn_3P_2 + 16CuCl_2 + 12ROH \longrightarrow 2(RO)_2(HO)PO + 3ZnCl_2 + 4R_2O + 16CuCl + 10HCl. \quad (120)$$

$$Cu_3P + 8CuCl_2 + 6ROH \longrightarrow (RO)_2(HO)PO + 11CuCl + 2R_2O + 7HCl; \quad (121)$$

R = CH_3, C_2H_5, C_3H_7, *iso*-C_4H_9, C_4H_9, *iso*-C_5H_{11}, C_5H_{11}.

$$Zn_3P_2 + 6R'OH + 12CuCl_2 \longrightarrow 2(R'O)_2HPO + 2R'Cl + 12CuCl + 4HCl + 3ZnCl_2. \quad (122)$$

$$Cu_3P + 3R'OH + 6CuCl_2 \longrightarrow (R'O)_2HPO + R'Cl + 9CuCl + 2HCl. \quad (123)$$

$$Zn_3P_2 + 8R'OH + 3O_2 \longrightarrow 2(R'O)_2HPO + 3Zn(OH)_2 + 2R_2'O. \quad (124)$$

$$Cu_3P + 4R'OH + 1.5O_2 \longrightarrow (R'O)_2HPO + 3Cu(OH) + R_2O. \quad (125)$$

After regeneration, the solution can be reused to decompose Zn_3P_2 and Cu_3P. Trialkyl phosphates and dialkyl phosphonates can be extracted with heptane and separated by vacuum distillation.

Reactions (114)–(121) take place in the topochemical regime. The kinetic and conversion curves have the shape typical for topochemical reactions and pass through a sharp maximum at low conversions $\alpha = 0.1–0.3$.[60] The specific rate (W_{sp}, mol m^{-2} s^{-1}) of the topochemical reaction in the kinetic region was found from Eqn (33). The rate of the reaction was calculated having determined the consumption of O_2 and copper(II) and the accumulation of $(RO)_3P$, $(RO)_2(HO)PO$, Cu(I), $(R'O)_2HPO$, and RCl.

During the search for the optimum conditions and during the study of the mechanism of the oxidative P–O coupling of phosphides to alcohols, the influence of the concentrations of ROH, $CuCl_2$, CuCl, O_2, HCl, LiCl, H_2O, CH_3CN, $C_6H_5CH_2NH_2$, and $C_2H_5NH_2$ on this process was traced. According to atomic-absorption spectroscopic data and the results of laser microanalysis, the Zn_3P_2 and Cu_3P specimens contained less than 1% of impurities. The average Zn_3P_2 and Cu_3P particle sizes and the specific surfaces measured with the aid of a Coulter counter were 13–47 μm and 90–850 cm^2 g^{-1} respectively.

As the HCl and H_2O concentrations are varied, the rates of the topochemical reactions pass through a maximum at very low concentrations of the additives. Amines inhibit the topochemical process, while LiCl has only a weak influence on the latter. With increase in the concentrations of Cu(II), ROH, and O_2, as well as temperature, the rate of reaction also increases.[115–122]

$$Cu_3P + (3-n)HCl \rightleftharpoons Cu_nH_{3-n}P + (3-n)CuCl. \quad (126)$$

The state of the copper(II) complexes during the experiment was investigated by magnetic susceptibility (MS) and UV and EPR spectroscopic methods. According to MS and EPR spectroscopic data, copper chlorides exist predominantly in the monomeric state in alcoholic solutions. It follows from the UV spectra that water readily displaces alcohols from the coordination sphere of copper(II). Alcohol-containing copper(II) complexes exist only for the ratio $H_2O/Cu(II) < 20$. In the alcohol, the stability constants of copper(II) chlorides are higher than in water. The chloroalcoholcopper complexes predominate already for the ratio $Cl^-/Cu(II) \sim 2$.[47]

$$Cu_nH_{3-n}P + Cu_2Cl_3(ROH) \rightleftharpoons Cu_nH_{3-n}PCu_2Cl_3(ROH). \quad (127)$$

The ^{31}P NMR spectra contain an intense band corresponding to $(RO)_3PO$ (−1 ppm) and a weak band due to $(RO)_2(HO)PO$ (−0.5 ppm). Data taken from Nifant'ev and Vasyanina[45] were used in the analysis of the spectra.

The results presented above, obtained by physicochemical methods, suggest the following mechanism of the oxidative P–O coupling of alcohols to metal phosphides. The process begins with the stage involving the activation of the metal phosphide surface by the acid (however, the metal atoms are not fully substituted by hydrogen atoms and phosphine is not liberated). Subsequently the metal hydrogen phosphide adsorbs the heterovalent copper(II)–copper(I) chloride dimer, which is present, according to UV spectroscopic data,[47] in alcoholic solutions of $CuCl_2$–$CuCl$.

The two-electron redox decomposition of the surface complex, formed in stage (127), leads to the formation of a surface phosphinite and metallic copper.

