Translated from *Uspekhi Khimii*, 50, 1601-1626 (1981) U.D.C. 547.26.119:541.6:541.57

The Basicity and Nucleophilicity of Arsenyl Compounds†

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Data are presented on the nature of the As=O bond in compounds of tetracoordinate arsenic. Problems associated with the manifestation of the electron-donating properties of arsenyl compounds, particularly their basicity in various media as well as their proton-accepting capacity in the formation of hydrogen-bonded complexes, are examined. The electron-donating and proton-accepting capacities of compounds of the type R_nEO, where E=N, P, As, Sb, S, Se, or Te, are compared. The reactions of arsenyl compounds with a wide variety of electrophiles as well as other reactions involving the arsenyl group are discussed. The bibliography includes 172 references.

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I. INTRODUCTION

A large amount of scattered data have now accumulated on the physicochemical and chemical properties of tetracoordinate arsenic compounds containing the arsenyl group. There are no reviews wholly devoted to this problem, but compounds containing the arsenyl group have been mentioned in monographs[1-4], reviews[5-18], and dissertations[19,20].

Substances containing the As=O bond constitute one of the most numerous groups of organoarsenic compounds, which play an important role both in laboratory practice and in certain branches of the economy (for example, as extractants in hydrometallurgy, medicinal preparations, herbicides, etc., [21,22]). Furthermore, the characterisation of the structure and properties of arsenyl compounds makes a definite contribution to the understanding of the structure and reactivity of compounds containing the E=O bonds (E=C, Si, P, Se, Te, etc.).

The aim of the present review is to survey the literature data, mainly for the last ten years, concerning the nature of the As=O bond as well as the basicity and nucleophilic reactivity of compounds of tetracoordinate arsenic. The nucleophilic properties of these compounds as well as their basicity, which, according to Edwards and Pearson[23], is a special case of the manifestation of nucleophilic reactivity, are determined by the presence of the arsenyl group. The review does not deal with methods for the synthesis arsenyl compounds, because these have been published in monographs[1-4] or, with their complex formation reactions with various metal salts, since the literature on this problem is extensive and its survey should be the subject of a special review.

Table 1. Certain physical characteristics of the As=O bond.

Type of compound	Compound	r (As=O) (r (As–O)), Å	$\nu_{As=O}$, cm^{-1}	$k_{As=O}$, mdyn Å^{-1}	Bond order	μ, D	$\mu_{As=O}$, D
Tertiary arsine oxides	Me_3AsO	1.65 [31]	903 [35]	7.24 [24]	1.50 [30]	—	—
ditto	Me_3AsO	1.62 [30]	—	10.30 [36]	1.47 [20]	5.12 [39]	5.20 [20]
»	Ph_3AsO	1.66[a] [32]	880 [1]	5.82 [38,30]	—	5.53 [40]	5.27 [20]
»	Ph_3AsO	1.64 [33]	885 [29]	6.01 [20]	—	—	5.84 [40]
Arsinic acids	$Me_2As(O)OH$	1.61[b] (1.63) [34]	869 [31]	5.77 [31]	1.43 [31]	—	—
Arsonic acids	$MeAs(O)(OH)_2$	1.65[f](1.75) [34]	913 [31]	6.39 [31]	1.54 [31]	—	—
Arsinate esters	$Me_2As(O)OMe$	1.64[c] (1.78) [24]	929 [24]	6.51 [24] 6.71 [20]	1.61 [20]	4.00[d] [20]	3.80[d] [20]
Arsonate esters	$MeAs(O)(OMe)_2$	1.62[c] (1.78) [24]	954 [24]	6.91 [24] 7.01 [20]	1.67 [20]	2.88 [20]	3.20 [26]
Arsonates	$(MeO)_3AsO$	1.61[c] (1.78) [24]	975 [24] 976 [36,37]	7.38 [20] 7.24 [24] 12.00 [36]	1.74 [20]	3.08[e] [20]	2,45 [26,20]

Remarks: *a*) monohydrate; *b*) the bond lengths r(As=O) and r(As–O) may become equalised as a result of the involvement of the oxygen of the arsenyl bond in a hydrogen bond[34]; *c*) calculated values; *d*) for $Bu_2As(O)OBu$; *e*) for $(EtO)_3AsO$; *f*) for $PhAs(O)(OH)_2$.

