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Structure and Properties of Oxide Halides of Phosphorus and Certain Transition Elements

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Published information is presented on the structure and the properties of phosphoryl compounds and certain others containing oxo-groups. Modern views on the structure of the phosphoryl group are related to the presence of a σ-bond and also to d_π-p_π interaction between the orbitals of the phosphorus and oxygen atoms; this type of interaction is observed also at other bonds involving phosphorus (P-Hal). Compounds containing oxo-groups exhibit donor properties, forming complexes with acceptor molecules. The general properties of donor-acceptor complex compounds are discussed. A list of 196 references is included.

CONTENTS

I. Introduction	485
II. Nature of bonding of atoms in oxide halides of Group III elements	485
III. Donor-acceptor properties of oxide halides in chemical reactions	489
IV. Reactions of phosphoryl chloride with Groups II-V chlorides	490

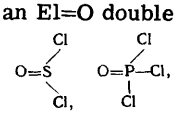
I. INTRODUCTION

Various halides containing an ElO group are of great practical value. They are widely used as non-aqueous solvents[1] and also for the separation of chlorides of different elements[2-5]. Interest is being taken at the present time in the application to laser technology of mixed-solvent solutions based on phosphoryl and other compounds containing ElO groups[6-11]. The structure of such compounds and their complexes involves several problems of theoretical inorganic chemistry, and therefore is of undoubted interest.

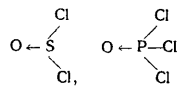
The present paper discusses certain aspects of the structure, chemical activity, and complex-forming power of halides containing an ElO group, attention being paid mainly to the phosphoryl group.

II. NATURE OF BONDING OF ATOMS IN OXIDE HALIDES OF GROUP III ELEMENTS

According to Werner the molecules NOCl, $POCl_3$, $SOCl_2$, $SeOCl_2$, etc. contain an El=O double bond:



According to the Lewis octet theory the bond between the central atom and the oxygen atom was regarded as of donor–acceptor type involving a pair of electrons on the central atom:

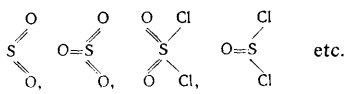


Experimental investigations of the molecular properties supported both views. The measured parachors for several compounds were lower than those calculated on the basis of Werner's formulae†, and compounds containing an El–O [type of] bond (S–O, P–O, P–S) exhibited less tendency to reactions involving addition than might have been expected for compounds containing a double bond. On the other hand, the El–O interatomic distances, the bond energies, and the dipole moments indicated the presence of a double bond[13–17].

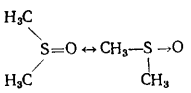
Siebert[13] characterised the ElO(S) bonds by their multiplicity, which he calculated in several oxides and oxide halides of non-metals by means of the rules that he had derived[18]. For sulphur compounds, for example, he obtained the values

SO_2	SO_3	SO_2Cl_2	$SOCl_2$	SO_2F_2	SOF_2
1.96	2.04	2.03	1.87	2.19	2.04

for the multiplicity of the SO bond. This is seen to be close to 2 in all the compounds, from which he concludes that a double bond S=O is present:



In the case of methyl derivatives, e.g. dimethyl sulphoxide, the multiplicity of the SO bond falls to 1.7, which Siebert attributes to an approach towards a donor–acceptor bond:

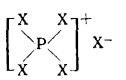


At one time Pauling regarded the resonance of two structures as the reason for the increase in the ElO bond energy‡. For phosphorus compounds the multiplicity of the PO bond is close to 2, and diminishes on passing from fluorides to bromides[20,21]; introduction of a methyl group diminishes the multiplicity considerably:

POF_3	2.34
$POCl_3$	2.09
$POBr_3$	2.02
$PO(CH_3)_3$	1.7

Discussion of the type of bond in ElO(S) groups in terms of its multiplicity is formal in character, and cannot give a complete idea of their structure.

According to modern views the nature of the (Hal)ElO bonds in Hal_3PO molecules is due to hybridisation of the atomic orbitals of the central atom, but the participation of *d*-orbitals of the central atom in bond formation is a matter of controversy[22,23]. Pauling, although the first to suggest the participation of *d*-orbitals in the formation of covalent bonds by elements in the third period, assumed for phosphorus compounds PX_5 the type of structure



in which the *d*-orbitals of phosphorus are not involved in bond formation. In the proposed formula combination of the five X atoms with the phosphorus atom can be effected by 3*s*- and 3*p*-orbitals together with electrostatic attraction between phosphorus and a unit negative charge distributed among the five X atoms. Atoms of elements in the second period—carbon, nitrogen—usually exhibit quadrivalency when they form covalent two-electron bonds. The participation of *d*-orbitals in the bond with elements in the third period may increase the coordination number of the central atom. On the other hand, the difference between the coordination numbers of elements in the second and third periods has been ascribed mainly to steric factors[24], not to the energy difference between the *d*-orbitals of the elements. The structure and the energies of the 3*d*-orbitals of isolated atoms of elements in the third period are such that their participation in bond formation is improbable[25–27].