In the presence of $CuCl_2$, copper dissolves rapidly.

$$Cu + CuCl_2 \rightleftarrows 2CuCl; \qquad K_c = 8 \times 10^6.$$

Thus the oxidative P–O coupling of the metal phosphide to an alcohol includes three main stages: acid hydrolysis of the metal phosphide to the metal hydrogen phosphide, reduction of the chloroalcoholcopper(II) complexes to copper(I) by the metal hydrogen phosphide, and regeneration of the copper(II) ions with oxygen. The acid–base stage (126) is accelerated with increase in the acidity of the medium and the alcohols. The oxidation–reduction stage (128) is retarded as the acidity of the medium increases, which hinders the formation of the alkoxy-ligand. When ROH is displaced from the coordination sphere of copper(II) by the addition of HCl, LiCl, and H_2O, the yield of organic phosphates is seen to fall from 100% to 20%.[115–122]
The oxidation–reduction decomposition reaction (128) takes place as follows:

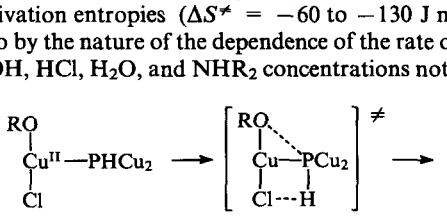
$$Cu_nH_{3-n}PCu_2Cl_3(ROH) \longrightarrow \longrightarrow Cu + CuCl + Cu_nH_{2-n}P(OR) + 2HCl. \qquad (128)$$

The subsequent stages of the oxidation of $(RO)PCu_2$ to $(RO)_2PCu$, $(RO)_3P$ and $(RO)_3PO$ are rapid.

The oxidation–reduction decomposition of (A) takes place with formation and subsequent reaction of a cyclic transition state.

$$Cu_2X_3(ROH)PCu_3 \underset{-CuX}{\overset{HX}{\rightleftarrows}} Cu_2X_3(ROH)PCu_2 \underset{-HX}{\rightleftarrows} \rightleftarrows Cu_2X_2(RO)PHCu_2 \longrightarrow Cu + CuX + (RO)PCu_2 + HX.$$
$$\mathbf{A} \qquad (129)$$

The coordination mechanism of reaction (130) is indicated by the low activation energies ($E^{\neq}$ = 50–70 kJ mol^{-1}) and activation entropies ($\Delta S^{\neq}$ = −60 to −130 J mol^{-1} K^{-1}), and also by the nature of the dependence of the rate of reaction on the ROH, HCl, H_2O, and NHR_2 concentrations noted above.



$$\longrightarrow (RO)PCu_2 + Cu + HCl. \qquad (130)$$

The coordination mechanism of reaction (130) has been investigated by the CNDO method.[120] The molecular model of adsorption was used in the calculation.[64] For this purpose, calculations were made for the surface cluster complexes differing in the numbers of H and Cu atoms in the copper hydrogen phosphide and by the number of molecules (H_2O, ROH) and ions (RO^-, HO^-, Cl^-) in the coordination sphere of copper(II). The surface complexes chosen for the investigation modelled the influence of the number of halide, alkoxide, and hydroxide ions and water and alcohol molecules as well as the degree of substitution of copper atoms by hydrogen atoms in the copper phosphide on the nature of the bond between the atoms of the cluster.[120]

The quantum-chemical study established that the adsorption of chloroaquoalcoholcopper(II) complexes on the hydrogen phosphide is accompanied by the formation of bonds not only between the copper(II) ion and the phosphorus atom but also between the chlorine and copper (in the phosphide) atoms, between phosphorus and the alcohol, between phosphorus and water, and between phosphorus and chlorine. These bonds stimulate the oxidation of phosphorus and the reduction of copper(II).[120] The alkoxide ion forms a stronger bond with the phosphorus atom than do ROH, H_2, and the X^- ions. Hence it follows that the products of the oxidative P–O coupling are obtained as a result of the direct reaction of RO^- with the phosphorus atom. The strength of the bond between phosphorus and the alkoxide ion in the adsorption complex increases as the metal atoms are replaced by hydrogen atoms. The greater the number of hydrogen atoms in the hydrogen phosphide, the greater the tendency of the inner-sphere nucleophiles (X^-, HO^-, RO^-) to interact with the phosphorus atom. However, the complete replacement of the metal atoms in the phosphide by hydrogen atoms is not convenient, since the energy of the bonds between the coordinated bases and the metal atoms is much higher than that of the bonds between such bases and hydrogen atoms. Consequently hydrogen phosphides react with chloroalkoxocopper(II) complexes faster than do metal phosphides and phosphine.[120] Hence the cause of the positive influence of a small amount of added acid (up to 0.6 mol litre^{-1}), leading to only partial replacement of metal atoms by hydrogen atoms in the phosphide, on the rate of the topochemical process can be understood. However, when the ligands Cl^-, OH^-, and RO^- are replaced by O^{2-} ions, which form much stronger bonds with the metal atom of the phosphide, the oxidation process is accelerated. Thus the highest catalytic activity is shown by metal halides in weakly acid media and by metal oxides in alkaline media.[63]

XII. Oxidative P–O coupling of zinc and copper phosphides to alcohols in the presence of chlorine

Dorfman observed for the first time[49] that trialkyl and dialkyl phosphates can be obtained rapidly and in high yield (50%–90%) on chlorination of Zn_3P_2 and Cu_3P in alcoholic solutions.

