Translated from *Uspekhi Khimii* **60** 1190–1228 (1991) U.D.C. 547+546+541

Oxidation of phosphine and arsine by metal complexes and free and bound oxygen

Ya A Dorfman, I M Yukht, L V Levina, G S Polimbetova, T V Petrova, V S Emel'yanova
Institute of Organic Catalysis and Electrochemistry, Academy of Sciences of the Kazakh SSR, Alma-Ata

ABSTRACT. Data on the oxidation of PH_3 and AsH_3 by metal complexes and oxygen compounds of metals and non-metals and on their catalytic and coupled oxidation by dioxygen, ozone, and peroxide compounds are analysed. The methods for the activation of oxidants, phosphine, and arsine, ensuring the acceleration of the oxidative reactions in processes involving the elimination of the extremely harmful impurities PH_3 and AsH_3 from gases, are examined.

The bibliography includes 176 references.

Contents

I.	Introduction	605
II.	The many-electron rate-limiting stage	605
III.	PH_3 and AsH_3 oxidation reactions and orbital symmetry rules	609
IV.	Oxidation by the halogens	610
V.	Oxidation by oxygen compounds of the halogens	612
VI.	Oxidation by oxygen compounds of nitrogen	612
VII.	Oxidation by oxygen compounds of sulphur, selenium, and tellurium	613
VIII.	Oxidation by oxygen compounds of 3*d* metals	614
IX.	Oxidation by metal complexes	617
X.	Oxidation by dioxygen, ozone, and peroxide compounds	618
XI.	Conclusion	619

I. Introduction

Reactions involving oxidation by metal complexes and free and bound oxygen are used widely to remove the extremely toxic impurities AsH_3 and PH_3 from gases.[1–4] These impurities are present in the effluent gases from phosphorus, carbide, metallurgical, phosphide, hypophosphite, and other industries and are evolved in the processing of phosphorus slags.[1–5] Reactions involving the oxidation of PH_3 and AsH_3 by dioxygen are used to purify oxygen-containing gases while oxidation of phosphine and arsine by bound oxygen is employed for the detoxification of oxygen-free gases.[1–4] However, there are no reviews in the literature of the oxidation reactions of PH_3 and AsH_3. Certain reactions of PH_3 and AsH_3 have been described.[6–12]

The present review discusses the principal features of the kinetics and mechanisms of the majority of the known reactions involving the oxidation of PH_3 and AsH_3 by metal complexes and the oxygen compounds of metals and non-metals as well as their catalytic and chemical oxidation by dioxygen, ozone, and peroxide compounds.

In the analysis of the oxidation reaction PH_3 and AsH_3, it was observed that a common feature of the fast reactions is the many-electron nature of the rate-limiting stage involving an even number of electrons in the case of PH_3 and an odd number of electrons in the case of AsH_3. On the other hand, in processes where an odd number of electrons is transferred in the rate-limiting stage of the oxidation of the PH_3 and an odd number of electrons is transferred in the corresponding stage in the oxidation of AsH_3 are slow. The observed effect made it possible to divide the PH_3 and AsH_3 oxidation reactions into two groups: complementary and non-complementary reactions.[13] The number of electrons involved in the oxidation-reduction reactions depends on the type of stable valence states of the oxidant and their redox potentials.[14] The rate of reaction increases with increase in the number of electrons participating in the rate-limiting stage. Four methods for the acceleration of the PH_3 and AsH_3 oxidation reactions are most common: (1) the use of solvents or carriers which stimulate the formation of polynuclear complexes ensuring the transfer of the necessary number of electrons: (2) the use of catalysts which are capable of being reduced by PH_3 and AsH_3 in the presence of an oxidant with participation of the required number of electrons and which are rapidly regenerated by the oxidant to the initial state; (3) the application of catalysts which permit the separation of the rate-limiting stage into two slow stages: the reduction of the catalyst by PH_3 or AsH_3 with participation of the required number of electrons and the reoxidation of the catalyst by the oxidant; (4) the introduction of additives (activators) which ensure the coupled oxenoid oxidation of PH_3 and the non-oxenoid oxidation of AsH_3. In a number of instances, several methods are used simultaneously to accelerate the reduction of metal complexes and free and bound oxygen by phosphine and arsine.[11,12]

II. The many-electron rate-limiting stage

The oxidation of PH_3 and AsH_3 to the phosphate and arsenate respectively, i.e.

$$PH_3 - 8e + 4O^{2-} \rightarrow PO_4^{3-} + 3H^+, \quad (1)$$

$$AsH_3 - 8e + 4O^{2-} \rightarrow AsO_4^{3-} + 3H^+, \quad (2)$$

proceeds with participation of eight electrons and can occur in principle as a multistage process. We shall consider the thermodynamics of such successive oxidation. The oxidation of PH_3 and AsH_3 reduces the electron density of the P and As atoms and converts them into electron acceptors. As a result, phosphate and arsenate as well as the intermediate and final products of the

oxidation of PH_3 (phosphinite, phosphonite, phosphite, and phosphate) and AsH_3 (arsenite and arsenate) are stabilised in basic media owing to the formation of bonds with the bases. Presumably the rate constants for the oxidation of PH_3 and AsH_3 by bound and free oxygen are higher, other conditions being equal, in alkaline media than in acid media as a consequence of the formation of a donor–acceptor bond with the bases in the transition state. Thus for identical oxidising capacities of the reactants, alkaline media are more favourable for the oxidation of PH_3 and AsH_3. Since at high pH many oxidants are sparingly soluble and have a low redox potential, the oxidation-reduction reactions of PH_3 and AsH_3 were investigated in greater detail at low pH.[11,12]

Fig. 1 illustrates the distribution of energy in the successive oxidation of PH_3 in two-, four-, six-, and eight-electron processes. The redox potentials of the two-, four-, six-, and eight-electron oxidation of PH_3 in acid and alkaline media were calculated from data in handbooks using the law of the conservation of energy.[15] It is possible to use weaker oxidants for the oxidation of PH_3 in an alkaline medium than in the acid medium (see Table 1 at the end of the review). Since in most cases the oxidation reactions of PH_3 were investigated in the presence of an acid, which ensured the homogeneous occurrence of the process, we shall consider the distribution of energy among different stages in an acid medium. Phosphorus gives rise to stable compounds of the following oxidation states: P^{-3}(PH_3, PR_3); P^{-1}(PH, R_3PO, H_3PO); P^{+}[$R_2(RO)PO$, $H_2(HO)PO$, HPO, R_2P_2, R_4P_4]; P^{+3}[$R(RO)_2PO$, P_2O_3, $P(RO)_3$, PCl_3, $H(HO)_2PO$]; P^{+5}[$(RO)_3PO$, $P(RO)_5$, $(HO)_3PO$, P_2O_5, PCl_3O, PCl_5].[16]

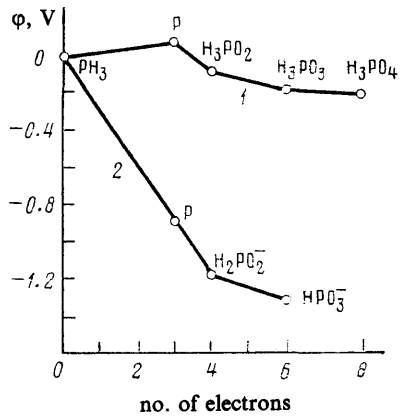


Figure 1. The oxidation-reduction potentials of three-, four-, six-, and eight-electron oxidation of phosphine to phosphorus, hypophosphorus, phosphorus, and phosphoric acids respectively in acid (curve *1*) and alkali (curve *2*) media.

The oxidation state varies in the above series in steps corresponding to an even number of electrons.[17] Other valence states of the P atom, differing from P^{-3} by an odd number of electrons (P^{-2}, P^{0}, P^{+2}, and P^{+4}), are unstable.[17] The stability of the P^{-2}, P^{0}, P^{+2}, and P^{+4} valence states increases somewhat in the presence of the P–P bond [P_2H_4, P_2R_4, P_4R_6, P_4, $P_2H_2(O)_2(OH)$, $P_2(RO)_4$, P_2Cl_4, $P_2(HO)(O)_2$].[18] However, diphosphorus compounds are obtained either from substances already containing P–P bonds or by the reaction of the P^{+3} acid chlorides with P^{-3} compounds (secondary phosphines, alkyl phosphides, alkali metals).[18] In the oxidation of PH_3, the formation of diphosphorus products is hindered by the necessity for the involvement of two PH_3 molecules in the rate-limiting stage.

One-, three-, five-, and seven-electron oxidation of PH_3, leading to the regeneration of unstable intermediates, is thermodynamically less viable than the two-, four-, six-, and eight-electron oxidation leading to the formation of stable intermediate or final products. Bearing in mind the rules stating that the variation of free energies is linear,[14] one can assume that the non-complementary oxidation of PH_3 should be appreciably slower and should require a higher activation energy than the complementary oxidation.[13] Similar rules are characteristic of the complementary and non-complementary transitions also in other oxidation-reduction reactions.[13,14,19,20]

The thermodynamic, activation, and kinetic parameters of the rate-limiting stage of the oxidation of PH_3 depend not only on the complementarity but also on the total number of participating electrons. Fig. 1 shows that, in the successive complementary oxidation of PH_3, the energy is distributed non-uniformly among different stages. If P^{-1} compounds are formed in the interaction as intermediates (two-electron rate-limiting stage), then the first stage can be carried out only using oxidants with a redox potential in excess of 0.06 V. If P^{+1} compounds are generated as intermediates (four-electron rate-limiting stage), then weaker oxidants with redox poentials in excess of −0.08 V are suitable for the initial step. The six- and eight-electron reactions can occur using oxidants having redox potentials in excess of −0.14 and −0.15 V respectively. Similar rules have been established also for the reduction reactions of many-electron reactants.[21–24].

The overall energy effect in the rate-limiting stage increases with increase in the number of active electrons and reaches a maximum when the process involves eight electrons of PH_3. Since a large number of molecules (phosphine, several oxidant and base molecules) usually participate in a many-electron rate-limiting stage, it follows that, with increase in the number of active electrons, the role of the entropy prohibition becomes more pronounced.[13] However, if the solvent or the carrier stimulate the formation of polynuclear complexes containing bases in the coordination sphere, the entropy barrier is lowered.[14] Positive changes in the activation entropy are observed when the polynuclear complex forms fairly stable compounds with PH_3. Metal complexes forming phosphides on interaction with PH_3 are especially effective. The phosphides generate the ions of d^8–d^{10} metals from CuCl, $AgNO_3$, $HgCl_2$, AuCl, $PdCl_2$, and $PtCl_2$.[16] The coordinated phosphide anion has more marked reducing properties than PH_3. The molecules deprotonated by the complex-forming agent are usually oxidised much faster than the initial molecules.[25] Polynuclear complexes can be detected by physical[26] and physicochemical methods.[27]

The formation of polynuclear metal complexes is promoted by solvents with a low dielectrical constant and mono- and poly-dentate ligands having at least two unshared electron pairs with similar energies (F^-, Cl^-, Br^-, I^-, O^{2-}, HO^-, S^{2-}, HS^-, Se^{2-}, Te^{2-}). The content of polynuclear complexes in solution increases in turn with increase in the total concentration of the metal.[26] As a rule, the amount of polynuclear complexes ($C_{Ox_iY_i}$) depends on the total

concentration of the oxidant ($C_{Ox\Sigma}$) and the ligands (C_Y) as described by the formula[26]

$$C_{Ox_jY_i} = \frac{C_{Ox\Sigma}\gamma C_{Ox}^{j-1} C_Y^i}{1 + \gamma C_{Ox}^{j-1} C_Y{}^i}.$$

When $\gamma C_{Ox}^{j-1} C_Y^i > 1$ and $C_{Ox_jY_i} = C_{Ox\Sigma}$, we have $\gamma = C_{Ox_jY_i}/C_{Ox}^j C_Y^i$.

Polynuclear metal complexes are reduced by phosphine in the following way: one of the metal ions of the polymeric complexes is bound to PH_3 and electrons are transferred from phosphine to other ions of the intermediate. This mechanism operates in the reduction of a many-electron oxidant.[21–24]

The stability of polynuclear oxygen-containing compounds depends on the acidity of the medium and usually increases as half the sum of the electronegativities of the central atom and oxygen approaches 2.5.[28] Since phosphine and arsine do not form complexes with high-valence forms of the metal, the oxygen compounds react with PH_3 and AsH_3 via an outer-sphere mechanism. Phosphine adds to an O atom of the polynuclear oxygen compound. The nearest central metal atom effects the transfer of electrons from PH_3 to the remaining ions of the intermediate and transfers non-bridging O atoms to phosphine. The loss of oxygen atoms by this centre is made good by the oxygen atoms from other oxygen compounds of the polynuclear ensemble.

Iodide and bromide ions are most often used as catalysts ensuring the oxidation of PH_3 and AsH_3 by metal complexes and bound oxygen via separate mechanisms. In order to estimate their catalytic properties in the reduction of various oxidants, a correlation equation has been proposed.[29] The oxidation reaction usually begins with the stage involving the formation of a complex of PH_3 with the oxidant. It follows from data on the mechanisms of the oxidative reactions of PH_3 that metal complexes form intermediates with a central atom–phosphorus bond, while oxygen compounds of metals and non-metals give rise to products with an O–P bond:

$$PH_3 + Ox_j \overset{K_1}{\rightleftarrows} Ox_j(PH_3). \quad (3)$$

Next comes the inner-sphere or outer-sphere redox reaction of the intermediate $Ox_j(PH_3)$. Coordinated bases (O^{2-}, OH^-, H_2O, ROH, RO^-, Cl^-, Br^-, I^-, etc.) add to phosphine:

$$(PH_3)Ox_j \overset{K_2}{\rightleftarrows} (PH_3O_m)\,Red_j. \quad (4)$$

The process terminates with the decomposition of the complex formed by the reduced form of the oxidant (Red_j) and the oxidised phosphine (PH_3O_m):

$$(PH_3O_m)\,Red_j \xrightarrow{k_0} PH_3O_m + j\,Red. \quad (5)$$

The equilibrium constant K_2 can be determined from the difference between the redox potentials φ_1 and φ_2:

$$\lg K_2 = \frac{(\varphi_1 - \varphi_2)\,RT}{nF}, \quad (6)$$

where n is the number of electrons which in the given instance are transferred from the reductant to the oxidant and F is the Faraday (96 500 coulomb mol^{-1}). According to this mechanism, the effective rate constant k is given by

$$k = k_0 K_1 K_2. \quad (7)$$

It follows from Eqns. (6) and (7) that

$$\lg k = \lg k_0 + \lg K_1 + \frac{RT}{nF}(\varphi_1 - \varphi_2). \quad (8)$$

The quantities φ_1 and φ_2 characterise the oxidation-reduction potentials of the oxidant and phosphine respectively in the intermediate complex.[30] On complex formation, the oxidation-reduction potentials of the reactants involved change and frequently in the opposite directions.[30] As K_1 varies, the effective rate constant k therefore passes through a maximum. The formation of a complex between Ox_j and PH_3 facilitates, on the one hand, the inner-sphere redox transfer of electrons and, on the other hand, lowers the redox potential of the oxidant φ_1. As a result of the formation of a stable complex with PH_3, the oxidant is converted into a reductant.[30] Metal phosphides [$(HgCl)_3P$, Cu_3P, Ag_3P, Au_3P] exhibit only reductive properties. It follows from Eqn. (8) that the rate constant for the reduction of the oxidant by phosphine increases with increase in the redox potential of the oxidant in the half-reaction involving an even number of electrons (n). Mononuclear and polynuclear complexes of the oxidant can participate in the rate-limiting stage. The transition state in the rate-limiting stage is stabilised if the system contains species capable of forming donor–acceptor and dative bonds with the oxidised P atom and the reduced oxidant. Since an increase and decrease in the positive charge on the P atom enhances the "hard" and "soft" properties respectively,[14] a combination of species of both types in the system is optimal. Since oxygen-containing molecules (H_2O, ROH) stabilise the positively charged states of the P atoms while iodide ions stabilise the reduced forms of the metal complexes, aqueous and alcoholic solutions of alkali metal iodides are most often employed as the solvent in PH_3 oxidation reactions.[11,12]

The concerted transfer of an appreciable number of electrons in the rate-limiting stage takes place stepwise via the formation and subsequent reactions of unstable intermediates which have definite albeit short lifetimes.[31] Such intermediates, formed as a result of one- or two-electron transfer, are present in shallow energy wells.[31] The energy profile of a many-electron rate-limiting stage involves several transition states. The saw-tooth form of the energy barrier in a many-electron rate-limiting stage is due to the fact that the simultaneous transfer of more than one electron is prohibited by the Franck–Condon principle.[13] The Franck–Condon barrier increases sharply in the transfer of two electrons.[13,14] The intermediate complex is rearranged in small energy wells, which makes it possible to overcome the Franck–Condon barrier. Other important limitations to the many-electron transfer in the rate-limiting stage arise from the rule of the conservation of electron spin[32] and of the symmetry of the interacting orbitals.[33,34] The energy wells are shallow if the successive transfer of a large number of electrons in the rate-limiting stage takes place without the infringement of these rules.

The main driving force of a many electron rate-limiting stage is the difference between the energies of the one-electron and many-electron stages [Eqn. (8)]. The greater this difference, the greater the probability of the many-electron transition. Exothermic reactions are preferred because a definite energy is required to rearrange the intermediates. Low activation energies are characteristic of all the steps in a many-electron rate-limiting stage owing to the high degree of utilisation of the energy of formation of new bonds in the dissociation of old ones.[35]

Eqn. (8) can be used to predict reactions with participation of other many electron-donors, since the known correlations (see, for example, Tobe[13] and Basolo and Pearson[14]) are used only for estimations relating to one-electron reactions. In conformity with Eqn. (8), a three-electron transfer in the rate-limiting stage is preferred in the oxidation of AsH_3. It can be seen from Fig. 2 that the redox potential $\varphi_{AsH_3 \rightarrow As} = -0.65$ V, while the redox potentials of the six- and eight-electron transfers reach -0.18 and 0.05 V respectively. Oxidants ensuring the energetically favourable three-electron oxidation of AsH_3 in the rate-limiting stage are therefore rapidly reduced by arsine.[6]

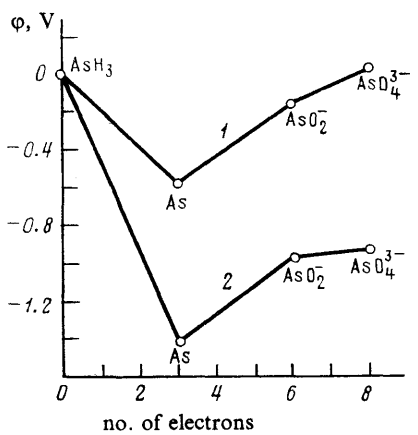


Figure 2. The oxidation-reduction potentials of three-, six-, and eight-electron oxidation of arsine to arsenic, arsenious, and arsenic acids in acid (curve *1*) and alkaline (curve *2*) media.

Oxidants capable of effecting the six- and eight-electron transfer (HIO_3 or H_5IO_6) convert AsH_3 directly into $HAsO_2$ or H_3AsO_4 without the preliminary liberation of As. The point is that the successive oxidation of AsH_3 to As and then of As to $HAsO_2$ or H_3AsO_4 is energetically less favourable than the direct transformation $AsH_3 \rightarrow HAsO_2$ (or H_3AsO_4). The $AsH_3 \rightarrow HAsO_2$ and $AsH_3 \rightarrow H_3AsO_4$ redox potentials are only -0.18 and 0.05 V respectively, while the $As \rightarrow HAsO_2$ and $As \rightarrow H_3AsO_4$ redox potentials are respectively 0.25 and 0.58 V. The rates of reduction of six- and eight-electron oxidants by AsH_3 and PH_3 are therefore similar. In reactions with oxidants promoting the transfer of an odd number of electrons, the reactivity of AsH_3 is appreciably higher than that of PH_3.