Note. Here and in the other tables the numbers in square brackets denote references (Ed.of Translation).

†By analogy with the phosphoryl bond P=O, the term arsenyl bond for As=O is more useful than another term sometimes encountered in the literature.

II. THE NATURE OF THE ARSENYL BOND

The nature of the arsenyl bond has been discussed in numerous studies[19,20,24-30]. All the investigators have concluded that the arsenyl bond is complex and differs from covalent, single, and double bonds and at the same time is not a purely semipolar bond. Certain physical characteristics of the arsenyl bond are listed in Table 1.

Comparison of the As=O and As–O bond lengths shows that the difference between them (up to 0.1 Å) is much smaller than the difference between the sums of the radii of As and O atoms involved in single and double bonds (0.17 Å).[34] Calculation of the lengths of formally double and single bonds, r(As=O) and r(As–O), from the Schomaker-Stevenson formula yields 1.58 and 1.74 Å respectively[29]. Table 1 shows that the experimental value of r(As=O) differs from the above values. Unfortunately the experimental values of r(As=O) refer to the arsenyl group whose oxygen atom is involved in a hydrogen bond.

It has proved convenient to investigate arsenyl compounds by vibrational spectroscopic methods, particularly by infrared spectroscopy[20,24,29,30,35,36,37,41-50]. It has been established that the vibration which is characteristic not only as regards frequency but also as regards mode, corresponds to the arsenyl group in the infrared spectrum. The As=O stretching vibration makes a contribution greater than 95% to the band assigned to the vibration of this bond, while in the case of the As–O bond there is no rigorously characteristic vibration[20,24,36]. Calculations of the stretching vibration frequencies ν(As–O) and ν(As=O) yielded 670 and 1010 cm^{-1}.[29] The calculated and experimental data for the arsenic–oxygen single bond are similar; ν(As=O) is active in the range 600–748 cm^{-1}.[29,50]. The regions where ν(As=O) is active for different derivatives of tetracoordinate arsenic are given in Table 2. Evidently ν(As=O) is active in the range 845–980 cm^{-1} and the experimental values thus differ from the values calculated for the double bond. The influence of substituents on the spectral characteristics of the As=O bond are as a rule additive, as for P=O.[44] A linear relation has been discovered between ν(As=O) and the sum of the constants χ of the substituents at the arsenic atom[29]: $\nu(As=O) = 720 + 30\Sigma\chi$, where χ are the substituent constants (the "group electronegativities" of the substituents derived for phosphoryl compounds). There is a similar relation also for the P=O bond[64]: $\nu(P=O) = 930 + 40\Sigma\chi$.

Such additivity shows that the phosphoryl and arsenyl groups are not directly involved in the resonance interaction with the substituents at the phosphorus and arsenic atoms, which does not, however, rule out the probability of a specific interaction of certain substituents with phosphorus and arsenic atoms[44]. Thus, for "narrow" series, for example, for *para*-substituted phenyl phosphonates and dialkylarylarsine oxides, p-$XC_6H_4P(O)(OEt)_2$ and p-XC_6H_4.$As(O)Et_2$, a linear relation has been found between ν(P=O) and ν(As=O), on the one hand, and the Hammett constants for *para*-substituents, on the other[42]: $\nu(As=O) = 904 + 5\sigma$, $r = 0.98$; $\nu(P=O) = 1260 + 9\sigma$, $r = 0.92$. Since the Hammett constants include a resonance component, the existence of such relations can be treated as evidence for the conjugation of the substituents with the phosphorus and arsenic atoms. Shagidullin[42,44] arrived at the same conclusion in the analysis of ultraviolet spectroscopic data. Analysis of the M=X vibrational frequencies in compounds of the type $R_3M=X$, where M=P, As, or Sb, X=O, S, Se, or Te, and R are alkyl groups, showed[35], that, for identical R, the frequency ν(M=X) depends on the mass of the molecule and the electronegativities of the M and X atoms:

$$\nu_{M=X} = k\left[\frac{\Sigma M}{(m_M\, m_X)}\right]^{1/2} E_M E_X,$$

where M is the mass of the molecule, m the mass of the given atom, and E the electronegativity of the atom.