The unreacted alcohol and the organophosphorus reaction products were separated from the inorganic substances by extraction with heptane and vacuum distillation.[115–122] A Cl_2–Ar gas mixture, supplied directly into the liquid phase, was used in the experiments. The rate of supply of the mixture was regulated in such a way that the potential of the Cl_2/Cl chlorine electrode remained constant during the study, while the Cl_2 concentration in the gas at the outlet from the reactor was close to zero. The rate of the reaction was inferred from the consumption of the phosphide, chlorine, and the alcohol and from the accumulation of the reaction products, which were analysed by gas chromatography and ^{31}P NMR spectroscopy.

The introduction of the phosphide into an alcoholic solution of chlorine at 10–80 ° is accompanied by a rapid cathodic shift of the reaction potential to a value which depends on the Cl_2 concentration in the Cl_2–Ar gas mixture. The potential shifts in the negative direction on lowering the Cl_2 concentration and with increase in the amount of the phosphide. On the other hand, it shifts in the anodic direction with increase in the Cl_2 content in argon and with decrease in the amount of the phosphide. The potentiometric method makes it possible to follow continuously during the experiment the chlorine/phosphide ratio in the reaction system.

$$Zn_3P_2 + 8Cl_2 + 8ROH \longrightarrow 2(RO)_3PO + 3ZnCl_2 + 8HCl + 2RCl. \quad (131)$$

$$2Cu_3P + 11Cl_2 + 8ROH \longrightarrow 2(RO)_3PO + 6CuCl_2 + 2RCl + 8HCl. \quad (132)$$

$$Zn_3P_2 + 8Cl_2 + 8ROH \longrightarrow 2(RO)_2(HO)PO + 3ZnCl_2 + 4RCl + 6HCl. \quad (133)$$

$$2Cu_3P + 11Cl_2 + 8ROH \longrightarrow 2(RO)_2(HO)PO + 6CuCl_2 + 4RCl + 6HCl; \quad (134)$$

R = C_4H_9, *iso*-C_4H_9, C_5H_{11}, *iso*-C_5H_{11}.

The sharp cathodic or anodic shift of the chlorine electrode potential depending on the chlorine/phosphide ratio indicates the high rate of the topochemical reaction of the phosphide with chlorine in the alcohol.

According to ^{31}P NMR data,[45] reactions (131)–(134) proceed relatively selectively. Mainly trialkyl and dialkyl phosphates are formed, their chemical shifts being −1 and −2 ppm respectively. The ^{31}P NMR spectra also contain small peaks due to the tetracoordinate phosphorus derivatives Cl_3PO (0.6 ppm), $(RO)_2ClPO$ (0.5 ppm), and $(RO)_2HPO$ (1 ppm). When phosphine is chlorinated in *iso*-C_3H_7OH the chemical shifts (ppm) are displaced upfield: (*iso*-$RO)_3PO$ (−4 ppm) and (*iso*-$RO)_2(HO)PO$ (−6 ppm). Hence it follows that reactions (131)–(134) proceed via the formation and subsequent reaction of phosphorus pentachloride.

The main feature of the reactions of PCl_5 with ROH and H_2O is the initial formation of phosphoryl chloride [reaction (136)], the rate of the subsequent alcoholysis of which increases with increase in the pH of the medium.[104] Such a sequence of reactions of phosphorus pentachloride with alcohols and water is due to the formation of the stable phosphoryl group P=O.[104] The reactions of phosphoryl chloride with ROH and H_2O proceed as stepwise elimination of HCl.[104] In the reactions of alcohols with phosphoryl chloride, phosphorodichloridates are generated initially. This is followed by the formation of phosphorochloridates and finally trialkyl phosphates. Reactions (136)–(138) are significantly accelerated in the presence of HCl binding agents. Without added pyridine, reaction (137) takes several hours, while in the presence of pyridine it reaches completion after several minutes. Therefore, in order to accelerate the reactions, the sample of the solution is treated with pyridine before chromatographic analysis.

$$Zn_3P_2 + 8Cl_2 \longrightarrow 2PCl_5 + 3ZnCl_2. \quad (135)$$

$$PCl_5 + ROH \longrightarrow Cl_3PO + RCl + HCl. \quad (136)$$

$$Cl_3PO + 2ROH \longrightarrow (RO)_2ClPO + 2HCl. \quad (137)$$

$$(RO)_2ClPO + ROH \longrightarrow (RO)_3PO + HCl. \quad (138)$$

$$(RO)_2ClPO + ROH \longrightarrow (RO)_2(HO)PO + RCl. \quad (139)$$

During the chlorination of Cu_3P, it was observed that the yield of trialkyl phosphate increases significantly when the Cl_2 concentration is reduced (to 10^{-3}–10^{-4} mol litre^{-1}) as fresh portions of Cu_3P are added. The autocatalysis is due to the fact that, following the appearance of $CuCl_2$ in the system as a result of the reaction

$$2Cu_3P + 11Cl_2 \longrightarrow 2PCl_5 + 6CuCl_2, \quad (140)$$

processes begin in which $CuCl_2$ becomes the catalyst and Cl_2 and Cu_3P are the reactants.