Other features are observed in the oxidation of ammonia. Nitrogen forms stable compounds when it exists in the following oxidation states: $N^{-3}(NH_3)$, $N^{-1}(NH_2OH, NH_2Cl)$, $N^0(N_2)$, $N^{+1}(NHCl_2)$, $N^{+3}(HNO_2)$, and $N^{+5}(HNO_3)$.[36] In contrast to the increase in the positive charge on As and P, its increase on nitrogen is accompanied by an increase in the redox potential (Fig. 3). It follows from Fig. 3 that, in the oxidation of NH_3 in an alkaline medium, two-, four-, six-, and eight-electron transfers take place preferentially in the rate-limiting stage. Similar transfers in an acid medium are distinguished by high redox potentials. The most favourable six-electron transfer is hindered by the necessity for the involvement of two NH_3 molecules in the slow stage. It follows from a comparison of Figs. 1–3 that concerted four-, six-, and eight-electron oxidation is preferred for PH_3, three- and six-electron oxidation is preferred for AsH_3 and two- and four-electron oxidation is preferred for NH_3. The above properties of PH_3, AsH_3, and NH_3 influence significantly the kinetics of the oxidation reactions of the hydrides. The different behaviour of the hydrides is due to the sharp decrease in the energies of the bonds formed by the heteroatoms with hydrogen in the sequence (energy in kJ mol^{-1}) N–H (380) > P–H (323) > As–H (281) > Sb–H (256) and in the heats of formation of the hydrides in the sequence (heats expressed in kJ mol^{-1}) NH_3 (−46.2) > PH_3 (9.6) > AsH_3 (67.0) > SbH_3 (144.6).[36] The probability of the concerted three-electron oxidation with abstraction of all the hydrogen atoms therefore increases in the same sequence and the tendency towards the synchronous two-electron oxidation, accompanied by the loss of only two hydrogen atoms, diminishes.

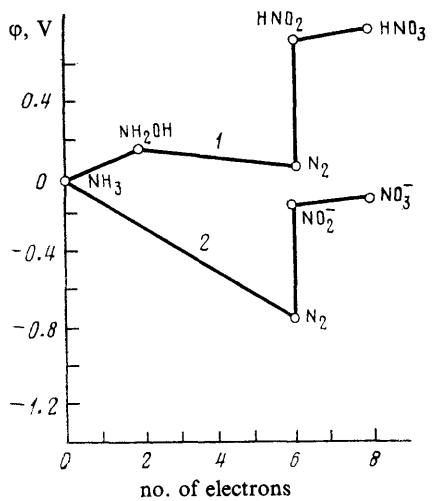


Figure 3. The oxidation-reduction potentials of two-, six-, and eight-electron oxidation of NH_3 to hydroxylamine, nitrogen, and nitrous and nitric acids respectively in acid (curve *1*) and alkaline (curve *2*) media.

The many electron single-state oxidation of PH_3 is facilitated by the fact that the intermediate phosphorus compounds (+1, −1, +3) are characterised by a much greater capacity for complex formation than phosphine. The intensification of the ligand properties of the phosphorus atom as it is oxidised lowers the entropy barrier in the multistep rate-limiting stage. On the other hand, the ligand properties of the nitrogen atom are rapidly weakened as ammonia is oxidised. This increases the energy barrier in the multistep rate-limiting stage and limits the number of electrons transferred simultaneously.

Thus oxidation mechanisms with many-electron rate-limiting stages are energetically favourable for PH_3 and AsH_3. The entropic obstacles are not so great if the intermediate complex is formed

before the rate-limiting stage. The barriers associated with the rules of the conservation of electron spin and the Franck–Condon principle are removed by virtue of the multistep nature of the slow stage where one or two electrons are transferred in each step.

III. PH_3 and AsH_3 oxidation reactions and orbital symmetry rules

In the analysis and prediction of the chemical properties of PH_3 and AsH_3, account is taken of the predominantly *s* character of the unshared electron pair,[37,38] of the relatively low ionisation potentials (10.5 and 9.8 eV respectively), of the high electron affinities (0.77 and 1.07 eV respectively), of the high polarisabilities and the large dimensions of the 3*s* and 3*p* orbitals,[39] of the presence of valence *d* levels,[10] and of the tendency of the diffuse σ*-bonds to effect the σ,*n*- and σ,π-coupling of these molecules.[40] In order to account for the mechanisms of the reactions of PH_3 and AsH_3, the orbital symmetry rules, which have found wide applications in organic and inorganic chemistry and catalysis,[32–43] will be used in the present review.

According to Hammond's postulate,[32] in exothermic reactions the energy and the structure of the transition state are close to those of the initial reactant while in endothermic reactions they are close to those of the product. In order to determine the nature of the activation, it is therefore necessary to have information about the nodal structures, energies, and populations of the frontier orbitals (HOMO and LUMO) of the reactants and products.[33,34] Data on the structures of PH_3, AsH_3 and their oxidation products, obtained by quantum-chemical,[34,41–52] photoelectron spectroscopic,[41,44] and X-ray spectroscopic[53–62] methods, are important. According to calculations,[34,42,43] the molecular orbitals of NH_3, PH_3, AsH_3 and SbH_3 have the following configurations:

$$\text{for } NH_3\text{: } (a_1)^2(e)^4(2a_1)^2(3a_1)^0(2e)^0,$$

$$\text{for } SbH_3,\ PH_3 \text{ and } AsH_3\text{: } (a_1)^2(e)^4(2a_1)^2(2e)^0(3a_1)^0.$$

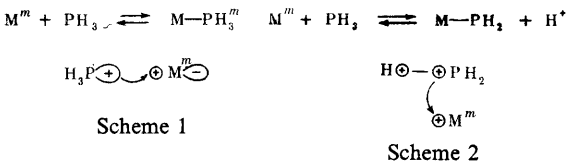
In contrast to NH_3, the 2*e* orbitals of the PH_3, SbH_3, and AsH_3 molecules occupy a lower energy level than the $3a_1$ orbitals, since the 2*e* molecular orbitals of stibine, phosphine, and arsine belong mainly to the 3*d* type.[34–41] The usual parallel decrease in the ionisation potentials of the molecule and atom are not observed in the series of hydrides NH_3, PH_3, AsH_3, and SbH_3:[41] the ionisation potentials of atoms diminish on passing from N to Sb and the ionisation potentials of the hydrides vary in the opposite sequence: $NH_3 < PH_3 < AsH_3 < SbH_3$.[34,41] This reversal of the sequence on passing from atoms to molecules of the hydride is induced by the increase in the contribution of the *s* orbital of the heteroatom to the occupied *n* orbital of the hydride with increase in the size of the heteroatom (E) and with decrease in the H–E–H bond angle.[34,41]

It follows from the data presented that, in contrast to NH_3, the PH_3 and AsH_3 molecules tend to form donor–acceptor and dative bonds with complex-forming agents. In contrast to the ammonia molecule, the HOMO and LUMO in phosphine and arsine form respectively P–H and As–H σ- and σ*-bonds. The frontier orbitals are predominantly of σ character and to a much lesser extent the n character, which is reflected, in our view, in the chemical properties of the hydrides PH_3 and AsH_3. Thus, the two-sided exchange reactions of PH_3 of the type [σ + σ], [σ + π], and [σ + ππ] are therefore symmetry-prohibited. Owing to the difference between the energies of the $2a_1$ and *e* orbitals, reactions of the type [σσ + σ], [σσ + π], and [σσ + ππ] are difficult for PH_3. The one-sided homolytic processes proceed at elevated temperatures or in the presence of radicals.[7] One-sided heterolytic reactions of the type [*n* + *n*] require the participation of (soft) electrophiles or nucleophiles.[8] Reactions involving the nucleophilic addition and the electrophilic substitution of H atoms are therefore typical for phosphines with a P–H bond.[8]

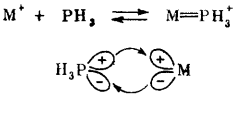
By virtue of the presence of valence *d* orbitals, phosphine exhibits a tendency to undergo both one-sided and two-sided exchange reactions with the reactants containing occupied *d* and π orbitals. Donor–acceptor electron transfer occurs on formation of complexes between phosphine and "hard" protic and aprotic acids (H_2SO_4, $TiCl_4$, $AlCl_3$, BCl_3).[6] Synchronous donor–acceptor and dative electron transfers are observed in the interaction of PH_3 with "soft" transition metal complexes having high redox potentials and low charges (Ag^I, Au^I, Cu^I, Hg^{II}, Pd^{II}, Pt^{II}) [16] and polar unsaturated molecules.[8]

The donor–acceptor one-sided interaction of PH_3 with a metal cation (M^+) leads to the appearance of an unstabilised phosphonium ion, in contrast to the ammonium ion. The dative one-sided electron transfer from the cation M^+ to PH_3 is thermodynamically unfavourable, since it leads to the formation of unstable negatively charged phosphine. The two-sided exchange interaction, in which two close *d* and *s* orbitals of the cation interact in concert with the frontier orbitals of PH_3, is more favourable. The reverse transfer is not accompanied by an appreciable localisation of electrons on one of the fragments. Complexes with close *d* and *s* levels, populated overall by two electrons, are most suitable for such interaction.[33] This is indicated by the particular tendency of PH_3 to form complexes with ions of d^{10} metals (Ag^I, Cu^I, Hg^{II}, Au^I).[63]

The orbital diagrams of single bond formation (Scheme 1), electrophilic substitution (Scheme 2), and double bond formation (Scheme 3) reactions with participation of phosphine and a d^{10} metal ion are presented below:



Scheme 1 Scheme 2



Scheme 3

Scheme 1 illustrates the unshared orbital of PH_3 and an unoccupied orbital of the *p* metal cation, while Scheme 2 illustrates the nodal structures of the P–H σ-bond and the unoccupied orbital of the cation. It follows from the comparison of the orbitals that nucleophilic addition and electrophilic substitution reactions are symmetry-allowed for PH_3.[33] The mode of reaction depends on the redox potential of the complex. The higher the redox potential, the more likely the formation of metal phosphide complexes. Thus $AgNO_3$, $CuHSO_3$, $HgCl_2$, and $PdCl_2$ form phosphides on interaction with PH_3, while AgCl, AuCl, CuI, BCl_3, $TiCl_4$, $AlCl_3$, and SiF_4 give rise to phosphine complexes.[6,16]

Scheme 3 illustrates the orbital diagram for the appearance of the $H_3P{=}M^+$ double bond. The PH_3 orbitals are presented as five equivalent sp^3d orbitals. Three of these are used for bonds with H atoms, while in the other two the remaining electrons are accommodated in two ways depending on whether they are paired or not. In the singlet state the electrons are paired and occupy one of the accessible orbitals. This form participates in complex formation reactions with d^{10} metal ions, whose frontier orbital are constructed similarly (Scheme 3).[32,33] In the triplet state, the electrons are located in different orbitals. This form is preferable for reactions with radicals.[32,33]

It is seen from Scheme 1 that, on interaction with complexes of *s* and *p* elements, phosphine is hardly activated, since the hybridisation of the phosphorus atom is not altered. On the other hand, on coordination to complexes of *d* metals, phosphine is activated because the hybridisation of the phosphorus atom becomes significantly different (Scheme 3). A similar change in the hybridisation of the phosphorus atom occurs also on formation of complexes of *d* metal phosphides.

In order to assess the nature of the activation of the reactants needed for the occurrence of the reaction, one must have information about the electronic structure of the products.[14,32] The point is that the activation energy falls as the electronic configurations of the initial and final substances are approached.[14,32] The PH_3 oxidation products (oxygen compounds of phosphorus) have been thoroughly investigated by quantum-chemical[41] and UV and X-ray spectroscopic[41,61] methods. The main conclusion is that, with increase in the number of P–O bonds, the *d* character of the phosphorus atom becomes more pronounced.[61] In order to accelerate the PH_3 oxidation reactions, it is therefore necessary to intensify, by means of activation, the *d* character of the phosphorus atom. This is achieved by coordinating PH_3 to d^{10} metal ions which have close *d* and *s* levels (Cu^I, Au^I, Ag^I, Hg^{II}).

IV. Oxidation by the halogens

In contrast to NH_3 and AsH_3, gaseous PH_3 does not react with the halogens.[64] The interaction of NH_3 with the halogens leads to the formation of haloamines.[37] Arsine reacts vigorously with chlorine; it ignites even at the temperature of liquid nitrogen.[6] The reaction with bromine and iodine is rapid at room temperature with formation of arsenic halides.[6] Ammonia, which possesses a distinct unshared electron pair, as already mentioned, reacts with the halogens (X_2) via an S_N2 mechanism. Arsine, which has a weak unshared electron pair and is characterised by weak As–H bond energy, interacts with the halogens via homolytic mechanisms. The rate of the reaction of NH_3 with X_2 increases with increase in the redox potential of the halogens and the N–X bond energy (i.e. on passing from Br_2 to Cl_2).[37] The reactivity of arsine in this reaction is determined mainly by the As–X bond energy. In the liquid phase, all three hydrides are readily oxidised by the halogens.[65]

These reactions are widely used for the liquid-phase purification of gases.[2–4] Phosphine,[65,66] phosphine derivatives,[10] phosphites, and phosphorus halides[67] readily react with the halogens,[16,17] hypohalites,[68] and alkyl halides:[10,68]

$$PH_3 + 4Cl_2 + 4H_2O \rightarrow (HO)_3PO + 8HCl, \quad (9)$$

$$PH_3 + 4Br_2 + 4H_2O \rightarrow (HO)_3PO + 8HBr, \quad (10)$$

$$PH_3 + 2I_2 + 2H_2O \rightarrow (HO)H_2PO + 4HI, \quad (11)$$

$$PH_3 + 4HXO \rightarrow (HO)_3PO + 4HX, \quad (12)$$

$$R_3P + Cl_2 \rightarrow R_3PCl_2, \quad (13)$$

$$(RO)_3P + Cl_2 \rightarrow (RO)_2ClPO + RCl, \quad (14)$$

$$Cl_3P + Cl_2 \rightarrow PCl_5, \quad (15)$$

$$(PhO)_3P + Cl_2 \rightarrow (PhO)_3PCl_2. \quad (16)$$

Phosphorus(III) derivatives, which possess, in contrast to PH_3, a distinct unshared electron pair, react vigorously with the halogens,[68] forming nucleophilic addition or substitution products[68]—phosphonium salts and phosphoranes. The nucleophilic attack by the tertiary phosphine is directed to the atom with the highest LUMO coefficient (effective positive charge). Despite the fact that the P–O bond is much stronger than the P–Cl bond, tertiary phosphines attack the halogen atom in alkyl hypohalites in which the LUMO is localised. The halophosphonium salts, formed on interaction of PR_3 with hypochlorites, i.e.

$$R_3P + Cl{-}OR \rightarrow [R_3PCl]OR \rightarrow [R_3POR]Cl,$$

rearrange to the stable alkoxyphosphonium salts.[68] When the reaction is carried out in methanol, optically active phosphines are converted into phosphine oxides with the inverted configuration:

$$[R_3PCl]OR + MeOH \rightarrow R_3PO + MeCl + ROH.$$

Compounds with the RCO–Br, CCl_3–Cl, and Br–$CHArSO_2Ph$ bonds behave similarly. However, compounds with the Cl–CH_2R and Cl–COR bonds attack tertiary phosphines via the carbon atom.[68]

NH_3 behaves similarly to a tertiary phosphine. The oxidation of NH_3 to N_2H_4 and N_2 by sodium hypochlorite takes place in stages with the intermediate formation of chloramine:[36]

$$NH_3 + NaClO \rightarrow NH_2Cl + NaOH,$$

$$NH_2Cl + NH_3 + NaOH \rightarrow N_2H_4 + NaCl + H_2O,$$

$$N_2H_4 + 2NH_2Cl \rightarrow N_2 + 2NH_4Cl.$$

The interaction of coordinated ammonia with Cl_2 leads to the formation of the products of the electrophilic substitution of hydrogen atoms by chlorine atoms. The oxidation of platinum(II) ammines with chlorine results in the formation of dichloramineplatinum(IV).[37]

Since, in contrast to PR_3 and NH_3, PH_3 has weak nucleophilic properties, the driving force of the attack is to a large extent the energy of the bond formed.

The kinetics and mechanism of the oxidation of PH_3 by the halogens [reactions (9)–(12)] in solutions have been investigated.[65,66] The rates of reactions (9)–(12) increase with increasing concentrations of X_2 and PH_3 and of temperature and fall with increase in the content of X^- and in the pH. When the pH and C_{X^-} are varied, the ratios of the different forms of X^+ (X_2, X_3^-, XOH, XO^-) also vary:

$$X_2 + H_2O \rightleftarrows XOH + HX, \quad (17)$$

$$XOH + OH^- \rightleftarrows XO^- + H_2O, \quad (18)$$

$$X_2 + X^- \rightleftarrows X_3^-, \quad (19)$$

The above species are characterised by different reactivities in relation to PH_3.[12] The reactivity of the halogen compounds diminishes sharply in the sequence $X_2 > XOH > X_3^- > XO^-$ (see Table 1 at the end of the review).[11] Since the rate constants for the hydrolysis of X_2 [reaction (17)] and XOH [reaction (18)] decrease appreciably on passing from Cl_2 ($pK \simeq 4$) to Br_2 ($pK \simeq 9$) and I_2 ($pK \simeq 12$) and from ClOH ($pK \simeq 8$) to BrOH ($pK \simeq 9$) and IOH ($pK \simeq 13$),[36] iodine reacts with PH_3 in both acid and weakly alkaline solutions while chlorine reacts only in neutral and acid solutions.[12] In neutral and weakly alkaline solutions, the mixed systems $ClOH-Br_2-H_2O$, $ClOH-I_2-H_2O$, and $BrOH-I_2-H_2O$ exhibit a high reactivity.[12] In such systems, the halogen characterised by low hydrolysis rate constants plays the function of the catalyst, while the halogen which exhibits a higher tendency towards hydrolysis is the oxidant. Thus the interaction in the $PH_3-ClOH-I_2-H_2O$ system takes place via a separate mechanism in the following manner: phosphine is oxidised via Eqn. (11), while the I^- ion is reoxidised back to I_2 by hypochlorous acid:

$$2HI + ClOH \rightarrow I_2 + HCl + H_2O. \quad (20)$$

The catalytic effect is due to the fact that in neutral and weakly alkaline media, reactions (11) and (20) are faster than reaction (12).[11] The equilibrium constants of reaction (19) increase significantly in the sequence Cl_3^- ($pK \simeq 1$) < Br_3^- ($pK \simeq -1$) < I_3^- ($pK \simeq -4$).[36] Therefore the addition of I^- ions has a negative effect on reaction (11).