Table 1. Energy of transition from ground state, eV.

Transition	Al	Si	P	S	Cl
One-electron					
$(s) \rightarrow (d)$	8.47	12.21	17.54	20.72	26.17
$(p) \rightarrow (d)$	3.90	5.51	7.23	7.89	11.07
Two-electron					
$(s)^2 \rightarrow (d)^2$	20.63	28.88	37.93		58.52
$(sp) \rightarrow (d)^2$	14.49	20.34	27.75	32.25	41.25
$(p)^2 \rightarrow (d)^2$		13.99	18.00		26.92

Table 1[28] shows that the $s \rightarrow d$ transition energy is rather lower in elements of the third period than in those of the second period, but is sufficiently high for the *d*-orbitals to take part in bond formation (in transition elements the energy of an $s \rightarrow d$ transition is ~ 8 eV). The radius of the 3*d*-orbitals of the phosphorus atom is 2.43 Å, considerably exceeding the radii of the 3*s*- and 3*p*-orbitals (0.47 and 0.55 Å respectively). The calculated overlap integrals of the *p*-orbitals of the ligands and the *d*-orbitals of an isolated phosphorus (sulphur) atom, e.g. the p_Z–d_{Z^2} overlap integrals, are negative, the *d*-orbitals being "smeared out" too much to form a σ-bond[28]. However the presence of ten or twelve electrons surrounding the central atom in the $POCl_3$, $SOCl_2$, etc. molecules, and the stable five- and six-coordinated compounds obtained with phosphorus, indicate the possible participation of *d*-orbitals of the central atom in the bonds. Additional interaction involving the *d*-orbitals of the central atom might explain also the high ElO, ElHal bond energies, the high vibration frequencies, and the short bond lengths between the central atom and oxygen in compounds of elements in the third period in comparison with those of elements in the second period. Quantum-mechanical calculations[29–34] have shown the possibility that *d*-orbitals of phosphorus and sulphur atoms may take part in forming σ- and π-bonds. The *d*-orbitals of the central atom undergo a considerable change of energy in the ligand field, which facilitates their participation in hybridisation.

The main factors influencing the size and energy of the *d*-orbital—(1) the spin contribution of unshared electrons, (2) the number of *d*-electrons, and (3) the formal charge on the atom—have been distinguished[22,35] according to the mode of excitation. The last factor has the greatest effect, and is explained in terms of formal concepts: electronegative substituents, by drawing electrons away from the central atom, increase its charge, which in turn leads to contraction of the *d*-orbitals.

† Sidgwick[12] showed that the parachor should decrease even with increase in the number of electrons around the atom from 8 to 10 or 12.

‡ The increase in bond energy has been discussed[19] in terms of hybridisation.

The contribution of d-orbitals to bond formation may vary. Cruickshank[36] suggested that they played an equivalent part together with s- and p-orbitals. The possibilities of sp^3d-hybridisation of the phosphorus atom have been discussed[27,37,38], and the energies of other excited states sp^2d^2, p^3d^2 have also been determined. Various energy levels have been calculated by the molecular orbital method for isolated P^0, P^+, and P^- atoms, although it is not possible to extrapolate data for individual atoms to molecules[39]. The sp^3d-hybridisation of a phosphorus atom represents the formation of five equivalent bonds.

The spatial arrangement of the hybrid orbitals may lead to various structures[40], among which a bipyramidial structure is energetically the most favourable. Phosphorus is then bound to oxygen by a σ-bond and a superimposed covalent π-bond resulting from overlapping of one of the five sp^3d-hybrid orbitals of the phosphorus atom and a p-orbital of the oxygen atom.

Molecular orbital calculations for Y_3PO molecules, taking into account the effect of substituents on the phosphorus–oxygen bond and the accompanying change in hybridisation of the phosphorus orbitals, led Wagner[41,42] to regard the σ-bond as of donor–acceptor type P → O. Two π-bonds, formed by $2p_x$- and $2p_y$-orbitals of oxygen and $3d_{xz}$- and $3d_{yz}$-orbitals of phosphorus, are superimposed on the σ-bond. This type of overlap of orbitals can be illustrated by Fig. 1[43,44], which shows the possibility of interaction between two d-orbitals of four-coordinated phosphorus and two p-orbitals of oxygen. If the molecule containing four-coordinated phosphorus is so oriented that the P=O bond lies along the x-axis, $d_\pi - p_\pi$ bonds can be formed by the binding of the phosphoryl oxygen to the phosphorus atom by a σ-bond produced by the overlapping of an sp^3-hybrid orbital of phosphorus with a p_x-orbital of oxygen and two π-bonds formed by $3d_{xy}$- and $3d_{xz}$-orbitals of phosphorus and p_y- and p_z-orbitals of the phosphoryl oxygen.