$$Cu_3P + 8CuCl_2 + 4ROH \longrightarrow 11CuCl + (RO)_3PO + RCl + 4HCl. \quad (141)$$

$$2CuCl + Cl_2 \longrightarrow 2CuCl_2. \quad (142)$$

Copper phosphide is oxidised to trialkyl phosphates by $CuCl_2$ in alcohols, while CuCl, a product of reaction (141), is reoxidised to $CuCl_2$. When there is a deficiency of Cl_2, copper phosphide reacts with $CuCl_2$ and not with Cl_2.

The catalytic pathway ensures a high selectivity of the reation, since the oxidative alcoholysis of Cu_3P proceeds without the preliminary formation of chloro-derivatives of phosphorus via the direct reaction of Cu_3P with ROH in the coordination sphere of copper(II). Tests showed that, in the absence of Cl_2, the stoichiometric reaction (141) taks place.[120,121]

It follows from the ^{31}P NMR spectra, indicating the presence of $(RO)_2HPO$ in the reaction mixture, that trialkyl phosphate is formed from the dialkyl phosphite produced on dealkylation of trialkyl phosphite.[61,62]

$$Cu_3P + 6CuCl_2 + ROH \longrightarrow (RO)_3P + 9CuCl + 3HCl. \quad (143)$$

$$(RO)_3P + HCl \longrightarrow (RO)_2HPO + RCl. \quad (144)$$

$$(RO)_2HPO + 2CuCl_2 + ROH \longrightarrow (RO)_3PO + 2CuCl + 2HCl. \quad (145)$$

According to Dorfman et al.[53] and Fridman et al.,[54] dialkyl phosphate is readily oxidised by $CuCl_2$ in the alcohol to trialkyl phosphate.

* * *

The studies described above were carried out in the little investigated field of the organic chemistry of phosphorus and phosphides, which, however, is of great practical importance. The principal features of the new reaction involving the oxidative phosphorylation of organic compounds by phosphorus and phosphides were described. Organophosphorus compounds can be obtained by this reaction much more simply than by the existing methods in which metallated organic substances and phosphorus halides or alkali metal phosphides and halo-derivatives of organic compounds are used.[1–6] By virtue of the high rates of the reactions considered, highly toxic waste from phosphorus factories with a low content of the phosphorylating agent (the effluent phosphine- and phosphorus-containing gases, dilute phosphorus sludge, transition metal phosphides, and red phosphorus) can be used as raw materials in these processes.[114,123]

It has been shown that the non-polar tetraphosphorus and the weakly polar phosphine, which tend to undergo homolytic reactions, enter vigorously into heterolytic organic reactions in the presence of metal complexes. The mechanism, rate, and mode of reaction depend on the nature of the ligands. The use of the ligand effect, described in 1972[46] and applied successfully by Lupi and Chubar,[124] makes it possible to alter significantly the nature of the process by adding simple alkali metal salts.

The mechanisms of the activation of phosphorus and phosphides and of the reactions involving the oxidative O-, N-, and C-coupling of alcohols, amines, aldehydes, carboxylic acids, glycols, and nitriles to phosphine, white and red phosphorus, and transition metal phosphides, described above, can be used to discover new reactions of this type with participation of other organic compounds.

References

1. R S Edmundson (Ed.) *Dictionary of Organophosphorus Compounds* (London: Chapman and Hall, 1987)
2. U Aufl (Ed.) *Methoden der Organischen Chemie* (Houben-Weyl) (Stuttgart: Georg Thieme, 1963) Vol. 12
3. Ch Fest, K T Schmidt *The Chemistry of Organophosphorus Pesticides* (Berlin: Springer, 1982)
4. C Hanson (Ed.) *Recent Advances in Liquid–Liquid Extraction* (Translated into Russian; Moscow: Khimiya, 1974)