The facts listed above show that reactions (9)–(12) proceed via the formation and hydrolysis of phosphorus halides in accordance with the mechanism

$$PH_3 \xrightarrow[-H^+]{X^+} PH_2X \xrightarrow[-HX]{H_2O} PH_2(OH) \xrightarrow[-H^+]{X^+} PH(OH)X \xrightarrow[-HX]{H_2O}$$

$$\rightarrow PH(OH)_2 \rightarrow (HO)H_2PO \xrightarrow[-H^+]{X^+} (HO)XHPO \xrightarrow[-HX]{H_2O}$$

$$\rightarrow (HO)_2HPO \xrightarrow[-H^+]{X^+} (HO)_2XPO \xrightarrow[-HX]{H_2O} (HO)_3PO. \quad (21)$$

Since the P–X bond energy diminishes rapidly in the sequence F > Cl > Br > I, it follows that PI_5 does not exist, in contrast to PF_5, PCl_5, and PBr_5.[10] Therefore the oxidation of PH_3 by iodine in water terminates in a stage involving the formation of $(HO)_2HP$, which isomerises to $(HO)H_2PO$.[11]

The hydrogen atoms of PH_3 are substituted by X^+ in the rate-limiting stage in accordance with the S_N2 mechanism (see Scheme 2). The intermediate halo-derivatives of phosphorus(III) and phosphorus(V) hydrolyse immediately after their formation, so that it is impossible to detect them.[11] The high rate of hydrolysis is due to the fact that the energies of the P–O (86 kcal mol^{-1}) and P=O (146 kcal mol^{-1}) bonds are higher than the energy of the P–X bond (44–79 kcal mol^{-1}).[10]

The parallel variation of the reactivities of the halogens (Cl_2 > Br_2 > I_2 > HClO > HBrO > HIO) and the ionisation potentials [Cl (12.97 V) > Br (11.81 V) > I (10.45 V)] and of the oxidation-reduction potentials [Cl_2 (1.36 V) > Br_2 (1.07 V) > I_2 (0.54 V), ClOH (0.94 V) > BrOH (0.76 V) > IOH (0.49 V)] and the electron affinities [Cl (3.8 eV) > Br (3.54 eV) > I (3.29 eV)] is observed.[36] The active species X^+ is formed as a result of the reactions

$$H_2O + X_2 \rightleftarrows H_2OX^+ + X^-, \quad (22)$$

$$XOH \rightleftarrows X^+ + OH^-. \quad (23)$$

The X^+ formation constant increases in the sequences Cl_2 ($pK \simeq 30$) < Br_2 ($pK \simeq 20$) < I_2 ($pK \simeq 10$) and HClO ($pK \simeq 58$) < HBrO ($pK \simeq 53$) < HIO ($pK \simeq 39$).[69] Since the electrophilicity and the equilibrium concentration of X^+ vary in parallel as a function of its nature, its reactivity depends only slightly on the nature of X_2 and HXO.[12]

The tendency towards the formation of X^+ increases sharply in the sequence $F^+ \ll Cl^+ < Br^+ < I^+$,[69] since the metallic properties of the halogens intensify in the same sequence.[36] There is little evidence for the existence of Cl^+ or Br^+, but the I^+, I_3^+, and I_5^+ ions as well as I_2Cl^+, I_2Br^+, and ICl^+ have been thoroughly investigated.[36] The I^+ ion is highly electrophilic. It exists in media with weakly nucleophilic properties, for example in acid solutions.[36] The Cl_2, Br_2, and I_2 molecules, which have the $(\sigma)^2(\sigma^*)^2(\pi)^4(\sigma)(\pi^*)^4$ structure,[36] tend to exhibit the delocalisation of the antibonding π^* electrons. Thus the delocalisation of the π^* electrons over the unoccupied *d* orbitals tends to strengthen the X–X bond. Since, as already mentioned, PH_3 tends to form dative bonds with complex-forming agent (Cu^+, Ag^+, Au^+, Hg^{2+}, Pt^{2+}, Pd^{2+}), the unusual reactivity of the halogens in the PH_3 oxidation reaction becomes understandable. This reactivity is caused by the two-sided exchange interaction of the halogens with phosphine, which facilitates the formation of an intermediate complex. The fairly inert PH_3 molecule is activated in this complex as a result of the change in hybridisation $sp^3 \rightarrow sp^3d$. The latter structure is better prepared for oxidation than the initial sp^3 structure.

Another feature of the halogens is their tendency to polymerise in the presence of X^-.[36] The energetically favourable single-stage many-electron oxidation of phosphine is associated with this important property. Since the fraction of polyhalides increases with increase in the concentration of the halogens, the latter exhibit reactivity at elevated concentrations (10^{-3}–10^{-1} M).[11]

Different features are observed in the oxidation of AsH_3 by the halogens in an aqueous medium:[70]

$$AsH_3 + 3X_2 + 2H_2O \rightarrow HAsO_2 + 6HX. \quad (24)$$

The rate constants for the reactions of AsH_3 with the halogens (see Table 1) are higher than those for the analogous reactions of PH_3.[70] In constrast to PH_3, arsine is oxidised at low concentrations of the halogens (10^{-4}–10^{-5} M for I_2). The oxidation of AsH_3 in the mixed systems $ClOH-KI-H_2O$ and $ClOH-NaBr-H_2O$ takes place readily at KI concentrations higher by an order of magnitude than in the oxidation of PH_3.[70] The point is that, in contrast to

PH_3, AsH_3 is oxidised by the halogens homolytically. Such behaviour of AsH_3 is caused by its tendency to dissociate into the elements.[6]

Thus phosphine reacts with the halogens via a heterolytic mechanism, while arsine reacts via a homolytic mechanism.

V. Oxidation by oxygen compounds of the halogens

Phosphine and arsine are very readily oxidised by the oxygen compounds of bromine(V),[71-74] iodine(V),[75-78] and iodine(VII):[79-81]

$$PH_3 + HIO_3 \rightarrow (HO)_2HPO + HI, \quad (25)$$

$$PH_3 + H_5IO_6 \rightarrow (HO)_3PO + HI + 2H_2O. \quad (26)$$

PH_3 undergoes substitutional oxidative hydroxylation in reactions (25) and (26). Iodine(V) and iodine(VII) react similarly with AsH_3:

$$AsH_3 + HIO_3 \rightarrow HAsO_2 + HI + H_2O, \quad (27)$$

$$AsH_3 + H_5IO_6 \rightarrow H_3AsO_4 + HI + 2H_2O. \quad (28)$$

Since the IO_3^- and $H_4IO_6^-$ ions do not react with PH_3 and AsH_3, the rates of reactions (25)–(28) increase sharply after the addition of a very small amount of acid.[75-81] At pH 3–4, phosphine and arsine are rapidly oxidised by HIO_3 and H_5IO_6.[75-81]

Bromine(V) and especially chlorine(V) and chlorine(VII) compounds exhibit a very low reactivity in reactions of type (25)–(28).[71-74]

The appreciable reactivity of HIO_3 and H_5IO_6 in dilute acid solutions is caused by the relatively high proton affinity:

$$IO_3^- + H^+ \rightleftharpoons HIO_3, \quad K = 10 ,$$
$$H_2IO_6^{3-} + H^+ \rightleftharpoons H_3IO_6^{2-} \quad K = 10^{15} ,$$
$$H_3IO_6^{2-} + H^+ \rightleftharpoons H_4IO_6^-, \quad K = 2 \cdot 10^{10} ,$$
$$H_4IO_6^- + H^+ \rightleftharpoons H_5IO_6, \quad K = 3 \cdot 10^3 .$$

In contrast to $HClO_3$, $HBrO_3$, and $HClO_4$, the molecules of HIO_3 and H_5IO_6 exhibit "soft" properties, which are necessary for the formation of adducts with diphilic PH_3. Reactions (25)–(28) are characterised by the presence of an induction period, which diminishes after the introduction of KI or $HClO_4$.[75,78] Even at low KI or $HClO_4$ concentrations (10^{-4} M), the induction period disappears.[80] In terms of their effectiveness, the KI and $HClO_4$ additives are similar.[75-81] The optimum acid concentration is equal to the initial concentration of $H_4IO_6^-$ or IO_3^-.[78,80] Potentiometric study has shown that the redox potential of the reacting system gradually increases during the induction period.[78,80] The point is that the redox potentials of the IO_3^- and $H_4IO_6^-$ ions are respectively 0.26 and 0.70 V, while those of the HIO_3 and H_5IO_6 molecules are 1.20 and 1.64 V. The system begins to absorb PH_3 actively only after the attainment of the redox potential characteristic of HIO_3 or H_5IO_6. Hence one may conclude that H_3PO_3 accumulates and the HIO_3 and H_5IO_6 molecules, responsible for the reaction, are formed during the induction period.

The geometry of the oxy-anions XO_4^- and XO_3^- is determined by the sp^3 hybridisation of all the valence electrons of the halogen atom.[36] The O–X–O angles are in all cases close to the tetrahedral value. However, the *d* orbitals also definitely participate in the formation of X–O π-bonds.[36] Judging from the redox potential, compound (IX) with a potential of 1.1 V is formed under the influence of iodide ions. Compounds in which iodine is present in intermediate valence states are not produced in reactions (25)–(28).

The substitutional hydroxylation of PH_3 by iodine(V) and iodine(VII) compounds can be represented as follows:

$$PH_3 \xrightarrow[-H^+]{IO_3OH} [(IO_2)\,PH_2OH]^- \xrightarrow[-H^+]{H^+} [(IO)PH(OH)_2]^- \xrightarrow{H^+} \longrightarrow OP(OH)_2H + HI, \quad (29)$$

$$PH_3 \xrightarrow[-H^+]{IO_3OH} [(IO_3)PH_2OH]^- \xrightarrow[-H^+]{H^+} [(IO_2)PH(OH)_2]^- \xrightarrow[-H^+]{H^+} \longrightarrow [(IO)P(OH)_3]^- \xrightarrow{H^+} (HO)_3PO + HI. \quad (30)$$

The six- and eight-electron reactions (29) and (30) apparently take place in one stage via three or four two-electron steps with shallow energy wells in the course of the reaction. The driving force of the many-electron rate-limiting stage is the increase in the exothermic heat evolution with increase in the number of electrons participating in the reaction (Fig. 1). The entropy barrier of the many-electron type is lowered as a consequence of the tendency of the phosphorus atom to form intermediates containing iodine in all possible intermediate valence states. The analogous bromine and chlorine compounds do not have this property and are incapable of effecting the many-electron process in one stage because of entropic factors. Therefore, as X varies in the sequence HIO_3 (1.08 V) < $HBrO_3$ (1.44 V) < $HClO_3$ (1.47 V) [36] (see Table 1 at the end of the review), the reactivity and the redox potential vary in opposition.

Arsine is oxidised by oxygen compounds of iodine(V) similarly to phosphine and the rates of oxidation are also similar. The formation of arsenious acid as the product indicates the many-electron nature of the rate-limiting stage in which six electrons participate. The direct oxidation $AsH_3 \rightarrow HAsO_2$ is energetically more favourable than the multistage oxidation via the formation of As and its subsequent oxidation to $HAsO_2$. The redox potential of the reaction $AsH_3 \rightarrow HAsO_2$ is −0.18 V and that of the reaction $As \rightarrow HAsO_2$ is 0.25 V. AsH_3 and PH_3 therefore have similar reactivities in relation to iodine(V) (see Table 1).

The oxygen compounds of the halogens are activated by metal ions in a high oxidation state as a result of the increase in the redox potential and the polarity of the oxidant. Thus the reactions involving the oxidation of PH_3 by halates and perhalates are accelerated by molybdenum(VI) [71,76] and tungsten(VI) [77,81] complexes. Metal ions in the highest oxidation states are coordinated to the oxygen compounds of the halogens via the O atom. Halates and perhalates add to PH_3 via the other oxygen atom. The oxidant activated in this way gives up an O atom to phosphine more readily. In the presence of Cl^- ions, ICl, characterised by a potential of 1.1 V, participates in reactions (25) and (26).

VI. Oxidation by oxygen compounds of nitrogen

The oxygen compounds of nitrogen oxidise PH_3 and AsH_3 fairly readily via the reactions[11-12,82-86]

$$PH_3 + 2N_2O_4 \rightarrow 4NO + (HO)_3PO, \quad (31)$$

$$AsH_3 + HNO_3 \rightarrow As + NO + 2H_2O. \quad (32)$$

These compounds are used to remove PH_3 and AsH_3 from gases[2-4] (see Table 1 at the end of the review). Under these conditions, PH_3 interacts effectively only with concentrated HNO_3 solutions (above 25%),[2] while AsH_3 reacts rapidly also with dilute nitric acid.[6] The conversion curve for the oxidation of PH_3 by nitric acid (dependence of the rate of reaction on the amount of absorbed PH_3) passes through a maximum, which indicates the involvement of N_2O_4, and not HNO_3, in the reaction. N_2O_4 is formed by the reaction

$$HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O. \quad (33)$$

The remaining oxygen compounds of nitrogen (NO, N_2O, HNO_2, and HNO_3) are relatively inactive.[11,12] These data show that, in contrast to AsH_3, PH_3 is oxidised only by oxygen compounds of nitrogen(IV), in the presence of which there is a possibility of a many-electron rate-limiting stage with participation of an even number of electrons. Phosphorus(III) compounds exhibit a tendency to interact with the O atoms of the oxygen compounds of nitrogen[7,87] owing to the high P=O bond energy (611 kJ mol^{-1}).[10] The rate-limiting stage in the oxidation of organophosphines and phosphites by *N*-oxides (R_3NO) is the nucleophilic addition of an O atom to phosphorus(III). The rate of oxidation of phosphorus(III) derivatives by pyridine *N*-oxide diminishes in the sequence

$$PCl_3 > PhCl_2P > Ph_2PCl \gg (PhO)_3P > (EtO)_3P \gg Ph_3P > > Bu_3P > Et_2PhP.$$

On the other hand, in the oxidation of phosphites by the oxide N_2O_4 the electrophilic addition of an O atom to the phosphorus(III) atom takes place in the rate-limiting stage. This is indicated by the series of reactivities of phosphorus(III) compounds in relation to N_2O_4: $P(RO)_3 \gg P(PhO)_3$.[10] When account is taken of the data presented, the mechanism of the oxidation of PH_3 by the oxide N_2O_4 can be represented as follows:

$$N_2O_4 + PH_3 \rightleftarrows (N_2O_4)PH_3 \xrightarrow[-NO]{} (NO_2)PH_2(OH) \xrightarrow[-NO]{} PH(OH)_2, \quad (34)$$

$$PH(OH)_2 + N_2O_4 \rightleftarrows (N_2O_4)PH(OH)_2 \xrightarrow[-NO]{} (NO_2)P(OH)_3 \xrightarrow[-NO]{} \longrightarrow (HO)_2PO. \quad (35)$$

Reaction (31) includes two four-electron stages. In each stage there are in its turn two two-electron steps to which shallow energy wells correspond. The entropy barrier in the many-electron transition is overcome by virtue of the formation of a complex between N_2O_4 and PH_3 or, in the general case, between N_2O_4 and phosphorus(III). As a result of complex formation with participation of the O atoms of the oxygen compounds of nitrogen and the phosphorus(III) atom, the reactions involving the oxidation of phosphorus(III) derivatives by nitrogen oxides are very rapid.[7]

The oxidation of phosphine by nitrogen dioxide is accelerated by Ag^+ ions. A small amount of added $AgNO_3$ (10^{-4} M) ensures a high reactivity of these and dilute (<10%) solutions of nitric acid.[2,11] The kinetic equation for the oxidation of PH_3 by nitric acid does not then change.[11] Like other d^{10} ions (Cu^+, Au^+, Hg^{2+}), Ag^+ ions form phosphides on interaction with phosphine.[6] The deprotonation of phosphine on formation of the phosphide tends to reduce the redox potential of the electron donor. Furthermore, as already mentioned above, on formation of *d* metal phosphides, the hybridisation of the P atom changes ($sp^3 \rightarrow sp^3d$). In contrast to the initial phosphine, activated phosphine interacts more readily with an O atom in N_2O_4 as a result of the enhancement of the role of the $d_\pi - p_\pi$ interaction. Reaction (31) is also accelerated by mercury(II) chlorides, which form the phosphides $(HgCl)_3P$ (see Table 1).[11]

The iodide ion is also an effective catalyst of the oxidation of phosphine by the acids HNO_3 and HNO_2.[12] In the presence of I^-, the oxidation of phosphine by nitric acid proceeds via a stepwise mechanism:[82-86]

$$2HNO_3 + 6KI + 2H_2O \rightarrow 3I_2 + 2NO + 6KOH, \quad (38)$$

$$2I_2 + PH_3 + 2H_2O \rightarrow (HO)H_2PO + 4HI. \quad (39)$$

Reactions (38) and (39) are faster than the direct oxidation of PH_3 by HNO_3 (see Table 1).[11,12]

Consequently reaction (31) is accelerated following the enhancement of the electron-accepting properties of the phosphorus atom as a result of the replacement of hydrogen atoms by metals or if a strong nucleophile (the I^- ion) is used as the electron transferring agent. The point is that the oxides N_jO_i are ambident oxidants.[32-34] The LUMO and HOMO are located on the N and O atoms respectively. For this reason, the N atom reacts preferentially with nucleophiles and the O atom with electrophiles. Thus amines, in which there is a distinct unshared orbital, enter preferentially into diazotisation or nitrosation reactions.[36] Phosphine, which is characterised by the presence of a weak non-bonding level, reacts with the oxygen atoms of nitrogen oxides. Furthermore, in contrast to amines, PH_3 has a valence *d* orbital capable of $d_\pi - p_\pi$ conjugation with an oxygen atom in N_jO_i.

Thus, a characteristic feature of PH_3 is a tendency to undergo outer-sphere oxidation by oxygen compounds in which an O atom is present as a bridge.

VII. Oxidation by oxygen compounds of sulphur, selenium, and tellurium

The oxidation of PH_3 by concentrated H_2SO_4 is widely used in industry[2-4] (see Table 1 at the end of the review):

$$3H_2SO_4 + PH_3 \rightarrow 3SO_2 + (HO)_2HPO + 3H_2O, \quad (40)$$

$$H_2SO_4 + PH_3 \rightarrow S + (HO)_2HPO + H_2O, \quad (41)$$

$$H_2SO_4 + PH_3 \rightarrow H_2S + (HO)_3PO. \quad (42)$$

Reactions (40)–(42) take place at a high rate only at H_2SO_4 concentrations in excess of 90 wt.%.[2,3] At such a concentration, the monomeric and trimeric SO_3 molecules, responsible for the reaction, are formed:[36]

$$2H_2SO_4 \rightleftarrows SO_3 + H_3O^+ + HSO_4^-,$$

$$3SO_3 \rightleftarrows (SO_3)_3, \quad (43)$$

and the redox potential of SO_3 also increases. Sulphur trioxide oxidises PH_3 in accordance with the mechanism

$$PH_3 + SO_3 \rightleftarrows SO_3PH_3,$$

$$SO_3PH_3 \rightarrow S + (HO)_2HPO,$$

$$H_2O + SO_3PH_3 \rightarrow SH_2 + (HO)_3PO,$$

$$(SO_3)_3PH_3 \xrightarrow[-SO_2]{} PH_2(OH)(SO_3)_2 \xrightarrow[-SO_2]{} \longrightarrow PH(OH)_2(SO_3) \xrightarrow[-SO_2]{} OPH(OH)_2. \quad (44)$$

Reactions (40)–(42) are accelerated appreciably after the addition of a small amount of $HgSO_4$,[2] which forms phosphides with PH_3. As already mentioned, on passing to the phosphide state, the reduction potential increases and the phosphorus atom undergoes sp^3d hybridisation, which is convenient for the $d_\pi-p_\pi$ interaction with an oxygen atom of sulphur trioxide. The participation of monomeric and trimeric sulphur trioxide in the process is indicated by the high order of the reaction with respect to H_2SO_4. The occurrence of reactions (41) and (42) is direct evidence for the real occurrence of the eight-electron single-stage oxidation of PH_3, since in the intermediate valence states (SO_2 and S) sulphur does not oxidise PH_3 but does oxidise organophosphines.[68] The low redox potential of H_2SO_4 (only 0.2 V) and the high rate of reactions (40)–(42) indicate unambiguously that many-electron single-stage PH_3 oxidation processes are preferred. The many-electron rate-limiting stage takes place stepwise and there are small energy wells in the reaction pathway. The entropy barrier in reaction (44) is lowered by virtue of the involvement in it of the associated species $(SO_3)_3$ and the formation of a complex with participation of the phosphorus atom and an oyxgen atom of sulphur trioxide. The depth of the energy wells diminishes as the hydrogen atoms of PH_3 are substituted by OH groups, since the tendency of the phosphorus atom towards complex formation increases as the redox potential of the intermediate products falls (see Scheme 1). The substitution of H by OH groups activates the phosphorus atom[10] and there is at the same time an increase in the bond angle between the substituents and a change in hybridisation.[38] The majority of phosphorus(III) derivatives have a bond angle of approximately 100°.[38]

Such an angle is as a rule formed by substituents tending to enter into a $p_\pi-d_\pi$ interaction (OH, F, Cl, Br, I, C_6H_5) and a $\sigma-d_\pi$ interaction (Me). Electron-accepting bonding is achieved via the unoccupied d orbital of the phosphorus atom and the non-bonding p_π orbital or the σ-bond of the substituent. As a result, a double bond is formed between the phosphorus atom and the substituent, which alters the hybridisation of phosphorus and intensifies the tendency towards the formation of a complex with SO_3. Substituents of the type of H, CN, and SiH_3, which are incapable of $p_\pi-d_\pi$ and $\sigma-d_\pi$ conjugation, form a bond angle much smaller than 100° and are characterised by weak ligand properties.[38]

The oxygen compounds of selenium and tellurium which are analogues of H_2SO_4 are reduced by phosphine to the elements[82–85,88] (see Table 1):

$$2H_2SeO_3 + PH_3 \rightarrow 2Se + (HO)_3PO + 2H_2O, \quad (45)$$

$$2H_2TeO_3 + PH_3 \rightarrow 2Te + (HO)_3PO + 2H_2O. \quad (46)$$

High rates of reactions (45) and (46) are attained at an acid concentration in excess of 0.1 M.[82–85,88] The rates of these reactions increase after the addition of HCl and especially HBr and HI.[82] Since halide ions stimulate the disproportionation of selenium(II) and tellurium(II) compounds,[36] i.e.

$$3H_2O + 2TeCl_2 \rightleftarrows H_2TeO_3 + Te + 4HCl, \quad (47)$$

$$3H_2O + 2SeCl_2 \rightleftarrows H_2SeO_3 + Se + 4HCl, \quad (48)$$

It follows that reactions (45) and (46) take place via the reduction of selenium(IV) and tellurium(IV) to selenium(II) and tellurium(II) respectively. The polymeric compounds $(TeO_2)_j(H_2O)_i$ and $(SeO_2)_j(H_2O)_i$, predominating in acid solutions,[84] take part in the rate-limiting stages of reactions (45) and (46):

$$(TeO_2)_4 + PH_3 + 8HX \rightarrow 4TeX_2 + (HO)_3PO + 4H_2O, \quad (49)$$

$$(SeO_2)_4 + PH_3 + 8HX \rightarrow 4SeX_2 + (HO)_3PO + 4H_2O. \quad (50)$$

The oxygen compounds of selenium(IV), tellurium(IV), and sulphur (VI), which are capable of forming polymeric compounds, ensure the synchronous many-electron oxidation of PH_3, which is energetically more favourable than the two-electron oxidation (Fig. 1). Therefore, despite the low redox potentials of the oxygen compounds, sulphur(VI) selenium(IV), and tellurium(IV) are fairly rapidly reduced by phosphine.[82–85] In the intermediates formed in reactions (45) and (46) the bond linking the oxygen compounds of selenium(IV) and tellurium(IV) to PH_3 is formed via an O atom. The oxidation-reduction decomposition of the intermediate takes place as a result of the transfer of an oxygen atom from the oxygen compounds of selenium(IV) and tellurium(IV) to the phosphorus atom in PH_3.