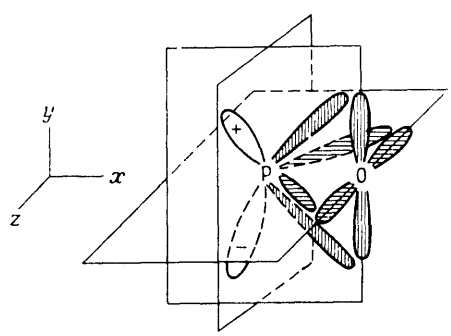


Figure 1. Scheme of $d_\pi - p_\pi$ interaction along the P–O bond.

Considering various types of substituents in the Y_3PO molecule, Wagner showed that the PO bond varies from single in trimethylphosphine oxide to almost triple in phosphoryl fluoride. The positive charge on the phosphorus atom passes through a minimum when the electronegativity of the substituent is 2.7 on Pauling's scale. In the two extreme cases—the most electronegative fluorine and the least electronegative methyl substituent—the charge distribution is

$$\underset{F_3}{-1.131} \equiv \underset{P}{+1.332} \equiv \underset{O}{-0.201} \quad \underset{(CH_3)_3}{+0.102} \equiv \underset{P}{+1.03} - \underset{O}{1.132}$$

This charge distribution shows that the dipole moment changes its direction on passing from phosphoryl fluoride to trimethylphosphine oxide. Fig. 2 illustrates the variation in the dipole moment with the electronegativity of the substituent. When the electronegativity of Y is 3.6, the dipole moment approaches zero§. Wagner's predicted variation in the dipole moment of the phosphorus–oxygen bond with the substituent has been confirmed experimentally[46,47]. It was found that the dipole moment, while depending almost solely on the electronic state of the phosphorus–oxygen (σ,π)-bond, does not vary monotonically on passing from some substituents to others, but passes through a minimum at certain substituent electronegativities. Analogous conclusions were reached from a consideration of the (σ,π)-bond of the sulphur atom in various derivatives[48].

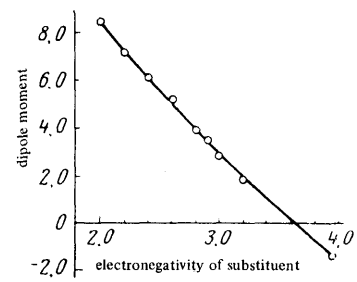


Figure 2. Variation in dipole moment of Y_3PO molecule with electronegativity of substituent Y.

In phosphoryl halides $POHal_3$ the d-orbitals of phosphorus may also interact with orbitals of the halogen atoms[49]: e.g. two $d_\pi - p_\pi$ bonds may be formed by the $d_{x^2-y^2}$ and d_{z^2} orbitals of phosphorus and the p-orbitals of the ligands[50,51]. Table 2 lists dissociation energies and bond multiplicities for several $POHal_3$ compounds[21,52]. The difference in the degree of interaction of the central atom with oxygen and with the halogen is evident. The degree of interaction diminishes in the sequence of substituents F → Br. It is apparent that $d_\pi - p_\pi$ interaction of the substituents has little effect on the P=O bond, since the presence of C_{3v} symmetry in the POX_3 system enables the orbitals of the X atoms to interact with d_π-orbitals of the phosphorus atom orthogonal to the orbitals used in the phosphorus–oxygen bond[44].

The way in which d-orbitals of the central atom are involved in the bonds has not yet been unequivocally settled. The phosphorus–oxygen and sulphur–oxygen bond lengths have been calculated[55] by the molecular orbital method for series of compounds with and without the involvement of

§ A triple phosphorus–oxygen bond has been found for the hypothetical molecule H_3PO calculated by the molecular orbital method, and the d-orbitals of the phosphorus atom are assumed to be involved in the bond[45].

d-orbitals. The results suggest that d-orbitals play a modest part in shortening these bonds, but the problem requires further consideration. The nitrogen–oxygen bond in nitrosyl trifluoride is shorter (1.15 Å) than the calculated value, as with compounds containing a P=O or an S=O bond, although the participation of d-orbitals is still less probable in this case. A possible explanation is the effect of the electronegative fluorine atom on the charge on the nitrogen.

Table 2. Energy of dissociation and multiplicity of bonds in the compounds $POHal_3$.

Hal	E, kcal mole^{-1} P–O	Multiplicity P–O	E, kcal mole^{-1} P–Hal	Multiplicity P–Hal
F	178*	2.47	90	1.35
Cl	161	2.24	61	0.91
Br	151	2.16	55	0.81

* Other numerical values have been given [53,54], but the general trend remains.

The presence of $p\pi-d\pi$ interactions is not indicated unambiguously by the experimental electronic, nuclear magnetic resonance, and nuclear quadrupole resonance spectra of series of compounds [56–59].

Table 3.

Compound	Force const.	Multiplicity	Compound	Force const.	Multiplicity
OPF_3	11.89	2.44	SPF_3	5.21	1.89
$OPCl_3$	10.24	2.15	$SPCl_3$	4.89	1.80
$OPBr_3$	9.74	—	$SPBr_3$	4.69	—
$OP(CH_3)_3$	9.14	1.88	$SP(CH_3)_3$	3.33	1.33

An examination has been made of the influence of the $3d_Z$-orbital component on several properties of sulphur- and phosphorus-containing molecules, including their ionisation potentials, electronic transition energies, dipole moments, and overlap integrals calculated by a semi-empirical method [60]. Introduction of this component only slightly improves the agreement between calculated and experimental values. Further investigation is required on these lines [22,23,27,39,55].