5. P A Kirpichnikov, L A Mukmenova, D G Pobedimskii *Usp. Khim.* **52** 1831 (1983) [*Russ. Chem. Rev.* **52** 1051 (1983)]
6. H R Allcock *Phosphorus–Nitrogen Compounds* (Translated into Russian; Moscow: Mir, 1976)
7. E E Nifant'ev, T S Kukhareva *Obzor Monografii i Obzorov po Khimii Fosfororganicheskikh Soedinenii* (A Survey of the Monographs and Reviews on the Chemistry of Organophosphorus Compounds) (Moscow: Mir, 1989)
8. Ya A Dorfman, L V Levina, T V Petrova, M M Aleshkova, G S Polimbetova, V S Emel'yanova *Zh. Obshch. Khim.* **60** 1275 (1990)
9. O A Erastov, G E Nikonov *Funktsional'no-Zameshchennye Fosfiny i Ikh Proizvodnye* (Phosphines with Functional Group Substituents and Their Derivatives) (Moscow: Nauka, 1986)
10. A I Rakhimov, S A Tungatarov, G S Polimbetova *Sintez Fosfororganicheskikh Soedinenii. Gomoliticheskie Reaktsii* (Synthesis of Organophosphorus Compounds. Homolytic Reactions) (Moscow: Nauka, 1986)
11. V M Koverya, V Ya Monin, V P Belyakov *Sposoby Ochistki Pechnogo Gaza ot Fosfora i Fosfina* (Methods for the Elimination of Phosphorus and Phosphine from Furnace Gas) (Moscow: Izd. NIITEKhIM, 1986)
12. N G Feshchenko, in *Uspekhi Khimii Fosfororganicheskikh i Seraorganicheskikh Soedinenii* (Advances in the Chemistry of Organophosphorus and Organosulfur Compounds) (Kiev: Naukova Dumka, 1970) p. 89
13. N G Feshchenko, L V Kirsanov, V G Kostin, L I Kudryavtseva, E A Mel'nichuk, Zh A Gorbatenko, I E Mitel'man, N D Gomelya, A G Matyusha, Yu P Makovetskii, T V Kovaleva, in *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Applications of Organophosphorus Compounds) (Leningrad: Nauka, 1987) p. 342
14. N G Feshchenko, E K Rutkovskii, Zh K Gorbatenko *Zh. Obshch. Khim.* **59** 1684 (1989)
15. A V Kirsanov, N G Feshchenko, in *Khimiya i Primenenie Fosfororganicheskikh Soedinenii. Trudy V Konferentsii* (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of the Vth Conference) (Moscow: Nauka, 1974) p. 37
16. L Maier *Forts. Chem. Fortschr.* **19** 1 (1971)
17. A W Frank, C F Baranauckas *J. Org. Chem.* **31** 1644 (1971)
18. G A Leman, in *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Applications of Organophosphorus Compounds) (Kiev: Naukova Dumka, 1981) p. 194
19. H F Lehmann, G Grobmann *Pure Appl. Chem.* **53** 205 (1980)
20. L Riesel, M Kant, R Helbing *Z. Anorg. Allg. Chem.* **580** 217 (1990)
21. A S Romakhin, I M Zarinov, Yu G Budnikova, Yu A Ignat'ev, E V Nikitin, A P Tomilov, Yu M Kargin *Elektrokhimiya* **25** 780 (1989)
22. C Broun, R F Hudson, L A Wartew, H Coates *Phosphorus Sulfur* **6** 481 (1979)
23. A P Tomilov, Yu M Kargin, I N Chernykh *Elektrokhimiya Elementoorganicheskikh Soedinenii. Elementy IV, V, VI Grupp Periodicheskoi Sistemy* (Electrochemistry of Organoelement Compounds. Group IV, V, and VI Elements) (Moscow: Nauka, 1986)
24. L V Kaabak, N Ya Shandrikov, A P Tomilov *Zh. Obshch. Khim.* **40** 548 (1970)
25. I M Osadchenko, A P Tomilov *Zh. Obshch. Khim.* **40** 698 (1970)
26. L F Filimonova, L V Kaabak, A P Tomilov *Zh. Obshch. Khim.* **39** 2174 (1969)
27. M V Tsikalova, D N Lobanov, I Ya Levitin *Dokl. Akad. Nauk SSSR* **308** 386 (1989)
28. Yu P Makovetskii, N G Feshchenko, A N Chernega *Zh. Obshch. Khim.* **61** 1075 (1991)
29. R A Cherkasov *Metalloorg. Khim.* **2** 13 (1989)
30. M Di Vaira, P Stohhioni, M Peryzzini *Polyhedron* **6** 351 (1987)
31. W E Lindsell, K J McCullough *J. Am. Chem. Soc.* **105** 4487 (1983)
32. P Dapporto, L Sacconi *Inorg. Chem.* **20** 3834 (1981)
33. V Di Vaira, L Sacconi *Angew. Chem.* **94** 338 (1982)
34. R A Trofimov, N K Gusarova, S F Malysheva, T N Rakhmatullina, S I Shaikhuddinova, V I Dmitriev, in *Mekhanizmy Reaktsii Nukleofil'nogo Zameshcheniya i Prisoedineniya* (The Mechanisms of Nucleophilic and Electrophilic Addition and Substitution Reactions) (Donetsk, 1990) p. 272