VIII. Oxidation by oxygen compounds of 3*d* metals

Sulphuric acid solutions of chromium(VI) and manganese(VII) are widely used in laboratory and industrial practice[2–4] for the removal of PH_3 and AsH_3 from gases.[11,12,89–91] PH_3 and AsH_3 are oxidised by oxygen compounds of chromium(VI) in accordance with the equations[89–91]

$$Na_2Cr_2O_7 + PH_3 + 4H_2SO_4 \rightarrow (HO)_2HPO + Cr_2(SO_4)_3 + Na_2SO_4 + 4H_2O, \quad (51)$$

$$2Na_2CrO_4 + 2AsH_3 + 5H_2SO_4 \rightarrow 2As + Cr_2(SO_4)_3 + 2Na_2SO_4 + 8H_2O. \quad (52)$$

Reaction (51) takes place satisfactorily only in very concentrated sulphuric acid solutions (>12 M) and in the presence of high contents of chromium(VI) ($>10^{-3}$ M). The oxidation of AsH_3 takes place vigorously in relatively dilute H_2SO_4 (>1–2 M) and at a lower chromium(VI) concentration ($<10^{-4}$ M).[89–91] The different behaviour of PH_3 and AsH_3 in sulphuric acid solutions of chromium(VI) is due to the fact that the oxidation of phosphine via a six-electron mechanism and of arsine via a three-electron mechanism to phosphorus(III) and arsenic respectively is energetically favourable (see Table 1 at the end of the review).

Chromium(VI) in solutions participates both in reversible dimerisation reactions and in acid–base reactions:[36,92]

$$CrO_4^{2-} + H^+ \rightleftarrows CrO_3(OH)^-, \quad K = 3.1 \cdot 10^8,$$
$$CrO_3(OH)^- + H^+ \rightleftarrows H_2CrO_4, \quad K = 2 \cdot 10^1,$$
$$2CrO_3(OH)^- \rightleftarrows Cr_2O_7^{2-} + H_2O, \quad K = 4.1 \cdot 10^3.$$

The scheme involving reversible reactions presented above is applicable only to solutions containing HNO_3 and $HClO_4$.[93] A chlorochromate ion is formed in solution in HCl and a sulphate complex is produced in H_2SO_4:[92]

$$CrO_3(OH)^- + HCl \rightleftarrows CrO_3Cl^- + H_2O, \quad K = 17,$$
$$CrO_3(OH)^- + HSO_4^- \rightleftarrows CrO_3(SO_4)^{2-} + H_2O, \quad K = 4.$$

It follows from the above equations that the predominance of a particular form of chromium(VI) in aqueous solutions depends on its concentration and the pH of the medium. The monomeric acid chromate ion exists in dilute solutions. With increase in concentration, the dichromate ion becomes the dominant form. The degree of protonation of these ionic species depends on the pH of the medium. Electron-accepting properties are characteristic of chromium trioxide. When CrO_3 is dissolved in the presence of HCl and H_2SO_4 in hydroxylated organic solvents, chromic acid esters are formed:[69]

$$AcOH + CrO_3 \rightleftarrows AcOCrO_3H,$$

$$2AcOH + CrO_3 \rightleftarrows (AcO)CrO_2 + H_2O\ .$$

In pyridine, CrO_3 exists as the complex $Py.CrO_3$ with a Cr–N bond.[69]

The interaction of monomeric chromium(VI) complexes with PH_3 is difficult owing to the complementary prohibition. The oxidising capacity of the chromium(VI) monomer corresponds to three electrons, while the reducing capacity of PH_3 corresponds to six or eight electrons.

In contrast to chromium(VI), chromium(V) readily oxidises triphenylphosphine:[93]

$$CrOL_2^+ + Ph_3P \rightarrow CrL_2^+ + Ph_3P{=}O,$$

where HL is 2-ethyl-2-hydroxybutyric acid. The reaction mechanism includes the transfer of an oxygen atom in accordance with the scheme

$$CrOL_2^+ + Ph_3P \rightleftarrows [Ph_3P{-}O{-}CrL_2]^+ \rightarrow Ph_3P{=}O + CrL_2^+.$$

The intermediate complex with a bridging O atom undergoes oxidation-reduction decomposition in the rate-limiting stage.[93] On the other hand, the oxidising capacity of the dimer, corresponding to six electrons, ensures the complementarity of the reaction involving the reduction of the dichromate by phosphine.

Another situation arises in the oxidation of AsH_3 by chromate. In this case, the requirement for the complementarity of the rate-limiting stage is satisfied also in the absence of dichromate. The reducing capacity of AsH_3 and the oxidising capacity of chromate are equal and corresponding to three electrons. As a result, AsH_3 is readily oxidised by chromates to arsenic at relatively low concentrations (1–2 M) and in the presence of a low chromium(VI) content ($< 10^{-4}$ M).[89–91] In the presence of added copper(II) and iron(III) salts, which tend to be involved in one-electron transfer, reactions (51) and (52) proceed readily at a much lower acidity (10^{-1} M). In weakly acid media at a chromium(VI) concentration of 10^{-4} M, monochromate ions, incapable of the complementary oxidation of AsH_3 and PH_3 to the acids, predominate. Copper(II) and iron(III) salts, which participate jointly with monochromate ions in the rate-limiting stage, make the reactions complementary. Chromium(VI), copper(II) ions, or iron(III) ions, used in isolation, oxidise phosphine at the concentrations indicated.[11] Jointly with monochromate, iron(III) or copper(II) ions ensure the occurrence of four-electron transfer in the slow stage:

$$[XCu(CrO_3OH)PH_3] + H_2O \rightarrow CuX + Cr(OH)_3 + (HO)_2HP,$$

$$[XCu(CrO_3OH)PH(OH)_2] + H_2O \rightarrow CuX + Cr(OH)_3 + (HO)_3PO.$$

Copper(II) ions are regenerated via the reaction

$$3CuX + NaCrO_3OH + 7HX \rightarrow 3CuX_2 + CrX_3 + 4H_2O + NaX.$$

Copper(II) and iron(III) ions promote the oxidation of phosphine by oxygen compounds of chromium(VI)[11,12] only at a low acidity of the medium[89–91] where chromate ions predominate in the system. At a high acidity, which promotes the formation of dichromates, iron(III) and copper(II) ions do not affect the rate of oxidation of PH_3 by chromium(VI). The effectiveness of copper(II) and iron(III) salts increases with decrease in acidity and decreases with increase in acidity, passing through a maximum as the X^- concentration rises.

The most significant promoting effect is exerted by added bromide and particularly iodide ions, which ensure the operation of the stepwise reaction mechanism.[11,12,89–91] In the presence of halide ions, phosphine and arsine do not interact directly with chromium(VI). Chromium(VI) oxidises halide ions to the halogens:

$$2Na_2CrO_4 + 6NaBr + 8H_2SO_4 \rightarrow 3Br_2 + Cr_2(SO_4)_3 + 5Na_2SO_4 + 8H_2O, \quad (53)$$

while halogens are in turn reduced back to the halide ion by phosphine or arsine:

$$4Br_2 + PH_3 + 4H_2O \rightarrow (HO)_3PO + 8HBr, \quad (54)$$

$$3Br_2 + AsH_3 + 2H_2O \rightarrow HAsO_2 + 6HBr. \quad (55)$$

Arsine is, as usual, effectively oxidised under milder conditions than phosphine.[89–91] The oxidation of AsH_3 requires chromium(VI), acid, and NaX concentrations lower by an order of magnitude than in the oxidation of PH_3. This is associated with the fact that the atomic halogen, stabilised in the coordination sphere of chromium, functions as the agent transferring electrons from AsH_3 to the chromate, while the transfer of electrons from PH_3 to the dichromate ion is effected by a polyhalide ion. The formation of polyhalide ions requires a higher concentration of halide ions than for the generation

of halogen atoms.[36] The catalytic activity of halide ions increases, as usual, in opposition to their redox potentials.[11,12,89–91] The oxidation of phosphine and arsine by oxygen compounds of manganese(VII) takes place in acid and alkaline media in the following way[82–85,94] (see Table 1):

$$2KMnO_4 + PH_3 + H_2SO_4 \rightarrow 2MnO_2 + (HO)_2HPO + + K_2SO_4 + H_2O, \quad (56)$$

$$2KMnO_4 + AsH_3 + H_2SO_4 \rightarrow 2MnO_2 + HAsO_2 + + K_2SO_4 + 2H_2O. \quad (57)$$

The oxidation of PH_3 and AsH_3 in alkaline and especially in neutral and acid media is rapid (Table 1).[94] Manganese(VII), which forms stable manganese(V) and manganese(VI) ions,[36] ensures both one- and two-electron oxidation of AsH_3 and PH_3. Furthermore, manganese(V) readily disproportionates to manganese(VI) and manganese(IV).[36]

The reactivity of manganese(VII) with respect to PH_3 in a neutral medium decreases in the presence of AsH_3. The coupled oxidation of PH_3 and AsH_3 by manganese(VII), which is fairly rapid, has been used in practice. The synergism is due to the fact that AsH_3 reduces manganese(VII) to manganese(VI), while PH_3 converts manganese(VI) into manganese(IV).

The rate of oxidation of PH_3 and AsH_3 increases significantly after the addition of halide ions.[82,94] The effectiveness of halide ions increases in opposition to the redox potentials.[82–85] In the presence of halide ions, manganese(VII) is reduced to manganese(II):

$$8KMnO_4 + 5PH_3 + 12H_2SO_4 \rightarrow 8MnSO_4 + 5(HO)_3PO + + 4K_2SO_4 + 12H_2O, \quad (58)$$

$$6KMnO_4 + 5AsH_3 + 9H_2SO_4 \rightarrow 6MnSO_4 + 5HAsO_2 + + 3K_2SO_4 + 14H_2O. \quad (59)$$

In the presence of halide ions, the mechanisms of reactions (58) and (59) change. In the absence of X^-, phosphine and arsine react with an O atom in oxygen compounds of manganese. The oxidation-reduction decomposition of the phosphine complex of manganese(VI) leads to the transfer of an O atom from manganese(VII) to PH_3, the decomposition being rapid as a consequence of complementarity. Manganese(VII) is reduced to a transfer of both an even number [reduction to Mn(V)] and an odd number [reduction to Mn(II, IV)] of electrons.

Manganese dioxide vigorously oxidises PH_3 and AsH_3 only above 300 °C. The reaction takes place in the gas phase and is inhibited by the PH_3 oxidation products—manganese(II) phosphates, which preclude the access of PH_3 to MnO_2. In the liquid phase, the reactivity of MnO_2 increases rapidly after the addition of iodide ions.[85] Halide ions ensure the occurrence of reactions (58) and (59) via a new, faster pathway.[85] In this case, PH_3 and AsH_3 do not react directly with manganese(VII), the latter oxidising the halide ions to the molecular halogen:

$$2KMnO_4 + 10KX + 8H_2SO_4 \rightarrow 2MnSO_4 + 5X_2 + 6K_2SO_4 + + 8H_2O. \quad (60)$$

Phosphine and arsine reduce in turn the halogen to the halide.[82–85] Halides are universal effective catalysts of the oxidation of PH_3 and AsH_3 for the majority of known oxidants.[11,12]

Being a strong nucleophile, the halide reacts more readily than PH_3 and AsH_3 with the central atom of the oxygen compound. The complementary oxidant converts X^- into X^+ while a non-complementary one generates from X^- the X^0 radical, which dimerises rapidly to X_2.[11] As a result, both complementary and non-complementary oxidants form the oxidant X_2, which is suitable for the oxidation of PH_3 and AsH_3. Furthermore, the X_2 molecules tend to form the polyhalides X_n.[36] Since the probability of the formation of X_n increases with decrease in the $2X^- \rightarrow X_2$ redox potential and with decrease in the X_2 concentration, a high rate of reaction is attained at fairly appreciable X^- concentrations.[11,12]

Solutions containing $10^{-3}-10^{-2}$ M of iodide ions or $10^{-2}-10^{-1}$ M bromide ions are most often used.[82]

Halogen atoms rather than molecules are the most suitable oxidants for the oxidation of AsH_3. In contrast to PH_3, AsH_3 is therefore oxidised at a lower X^- concentration[94] (Table 1).

It was noted above that the reactivity of the halogens with respect to PH_3 and AsH_3 decreases in parallel with their redox potentials: $Cl_2 > Br_2 > I_2$.[11,12] On the other hand, the catalytic activity of the halogens increases in opposition to the redox potentials of the halide ions: $I^- \gg Br^- > Cl^-$. The point is that the reactivity of X_2 is described by the equation

$$\frac{W}{[X_2][PH_3]} = k_{X_2},$$

while the catalytic activity of halide ions is described by the formula

$$\frac{W}{[PH_3][Ox][X^-]} = kK = k_{X^-},$$

where k is the rate constant and K the equilibrium constant of the reaction

$$Ox + 2X^- \rightleftarrows Red + X_2.$$

Since K increases with decrease in the $2X^- \rightarrow X_2$ redox potential, it follows that k_{X^-} and k_{X_2} form antiparallel series.[11,12]

The behaviour of oxygen compounds of chromium(VI) and manganese(VII), widely used for the removal of PH_3 and AsH_3 from gases,[82–85] was examined above. The oxygen compounds of other 3*d* metals are used for the oxidation of PH_3 in analytical practice.[11] In a strongly acid medium (~10 M), vanadium(V) is slowly reduced by phosphine[95] (see Table 1):

$$8NH_4VO_3 + PH_3 + 12H_2SO_4 \rightarrow (HO)_3PO + 8VOSO_4 + + 4(NH_4)_2SO_4 + 12H_2O. \quad (61)$$

A high acidity is necessary for the formation of polynuclear vanadates, capable of ensuring the complementary many-electron single-stage oxidation of PH_3. In order to accelerate reaction (61), halide ions are usually introduced.[95] Iodide ions exhibit the highest activity.[95] Heteropolyacids, the active principle of which is free VO_2 ions,[96] also oxidise PH_3 slowly. In contrast to PH_3, arsine is oxidised rapidly by heteropolyacids.[97] The rate of oxidation of AsH_3 by a heteropolyacid increases after the introduction of iodide ions.[97] In the HCl–HX system, phosphine and arsine are oxidised by the compounds ClBr and ClI.

The data presented show that, although the oxygen compounds of 3*d* metals do possess high redox potentials, they are reduced slowly by phosphine owing to their inability to ensure the complementary

many-electron single-stage oxidation of PH_3. However, they vigorously oxidise AsH_3, which reduces, in contrast to PH_3, the oxygen compounds of *d* metals via a homolytic mechanism. In the presence of X^- ions, phosphine is rapidly oxidised also by one-electron oxidants.

IX. Oxidation by metal complexes

Iron(III) and copper(II) chlorides are widely used to remove phosphines and arsine from gases,[2-4,12] since iron(II) [98,99] and copper (I) [100,101] chlorides are readily regenerated by dioxygen.[11] For the purification of oxygen-free gases, use is made of periodic action apparatus, on which the PH_3 and AsH_3 oxidation and regeneration stages are separated in time, while continuous operation apparatus is used for the detoxification of oxygen-containing gases.[2-4] Iron(III) chloride oxidises PH_3 in accordance with the scheme

$$8FeCl_3 + PH_3 + 4H_2O \rightarrow 8FeCl_2 + (HO)_3PO + 8HCl. \quad (62)$$

The reaction proceeds only at a high phosphine concentration. At low PH_3 concentrations, reaction (62) is very slow.[102-104] The rate of reaction increases sharply when concentrated (>3 M) $FeCl_3$ solutions are used.[105-107] Such a concentration is attained after the deposition of $FeCl_3$ from aqueous solution onto a carrier.[105-107] The high order of the reaction with respect to $FeCl_3$ indicates the involvement in the process of polynuclear iron(II) complexes, which are generated only at high iron(III) chloride concentrations.

The reactivity of polynuclear iron(III) complexes on carriers increases after the introduction of small amounts of $HgCl_2$ (10^{-4} M).[2,3] At a low $FeCl_3$ concentration ($<10^{-1}$ M), the reactivity is independent of the added $HgCl_2$. Iron(III) sulphates do not exhibit an appreciable reactivity in relation to PH_3 in an acid medium.[102] In weakly acid media, where polynuclear iron(III) complexes arise, phosphine is oxidised rapidly in the presence of silver(I) sulphate. In the absence of silver(I) ions, the reaction does not occur. In acetic acid media, which ensure the formation of the trinuclear complexes $Fe_3(OH)_2(AcO)_6^+$,[27] phosphine is also not oxidised.[103]

Silver(I) and mercury(II) ions stimulate the process by virtue of the formation of the phosphides AgH_2P and $(HgCl)_3P$, which, as already mentioned, have a higher reactivity than the initial phosphine. Only the dinuclear complexes $Fe_2Cl_9^{3-}$ arise in chloride solutions,[36] ensuring the two-electron oxidation of phosphine. In heterogenised systems, more reactive polynuclear iron(III) complexes are formed. They effect the many-electron energetically more favourable single-stage oxidation of PH_3 to $(HO)_3PO$. The reactivities of the deposited and dissolved iron(III) chlorides therefore differ significantly.[105-107] Dissolved iron(III) chlorides have a low reactivity,[104] whilst deposited ones have a high reactivity.[105] Iodide ions accelerate reaction (62) effectively,[102-104] exhibiting the highest activity when dissolved (and not deposited) iron(III) chlorides are used.[102-104,106] In the presence of iodide ions, reaction (62) proceeds via two stages: iron(III) chloride oxidises iodide ions to polyiodides and the latter are then reduced by phosphine, which regenerates iodide ions.[102-104,106]

Thus iodide ions are more suitable for the acceleration of the oxidation of phosphine by non-complementary oxidants, while silver(I) and mercury(II) are best for complementary oxidants. Cerium(IV) behaves similarly to iron(III).[108,109] Despite its very high redox potential (1.5 V), cerium(III) sulphate hardly interacts with PH_3 in the absence of catalysts. In the presence of halide ions, cerium(IV) is rapidly reduced by phosphine via the reaction

$$8Ce(SO_4)_2 + PH_3 + 4H_2O \rightarrow (HO)_3PO + 4Ce_2(SO_4)_3 + 4H_2SO_4. \quad (63)$$

In the presence of halide ions, the reaction is divided into two slow stages: the first of these involves the formation of Cl_2, ClBr, and ClI, which are reduced by phosphine in the second stage.[108,109] When these stages take place separately, they obey the same rules as in a catalytic process.[110] As usual, the catalytic activity of halide ions in reactions (63) increases in opposition to the redox potential: $I^- \gg Br^- > Cl^-$ [108-110] (see Table 1 at the end of the review).