When the oxygen atom in $\rangle P{=}O$ is replaced by a sulphur atom, the multiplicity of the phosphorus–sulphur bond, the force constants, and the corresponding bond energies are smaller than in the original compound. Table 3 lists force constants and bond multiplicities for several compounds [61]. The phosphorus–chlorine bond length increases on passing from phosphoryl to thiophosphoryl chloride [62–64].

The influence of substituents on the P=O bond is probably mainly an inductive effect [65,66]. As mentioned earlier, $d\pi-p\pi$ interaction of the phosphorus atom with a substituent has little effect on the P=O bond. Bell et al. [67] showed that the vibration frequencies of the latter bond in the infrared and the Raman spectra vary linearly with the electronegativity of the other substituents attached to phosphorus.

Some authors regard the vibration frequencies as functions of the Taft σ^*-constants [68,69] characterising the inductive and mesomeric effect of the substituents, and also introduce into the equation constants to represent the electronic shielding of the phosphorus nucleus [70]. The force constants of the P=O bond vary linearly with the calculated π-bond energies [71]; the coefficients in the equation $K = a + bE$ depend on the nature of the substituents.

The integral intensity of the vibrational bands involving the P=O bond depends on the electronic properties of the whole POX_3 molecule, and is 80% determined [72,73] by the product

$$\left(\frac{\partial\mu_{P=O}}{\partial Q}+\frac{\partial\mu_{P-Cl}}{\partial Q}\right)Q$$

where Q is the normal coordinate of the bond and μ the dipole moment of the bond. The non-unique character of the vibrational bands of the PO bond in a series of substituted phosphoryl compounds has also been noted elsewhere [74]. No effect of the nitrogen and sulphur atoms on the vibrational frequencies and force constants of the P=O bonds was apparent in the series of compounds $(RS)_3PO$ and $(R_2N)_3PO$, and the difference found in the π-charge on nitrogen and sulphur atoms (+0.187 and −0.004) [75] was expressed in a corresponding change in the integral intensity of the P=O vibrational bands.

Table 4. Force constants of P–X bonds as function of type of hybridisation of atomic orbitals.

Force constant	pd	p	sp^3	sp^2
K_{P-H}		3.10[a]	3.30[b]	3.59[c]
K_{P-CH_3}		2.77[d]	3.05[e]	—
K_{P-F}	4.52[f]	5.19[g]	6.34[h]	6.38[f]
K_{P-Cl}	1.63[i]	2.36[j]	2.66[k]	2.78[i]
K_{P-Br}		1.84[l]	2.66[m]	
K_{P-OCH_3}		3.37[n]	4.87[o]	

Compounds
[a] PH_3, [b] $BH_3{\cdot}PH_3$, [c] H_2PF_3, [d] $P(CH_3)_3$, [e] $SP(CH_3)_3$, [f] $OP(CH_3)_3$, [g] PF_3, [h] OPF_3, [i] PCl_3, [j] $OPCl_3$, [k] $SPCl_3$, [l] PBr_3, [m] $SPBr_3$, [n] $P(OCH_3)_3$, [o] $OP(OCH_3)_3$.

Examination of the effect of various factors on the force constants of the phosphorus bonds in series of compounds is of interest [61]. Table 4 lists force constants as a function of the type of hybridisation of the orbitals of the central atom. Increase in the s-character of the bond is accompanied by an increase in the force constants. A similar effect is produced by increasing the electronegativity of the substituents and also the charge on the ions.

The above regularities are less clearly exhibited by thiophosphoryl compounds [61,76,77]. In view of the diminished ionic character of the phosphorus–sulphur bond in comparison with the phosphorus–oxygen bond, it may be supposed that the mass of the atoms in the substituents and the force constants of P–X bonds—not the electronegativity—will have the decisive effect on the P–S stretching frequencies. However, Zingaro [78], in calculating the frequencies of the P–S vibrations in thiophosphoryl compounds, attributed the decisive role to the electronegativity of the substituents. These two conclusions on the effect of substituents on the phosphorus–sulphur bond are not mutually inconsistent, as might appear at first glance.

It has been proposed[79] to separate thiophosphoryl compounds into different groups containing strongly electronegative and less electronegative substituents. The regular variation in the force constant of the P–S bond within the groups is explained by mechanical interaction with P–X stretching vibrations, in agreement with conclusions reached by other workers[76]. When, however, compounds having substituents differing strongly in electronegativity are compared, this difference must be regarded as the cause of the variation in the phosphorus–sulphur vibration, in agreement with Zingaro's conclusions. Thus, similarly to phosphoryl molecules, the position of the phosphorus–sulphur band in thiophosphoryl compounds is determined by the immediate environment of the phosphorus atom[80-83].