35. N K Gusarova, S F Malysheva, T N Rakhmatullina *Zh. Obshch. Khim.* **60** 828 (1990)
36. B A Trofimov, N K Gusarov, S F Malysheva, V I Dmitriev, T N Rakhmatullina, M G Voronkov *Dokl. Akad. Nauk SSSR* **60**, 828 (1990)
37. B A Trofimov, N K Gusarova, S F Malysheva *Phosphorus Sulfur Silicon Relat. Elem.* **55** 271 (1991)
38. B A Trofimov, N K Gusarova, T N Rakhmatullina, V I Dmitriev, S I Shaikhuddinova *Zh. Obshch. Khim.* **61** 1310 (1991)
39. D E C Corbridge *Phosphorus. An Outline of Its Chemistry, Biochemistry, and Technology* [Amsterdam: Elsevier, 1978] (Translated into Russian; Moscow: Mir, 1982)
40. D Purdela, R Vilceanu *Chimiya Compusilor Organici al Fosforului* [Chemistry of Organophosphorus Compounds) (Translated into Russian; Moscow: Khimiya, 1972)
41. Ya A Dorfman, R R Abdreimova, L V Levina, T V Petrova *Kinet. Katal.* **30** 1484 (1989)
42. Ya A Dorfman, R R Abdreimova, L V Levina, T V Petrova *Zh. Obshch. Khim.* **59** 481 (1989)
43. Ya A Dorfman, R R Abdreimova, D M Doroshkevich *Teor. Eksp. Khim.* 659 (1991)
44. A E Arbuzov *Izbrannye Trudy po Khimii Fosfororganicheskikh Soedinenii* (Selected Works on the Chemistry of Organophosphorus Compounds) (Moscow: Nauka, 1977)
45. E E Nifant'ev, L K Vasyanina *Spektroskopiya YaMR ^{31}P* (^{31}P NMR Spectroscopy) (Moscow: Izd. MGPI im. V I Lenina, 1986)
46. Ya A Dorfman, D V Sokol'skii *Kataliz Ligandami v Vodnykh Rastvorakh* (Catalysis by Ligands in Aqueous Solutions) (Alma-Ata: Nauka, 1972)
47. E V Gusevskaya, V A Likholobov, E P Toyazi, Yu I Ermakov *Kinet. Katal.* **24** 53 (1983)
48. A J Kirby, S G Warren *The Organic Chemistry of Phosphorus* (Translated into Russian; Moscow: Mir, 1971)
49. Ya A Dorfman *Katalizatory Organicheskogo Sinteza* (Catalysts for Organic Synthesis) (Alma-Ata: Nauka, 1992) Vol. 2, p. 166
50. G I Dergach, I N Khmurova, A V Kirsanov, V I Shevchenko, A S Shtepanek *Fosfazosoedineniya* (Phosphazo-Compounds) (Kiev, 1965)
51. A P Marchenko, A M Pinchuk *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Applications of Organophosphorus Compounds) (Moscow: Nauka, 1987) p. 153
52. V P Kukhar, V F Gilyarov *Pure Appl. Chem.* **52** 891 (1980)
53. Ya A Dorfman, L V Levina, Shch M Pakhorukova *Kinet. Katal.* **32** 617 (1991)
54. Ya D Fridman, M G Levina, N V Dolgasheva, T V Danilova, R A Veresova, A Ya Fridman *Ustoichivost' Smeshannykh Kompleksnykh Soedinenii v Rastvorakh* (The Stability of Mixed Complexes in Solution) (Frunze: Ilim, 1971)
55. V A Gilyarov *Usp. Khim.* **47** 1628 (1978) [*Russ. Chem. Rev.* **47** 870 (1978)]
56. Ya A Dorfman, M M Aleshkova, M M Kebekbaeva, A S Karinskaya, A K Borangazieva *Zh. Obshch. Khim.* **61** 1101 (1991)
57. Ya A Dorfman, M M Aleshkova, A S Karinskaya *Kinet. Katal.* **32** 188 (1991)
58. Ya A Dorfman, M M Aleshkova, M M Kebekbaeva *Kinet. Katal.* **32** 1349 (1991)
59. Ya A Dorfman, D M Doroshkevich, M M Aleshkova *Kinet. Katal.* **32** 1357 (1991)
60. A Ya Rozovskii *Kinetika Topokhimicheskikh Reaktsii* (Kinetics of Topochemical Reactions) (Moscow: Khimiya, 1974)
61. J Okamoto, T Kusano, S Takamuku *Bull. Chem. Soc. Jpn.* **61** 3359 (1988)
62. J Okamoto, T Kusano, S Takamuku *Phosphorus Sulfur Silicon Relat. Elem.* **55** 195 (1991)
63. Ya A Dorfman, I M Yukht, L V Levina, G S Polimbetova, T V Petrova, V S Emel'yanova *Usp. Khim.* **60** 1190 (1991) [*Russ. Chem. Rev.* **60** 605 (1991)]
64. H H Dunken, V I Lygin *Quantum Chemistry of Adsorption on the Surfaces of Solids* (Translated into Russian; Moscow: Mir, 1980)
65. Ya A Dorfman, L V Levina, E Zh Aibasov, S A Tungatarov, G S Polimbetova *Zh. Obshch. Khim.* **60** 1987 (1991)
66. Ya A Dorfman, L V Levina, T V Petrova, V S Emel'yanova, I V Kel'man, A S Karinskaya *Zh. Obshch. Khim.* **60** 840 (1990)
67. Ya A Dorfman, L V Levina, G S Polimbetova *Koord. Khim.* **17** 280 (1991)