In contrast to iron(III) and cerium(IV) salts, the reactivity of copper(II) chlorides and sulphates increases sharply in the presence of copper(I).[113-115] In the presence of copper(I) ions in concentrated solutions of copper(II) salts (>1 mM), the following reactions proceed at a satisfactory rate:

$$3CuSO_4 + PH_3 + 3H_2O \rightarrow 3Cu + 3H_2SO_4 + (HO)_2HPO, \quad (64)$$

$$8CuCl_2 + PH_3 + 4H_2O \rightarrow 8CuCl + (HO)_3PO + 8HCl, \quad (65)$$

$$3CuCl_2 + AsH_3 \rightarrow As + 3CuCl + 3HCl. \quad (66)$$

Copper(II) ions, which are characterised by high redox potentials of the $Cu^{II} \rightarrow Cu^{I}$ (+0.153 V) and $Cu^{II} \rightarrow Cu^{0}$ (+0.337 V) transitions, oxidise PH_3 and AsH_3 at high rates[111,112] (Table 1). In concentrated solutions[113-115] and when carriers are used,[116,117] polynuclear saturated copper(II) and copper(I) complexes, which exhibit an enhanced reactivity,[111-115] play a dominant role.[118,119] Reactions (64)-(66) are accelerated by the CNS^-,[120] Br^-,[121-123] and I^- [124-126] ions (see Table 1).

Calculations by the CNDO, MVG, and HMO quantum-chemical methods have been performed for the aquophosphine complexes of copper(II) and iron(III) with different contents of X^- ions.[127-133] The $P-H_P$ and $HO-H_O$ bonds are weakened and the amount of their ionic character increases, a positive charge appears on the phosphorus atom, a negative charge appears on H_2O, and strong bonds are formed with the P, H_P, and H_O atoms, especially in the case of oxygen-containing anions. With increase in the negative charge on the complex, the $P-OH_2$ and $Cu-H_P$ bonds are strengthened while the P-Cu bond is loosened. This stimulates the oxidation-reduction decomposition of the complex involving the oxidation of phosphine and the reduction of copper(II). With decrease in the negative charge on the complex, the P-Cu and H_P-OH bonds are strengthened, which induces an acid-base reaction, copper(II) being reduced to copper(I) as a result of the oxidation-reduction decomposition of zerovalent copper. Reaction (65) is effectively accelerated by palladium(II) [134-136] of mercury(II) and copper(I) [134-138] chlorides. The synergistic effects arising under the joint action of copper(I) and palladium(II) or mercury(II) is due to the fact that copper(I) chlorides activate PH_3 differently compared with palladium(II) or mercury(II) chlorides.[137,138] Mercury(II) [138,139] and palladium(II) [140] chlorides activate phosphine by substituting the H atoms by $HgCl^+$ or $PdCl^+$ with formation of the phosphides $(HgCl)_3P$ or $(PdCl)_3P$.[138] Copper(I) chlorides promote the loosening

of the electron cloud of the phosphorus atom by forming a complex with palladium(II) or mercury(II) phosphide.[138] In the mixed complex, the phosphorus atom assumes the sp^3d configuration, which is convenient for oxidation. It is known[32] that the activation energy diminishes as the electronic configurations of the initial reactants and products approach one another. Since according to literature data[61] the phosphorus atom in phosphates has a pronounced d character, the change in hybridisation of the type $sp^3 \rightarrow sp^3d$ favours PH_3 oxidation reactions.

Gold(III) chlorides, which react very rapidly with phosphine even in dilute solutions (see Table 1), are reduced by phosphine in a different way:[141]

$$8AuCl_3 + 3PH_3 + 12H_2O \rightarrow 8Au + 3(HO)_3PO + 24HCl. \quad (67)$$

Like reaction (65), reaction (67) is accelerated by gold(I) chlorides.[11] However, in contrast to copper(II) in reaction (65), gold(III) is reduced also in the absence of gold(I) chlorides.[141] Gold(I) performed a dual function in this reaction. On the one hand, it activates phosphine, like other d^{10} ions, by virtue of the formation of phosphine complexes and, on the other hand, gold(I) ions participate together with gold(III) in the oxidation of PH_3. A mixed heteronuclear gold(III, I) phosphine complex undergoes inner-sphere decomposition with transfer of four electrons from PH_3 to Au(III) and Au(I). Reaction (67) is accelerated particularly effectively by added HBr, HI, and HCl as a result of the formation of ClBr and ClI. Gold(I) is continuously regenerated as a consequence of the oxidation of zerovalent gold by gold(III).

Platinum(IV) chlorides are reduced by phosphine similarly to gold(III):[142]

$$3Na_2PtCl_6 + 2PH_3 + 6H_2O \rightarrow 3Pt + 2(HO)_2HPO + 6NaCl + 12HCl. \quad (68)$$

The reaction is accelerated by platinum(II) chlorides, which perform a dual function: they activate PH_3, forming a phosphine complex, and, together with platinum(IV), they oxidise phosphine via a six-electron mechanism. Platinum(II) is continuously regenerated as a result of the oxidation of zerovalent platinum by platinum(IV). In a HCl–HX solution, reaction (68) is propagated by the ClBr and ClI species. Phosphine reduces platinum(II) chlorides very rapidly[138,140] (Table 1):

$$4PdCl_2 + PH_3 + 4H_2O \rightarrow Pd + (HO)_3PO + 8HCl. \quad (69)$$

The reactions of PH_3 with palladium(II) complexes [$PdCl_2(PhCH)_2$, $Pd(AcO)_2$, $(PPh_3)_2Pd(OAc)_2$] in non-aqueous solvents (chloroform, dioxane) leads to the formation of insoluble palladium compounds.[140] In all the compounds isolated, the oxidation state of palladium has been shown by the X-ray photoelectron spectroscopic method to be close to 2+, Pd–P bonds are present (demonstrated by the EXAFS method), and an acid (HCl, HOAc) is formed in the solutions over the precipitate. This indicates the acid–base nature of the interaction of PH_3 with palladium(II) complexes in a non-aqueous medium, which is accompanied by the heterolysis of the P–H bond and the formation of the PH_2 phosphide species coordinated to palladium (this is indicated by the ^{31}P NMR spectra of the chloride complex):

$$PH_3 + n\,PdX_2 \rightarrow PH_{3-n}(PdX)_n + nHX.$$

The extent of this process is regulated by selecting the basicity of the solvent. After the interaction of palladium acetate complexes with PH_3, an appreciable amount of acetic anhydride is formed in solution over the deposit.[140] This fact (together with ^{31}P MAS NMR data for the deposit) indicates the presence of oxidised forms of phosphine in the coordination sphere of palladium. All the palladium compounds isolated after interaction with PH_3 in non-aqueous media are readily hydrolysed in water with formation of $(HO)_3PO$ and zerovalent palladium. Thus the coordinated phosphine is oxidised via the formation of bonds between the coordinated phosphorus and the O atoms of the ligand. In contrast to oxygen compounds of metals and non-metals, forming outer-sphere complexes with PH_3 via an O atom, the metal complexes oxidise PH_3 via inner-sphere mechanisms.

As already mentioned, phosphine is activated only by metal ions capable of a two-sided exchange interaction. Low-valence forms of the metal usually possess such properties. Therefore the high-valence metal complex reduction reactions are as a rule activated by complexes of metals in low valence states. In a two-sided exchange interaction, the phosphorus atom of phosphine assumes an electronic configuration similar to that of the phosphorus atom in the products. Such activation of the reactant lower significantly the activation energies for the reactions.[143]

X. Oxidation by dioxygen, ozone, and peroxide compounds

The use of O_2, O_3, H_2O_2, and $Na_2S_2O_8$ for the oxidation of PH_3 is an extremely promising procedure, since the reaction products are harmless.[2–4] However, despite the high redox potentials of the oxidants listed above, the reactions

$$2O_2 + PH_3 \rightarrow (HO)_3PO, \quad (70)$$

$$4O_3 + PH_3 \rightarrow (HO)_3PO + 4O_2, \quad (71)$$

$$4H_2O_2 + PH_3 \rightarrow (HO)_3PO + 4H_2O, \quad (72)$$

$$4Na_2S_2O_8 + PH_3 + 4H_2O \rightarrow (HO)_3PO + 4Na_2SO_4 + 4H_2SO_4, \quad (73)$$

are very slow.[11,12,144–146]

The two-electron reduction of dioxygen to the peroxide or the four-electron reduction to water is thermodynamically very favourable, while the one-electron reduction of O_2 to O_2^- or HO_2^- takes place with absorption of heat.[147] On the other hand, the transfer of a pair of electrons to an O_2 molecule is impossible as a consequence of the spin prohibition, since dioxygen has a triplet ground state. The oxidation of organic and inorganic substances by dioxygen therefore proceeds via successive one-electron stages involving radical exchange mechanisms.[147] The rate of these processes is limited by the thermodynamic difficulty of the transition $O_2 \rightarrow O_2^-$. The one-electron transition generates the radicals O_2^- and HO_2^- with a very high redox potential. The non-complementarity and the negative potential of the one-electron transition $O_2 \rightarrow O_2^-$ hinder the oxidation of PH_3 at low concentrations of the latter (10^{-2}–10^{-1} vol.%) and at the normal temperature.[7,9,10] At elevated temperatures and high PH_3 and O_2 concentrations, conditions are created for the transfer of two electrons:[9,10]

$$PH_3 + O_2 \rightarrow PH + H_2O + O. \quad (74)$$

Severe conditions are necessary to overcome the spin prohibition in redox transitions. As mentioned above, the $sp^3 \rightarrow sp^3d$ transition to the triplet state, necessary for the removal of the spin prohibition, is facilitated at elevated temperatures. The O atom deformed by reaction (74) stimulates the explosive oxidation of PH_3.[9]

The oxidation of phosphine at low concentrations by dioxygen is fairly rapid in the presence of $CuCl_2$ and $FeCl_3$.[148–151] Phosphine reduces $CuCl_2$ and $FeCl_3$ to CuCl and $FeCl_2$ respectively. The initial state of the copper and iron salts is regenerated on treatment with O_2.[11] The addition of iodide and bromide ions accelerates the stages involving the reduction of copper(II) and iron(III) by phosphine,[124] but retards the stage in which copper(I) and iron(II) are oxidised by oxygen.[98] Palladium(II) [138] and mercury(II) [152] chlorides have a positive influence on the first stage and do not affect the second.[134,135] Single step mechanisms of the oxidation of PH_3 by dioxygen in the presence of metal complexes have not been described.[11] The I^-/C and PdO/C systems exhibit a high activity (Table 1).

The relative inertness of H_2O_2 in reaction (73) mentioned above is associated with the unusual properties of the frontier orbitals.[153,154] The peroxide bond in H_2O_2 is altogether unpolarised, since the high dipole moment, induced by the presence of the lone electron pairs on the oxygen atom in the peroxide group, is compensated by the uniform charge distribution and does not affect the dipole moment of the O–O bond.[153] The dipole moment of the H_2O_2 molecule is determined by the dipole moments of the H–O bonds and is equal to 2.2 D.[153] A π^*-type antibonding orbital plays the role of the HOMO, while the role of the LUMO is assumed by a σ^*-type antibonding orbital.[153] The type $[\sigma+\sigma]$ interaction of H_2O_2 with PH_3 is symmetry-prohibited, while the oxidative addition of H_2O_2 to PH_3 requires that a high symmetry barrier be overcome owing to the pronounced *s* character of the lone pair. The nucleophilic substitution of the OH^- group in H_2O_2 by phosphine is difficult because of the low polarity of the HO–HO bond and of phosphine. The reaction is accelerated somewhat in highly acid media by virtue of the protonation of the H_2O_2 with formation of the polar $H_3O_2^+$ species.[154] The addition of bromide and iodide ions[144] and also of $FeCl_3$ and $CuCl_2$ [145] accelerates reaction (72). In contrast to the dioxygen, hydrogen peroxide oxidises PH_3 via a single step mechanism in the presence of metal complexes.[145,146]

As a result of complex formation, metal ions increase the polarity of H_2O_2 and facilitate the interaction of PH_3 with an O atom of the peroxide bond. Iron(III) and copper(II) halides are therefore particularly effective at low acidities of the medium where there are no $H_3O_2^+$ ions. Metal and hydrogen ions act similarly, but their effectiveness is significantly different. In order to attain the same effect, a lower concentration of the metal ions than that of hydrogen ions is required.[144,145] The oxidation of AsH_3 by H_2O_2 takes place at lower concentrations of X^-, $CuCl_2$, and $FeCl_3$ than the oxidation of PH_3.[146]

Ozone is one of the most vigorous oxidants[155] and yet reaction (71) is very slow. The low reactivity of O_3 compared with PH_3 [154] is caused by the unusual electronic structure of ozone. The following filling of molecular orbitals corresponds to the unexcited state of the O_3 molecule: $(\sigma)^4(\pi)^2(2p)^4(\pi)^2(\sigma)^2$.[36] The O_3 molecule has an angular shape and a low polarity (0.17 D).[36] Two-sided $[\sigma+\sigma]$ reactions are therefore symmetry-prohibited and one-sided reactions are hindered by the very low basicity of PH_3 ($pK = -14$).

The configurations of the HOMO and LUMO of ozone, like those of H_2O_2, are favourable to the reactions with OH^- and X^-. In an alkaline medium, O_3 reacts with OH^-, generating an OH radical.[155] However, despite the extremely high redox potential, the OH radical oxidises PH_3 only weakly, since it is a one-electron oxidant. The most active catalyst of reaction (71) at pH 11–12 is the iodide ion.[146]

In the presence of SO_2 or P_2O_3, phosphine undergoes coupled oxidation by dioxygen in an alkaline medium:

$$PH_3 + 4SO_2 + 4O_2 + 4NaOH \rightarrow 4Na_2SO_4 + (HO)_3PO + 4H_2O, \quad (75)$$

$$PH_3 + 2P_2O_3 + 4O_2 + 5NaOH + H_2O \rightarrow 5NaH_2PO_4. \quad (76)$$

The addition of alcohol lowers somewhat the rates of reactions (75) and (76) but does not stop them completely. The oxenoid reaction (75) begins with the formation of peroxomonosulphuric acid:

$$HSO_3^- + O_2 \rightarrow HSO_5^-. \quad (77)$$

Subsequently the HSO_5^- anion oxidises PH_3:

$$4H_2SO_5 + PH_3 \rightarrow 4H_2SO_4 + (HO)_3PO. \quad (78)$$

In contrast to H_2O_2 and $H_2S_2O_8$, Caro's acid transmits its oxygen atoms to phosphine. In the rate-limiting stage, the phosphine molecule approaches the peroxide oxygen atom in H_2SO_5 along the O–O bond line; by virtue of the high polarity of the oxidant,[154] its occupied non-bonding *s* orbital overlaps the unoccupied p_{σ^*} orbital of the peroxide bond. The appearance of electrons in the antibonding orbital leads to the weakening and successive dissociation of the O–O bond.[154] This entails the formation of a new bond between the phosphorus atom of phosphine and an oxygen atom of the peroxomonosulphate. The unusual properties of H_2SO_5 are associated with the presence in peroxo-monoacids of a polarised peroxide bond (0.9 D) with a relatively low energy of the LUMO (−9.3 eV). The occurrence of reaction (76) is ensured by the monoperphosphoric acid H_3PO_5, the polarity of the peroxide bond of which is similar to that in H_2SO_5.[153]

Thus phosphine can undergo coupled oxidation by dioxygen in the presence of additives inducing oxenoid oxidation.

XI. Conclusion

The principal features of the kinetics and mechanisms of the majority of the reactions, described in the literature, involving the oxidation of PH_3 and AsH_3 by complexes and oxygen compounds with metals and non-metals and the catalytic and coupled oxidation by dioxygen, ozone, and peroxide compounds were analysed above.

Table 1 presents the rate constants for the majority of the catalytic and non-catalytic low-temperature reactions involving the oxidation of PH_3 and AsH_3 by various oxidants in acid, neutral, and alkaline solutions and in the gas phase. The halogens (Cl_2, Br_2, I_2) and their derivatives (HClO, HBrO, HIO, HIO_3, HIO_4, $HBrO_3$), the oxygen compounds of nitrogen (NO_2), sulphur, selenium, and tellurium (H_2SO_4, H_2SeO_3, H_2TeO_3) as well as transition metals ($KMnO_4$, $H_2Cr_2O_7$, HVO_3), and *d* metal complexes ($AuCl_3$, $AuBr_3$, $AuCl_2I$, $AuCl_2Br$, $CuCl_2$, $CuBr_2$, CuClBr, CuClI, CuBrI, H_2PtCl_6, H_2PtBr_6, H_2PtI_6, Na_2PdCl_4, $FeCl_2I$, $FeBr_2I$, $CeCl_3I$) react faster with PH_3 and AsH_3 than any other oxidants. The most effective catalysts of the reactions in which PH_3 and AsH_3 are oxidised by various oxidants are alkali metal iodides and copper(II) halides.

Table 1. Kinetic parameters of the reactions involving the oxidation of PH_3 and AsH_3 by metal complexes and free and bound oxygen at 298 K and 10^{-2}–10^{2} Pa.