The nuclear magnetic resonance spectra of phosphoryl compounds do not enable a similar relation to be established between the chemical shifts and the electronegativities of substituents adjacent to phosphorus. Electronic shielding of the nucleus of the central atom by substituents adjacent to the phosphoryl P–O and thiophosphoryl P–S groups increases in the sequence

$$Se < S < C_{aliph} < C_{arom} \approx P < N \approx Cl < H < O < F$$

the more electronegative the substituent element, the greater the shielding at the phosphorus atom. An explanation is provided by interaction between the substituent and the P=O or P=S electron cloud: the more electronegative the substituent, the more strongly it "draws out" the electrons of the π-bond of this group and the greater becomes the shielding of the phosphorus.

In sum the structure of molecules of the type XYZElO, containing oxo-groups, depends on the presence in the El–O group of coordinate bonds superimposed on and opposite to the σ-bond. sp^3d-Hybridisation is improbable. The $d_\pi - p_\pi$ interaction of phosphorus and halogen atoms is possible in the Hal_3PO molecule.

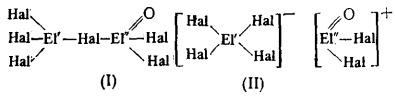
The geometrical configuration of the molecules corresponds to a distorted tetrahedron. For $POCl_3$ the P–Cl and P–O distances are 1.99 ± 0.02 and 1.45 ± 0.03 Å respectively, and the Cl–P–Cl angle is 103.6 ± 2°.[63]

III. DONOR–ACCEPTOR PROPERTIES OF OXIDE HALIDES IN CHEMICAL REACTIONS

Structural features of molecules containing oxo-groups govern their behaviour towards other compounds. The reactivity of such molecules, which is apparent in many reactions and has been discussed in detail, e.g. for organophosphorus compounds[40,44], is determined by the properties of the molecular and atomic non-bonding orbitals. Nucleophilic substitution at the phosphorus atom involves rupture of that one of the four phosphorus bonds that has the lowest electron density. Electrophilic reagents interact with the phosphoryl oxygen atom, which has the highest ME1 electrophilic superdelocalisability[84]. In the molecules XYZElO [or S] the O(S) atom and also the atoms X, Y, Z possess not only molecular orbitals but also non-bonding atomic orbitals with electron pairs, which may take part in the formation of bonds[85,86]. The possibility of their involvement in interaction with acceptor molecules depends on the factors discussed above, the interaction of hybrid molecular and atomic orbitals determining the donor properties of these molecules[87,88].

In view of the properties of the atomic orbitals of oxygen and chlorine (or other substituent) in molecules, we can in general imagine two mechanisms of interaction of molecules containing PO, SO, SeO, PS groups with various acceptors (e.g. chlorides of Groups III–V elements).

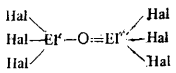
1. The donor–acceptor bond is formed by lone pairs of the halogen atom[89-96]:



(I) (II)

These structures differ in the share of the halogen Hal in the donor–acceptor bond. Case (II) involves formation of a tetrahedral ion of the type $ElHal_4^-$, which is stable with several metal chlorides.

2. The donor is the oxo-oxygen[97-108]¶:



Interaction occurs considerably more rarely according to scheme *1*, and is governed to a greater extent by the properties of the acceptor—the second component of the reaction—which is capable of forming a complex anion. The actual donor–acceptor interaction (scheme *2*) is the subject of discussion.

Substituents in XYZElO molecules, by exerting an inductive effect on the El–O bond, change its donor ability. For example, the donor power of the oxygen atom is weaker in oxide chlorides than in organic phosphoryl compounds, owing to the greater electronegativity of chlorine than of organic radicals and the stronger inductive effect of chlorine on the P=O bond. By "drawing out" the electrons from oxygen, chlorine lowers its capacity for participation in a donor–acceptor bond. The donor capacity of the compounds increases in the sequence

$$POF_3 < POCl_3 < POBr_3 < PO(CH_3)_3.$$

The electronegativity of the various organic substituents has the same effect[111].

The influence of the central atom on the properties of XYZElO molecules might be connected directly with the possibility and degree of participation of *d*-orbitals in the ElO bond: increased participation of those of the central atom should diminish the donor properties of the molecule. Phosphoryl chloride possesses donor properties; oxygen in the vanadyl(V) chloride molecule does not; while the molecules of transition elements—$TiOCl_2$, $MoOCl_2$, etc.—possess well defined acceptor properties[112,113].

On the other hand, the compound $(CH_3)_3NO$ is a poorer donor than is $(CH_3)_3PO$: the most convincing explanation here, as in the analogous case of bond shortening in the compound F_3NO, is based on the formal charge on the central atom[114].

Investigation of the complexing power of phosphoryl[89], seleninyl[115], acetyl[116-120], and thionyl[121] chlorides has made it possible to compare the donor properties of these molecules towards such acceptors as arsenic trichloride, tin tetrachloride, and titanium tetrachloride[97]. The donor properties of these molecules are found to decrease in the sequence

$$POCl_3 > SeOCl_2 > CH_3COCl > SOCl_2.$$

This donor sequence is consistent with the electronegativities of the central atoms in these molecules. It may

¶ Electrostatic interaction may be possible[110] as a consequence of the highly polar character of the phosphoryl P=O group.