68. Ya A Dorfman, L V Levina, T V Petrova, V S Emel'yanova, G S Polimbetova *Kinet. Katal.* **30** 1483 (1989)
69. G D Zakumbaeva, Ya A Dorfman, N M Popova, in *Soviet-Japanese Seminar on Catalysis , Novosibirsk, 1990* p. 240
70. Ya A Dorfman, L V Levina, T V Petrova, R R Sagandykova, Zh U Ibraimova *Zh. Obshch. Khim.* **59** 1454 (1989)
71. Yu N Kukushkina *Reaktsionnaya Sposobnost' Koordinatsionnykh Soedinenii* (Reactivity of Coordination Compounds) (Leningrad: Nauka, 1987)
72. D S Dohle, T C Jones, C E A Richard, W R Poper *J. Chem. Soc., Chem. Commun.* 865 (1984)
73. C D Ziegler, R F Heck *J. Org. Chem.* **42** 2941 (1978)
74. Ya A Dorfman *Katalizatory i Mekhanizmy Gidrirovaniya i Okisleniya* (Catalysts and Mechanisms of Hydrogenation and Oxidation (Alma-Ata: Nauka, 1984)
75. I V Kel'man, Ya A Dorfman *Razvitie Rabot v Oblasti Kataliza v Kazakhstane* (Development of Studies in the Field of Catalysis in Kazakhstan) (Alma-Ata: Nauka, 1990)
76. Ya A Dorfman, I V Kel'man *Koord. Khim.* **15**, 1022 (1989)
77. Ya A Dorfman, I V Kel'man *Teor. Eksp. Khim.* 654 (1991)
78. N Fischer, N Kollmar *Theor. Chim. Acta* **6** 163 (1970)
79. B N Tsvetkov, N A Bondarenko, N G Malakhova, M I Kabachnik, in *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Applications of Organophosphorus Compounds) (Leningrad: Nauka, 1987)
80. N Beck, I Nadpal *Studies on Complex Formation by the Latest Methods* (Translated into Russian; Moscow: Mir, 1989)
81. G B Shul'pin *Kataliticheskie Reaktsii, Kataliziruemye Kompleksami Metallov* (Catalytic Reactions Catalysed by Metal Complexes) (Moscow, 1989)
82. A E Shilov, G B Shul'pin *Usp. Khim.* **56** 754 (1987) [*Russ. Chem. Rev.* **56** 442 (1987)]
83. A E Shilov, G B Shul'pin *Usp. Khim.* **59** 1468 (1990) [*Russ. Chem. Rev.* **59** 853 (1990)]
84. V I Spitsin, I V Fedoseev *Karbonil'nye Kompleksy Platinovykh Metallov* (Platinum Metal Carbonyl Complexes) (Moscow: Nauka, 1980)
85. V I Perevalova, N B Shitova, L Ya Alyi, V K Duplyakin *Zh. Obshch. Khim.* **58** 1715 (1988)
86. V I Perevalova, N B Shitova, L Ya Alyi *Zh. Obshch. Khim.* **58** 1994 (1988)
87. V I Peshchevitskii, A V Belyaev, R L Shchekochikhina, G D Mal'chikov *Kinetika Reaktsii Zameshcheniya Ligandov v Kompleksnykh Soedineniyakh Platinovykh Metallov i Zolota* (Kinetics of the Ligand Substitution Reactions in Platinum Metal and Gold Complexes) (Novosibirsk: Nauka, 1974)
88. Ya A Dorfman, L V Levina, G S Polimbetova, E Zh Aibasova, A O Kokpanbaeva, T D Ualieva, in *Khimicheskie Sintezy na Osnove Odnouglerodnykh Molekul* (Chemical Syntheses Based on One-Carbon Molecules) (Moscow, 1991) p. 154
89. Ya A Dorfman, L V Levina, E Zh Aibasova, S A Tungatarov, in *Primenenie Metallokompleksnogo Kataliza v Organicheskom Sinteze* (Application of Metal Complex Catalysis in Organic Synthesis (Ufa: Izd. BNTSUrO Akad. Nauk SSSR, 1989) p. 100
90. Ya A Dorfman, L V Levina, D M Doroshkevich *Koord. Khim.* **18** 109 (1992)
91. R C Mehrotra *Coord. Chem. Rev.* **68** 101 (1985)
92. A D Troitskaya, in *Problemy Koordinatsionnoi Khimii. Reaktsionnaya Sbosobnost' Koordinatsionnykh Soedinenii* (Problems of Coordination Chemistry. The Reactivity of Coordination Compounds) (Moscow: Nauka, 1976) p. 7
93. A D Troitskaya, Z L Shmakova *Zh. Neorg. Khim.* **16** 1650 (1971)
94. D E Berry, K A Reverige, J Browning *Can. J. Chem.* **64** 1903 (1986)
95. W Keim *Catalysis in C1 Chemistry* (Translated into Russian; Leningrad, 1987) p. 18
96. C Masters *Homogeneous Catalysis by Transition Metals* (Translated into Russian; Moscow: Mir, 1983)
97. G Klopman, in *Chemical Reactivity and Reaction Paths* (Translated into Russian; Moscow: Mir, 1977) p. 62