Reaction	Catalyst	Rate constant	Refs.
$PH_3+3Cu(OAc)_2+3NaOH \rightarrow 3Cu+(NaO)_2HPO+NaOAc+5HOAc$	$CuOAc-C_3H_5(OH)_3$	$k_3=2.5\cdot10$	[166–169]
	$En-CuOAc-C_2H_4(OH)_2$	$k_3=8.5\cdot10^2$	
	$NH_4OH-CuOAc-C_3H_5(OH)_3$	$k_3=2.1\cdot10^2$	
	$NaOH-CuOAc-C_3H_5(OH)_3$	$k_3=6.2\cdot10^4$	
$PH_3+3CuCl_2+3H_2O \rightarrow 3Cu+(HO)_2HPO+6HCl$	$CuCl-PhCN$	$k_3=4.2\cdot10^2$	[166–169]
	$CuCl-MeCN$	$k_3=6.2\cdot10^2$	
	$CuCl-Py$	$k_3=2.8\cdot10^2$	
	$CuCl-R_2HN$	$k_3=4.5\cdot10^2$	
	$CuCl-R_3N$	$k_3=3.2\cdot10^2$	
	$CuCl-NH_4OH$	$k_3=1.2\cdot10^{-1}$	
$PH_3+1.5Na_2PtCl_6+3H_2O \rightarrow 1.5Pt+(HO)_2HPO+3NaCl+6HCl$	$PtCl_2-ROH$	$k_3=3.2\cdot10^2$	[170]
	$PtBr_2-ROH$	$k_3=8.2\cdot10^2$	
	PtI_2-ROH	$k_3=2.5\cdot10^3$	
$PH_3+2KMnO_4+H_2O \rightarrow 2MnO_2+(OH)_2HPO+2KOH$	–	$k_2=4.5\cdot10^4$	[82–85, 94]
$AsH_3+KMnO_4 \rightarrow As+MnO_2+KOH+H_2O$	–	$k_2=6.5\cdot10^4$	[160]
$PH_3+3NaClO \rightarrow (HO)_2HPO+3NaCl$	$HgCl_2$	$k_3=2.5\cdot10^7$	[11, 156]
$PH_3+4Cl_2+4H_2O \rightarrow (HO)_3PO+8HCl$	–	$k_2=1.3\cdot10^6$	[11, 12, 65, 66]
$PH_3+3Br_2+3H_2O \rightarrow (HO)_2HPO+6HBr$	–	$k_2=1.4\cdot10^5$	[11, 12, 65, 66]
$PH_3+2I_2+2H_2O \rightarrow (HO)H_2PO+4HI$	–	$k_2=9.8\cdot10^4$	[11, 12, 65, 66]
$PH_3+4HClO \rightarrow (HO)_3PO+4HCl$	–	$k_2=5.1\cdot10^4$	[11, 12, 65, 66]
$PH_3+3HBrO \rightarrow (HO)_2HPO+3HBr$	–	$k_2=3.1\cdot10^4$	[11, 12, 65, 66]
$PH_3+2HIO \rightarrow (HO)H_2PO+2HI$	–	$k_2=4.0\cdot10^3$	[11, 12, 65, 66]
$AsH_3+3Cl_2+2H_2O \rightarrow HAsO_2+6HCl$	–	$k_2=9.8\cdot10^6$	[70]
$AsH_3+3Br_2+2H_2O \rightarrow HAsO_2+6HBr$	–	$k_2=1.2\cdot10^6$	[70]
$AsH_3+1.5I_2 \rightarrow As+3HI$	–	$k_2=4.8\cdot10^5$	[70]
$AsH_3+3HClO \rightarrow HAsO_2+H_2O+3HCl$	–	$k_2=5.8\cdot10^5$	[70]
$AsH_3+3HBrO \rightarrow HAsO_2+II_2O+3HBr$	–	$k_2=2.8\cdot10^5$	[70]
$AsH_3+1.5HIO \rightarrow As+1.5H_2O+1.5HI$	–	$k_2=3.4\cdot10^4$	[70]
$PH_3+2NaClO \rightarrow (HO)H_2PO+2NaCl$	$KI-HClO_4$ ($<10^{-6}$ M)	$k_4=5.5\cdot10^{18}$	[11, 12, 65, 66]
$PH_3+3NaClO \rightarrow (HO)_2HPO+3NaCl$	$KBr-HClO_4$ ($<10^{-6}$ M)	$k_4=4.5\cdot10^{15}$	[11, 12, 65, 66]
$AsH_3+1.5NaClO \rightarrow As+1.5NaCl+1.5H_2O$	$KI-HClO_4$ ($<10^{-6}$ M)	$k_4=4.5\cdot10^{14}$	[11, 12, 65, 66]
$AsH_3+3NaClO \rightarrow HAsO_2+H_2O+3NaCl$	$KBr-HClO_4$ ($<10^{-6}$ M)	$k_4=8.3\cdot10^{15}$	[11, 12, 65, 66]
$PH_3+2NaIO \rightarrow (HO)H_2PO+2NaI$	$HClO_4$ ($<10^{-9}$ M)	$k_3=4.0\cdot10^{13}$	[11, 12, 65, 66]
$PH_3+3NaBrO \rightarrow (HO)_2HPO+3NaBr$	$HClO_4$ ($<10^{-8}$ M)	$k_3=2.10\cdot10^{12}$	[11, 12, 65, 66]
$PH_3+3NaClO \rightarrow (HO)_2HPO+3NaCl$	$HClO_4$ ($<10^{-6}$ M)	$k_3=2.5\cdot10^{11}$	[11, 12, 65, 66]
	$KBr-HClO_4$ ($<10^{-6}$ M)	$k_4=7.5\cdot10^{15}$	
$PH_3+NaIO_3 \rightarrow (HO)_2HPO+NaI$	$HClO_4-KBr$	$k_4=7.2\cdot10^7$	[11, 12, 71–81]
	$HClO_4$	$k_3=6.7\cdot10^4$	
$PH_3+NaIO_4 \rightarrow (HO)_3PO+NaI$	$HClO_4$	$k_3=1.2\cdot10^4$	[71–81]
$PH_3+NaBrO_3 \rightarrow (HO)_2HPO+NaBr$	$HClO_4$	$k_3=2.7\cdot10^3$	[71–81]
	$HClO_4-KBr$	$k_4=9.2\cdot10^7$	
	$HClO_4-KBr-K_2MoO_4$	$k_5=3.5\cdot10^{13}$	
$PH_3+NaClO_3 \rightarrow (HO)_2HPO+NaCl$	$HClO_4$	$k_3=1.2\cdot10^2$	[71–81]
	$HClO_4-LiCl$	$k_4=2.1\cdot10^4$	
$PH_3+NaIO_4 \rightarrow (HO)H_2PO+NaI$	$HClO_4-KI$	$k_4=2.2\cdot10^8$	[71–81]
	$HClO_4-KI-K_2MoO_4$ ($<10^{-5}$ M)	$k_5=2.5\cdot10^{17}$	
	$HClO_4-KI-LiWO_4$ ($<10^{-5}$ M)	$k_5=3.6\cdot10^{17}$	
$PH_3+NaIO_3 \rightarrow (HO)H_2PO+NaI$	$HClO_4-KI$	$k_4=4.5\cdot10^9$	[71–81]
	$HClO_4-KI-LiWO_4$ ($<10^{-5}$ M)	$k_5=4.2\cdot10^{17}$	
$PH_3+8HNO_3 \rightarrow (HO)_3PO+8NO_2+4H_2O$	H_2SO_4	$k_3=2.0\cdot10^{-2}$	[11, 12, 82–86]
$PH_3+\frac{8}{3}HNO_3 \rightarrow (HO)_3PO+\frac{8}{3}NO+\frac{4}{3}H_2O$	$H_2SO_4-HNO_2$	$k_4=2.1\cdot10^3$	[11, 12, 82–86]
$PH_3+1.5HNO_3 \rightarrow (HO)_2HPO+0.75N_2O+0.75H_2O$	$H_2SO_4-HNO_2-AgNO_3$	$k_5=6.3\cdot10^8$	[11, 12, 82–86]
	$H_2SO_4-HNO_2-HgCl_2$	$k_5=2.3\cdot10^5$	
	$H_2SO_4-HNO_2-KI$	$k_5=3.2\cdot10^7$	
	$H_2SO_4-HNO_2-LiBr$	$k_5=8.5\cdot10^5$	
	$H_2SO_4-HNO_2-LiCl$	$k_5=6.7\cdot10^3$	
$PH_3+6NO \rightarrow (HO)_2HPO+3N_2O$	H_2SO_4	$k_3=2.2\cdot10$	[11, 12, 82–86]
	H_2SO_4-LiCl	$k_4=2.1\cdot10^2$	
	H_2SO_4-LiBr	$k_4=1.1\cdot10^4$	
	H_2SO_4-KI	$k_4=3.4\cdot10^6$	
$PH_3+6HNO_2 \rightarrow (HO)_2HPO+6NO+3H_2O$	H_2SO_4	$k_3=8.5\cdot10^2$	[11, 12, 82–86]
	H_2SO_4-LiCl	$k_4=6.7\cdot10^3$	
	H_2SO_4-LiBr	$k_4=8.5\cdot10^5$	
	H_2SO_4-KI	$k_4=2.3\cdot10^7$	
$PH_3+3HNO_2 \rightarrow (HO)_2HPO+1.5N_2O+1.5H_2O$	$H_2SO_4-AgNO_3$	$k_4=4.8\cdot10^6$	[11, 12, 82–86]
$AsH_3+HNO_3 \rightarrow As+NO+2H_2O$	$H_2SO_4-HNO_2$	$k_4=6.5\cdot10^5$	[11, 12, 82–86]
	$H_2SO_4-HNO_2-AgNO_3$	$k_5=8.5\cdot10^8$	

Table 1 (continued).

Reaction	Catalyst	Rate constant	Refs.
$PH_3+3H_2SO_4 \rightarrow 3SO_2+(HO)_2HPO+3H_2O$	H_2SO_4	$k_3=6.5\cdot10^2$	[2, 3]
	H_2SO_4–$HgSO_4$	$k_4=6.5\cdot10^5$	
$PH_3+2H_2SeO_3 \rightarrow 2Se+(HO)_3PO+2H_2O$	$HClO_4$	$k_3=2.5\cdot10^5$	[82–85, 88]
	$HClO_4$–LiCl	$k_4=8.2\cdot10^5$	
	$HClO_4$–LiBr	$k_4=3.2\cdot10^6$	
	$HClO_4$–KI	$k_4=1.4\cdot10^8$	
$PH_3+2H_2TeO_3 \rightarrow 2Te+(HO)_3PO+2H_2O$	HCl–LiCl	$k_4=9.1\cdot10^4$	[82–85, 88]
	HCl–LiBr	$k_4=2.2\cdot10^5$	
	HCl–KI	$k_4=1.8\cdot10^7$	
$PH_3+\frac{4}{3}Na_2Cr_2O_7+\frac{16}{3}H_2SO_4 \rightarrow (HO)_3PO+\frac{4}{3}Cr_2(SO_4)_3+\frac{4}{3}Na_2SO_4+\frac{16}{3}H_2O$	H_2SO_4	$k_3=1.3\cdot10^4$	[11, 12]
	H_2SO_4–$CuCl_2$–LiCl	$k_5=2.4\cdot10^6$	
$PH_3+Na_2Cr_2O_7+4H_2SO_4 \rightarrow (HO)_2HPO+Cr_2(SO_4)_3+Na_2SO_4+4H_2O$	H_2SO_4–$CuSO_4$–LiBr	$k_5=5.6\cdot10^7$	[89–91]
	H_2SO_4–$Fe_2(SO_4)_3$–LiBr	$k_5=6.8\cdot10^7$	
	H_2SO_4–LiBr	$k_4=3.3\cdot10^6$	
$PH_3+\frac{4}{6}Na_2Cr_2O_7+\frac{16}{6}H_2SO_4 \rightarrow (HO)H_2PO+\frac{4}{6}Cr_2(SO_4)_3+\frac{4}{6}Na_2SO_4+\frac{16}{6}H_2O$	H_2SO_4–KI	$k_4=4.6\cdot10^8$	[89–91]
$AsH_3+Na_2Cr_2O_7+4H_2SO_4 \rightarrow HAsO_2+Cr_2(SO_4)_3+Na_2SO_4+5H_2O$	H_2SO_4–LiCl	$k_4=4.5\cdot10^6$	[89–91]
	H_2SO_4–$CuCl_2$–LiCl	$k_5=3.5\cdot10^7$	
$AsH_3+Na_2Cr_2O_7+5H_2SO_4 \rightarrow As+Cr(HSO_4)_3+2NaHSO_4+4H_2O$	H_2SO_4 – $CuSO_4$ – LiBr	$k_5=4.5\cdot10^8$	[89–91]
	H_2SO_4–$Fe_2(SO_4)_3$–LiBr	$k_5=8.9\cdot10^8$	
	H_2SO_4–LiBr	$k_4=9.1\cdot10^6$	
	H_2SO_4–KI	$k_4=8.2\cdot10^8$	
	H_2SO_4	$k_3=6.5\cdot10^4$	
$PH_3+\frac{8}{3}KMnO_4+\frac{4}{3}H_2SO_4 \rightarrow \frac{8}{3}MnO_2+(HO)_3PO+\frac{4}{3}K_2SO_4+\frac{4}{3}H_2O$	H_2SO_4	$k_3=1.2\cdot10^{12}$	[82–85]
$AsH_3+2KMnO_4+H_2SO_4 \rightarrow 2MnO_2+HAsO_2+K_2SO_4+2H_2O$	H_2SO_4	$k_3=5.4\cdot10^{12}$	[94]
$PH_3+\frac{6}{5}KMnO_4+\frac{9}{5}H_2SO_4 \rightarrow \frac{6}{5}MnSO_4+(HO)_2HPO+\frac{3}{5}K_2SO_4+\frac{9}{5}H_2O$	H_2SO_4–LiBr	$k_4=3.2\cdot10^{13}$	[94]
$PH_3+\frac{4}{5}KMnO_4+\frac{6}{5}H_2SO_4 \rightarrow \frac{4}{5}MnSO_4+(HO)H_2PO+\frac{2}{5}K_2SO_4+\frac{6}{5}H_2O$	H_2SO_4–KI	$k_4=2.1\cdot10^{14}$	[94]
$AsH_3+\frac{3}{5}KMnO_4+\frac{4.5}{5}H_2SO_4 \rightarrow \frac{1.5}{5}K_2SO_4+\frac{3}{5}MnSO_4+\frac{5}{12}H_2O+As$	H_2SO_4–LiBr	$k_4=8.4\cdot10^{13}$	[94]
	H_2SO_4–KI	$k_4=7.9\cdot10^{14}$	
$PH_3+8NH_4VO_3+12H_2SO_4 \rightarrow (HO)_3PO+8VOSO_4+4(NH_4)_2SO_4+12H_2O$	H_2SO_4	$k_3=5.0\cdot10^5$	[95]
	H_2SO_4–LiBr	$k_4=8.2\cdot10^6$	
	H_2SO_4–KI	$k_4=3.0\cdot10^9$	
$PH_3+8FeCl_3+4H_2O \rightarrow 8FeCl_2+(HO)_3PO+8HCl$	HCl	$k_3=1.2\cdot10$	[102–104]
$PH_3+3Fe_2(SO_4)_3+3H_2O \rightarrow 6FeSO_4+(HO)_2HPO+3H_2SO_4$	Ag_2SO_4	$k_3=3.2\cdot10^7$	[105–107]
$PH_3+2Fe_2(SO_4)_3+2H_2O \rightarrow 4FeSO_4+(HO)H_2PO+2H_2SO_4$	H_2SO_4–KI	$k_4=1.2\cdot10^8$	[105–107]
$PH_3+6FeX_3+3H_2O \rightarrow 6FeX_2+(HO)_2HPO+6HX$	HCl–KI	$k_4=2.3\cdot10^5$	[105–107]
	HBr–KI	$k_4=4.2\cdot10^6$	
$AsH_3+3FeCl_3 \rightarrow As+3FeCl_2+3HCl$	HCl	$k_3=2.6\cdot10^3$	[105–107]
	HCl–KI	$k_4=4.6\cdot10^5$	
$PH_3+8Ce(SO_4)_2+4H_2O \rightarrow (HO)_3PO+4Ce_2(SO_4)_3+4H_2SO_4$	HCl–LiCl	$k_4=2.4\cdot10^3$	[108, 109]
	HCl–LiBr	$k_4=4.2\cdot10^5$	
	HCl–KI	$k_4=3.4\cdot10^7$	
$PH_3+3CuSO_4+3H_2O \rightarrow 3Cu+3H_2SO_4+(HO)_2HPO$	Cu_2SO_4	$k_3=1.2\cdot10^{-1}$	[113–115]
$PH_3+8CuCl_2+4H_2O \rightarrow 8CuCl+8HCl+(HO)_3PO$	HCl–CuCl–LiCl	$k_5=2.5\cdot10^2$	[134–138]
	HCl–CuCl–$PdCl_2$	$k_5=3.4\cdot10^9$	
	HCl–CuCl–$HgCl_2$	$k_5=8.6\cdot10^9$	
$PH_3+6CuCl_2+3H_2O \rightarrow 6CuCl+6HCl+(HO)_2HPO$	HCl–CuCl–LiBr	$k_5=3.3\cdot10^5$	[157–159]
$PH_3+4CuCl_2+2H_2O \rightarrow 4CuCl+4HCl+(HO)H_2PO$	HCl – CuCl – KI	$k_5=5.8\cdot10^9$	[120–126]
$AsH_3+3CuCl_2 \rightarrow As+3CuCl+3HCl$	HCl–CuCl–LiCl	$k_5=3.2\cdot10^4$	[111, 112,
	HCl–CuCl–LiBr	$k_5=5.4\cdot10^8$	120–126, 161]
	HCl–CuCl–KI	$k_5=6.2\cdot10^{12}$	
$PH_3+\frac{8}{3}AuCl_3+4H_2O \rightarrow \frac{8}{3}Au+8HCl+(HO)_3PO$	HCl–AuCl–LiCl	$k_5=8.2\cdot10^9$	[141]
	HCl – AuCl – LiBr	$k_5=7.8\cdot10^{11}$	
	HCl–AuCl–KI	$k_5=6.8\cdot10^{12}$	
$PH_3+1.5Na_2PtCl_6+3H_2O \rightarrow 1.5Pt+(HO)_2HPO+3NaCl+6HCl$	HCl–$PtCl_2$–KI	$k_5=5.6\cdot10^{11}$	[142]
	HCl–$PtCl_2$–LiBr	$k_5=6.4\cdot10^9$	
	HCl–$PtCl_2$–LiCl	$k_5=4.2\cdot10^7$	
$PH_3+4PdCl_2+4H_2O \rightarrow Pd+(HO)_3PO+8HCl$	HCl–$PdCl_2$–LiCl	$k_5=4.5\cdot10^8$	[138–140]
$PH_3+4H_2O_2 \rightarrow (HO)_3PO+4H_2O$	HCl–HBr	$k_4=2.6\cdot10^4$	[144–146]
	HCl–HI	$k_4=1.5\cdot10^6$	
	HCl–$CuBr_2$	$k_4=8.4\cdot10^5$	
	HCl–$FeBr_3$	$k_4=5.2\cdot10^5$	
$AsH_3+3H_2O_2 \rightarrow HAsO_2+4H_2O$	HCl–LiCl	$k_4=3.2\cdot10^5$	[146]
	HCl–LiBr	$k_4=4.8\cdot10^6$	
	HCl–$FeBr_3$	$k_4=1.5\cdot10^8$	
	HCl–$FeCl_3$	$k_4=2.2\cdot10^6$	

Table 1 (continued).

Reaction	Catalyst	Rate constant	Refs.
$AsH_3+1.5H_2O_2 \rightarrow As+3H_2O$	HCl–KI	$k_4=7.8\cdot10^8$	[146]
$AsH_3+3Na_2S_2O_8+3H_2O \rightarrow HAsO_2+3H_2SO_4+3Na_2SO_4$	H_2SO_4–KI	$k_4=3.2\cdot10^8$	[146]
$PH_3+4Na_2S_2O_8+4H_2O \rightarrow (HO)_3PO+4Na_2SO_4+4H_2SO_4$	$HClO_4$–KI	$k_4=1.2\cdot10^8$	[146]
$PH_3+1.5O_2 \rightarrow (HO)_2HPO$	$HClO_4$–LiBr	$k_4=6.2\cdot10^6$	[162–165]
	KI–C	$k_1=2.3$	
	PdO–C	$k_1=1.8$	
	$CuCl_2$–$PdCl_2$–C	$k_1=1.2\cdot10$	
	$CuCl_2$–$HgCl_2$–C	$k_1=2.6\cdot10$	
$AsH_3+1.5O_2 \rightarrow HAsO_2+H_2O$	KI–C	$k_1=4.5$	[163]
$Ph_3+8CuCl_2+4ROH \rightarrow (RO)_3PO+RCl+8CuCl+7HCl$	CuCl–LiCl	$k_3=2.4\cdot10^3$	[166–172]
$PH_3+6CuCl_2+3R'OH \rightarrow (R'O)_2HPO+6CuCl+R'Cl+5HCl$	CuCl–LiCl	$k_3=1.2\cdot10^3$	[173]
$PH_3+3Na_2PtCl_6+3ROH \rightarrow 3Na_2PtCl_4+(RO)_3P+6HCl$	$PtCl_2$	$k_3=4.3\cdot10^2$	[170]
	$PtBr_2$	$k_3=1.2\cdot10^3$	
	PtI_2	$k_3=4.6\cdot10^3$	
$PH_3+6CuCl_2+3R_2HN \rightarrow 6CuCl+(R_2N)_3P+6HCl$	CuCl	$k_3=9.2\cdot10^3$	[174]
$PH_3+3CH_3CN+6Cu(OAc)_2 \rightarrow 6CuOAc+6HOAc+(CNCH_2)_3P$	CuOAc	$k_3=4.8\cdot10^2$	[166–171]
$PH_3+3(EtCH_2CH_2)_3N+18Cu(OAc)_2 \rightarrow 18CuOAc+18HOAc+[(Et-CH=CH)_2(PrCH)N]_3P$	CuOAc	$k_3=5.6\cdot10^2$	[166–171]
$PH_3+3C_5H_5N+6Cu(OAc)_2 \rightarrow 6CuOAc+6HOAc+(o\text{-}C_5H_4N)_3P$	CuOAc	$k_3=6.2\cdot10^2$	[166–171]
$PH_3+3C_6H_5CN+6Cu(OAc)_2 \rightarrow 6CuOAc+6HOAc+(o\text{-}C_6H_4CN)_3P$	CuOAc	$k_3=8.2\cdot10^2$	[166–171]
$PH_3+3C_6H_6+6Cu(OAc)_2 \rightarrow 6CuOAc+(C_6H_5)_3P$	CuOAc	$k_3=1.5\cdot10^3$	[166–171]
	Py		
$PH_3+3Cu(OAc)_2+3CH_3(CH_2)_nOH \rightarrow [HO(CH_2)_{n+1}]_3P+3Cu+6AcOH$	CuOAc	$k_3=6.8\cdot10^2$	[173]
$PH_3+3Na_2PtCl_4+3RCH_2OH \rightarrow (HOCHR)_3P+3Pt+6NaCl+6HCl$	—	$k_2=2.8\cdot10$	[170]

The catalytic activity of catalysts deposited on carbon (C) in reactions involving the oxidation of PH_3 and AsH_3 by oxygen is characterised by first-order rate constants (k_1, min^{-1}). The reactivity of substances oxidising PH_3 and AsH_3 without catalysts is characterised by second-order rate constants:

$$k_2 = W/[Ox][Red], \text{ litre mol}^{-1} \text{ min}^{-1},$$

where W is the reaction rate (mol litre^{-1} min^{-1}) and [Ox] and [Red] are the molar concentrations of the oxidant and reductant in the liquid phase.