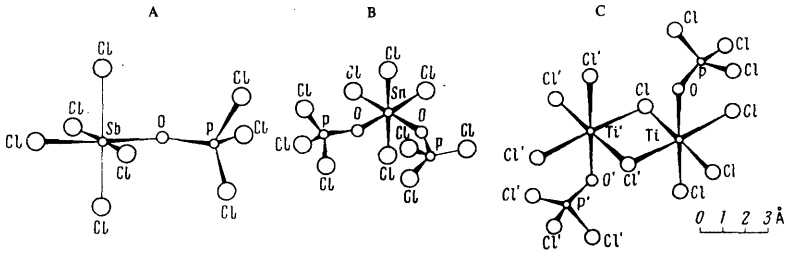


Figure 3. Structure of the compounds $SbCl_5.POCl_3$, $SnCl_4.2POCl_3$, and $(TiCl_4.POCl_3)_2$.

be supposed to a first approximation that the oxygen atom will have its maximum charge when the electronegativity of the central atom is least. The electronegativities of phosphorus, sulphur, selenium, and carbon are respectively 2.1, 2.4, 2.5, and 2.5. Increase in electronegativity increases the El–O bond order, by diminishing the donor power of the oxygen.

In view of the above mentioned inductive effect of substituents on the central atom in XYZElO(S) molecules and the appearance of a positive charge on the atom, such molecules can be assumed to possess acceptor properties. Indeed several molecules—those possessing the weakest donor properties—develop acceptor properties [97]. In this connection it is interesting that compounds are formed in mixtures of seleninyl chloride with carbon tetrachloride and of acetyl and thionyl chlorides with silicon tetrachloride, where these workers consider that the oxide chlorides are acting as acceptors, and the tetrachlorides in the uncharacteristic role of donors†. The investigation of binary mixtures with pyridine, which develops clearly defined donor properties, has established the presence of compounds when the second component of the mixture is seleninyl, acetyl, or thionyl chloride, etc.

The above considerations on the donor power of various oxo-compounds are based on experimental investigation of the complex compounds formed in mixtures and are fully valid only on the assumption of bond formation in them through oxygen.

A diminution in donor power is observed on passing from phosphoryl to thiophosphoryl chloride: thus mixtures of phosphoryl chloride with zirconium tetrachloride and niobium pentachloride are characterised by the formation of complex compounds [124–128]; no compounds are formed in the corresponding mixtures with thiophosphoryl chloride [129–131], the donor properties being determined in this case by the atomic orbitals of the sulphur atom.

IV. REACTIONS OF PHOSPHORYL CHLORIDE WITH GROUPS II–V CHLORIDES

A characteristic feature of molecules containing an oxo-group is the ability to react with valency-unsaturated chlorides of Groups III–V elements, their derivatives, and also halides of bivalent metals [132–134]. Examination of the equilibrium diagrams for systems formed by phosphoryl chloride with the chlorides $ElCl_3$ ($ElCl_4$, $ElCl_5$) by thermal analysis has established the presence of complex compounds, usually having the 1 : 1 composition, more rarely 1 : 2 and 2 : 1. [135–151] It is interesting that analogous compounds are obtained in the systems formed by two compounds containing oxo-groups—by phosphoryl chloride with molybdyl, tungstyl [112], or titanyl [113] chloride.

The resulting complexes are easily hydrolysed and are decomposed by alcohol. The melting point does not usually exceed 200°C. They are stable compounds, which can be isolated in the pure state; they dissolve in carbon tetrachloride and in nitrobenzene, while being less soluble in benzene. Dissolution in nitrobenzene is accompanied only by slight dissociation, and their stability in solution increases in the sequence

$$SbCl_5 \cdot POCl_3 < NbCl_5 \cdot POCl_3 < TaCl_5 \cdot POCl_3 < AlCl_3 \cdot POCl_3.$$

Coordination with oxygen has been found in several compounds of elements in Groups IV and V of the Periodic System [107,152–162], but the type of coordination is a matter of controversy for some double compounds with chlorides of Group III elements—boron, aluminium, gallium—and iron [94–96,104].

The main conclusions concerning the structure of these compounds were reached from a study of their infrared spectra. A shift in electron density from the El=O bond to M (scheme *2* in Section III) may be imagined to lead to an increase in the electronegativity of the phosphorus atom, influencing the displacement of electron density along the El–Cl bond: this is accompanied in the infrared spectrum by a fall in the vibrational frequency of the El=O bond and a rise in the El–Cl frequency. The newly formed M–O bond does not usually appear in the spectrum, evidently because of its low electron density [102]. On the other hand, formation of an El–Cl bond should lead to a slight shift in the El=O vibrational absorption band, but to a decrease in the El–Cl vibration frequency, as was established from investigation of complexes of nitrosyl halides [163–165]. The difficulties arising in recording the spectra of these hydrolysable substances prevent us from drawing unambiguous conclusions from the results.