98. R G Pearson *Symmetry Rules for Chemical Reactions* (Translated into Russian; Moscow: Mir, 1979)
99. Ya A Dorfman, V I Zakharov, I V Kel'man *Zh. Neorg. Khim.* **36** 2699 (1991)
100. V V Azatyan, S G Gagarin, V I Zakhar'in *Kinet. Katal.* **26** 222 (1985)
101. N P Machara, B S Ault *J. Phys. Chem.* **92** 73 (1988)
102. Ya A Dorfman, G S Polimbetova, G N Nadyrova *Zh. Prikl. Khim.* **64** 1510 (1991)
103. T A Tumanova, I E Flis *Fiziko-khimicheskie Osnovy Otbelki Tsellyulozy* (Physicochemical Foundations of the Bleaching of Cellulose) (Moscow: Lesnaya Prom., 1972)
104. A I Klochkov, V V Malzurin, V P Savel'yanov *Zh. Obshch. Khim.* **60** 71 (1990)
105. L N Mazalov, V D Yumatov, G N Dolenko, in *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Applications of Organophosphorus Compounds) (Leningrad: Nauka, 1987) p. 105
106. K Kellner, A Izschach *Z. Chem.* **24** 365 (1984)
107. R F Hudson *Structure and Mechanism in Organophosphorus Chemistry* (Translated into Russian; Moscow: Mir, 1967)
108. Ya A Dorfman, L V Levina, L I Grekov, in *Mekhanizmy Reaktsii Nukleofil'nogo Zameshcheniya i Prisoedineniya* (The Mechanisms of Nucleophilic and Electrophilic Addition and Substitution Reactions) (Donetsk: 1991) p. 180
109. Ya A Dorfman, L V Levina, L I Grekov *Kinet. Katal.* **30** 662 (1989)
110. Ya A Dorfman, R K Valetdinov, I T Shaikhutdinova, A A Kutuev, in *Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii i Polimerov* (The Chemistry and Technology of Organoelement Compounds and Polymers) (Kazan: Izd. Kaz. KhTi, 1984) p. 22
111. M A Glushkova, N A Chumaevskii, M M Ershova *Koord. Khim.* **11** 193 (1985)
112. T A Sumarukova, in *Kataliticheskie Reaktsii v Zhidkoi Faze* (Catalytic Liquid-Phase Reactions) (Alma-Ata: Nauka, 1980) p. 154
113. E E Grigoryan, L G Bykova, R F Eremova *Poluchenie Akrilamida Kataliticheskoi Gidratatsiei Akrilonitrila* (The Synthesis of Acrylamide by the Catalytic Hydration of Acrylonitrile) (Moscow: Izd. NIITEKhIM, 1978)
114. V B Chernogorenko, in *Novoe v Poluchenii i Primenenii Fosfidov i Fosfosoderzhashchikh Splavov* (New Developments in the Synthesis and Application of Phosphides and Phosphorus-Containing Alloys) (Alma-Ata: Nauka, 1988) Vol. 1, p. 5
115. Ya A Dorfman, T V Petrova, M Maleshkova, R R Abdreimova, L D Savel'eva, G S Polimbetova, V S Emel'yanova, L V Levina, in *Primenenie Metallokompleksnogo Kataliza v Organicheskom Sinteze* (Application of Metal Complex Catalysis in Organic Synthesis) (Ufa: Izd. BNTS UrO Akad. Nauk SSSR, 1989) p. 98
116. Ya A Dorfman, T V Petrova, L D Savel'eva *Kinet. Katal.* **33** 304 (1992)
117. Ya A Dorfman, T V Petrova, R R Sagadykova *Zh. Obshch. Khim.* **59** 1452 (1989)
118. Ya A Dorfman, T V Petrova, R R Sagadykova *Zh. Obshch. Khim.* **62** 1077 (1992)
119. Ya A Dorfman, T V Petrova, L D Savel'eva, Zh U Ibragimova, R R Sagandykova *Kinet. Katal.* **31** 480 (1990)
120. Ya A Dorfman, T V Petrova, L D Savel'eva *Kinet. Katal.* **33** 304 (1992)
121. Ya A Dorfman, M M Aleshkova, T V Petrova, in *Khimicheskie Sintezy na Osnove Odnouglerodnykh Molekul* (Chemical Syntheses Based on One-Carbon Molecules) (Moscow: Khimiya, 1991) p. 156
122. Ya A Dorfman, T V Petrova, L D Savel'eva, R R Abdreimova, M M Kebekbaeva, R R Sagandykova, L D Savel'eva, D M Doroshkevich *Zh. Obshch. Khim.* **62** 2710 (1992)
123. E Ya Tarat, O G Vorob'ev, O S Balabekov *Ochistka Gazov v Proizvodstve Fosfora i Fosfornykh Udobrenii* (Purification of Gases in the Manufacture of Phosphorus and Phosphorus Fertilisers) (Moscow: Khimiya, 1979)
124. A Lupi, B Chubar *Salt Effects in Organic and Organometallic Chemistry* (Translated into Russian; Moscow: Mir, 1991)