The catalytic activity of hydrogen ions and metal complexes is characterised by third-order rate constants:

$$k_3 = W/[Ox][Red][H^+], \text{ litre}^2 \text{ mol}^{-2} \text{ min}^{-1},$$

$$k_3 = W/[Ox][Red][M^{n+}], \text{ litre}^2 \text{ mol}^{-2} \text{ min}^{-1},$$

where $[H^+]$ and $[M^{n+}]$ are the molar concentrations of hydrogen and metal ions.

The catalytic activity of two-component mixed systems containing H^+ and X^- ($X^- = Cl^-, Br^-, I^-$) ions is characterised by fourth-order rate constants:

$$k_4 = W/[Ox][Red][H^+][X^-], \text{ litre}^3 \text{ mol}^{-3} \text{ min}^{-1},$$

where $[X^-]$ is the molar concentration of X^- ions.

The catalytic activity of three-component mixed systems incorporating the H^+, X^-, and M^{n+} ions is characterised by fifth-order rate constants:

$$k_5 = W/[Ox][Red][H^+][X^-][M^{n+}], \text{ litre}^4 \text{ mol}^{-4} \text{ min}^{-1}.$$

The rate constants were measured with a relative error of $\pm 10\%$. The catalysts based on *d* metal ions in the highest oxidation states [W(VII), Mo(VII)] propagate the process, like hydrogen ions, via an associative mechanism. They activate oxidants via coordination, which increases their redox potential and polarity.

The ions of *d* metals in intermediate oxidation states [Cu(II), Pd(II), Ag(I)] and alkali metal halides effect the reaction via a separate stage (oxidation-reduction) mechanism. Arsine and phosphine reduce the halogens and metal ions to halide ions and the metals, which oxidants regenerate the initial states of the metal ions and the halogens.

The complexes of *d* metals in the highest oxidation states [Hg(II), Cu(I)] activate phosphine and arsine via coordination. By virtue of the close positions of the *d* and *s* orbitals and the tendency towards a two-sided exchange interaction, they stimulate the $sp^3 \rightarrow sp^3d$ hybridisation of the phosphorus atom in PH_3. The oxygen compounds of high valence metal and non-metal ions oxidise phosphine via an outer-sphere mechanism, oxygen ions acting as a bridge, while metal complexes in an intermediate valence state oxidise phosphine via an inner-sphere mechanism.

In contrast to metal ions, halide ions are poorly coordinated to non-polar oxidants. Alkali metal halides therefore exhibit a high catalytic activity only in the presence of protic acids or metal ions which intensify the electrophilicity of oxidants.

In order to reduce the acidity of the medium, mixed systems containing a protic and an aprotic acid simultaneously are frequently employed. Thus negatively charged oxidants, present in the form of anions, oxidise PH_3 and AsH_3 acted upon jointly by hydrogen, metal, and halide ions. With the aid of H^+ and M^{n+} ions, it is possible to ensure in a three-component system in a weakly acid medium an effective positive charge in the oxidant, which is necessary for the manifestation of the catalytic properties of halide ions.

In neutral and alkaline solutions, the complexes of *d* metals in an intermediate valence state, which are soluble in such media, exhibit a high reactivity in relation to PH_3. The solubility of metal ions at high pH is increased sharply by ammonia, amines, polyhydric alcohols and hydroxyacids. An increased rate of oxidation of PH_3 by metal complexes is attained in an alkaline solution by virtue of the joint action of hydroxide and metal ions, generating the phosphite ion, which is a stronger reductant than PH_3. In alkaline systems, the reduced metal complexes are regenerated by oxygen. Metal complexes are therefore highly active catalysts of the oxidation of PH_3 by oxygen in an alkaline medium.

The phosphide ion is generated not only in an alkaline solution but also in a neutral medium under the influence of metal complexes containing "hard" ligands (AcO^-, SO_4^{2-}, Py, NR_3). Such ligands induce the inner-sphere acid–base decomposition of phosphine complexes of metals with formation of metal phosphides. The acid–base mechanism predominates as a result of the strengthening of the bonds between the metal and the phosphorus atom of PH_3. Phosphine is converted into the phosphite ion and acquires nucleophilic reactivity. In the presence of "soft" ligands (Cl^-, Br^-), phosphine becomes an electrophile by virtue of the manifestation of an effective positive charge on the phosphorus atom and reacts vigorously with the nucleophiles in the coordination sphere. By varying the nature of the ligands, it is therefore possible to induce either nucleophilic or electrophilic reactivity in the coordinated phosphine.

In the presence of Cl^-, Br^-, and I^- ions in aqueous solutions, phosphine reacts with coordinated H_2O molecules to form the products of its oxidative hydroxylation [$(OH)_3PO$, $(OH)_2HPO$, $(OH)H_2PO$]. In non-aqueous solutions with metal salts, the previously unknown reactions involving the O-, N-, and C-phosphorylation of organic compounds proceed selectively and rapidly. In alcoholic solutions of copper(II), platinum(IV), and iron(III) halides, phosphine interacts with the inner-sphere ROH molecules (R = Me, Et, Pr, iso-Pr, Bu, iso-Bu, Pe, iso-Pe, Oct) with formation of the products of the oxidative alkoxylation of phosphine—trialkyl phosphates [$(RO)_3PO$] and dialkyl phosphites [$(RO)_2HPO$]. In solutions of $CuCl_2$ or $Cu(OAc)_2$ in primary or secondary amines (NRH_2, NR_2H), the products of the oxidative amination of phosphine are formed—phosphorus triamides [$P(NR_2)_3$ and $P(NRH)_3$]. In alcoholic solutions of PtX_2 and $Cu(OAc)_2$, the products of the oxidative hydroxyalkylation of phosphine are obtained—the tris(α-hydroxyalkyl)phosphines $P(HOCRH)_3$ and $P[HO(CH_2)_n]_3$. In solutions of $Cu(OAc)_2$ in acetonitrile (MeCN) and benzonitrile (PhCN), the products of the oxidative cyanomethylation [tricyanomethylphosphine $P(CNCH_2)_3$] and cyanoarylation [tris(*o*-cyanoaryl)phosphine $P(o\text{-}CNC_6H_4)_3$] are formed. The product of the oxidative C-phosphorylation of pyridine by phosphine is synthesised in pyridine solutions of $CuCl_2$ or $Cu(OAc)_2$—tris(*p*-pyridyl)phosphine $P(o\text{-}C_5H_4N)_3$.

In mixed non-aqueous solutions of copper(II) salts, a mixture of products is obtained, in contrast to single component solutions. Thus the products of the oxidative C-phosphorylation of benzene (PPh_3) and pyridine [$P(o\text{-}C_5H_4N)_3$] are formed in solution in C_6H_6–C_5H_5N in the presence of $CuCl_2$ or $Cu(OAc)_2$.

The processes involving the oxidative O-, N-, and C-phosphorylation of organic compounds by phosphine and $CuCl_2$ and $Cu(OAc)_2$ solutions are accelerated by copper(I) ions like other reactions of PH_3. The yield of the products of the oxidative O-, N-, and C-phosphorylation by phosphine falls sharply after the addition of H_2O (> 5%), since there is an increase in the yield of inorganic phosphates.

In processes involving the O-, N-, and C-phosphorylation by phosphine, copper(II) ions are reduced to copper(I) ions or zerovalent copper. These products are readily regenerated by oxygen. A solution containing $CuCl_2$ or $Cu(OAc)_2$ after regeneration can be used again for the absorption of PH_3. The copper salts are separated by vacuum distillation from the products of the oxidative phosphorylation by phosphine and can be reused.

The new oxidative O-, N-, and C-phosphorylation reactions are much simpler than those known previously. Either metallated organic products and phosphorus halides or alkali metal phosphides and halo-derivatives of organic compounds participate in these reactions.[175,176]

By virtue of the high rates of the new oxidative O-, N-, and C-phosphorylation reactions, gases with a low PH_3 content (< 1.0%), for example, the effluent gases from phosphorus and hypophosphite factories, can be used as the raw materials in these processes.[4]

References

1. 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), Khimiya, Leningrad, 1979, 208 pp
2. I I Strizhevskii *Tekhnika Bezopasnosti pri Proizvodstve Atsetilena* (Safety Techniques in the Manufacture of Acetylene), Khimiya, Moscow, 1978, 248 pp
3. S A Miller *Atsetilen, Ego Svoistva, Poluchenie i Primenenie* (Acetylene—Its Properties, Preparation, and Applications), Khimiya, Leningrad, 1969, 678 pp
4. 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), Izd. NIITEKhIM, Moscow, 1986, 43 pp
5. V B Chernogorenko *Novoe v Poluchenii i Primenenii Fosfidov i Fosforsoderzhashchikh Splavov* (New Developments in the Preparation and Application of Phosphides and Phosphorus-containing Alloys), Nauka, Alma-Ata, 1988, Vol. 1, p. 5
6. A F Zhigach, D S Stasinevich *Khimiya Gidridov* (The Chemistry of Hydrides), Khimiya, Leningrad, 1969, 675 pp
7. A I Rakhimov *Sintez Fosfororganicheskikh Soedinenii. Gomoliticheskie Reaktsii* (Synthesis of Organophosphorus Compounds. Homolytic Reactions), Nauka, Moscow, 1985, 230 pp
8. O A Erastov, G E Nikonov *Funktsional'no-Zameshchennye Fosfiny i Ikh Proizvodnye* (Phosphines with Functional Group Substituents and Their Derivatives), Nauka, Moscow, 1986, 306 pp
9. J R van Wazer *Phosphorus and Its Compounds* (Translated into Russian), Inostr. Lit., Moscow, 1962, 672 pp
10. R Hudson *Structure and Mechanism in Organophosphorus Chemistry* (Translated into Russian), Mir, Moscow, 1967, 355 pp
11. D V Sokol'skii, Ya A Dorfman *Kataliz Ligandami Okislitel'no-Vosstanovitel'nykh Reaktsii v Vodnykh Rastvorakh* (Catalysis of Oxidation-Reduction Reactions in Aqueous Solutions by Ligands), Nauka, Alma-Ata, 1972, 337 pp

12. D V Sokol'skii, Ya A Dorfman, T L Rakitskaya *Protonno-Aprotonnyi Kataliz v Rastvorakh* (Protic-Aprotic Catalysis in Solutions), Nauka, Alma-Ata, 1976, 245 pp
13. M Tobe *The Mechanisms of Inorganic Reactions* (Translated into Russian), Mir, Moscow, 1965, 270 pp
14. F Basolo, R G Pearson *Mechanisms of Inorganic Reactions* (Translated into Russian), Mir, Moscow, 1971, 590 pp
15. J Huheey *Inorganic Chemistry. The Structure of Matter and Reactivity* (Translated into Russian), Khimiya, Moscow, 1987, 695 pp
16. D Corbridge *Phosphorus. Fundamentals of the Chemistry, Biochemistry and Technology* (Translated into Russian), Mir, Moscow, 1982, 680 pp
17. D Purdela, R Vilceanu *Chemistry of Organophosphorus Compounds and Their Acid Derivatives* (Translated into Russian), Khimiya, Moscow, 1973, 840 pp
18. I F Lutsenko, M V Proskurina *Usp. Khim.*, 1978, **47**(9) 1648 [Engalish translation in *Russ. Chem. Rev.*, 1978(9)]
19. Yu N Kozlov, A B Purmal' *Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii* (All-Union Conference on the Mechanisms of Catalytic Reactions), Nauka, Moscow, 1978, Vol. 1, p. 82
20. Zh P Kachanova, Yu M Azizov, A P Purmal' *Kompleksoobrazovanie v Katalize* (Complex Formation in Catalysis), Nauka, Moscow, 1968, Vol. 13, p. 121 [*Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis)]
21. A E Shilov *Problemy Khimicheskoi Kinetiki* (Problems of Chemical Kinetics), Nauka, Moscow, 1979, p. 180
22. A E Shilov *Problemy Fiksatsii Azota* (Problems of Nitrogen Fixation), Mir, Moscow, 1982, p. 37
23. A E Shilov *Novoe v Khimicheskoi Fiksatsii Azota* (New Developments in the Chemical Fixation of Nitrogen), Mir, Moscow, 1983, p. 132
24. A E Shilov *Mekhanizm Kataliza* (The Mechanism of Catalysis), Part 2, *Metody Issledovaniya Kataliticheskikh Reaktsii* (Methods for the Investigation of Catalytic Reactions), Nauka, Novosibirsk, 1984, p. 57
25. O S Fedorova, D V Lim, V M Berdnikov *React. Kinet. Catal. Lett.*, 1978, **8** 371
26. M Beck, I Nadpal *Studies on Complex Formation by the Latest Methods* (Translated into Russian), Mir, Moscow, 1989, 406 pp
27. V I Kravtsov *Ravnovesie i Kinetika Elektrodnykh Reaktsii Kompleksov Metallov* (Equilibria and Kinetics in the Electrode Reactions of Metal Complexes), Khimiya, Leningrad, 1985, 208 pp
28. A S Goncharenko *Zh. Neorg. Khim.*, 1966, **11**(4) 943 [English translation in *Russ. J. Inorg. Chem.*, 1966(4)]
29. D V Sokol'skii, Ya A Dorfman, V S Emel'yanova *Dokl. Akad. Nauk SSSR*, 1971, **201** 1125
30. Ya D Fridman *Okislitel'no-Vosstanovitel'nye Svoistva Kompleksnykh Soedinenii Metallov i Ikh Ustoichivost' v Rastvorakh* (Oxidation-Reduction Properties of Metal Complexes and Their Stability in Solutions), Ilim, Frunze, 1966, 310 pp
31. T Gilchrist, R C Storr *Organic Reactions and Orbital Symmetry* (Translated into Russian), Mir, Moscow, 1976, 352 pp
32. L Salem *Electrons in Chemical Reactions* (Translated into Russian), Mir, Moscow, 1985, 280 pp
33. G Klopman *Reactivity and Reaction Pathways* (Translated into Russian), Mir, Moscow, 1979, p. 63
34. R G Pearson *Symmetry Rules for Chemical Reactions* (Translated into Russian), Mir, Moscow, 1979, 592 pp
35. G K Boreskov *Kataliz. Voprosy Teorii i Praktiki* (Catalysis. Problems in Theory and Practice), Nauka, Novosibirsk, 1987, 535 pp
36. F A Cotton, G Wilkinson *Advanced Inorganic Chemistry: A Comprehensive Text* (Translated into Russian), Mir, Moscow, 1979, 670 pp
37. Yu N Kukushkin *Reaktsionnaya Sposobnost' Koordinatsionnykh Soedinenii* (Reactivity of Coordination Compounds), Khimiya, Leningrad, 1987, 288 pp
38. E N Tsvetkov, M I Kabachnik *Usp. Khim.*, 1971, **40**(1) 177 [English translation in *Russ. Chem. Rev.*, 1971(1)]
39. D A Bochvar, N P Gambaryan, L M Epshtein *Usp. Khim.*, 1976, **45**(7) 1316 [English translation in *Russ. Chem. Rev.*, 1976(7)]
40. E N Tsvetkov, A A Korkin *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Applications of Organophosphorus Compounds), Nauka, Moscow, 1987, p. 211
41. V V Zverev, Yu P Kitaev *Usp. Khim.*, 1977, **56**(9) 1515 [English translation in *Russ. Chem. Rev.*, 1977(9)]
42. S Elbel, H Bergmann, W Eusslin *J. Chem. Soc., Faraday Trans. 2*, 1974, 555
43. J H Hillier, V R Saunders *J. Chem. Soc. A*, 1970, 2475
44. H Bock *Pure Appl. Chem.*, 1975, **44** 343
45. F Keil, W Kutzelnigg *J. Am. Chem. Soc.*, 1975, **97** 3623
46. [there is no reference numbered 46 in Russian text (Ed. of Translation)]
47. F J Chu, T Oka *J. Chem. Phys.*, 1974, **60** 4612
48. K Kijima, T Tanaka *J. Mol. Spectrosc.*, 1981, **89** 62
49. N Zumbulyadis, B P Dailey *Mol. Phys.*, 1974, **27** 663
50. J M Zehn, B Munsch *Mol. Phys.*, 1972, **23** 91
51. D C Marinyck, D Dixon *J. Phys. Chem.*, 1982, **86** 914
52. J D Petke, J L Whitten *J. Chem. Phys.*, 1973, **59** 910
53. J J Norman *J. Chem. Phys.*, 1974, **61** 4630
54. W B Perry, T F Schaaf, W L Jolley *J. Am. Chem. Soc.*, 1975, **97** 4899
55. E Fluck, D Z Weber *Z. Naturforsch.*, 1974, **29b** 603
56. E Fluck, D Weber *Z. Anorg. Chem.*, 1977, **429** 247
57. S Hoste *J. Electron Spectrosc. Relat. Phenom.*, 1979, **17** 191
58. A A Bakke, Hsiang-Wen Chen, W L Jolley *J. Electron Spectrosc. Relat. Phenom.*, 1980, **20** 333
59. G N Dolenko, S A Krupoder, L N Mazalov *Zh. Strukt. Khim.*, 1979, 332
60. E A Gol'tsova, L N Mazalov, V D Yumatov, et al. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1976, No. 4(9) 41
61. L N Mazalov, V D Yumatov, G N Dolenko *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Applications of Organophosphorus Compounds), Nauka, Leningrad, 1987, p. 105
62. V I Nefedov *Rentgenoelektronnaya Spektroskopiya Khimicheskikh Soedinenii* (X-Ray Electronic Spectroscopy of Chemical Compounds), Khimiya, Moscow, 1984, 256 pp
63. B E Ivanov, V F Zheltukhin *Usp. Khim.*, 1970, **39**(5) 773 [English translation in *Russ. Chem. Rev.*, 1970(5)]
64. V V Azatyan, S G Gagarin, V I Zakhar'in, et al. *Kinet. Katal.*, 1985, **26** 222
65. D V Sokol'skii, Ya A Dorfman, G P Pole *Zh. Prikl. Khim.*, 1977, **44** 2571