X-Ray results obtained for the compounds $SbCl_5.POCl_3$, [156] $SnCl_4.2POCl_3$, [157] and $TiCl_4.POCl_3$ [158] indicate unequivocally the presence of coordination with oxygen. Fig. 3 shows the arrangement of the atoms in these compounds. The interatomic distances of the M–O donor–acceptor bond are (in Å)—TiO 2.10, SbO 2.18, $SnO_{(1)}$ 2.25, and $SnO_{(2)}$ 2.30 (for the 1 : 2 complex)—formation of an M ← O bond having hardly any effect on the P–O length, which is 1.46 Å for the compound with titanium tetrachloride, 1.46 Å for $SbCl_5.POCl_3$, and 1.41 and 1.49 Å for the tin complex (P–O bond length 1.45 Å for the $POCl_3$ molecule), and slightly increasing the ClPCl angle (by 3–4°)‡.

† The donor properties of these molecules have been noted by other workers [122,123].

‡ The mean phosphorus–oxygen distance in $POCl_3$ in the mixed complex $Mg(PO_2Cl_2)(POCl_3)$ is 1.42 Å, the molecules being slightly deformed [166].

The nuclear magnetic resonance spectra of the complex $TiCl_4.POCl_3$ (^{31}P) indicate an increase in the chemical shift δ from 2.2×10^{-6} for phosphoryl chloride to 16.6×10^{-6}, which is evidence of a decrease in the degree of shielding of the phosphorus nucleus in the complex and a diminution in the degree of π-overlap along the P=O bond[107].

Study of the chlorine-35 nuclear quadrupole resonance spectra of the complex compounds formed by antimony, iron, and titanium chlorides[167] enabled the type of chemical bond to be ascertained by comparing the state of the PCl_3 groups in the free phosphoryl chloride molecule and in the complex. The shift in the spectral bands was estimated by means of the formula

$$\Delta\rho = -\Delta I - \Delta\pi - \Delta(\alpha\sigma)$$

where I is the degree of ionic character of the bond, π is the degree of π-character, and α and σ are the degrees of s- and d-hybridisation of the bond. The state of the PCl_3 group is almost the same in the phosphoryl chloride molecule and in the complex, so that the frequency shifts obtained can be ascribed to a change ΔI in the ionic character of the bond. The frequency shifts found experimentally in the spectra of the complexes indicated that ΔI, representing the displacement of the electronic charge from chlorine to phosphorus on formation of the complex, varies in the sequence

$$SbCl_5 > FeCl_3 > SnCl_4 > TiCl_4.$$

The donor–acceptor bond M←O is stable: the compounds exist in the melt and in the vapour state. The calculated heats of dissolution of the complexes (ΔH, kcal mole^{-1})—$ZrCl_4.POCl_3$ 24.3,[131] $TiCl_4.POCl_3$ 23.3,[168] $FeCl_3.POCl_3$ 18.2,[169] $BCl_3.POCl_3$ 17.9,[151] $AlCl_3.POCl_3$ 28.4,[170] and $GaCl_3.POCl_3$ 22.6[171,172]—provide an energetic characteristic of the donor–acceptor bond.

The formation of a donor–acceptor bond can be characterised directly by a calorimetric study of reactions between donors and acceptors[111,171]. Heats of dissolution of acceptor chlorides in phosphoryl chloride have been measured according to the scheme

$$MCl_n + POCl_3 = Cl_nMOPCl_{3\,soln} \quad \Delta H_1\ n = 3\text{—}5$$
$$Cl_nMOPCl_{3\,solid} + POCl_3 = Cl_nMOPCl_{3\,soln} \quad \Delta H_2\ n = 3\text{—}5$$

The quantity $\Delta H_3 = \Delta H_1 - \Delta H_2$ is taken to be a direct measure of the donor-acceptor interaction:

$$MCl_{n\,solid\ soln} + POCl_{3\ soln} = Cl_nMOPCl_{3\,solid} \Delta H_3\ n = 3\text{—}5$$

Table 5 lists these thermal effects for a series of chlorides, among which those of Group III elements have the smallest values of ΔH_3. The nature of the coordination in them is a matter of controversy, and the general trend is due to an increase in the electronegativity of the acceptor metal atom. However, calorimetric results are only relative in character[111], since several secondary factors, e.g. changes in the structure of acceptor and donor, etc., are superimposed on the donor–acceptor interaction. Transfer of these compounds to the liquid phase involves their ionisation.

The Raman spectra of the complexes—$SnCl_4.2POCl_3$, $TiCl_4.2POCl_3$, and $SbCl_3.POCl_3$—in solution[102] indicate strong intermolecular interaction between phosphoryl chloride and the metal halide. It is usually difficult to isolate the solid adducts from solutions because of their tendency to supercooling[173] or because of the slowness of reaction between the components[89]. The composition of the solutions is complicated, and complex ions are present[174–179].