66. D V Sokol'skii, Ya A Dorfman, G P Pole *Dokl. Akad. Nauk SSSR*, 1971, **201** 875
67. A J Kirby, S G Warren *The Organic Chemistry of Phosphorus* (Translated into Russian), Mir, Moscow, 1971, 400 pp
68. D Barton, W D Ollis (Editors), *Organic Chemistry* (Translated into Russian), Khimiya, Moscow, 1983, Vol. 4, p. 595; Vol. 5, p. 16
69. T A Turney *Mechanisms of Inorganic Reactions* (Translated into Russian), Mir, Moscow, 1968, 250 pp
70. Ya A Dorfman, M M Aleshkova, D M Doroshkevich, I L Zil'berberg *Zh. Neorg. Khim.*, 1988, **33**(6) 1382 [English translation in *Russ. J. Inorg. Chem.*, 1988(6)]
71. D V Sokol'skii, Yu A Dorfman, T L Rakitskaya *Dokl. Akad. Nauk SSSR*, 1974, **216** 353
72. D V Sokol'skii, Ya A Dorfman, T L Rakitskaya *Kinet. Katal.*, 1973, **14** 1406
73. D V Sokol'skii, Ya A Dorfman, T L Rakitskaya *Zh. Fiz. Khim.*, 1973, **14**(1) 59 [English translation in *Russ. J. Phys. Chem.*, 1973(1)]
74. Ya A Dorfman, T L Rakitskaya, R K Kaidarova *Kinet. Katal.*, 1976, **17** 1197
75. Ya A Dorfman, T L Rakitskaya, R K Kaidarova *Zh. Fiz. Khim.*, 1977, **51**(6) 1434 [English translation in *Russ. J. Phys. Chem.*, 1977(6)]
76. Ya A Dorfman, T L Rakitskaya, R K Kaidarova *Zh. Obshch. Khim.*, 1976, **46** 2643
77. Ya A Dorfman, T L Rakitskaya, R K Kaidarova *Zh. Prikl. Khim.*, 1975, **48** 2742
78. D V Sokol'skii, T L Rakitskaya, R K Kaidarova *Dokl. Akad. Nauk SSSR*, 1973, **209** 1354
79. Ya A Dorfman, T L Rakitskaya, R K Kaidarova *Zh. Obshch. Khim.*, 1976, **46** 1668
80. Ya A Dorfman, T L Rakitskaya, R K Kaidarova *Elektrokhimiya*, 1976, **12** 479
81. Ya A Dorfman, T L Rakitskaya, R K Kaidarova *Zh. Fiz. Khim.*, 1977, **51**(5) 1103 [English translation in *Russ. J. Phys. Chem.*, 1977(5)]
82. Ya A Dorfman, V S Emel'yanova, A S Amanzholova, et al. *Kompleksnye Soedineniya v Katalize* (Complex Compounds in Catalysis), Nauka, Alma-Ata, 1980, p. 64
83. Ya A Dorfman, V S Emel'yanova, G S Polimbetova, et al. *Metallokompleksnyi Kataliz Okislitel'no-Vosstanovitel'nykh Protsessov* (Metal Complex Catalysis of Oxidation-Reduction Processes), Nauka, Alma-Ata, 1981, p. 3
84. Ya A Dorfman, T L Rakitskaya, T V Petrova, et al. *Gomogennoe Okislenie* (Homogeneous Oxidation), Nauka, Alma-Ata, 1978, p. 34
85. Ya A Dorfman, T L Rakitskaya, L V Tyuleneva, et al. *Koordinatsionnyi Kataliz* (Coordination Catalysis), Nauka, Alma-Ata, 1977, p. 3
86. Ya A Dorfman, V S Emel'yanova, I V Kel'man, et al. *IV Mezhdunarodnyi Simpozium po Gomogemmonu Katalizu. Tezisy Dokladov* (The IVth International Symposium on Homogeneous Catalysis. Abstracts of Reports), Nauka, Leningrad, 1984, Vol. 2, p. 195
87. R G Kolbandkeri, D K Padma, A R Murthy *Indian J. Chem., Sect. A*, 1981, **20** 83
88. Ya A Dorfman, T L Rakitskaya, A S Amanzholova *Zh. Prikl. Khim.*, 1979, **52** 2385
89. D V Sokol'skii, Ya A Dorfman, G S Utegenova *Zh. Fiz. Khim.*, 1972, **46**(2) 507 [English translation in *Russ. J. Phys. Chem.*, 1972(2)]
90. Ya A Dorfman, G S Polimbetova, B A Mansurov, A K Kamaletdinova *Zh. Prikl. Khim.*, 1982, **55** 761
91. Ya A Dorfman, G S Polimbetova, I V Kel'man, et al. *Koord. Khim.*, 1989, **15** 77
92. H B Mark, G A Rechnitz *Kinetics in Analytical Chemistry* (Translated into Russian), Mir, Moscow, 1972, 362 pp
93. A Riavely, S Srinivasan Vangular *Indian J. Chem., Sect. A*, 1986, **25** 836
94. Ya A Dorfman, G S Polimbetova, B A Mansurov *Koord. Khim.*, 1988, **14** 1219
95. Ya A Dorfman, V S Emel'yanova, T N Kisanova, et al. *Koordinatsionnyi Kataliz* (Coordination Catalysis), Nauka, Alma-Ata, 1977, p. 41
96. I V Kozhevnikov, K I Matveev *Usp. Khim.*, 1982, **51**(11) 1875 [English translation in *Russ. Chem. Rev.*, 1982(11)]
97. Ya A Dorfman, M M Aleshkova, D M Doroshkevich, I V Kel'man *Zh. Fiz. Khim.*, 1984, **58**(12) 2975 [English translation in *Russ. J. Phys. Chem.*, 1984(12)]
98. D V Sokol'skii, Ya A Dorfman, T L Rakitskaya *Dokl. Akad. Nauk SSSR*, 1971, **201** 123
99. D V Sokol'skii, Ya A Dorfman, T L Rakitskaya *Kinet. Katal.*, 1973, **14** 608
100. D V Sokol'skii, Ya A Dorfman, L S Ernestova *Zh. Fiz. Khim.*, 1972, **46**(7) 1855 [English translation in *Russ. J. Phys. Chem.*, 1972(7)]
101. D V Sokol'skii, Ya A Dorfman, L S Ernestova *Zh. Prikl. Khim.*, 1973, **46** 2079
102. D V Sokol'skii, Ya A Dorfman, T L Rakitskaya *Dokl. Akad. Nauk SSSR*, 1971, **199** 618
103. D V Sokol'skii, Ya A Dorfman, G B Protopopova *Zh. Fiz. Khim.*, 1973, **47**(8) 1982 [English translation in *Russ. J. Phys. Chem.*, 1973(8)]
104. D V Sokol'skii, Ya A Dorfman, T L Rakitskaya *Kinet. Katal.*, 1973, **14** 507
105. T L Rakitskaya, I S Kostyukova, T D Red'ko *Kataliticheskie Reaktsii v Zhidkoi Faze* (Catalytic Reactions in the Liquid Phase), Nauka, Alma-Ata, 1988, Part 3, p. 71
106. T L Rakitskaya *Metallokompleksnyi Kataliz Okislitel'no-Vosstanovitel'nykh Protsessov* (Metal Complex Catalysis of Oxidation-Reduction Processes), Nauka, Alma-Ata, 1981, p. 94
107. T L Rakitskaya *IV Mezhdunarodnyi Simpozium po Gomogennomu Katalizu. Tezisy Dokladov* (The IVth International Symposium on Homogeneous Catalysis. Abstracts of Reports), Nauka, Leningrad, 1984, Vol. 1, p. 163
108. D V Sokol'skii, Ya A Dorfman, Z I Rogova *Zh. Fiz. Khim.*, 1972, **46**(10) 2566 [English translation in *Russ. J. Phys. Chem.*, 1972(10)]
109. D V Sokol'skii, Ya A Dorfman, Z I Rogova *Zh. Fiz. Khim.*, 1974, **48**(3) 585 [English translation in *Russ. J. Phys. Chem.*, 1974(3)]
110. Ya A Dorfman, V S Emel'yanova, T N Kisanova, et al. *Koordinatsionnyi Kataliz* (Coordination Catalysis), Nauka, Alma-Ata, 1977, p. 41
111. Ya A Dorfman, G S Polimbetova, V S Emel'yanova, et al. *Kinet. Katal.*, 1985, **26** 615

112. I V Kel'man, Ya A Dorfman *Razvitie Rabot v Oblasti Kataliza v Kazakhstane* (Development of Research in the Field of Catalysis in Kazakhstan), Nauka, Alma-Ata, 1990, Part 1, p. 145
113. E A Boguslavskii, N M Lanshina, L N Erler *Dokl. Akad. Nauk SSSR*, 1978, **60** 1783
114. E A Boguslavskii, N M Lanshina, L N Erler *Dokl. Akad. Nauk SSSR*, 1978, **60** 1750
115. I A Antonov, L M Kuznetsov, S N Neshumova *Poluchenie Atsetilena iz Karbida Kal'tsiya* (Preparation of Acetylene from Calcium Carbide), Khimiya, Moscow, 1980, 110 pp
116. Ya A Dorfman *Katalizatory, Soderzhashchie Nanesennye Kompleksy* (Catalysts Containing Deposited Complexes), Izd. IK SO Akad. Nauk SSSR, 1977, p. 199
117. T L Rakitskaya *Katalizatory, Soderzhashchie Nanesennye Kompleksy* (Catalysts Containing Deposited Complexes), Izd. IK SO Akad. Nauk SSSR, 1980, p. 163
118. O N Temkin *Vvedenie v Metallokompleksnyi Kataliz* (Introduction to Metal Complex Catalysis), Izd. MITIKhT, Moscow, 1980, 530 pp
119. S N Andreeva, S V Sapozhnikova *Dokl. Akad. Nauk SSSR*, 1967, **172** 837
120. D V Sokol'skii, Ya A Dorfman, V S Emel'yanova *Zh. Obshch. Khim.*, 1971, **41** 1918
121. T L Rakitskaya, N N Kosheleva, O L Shkol'nikova *Koord. Khim.*, 1981, **7** 365
122. D V Sokol'skii, Ya A Dorfman, N I Evtikov *Zh. Fiz. Khim.*, 1972, **46**(12) 3118 [English translation in *Russ. J. Phys. Chem.*, 1972(12)]
123. D V Sokol'skii, Ya A Dorfman, N I Evtikov *Zh. Org. Khim.*, 1973, **9** 735
124. D V Sokol'skii, Ya A Dorfman, V S Emel'yanova *Dokl. Akad. Nauk SSSR*, 1971, **201** 1125
125. D V Sokol'skii, Ya A Dorfman, L S Ernestova *Zh. Prikl. Khim.*, 1972, **45** 1344
126. D V Sokol'skii, Ya A Dorfman, L S Ernestova *Dokl. Akad. Nauk SSSR*, 1972, **205** 865
127. Ya A Dorfman, I V Kel'man *Teor. Eksp. Khim.*, 1980, **16** 692
128. Ya A Dorfman, I V Kel'man, D M Doroshkevich *Teor. Eksp. Khim.*, 1982, **18** 621
129. Ya A Dorfman, I V Kel'man, D M Doroshkevich *Teor. Eksp. Khim.*, 1983, **19** 300
130. Ya A Dorfman, I V Kel'man, D M Doroshkevich *Koord. Khim.*, 1984, **10** 320
131. Ya A Dorfman, I V Kel'man *Teor. Eksp. Khim.*, 1984, **20** 485
132. Ya A Dorfman, I V Kel'man *Teor. Eksp. Khim.*, 1985, **21** 718
133. Ya A Dorfman, I V Kel'man, D M Doroshkevich *Zh. Neorg. Khim.*, 1985, **30**(1) 132 [English translation in *Russ. J. Inorg. Chem.*, 1985(1)]
134. Ya A Dorfman, G S Polimbetova, G A Prazdnikova, I G Zil'bert *Katalizatory, Soderzhashchie Nanasennye Kompleksy* (Catalysts Containing Deposited Complexes), Izd. IK SO Akad. Nauk SSSR, 1980, p. 144
135. T L Rakitskaya, V Ya Paina, N N Kosheleva, et al. *Katalizatory, Soderzhashchie Nanasennye Kompleksy* (Catalysts Containing Deposited Complexes), Izd. IK SO Akad. Nauk SSSR, 1980, p. 159
136. T L Rakitskaya, N N Kosheleva, N S Poklad, et al. *XIV Vsesoyuznoe Chugaevskoe Soveshchanie po Khimii Kompleksnykh Soedinenii, Ivanovo* (The XIVth All-Union Chugaev Conference on the Chemistry of Complex Compounds, Ivanovo), Ivanovo, 1981, p. 410
137. D V Sokol'skii, Ya A Dorfman, I A Kazantseva *Dokl. Akad. Nauk SSSR*, 1973, **213** 103
138. Ya A Dorfman, T V Petrova, L V Levina, et al. *Metallokompleksnyi Kataliz Okislitel'no-Vosstanovitel'nykh Protsessov* (Metal Complex Catalysis of Oxidation-Reduction Processes), Nauka, Alma-Ata, 1981, p. 69
139. D V Sokol'skii, Ya A Dorfman, I A Kazanstseva, T S Utegenova *Zh. Fiz. Khim.*, 1970, **44**(9) 2262 [English translation in *Russ. J. Phys. Chem.*, 1970(9)]
140. G A Makarova, V N Zudin, A V Pashis, et al. *VII Vsesoyuznaya Konferentsiya po Kataliticheskim Reaktsiyam v Zhidkoi Faze* (The VIIth All-Union Conference on Catalytic Reactions in the Liquid Phase), Nauka, Alma-Ata, 1988, p. 90
141. D V Sokol'skii, Ya A Dorfman, V S Emel'yanova *Kinet. Katal.*, 1973, **14** 1573
142. D V Sokol'skii, Ya A Dorfman, V S Emel'yanova *Dokl. Akad. Nauk SSSR*, 1971, **198** 1110
143. O P Charkin *Stabil'nost' i Struktura Gazoobraznykh Neorganicheskikh Molekul, Radikalov i Ionov* (The Stability and Structure of Gaseous Inorganic Molecules, Radicals, and Ions), Nauka, Moscow, 1980, 276 pp
144. Ya A Dorfman, T L Rakitskaya, R G Sapova *Kataliticheskoe Gidrirovanie i Okislenie* (Catalytic Hydrogenation and Oxidation), Nauka, Alma-Ata, 1975, p. 3
145. Ya A Dorfman, T L Rakitskaya, R G Sapova *Gomogennyi Kataliz* (Homogeneous Catalysis), Nauka, Alma-Ata, 1975, p. 59
146. Ya A Dorfman, T V Petrova, L V Tyuleneva, et al. *Kompleksnye Soedineniya v Katalize* (Complex Compounds in Catalysis), Nauka, Alma-Ata, 1980, p. 3
147. A V Savitskii, V I Nelyubin *Usp. Khim.*, 1975, **44**(2) 214 [English translation in *Russ. Chem. Rev.*, 1975(2)]
148. T L Rakitskaya, I S Kostyukova, T D Red'ko *Kinet. Katal.*, 1987, **728** 1501
149. T L Rakitskaya, N N Abramova, N S Poklad, T D Red'ko *Kinet. Katal.*, 1987, **28** 872
150. D V Sokol'skii, Ya A Dorfman, T L Rakitskaya *Dokl. Akad. Nauk SSSR*, 1972, **203** 155
151. D V Sokol'skii, Ya A Dorfman, L S Ernestova *Zh. Prikl. Khim.*, 1973, **46** 1127
152. D V Sokol'skii, Ya A Dorfman, I A Kazantseva *Izv. Akad. Nauk Kazakh. SSR, Ser. Khim., Nauk*, 1972, (2) 36
153. A G Miroshnichenko, V A Lunenok-Burmakina *Neorganicheskie Perekisnye Soedineniya* (Inorganic Peroxide Compounds), Nauka, Moscow, 1975, p. 72
154. V A Lunenok-Burmakina *Neorganicheskie Soedineniya* (Inorganic Compounds), Nauka, Moscow, 1975, p. 27
155. D S Gorbenko-Germanov *Neorganicheskie Perekisnye Soedineniya* (Inorganic Peroxide Compounds), Nauka, Moscow, 1975, p. 161
156. D V Sokol'skii, Ya A Dorfman, L S Solov'eva, et al. *Zh. Prikl. Khim.*, 1971, **44** 1239
157. D V Sokol'skii, Ya A Dorfman, Z F Prazdnikova *Zh. Org. Khim.*, 1971, **7** 2048
158. D V Sokol'skii, Ya A Dorfman, Z F Prazdnikova, I V Rodnikova *Dokl. Akad. Nauk SSSR*, 1971, **197** 365

159. D V Sokol'skii, Ya A Dorfman, Z F Prazdnikova, I V Rodnikova *Zh. Org. Khim.*, 1973, **9** 1569
160. Ya A Dorfman, G S Polimbetova, B A Mansurov, D M Doroshkevich *Zh. Obshch. Khim.*, 1989, **59** 2007
161. Ya A Dorfman, G S Polimbetova, V S Emel'yanova, et al. *IV Mezhdunarodnyi Simpozium po Gomogennomu Katalizu. Tezisy Dokladov* (The IVth International Symposium on Homogeneous Catalysis. Abstracts of Reports), Nauka, Leningrad, 1984, Vol. 2, p. 197
162. Ya A Dorfman, G S Polimbetova, L V Levina, et al. *IV Vsesoyuznaya Konferentsiya po Kinetike Geterogenno-Kataliticheskikh Reaktsii: Materialy Konferentsii* (The IVth All-Union Conference on the Kinetics of Heterogeneous Catalytic Reactions: Conference Proceedings), Nauka, Moscow, 1988, p. 80
163. Ya A Dorfman, G S Polimbetova, I M Yukht, et al. *I Vsesoyuznyi Simpozium po Makroskopicheskoi Kinetike i Khimicheskoi Termodinamike: Tezisy Dokladov, Chernogolovka* (The 1st All-Union Symposium on Macroscopic Kinetics and Chemical Thermodynamics: Abstracts of Reports, Chernogolovka), Chernogolovka, 1984, Vol. II, Part 2, p. 90
164. V M Bogdanov, O V Moiseichuk, Yu I Shumyatskii *Zh. Prikl. Khim.*, 1987, **60** 1119
165. U I Yunusov, E A Karpenko, S Zh Suleimenova *Okhrana Vozdushnogo Basseina ot Vrednykh Vybrosov Fosfornykh Proizvodstv* (Protection of Local Air Against the Harmful Waste from Phosphorus Industries), Khimiya, Moscow, 1985, 47 pp
166. Ya A Dorfman, L V Levina, T V Petrova, et al. *Zh. Obshch. Khim.*, 1990, **60** 1275
167. Ya A Dorfman, L V Levina, T V Petrova, et al. *Zh. Obshch. Khim.*, 1990, **60** 840
168. Ya A Dorfman, L V Levina, T V Petrova, et al. *Kinet. Katal.*, 1989, **30** 1487
169. Ya A Dorfman, L V Levina, T V Petrova, et al. *Zh. Obshch. Khim.*, 1989, **59** 1454
170. Ya A Dorfman, L V Levina, E Zh Aibasov, S Tungatorov *Vsesoyuznaya Konferentsiya po Primeneniyu Metallo-kompleksnogo Kataliza v Organicheskom Sinteze: Tezisy Dokladov, Ufa* (All-Union Conference on the Application of Metal Complex Catalysis in Organic Synthesis: Abstracts of Reports, Ufa), Ufa, 1989, p. 100
171. J D Zakumbarova, A B Fasman, N M Popova, et al. *Soviet–Japanese Seminar on Catalysis*, Novosibirsk, 1990, p. 240
172. Ya A Dorfman, L V Levina, E Zh Aibasov, et al. *Zh. Obshch. Khim.*, 1991, **61** 626
173. Ya A Dorfman, L V Levina, G S Polimbetova, et al. *Koord. Khim.*, 1991, **17** 287
174. Ya A Dorfman, L V Levina, O M Pakhorukova *Kinet. Katal.*, 1991, **32** 320
175. E N Tsvetkov, N A Bondarenko, I G Malakhova *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Applications of Organo-Phosphorus Compounds), Nauka, Leningrad, 1987, p. 50
176. E E Nifant'ev, T S Kukhareva *Obzor Monografii i zorov po Khimii Fosfororganicheskikh Soedinenii* (Survey of the Monographs and Reviews on the Chemistry of Organophosphorus Compounds), Nauka, Moscow, 1989, 160 pp