The ionisation of the complex compounds in solutions usually involves ionisation of the M–Hal bond with preservation of the MO...P donor–acceptor bond. The general scheme of ionisation is[180]

$$2\,DACl_n \rightleftarrows [D_2ACl_{n-1}]^+ + [ACl_{n+1}]^-$$

With variation in the donors the general tendency is for the degree of ionisation of the compounds in solution to increase with the donor strength[181–183].

Table 5. Heats of dissolution of acceptor chloride (ΔH_1) and of solvate (ΔH_2) in phosphoryl chloride and heats of donor–acceptor interaction [ΔH_3].

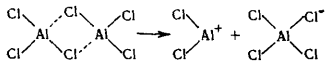
Acceptor chloride	$-\Delta H_1$	Solvate	$-\Delta H_2$	$-\Delta H_3$
$SbCl_5$	17.9	$Cl_5SbOPCl_3$	0.8	17.1
$TiCl_4$	20.7	$Cl_4Ti(OPCl_3)_2$	−1.7	22.4
		$Cl_4TiOPCl_3$	−2.7	
$SnCl_4$	20.2	$Cl_4Sn(OPCl_3)_2$	−2.1	22.3
$FeCl_3$	15.0	$Cl_3FeOPCl_3$	1.7	13.3
BCl_3	9.4	Cl_3BOPCl_3	1.5	7.9
$AlCl_3$	16.6	$Cl_3AlOPCl_3$	—	—
$GaCl_3$	11.0	$Cl_3GaOPCl_3$	0.8	10.2

Solutions of mixtures of aluminium, iron, titanium, etc. chlorides contain both cationic and anionic forms. Analysis of conductometric titration and electrical conductivity data for the solutions indicates that interaction in solution can be represented by the equation[173]

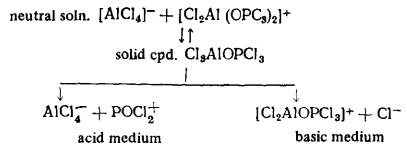
$$\text{Polymer} \rightleftarrows \text{Anion} + POCl_2^+ \rightleftarrows FeCl_4^- + POCl_2^+$$

which involves coordination with oxygen. The existence of iron in both cationic and anionic forms has been confirmed by the electrolysis of solutions of complexes of phosphoryl and thiophosphoryl chlorides with iron(III) chloride[184].

The structure of solutions of mixtures of aluminium and phosphoryl chlorides was examined in the light of possible simultaneous coordination with oxygen and chlorine[173,185]. Formation of such a complex can be pictured from a consideration of the breakdown of the dimer Al_2Cl_6:



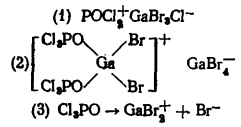
and the cation $AlCl_2^+$ combines with a donor molecule. The structure of a solution of aluminium and phosphoryl chlorides is then represented as



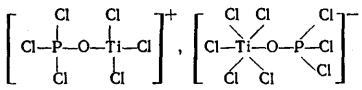
The dual character of oxygen and chlorine coordination in such solutions is supported by other work[186–188]: both a solvated O-coordinated complex and the ion $AlCl_4^-$ are present, the latter being formed in two ways:

$$1)\ AlCl_3 + POCl_3 \rightarrow AlCl_4^- + POCl_2^+$$
$$2)\ 4AlCl_3 + 6\,POCl_3 \rightarrow 3\,AlCl_4^- + [Al(POCl_3)_6]^{3+}$$

The investigation of mixed compounds in solutions of $GaBr_3.POCl_3$ suggests three possible ionisation paths with formation of the products[189]



Structure (3) is regarded[189] as the most probable; the P–O→M bond is preserved on dissociation, as in the above cases. This bond is stable also when the complex $TiCl_4.POCl_3$ dissociates in solution, and the ions



are assumed to be present[179]. A study of solutions of various donor–acceptor pairs ($GeCl_4$–acceptor) in phosphoryl chloride has established the presence of associated complexes containing the anion $[GeCl_6]^{2-}$.[190]

Binary mixtures from which individual complex compounds do not separate are of great interest. Such binary mixtures exhibit considerable departures from ideality. A positive deviation from Raoult's laws is characteristic of solutions of the mixtures $GeCl_4$–$POCl_3$, $SiCl_4$–$POCl_3$,[191,192] and $SeOCl_2$–$AsCl_3$,[193] the degree of departure from the laws of ideal solutions being proportional to the donor power of the donor (and the strength of the acceptor). Thus the $VOCl_3$–$TiCl_4$ system[194,195] can be regarded as ideal, which corresponds to the decrease in donor power in the sequence—$POCl_3 > SeOCl_2 > VOCl_3$.

We have already noted a decrease in the donor power of the P–S bond on passing from phosphoryl to thiophosphoryl chloride, but intermolecular interaction occurs between $PSCl_3$ and $SiCl_4$ in solution, producing a departure from ideal behaviour, though smaller than in the $POCl_3$–$SiCl_4$ system[196].

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