The differences between the stretching vibration frequencies ν(As=O) in the spectra of various compounds of tetracoordinate arsenic, the differences between the force constants of the As=O bond, and calculations of the order of this bond based on infrared spectroscopic data (Tables 1 and 2) showed, that, depending on the environment of the arsenic atom, the bond multiplicity N varies from 1.4 to approximately 1.8 $N \cong 1.5$ for arsine oxides, $k_{P=O} = 8.25$ and $N \cong 1.9$ for the oxide Me_3PO, and $k_{N\to O} = 3.90$ and $N = 0.65$ for Me_3NO.[30] Many investigators explain such differences in the multiplicities of the NO, PO, and AsO bonds on the basis of the concept of vacant d orbitals[19,20,30,55,56]. Although the NO bond in amine oxides can be regarded as the semipolar $(CH_3)_3\overset{+}{N}-O^-$ linkage, nevertheless calculations of the electronic structures of the compounds X_3NO have shown that there is some displacement of the electrons of the oxygen atom to the nitrogen atom: $p_\pi(O) \to p_\pi(N)$.[56] In phosphorus and arsenic compounds there is a possibility of p_π–d_π interaction between the vacant

Table 2. The regions where the ν(As=O) stretching vibrations are active in the infrared spectra of compounds of tetracoordinate arsenic.

Compound	R_3AsO_H ‖ O	$RAs(OH)_2$ ‖ O	R_3AsO	R_3AsOR' ‖ O	$RAs(OR')(NR''_2)$ ‖ O	$RAs(OR')_2$ ‖ O	$(RO)_2AsNR'_2$ ‖ O	$(RO)_3AsO$
$\nu_{As=O}$, cm^{-1}	870 [22]	845–940 [31,51]	880–910 [35,41]	920–930 [48,49]	940–950 [52]	950–960 [29,43]	940–960 [53]	955–978 [24,50]

2*p* orbitals of oxygen and the corresponding 3*d* and 4*d* orbitals of the heteroatoms, which leads to an increase of the multiplicity of the phosphoryl and arsenyl bonds. Since $2p_\pi-3d_\pi$ interaction is energetically more favourable than the $2p_\pi-4d_\pi$ interaction, the above interaction plays a more important role in the phosphorus compounds and leads to a greater increase in the multiplicity of the P=O bond.

This situation has also been confirmed by the dissociation energies of the E=O bonds. The dissociation energy of the arsenyl bond has been determined from thermochemical data for the oxides As_4O_{10} [57] and Ph_3AsO.[58] For comparison, Table 3 presents the dissociation energies of the element–oxygen bonds. It is seen from these data that the dissociation energy of the phosphoryl bond is much higher than for other E=O bonds (cf. also the dissociation energies of the N→O and P=O bonds in F_3NO and F_3PO, which are 410 and 540 kJ mol^{-1} respectively[69]). The difference between the dissociation energies of single element–oxygen bonds is much smaller. If the difference between the dissociation energies of single and double bonds is assumed to be, after Mitchell[55], the contribution of the π-component to the formation of the E=O bond, then, according to the data in Table 3, this contribution is 217–301 kJ mol^{-1} (159 kJ mol^{-1} according to Mitchell[55]) for phosphorus and 88–142 kJ mol^{-1} for arsenic. In the carbonyl group the contribution of the π-component is much greater, amounting to 335–377 kJ mol^{-1}, which can be explained by certain factors, including the shorter length of the CO bond and the more effective $p_\pi-p_\pi$ overlap[55].

Table 3. The element–oxygen bond dissociation energies.

Compound	Bond	Bond energy, kJ mol^{-1}	Compound	Bond	Bond energy, kJ mol^{-1}	Compound	Bond	Bond energy, kJ mol^{-1}
E_4O_6 [57]	P–O	335	E_4O_{10} [57]	P=O	653	Ph_3EO [58]	P=O	552
»	As–O	301	»	As=O	389	»	As=O	443
»	Sb–O	297	»	Sb=O	399	»	Sb=O	439

Measurements of the dipole moments of compounds of tetracoordinate arsenic and calculations of the dipole moments of the As=O bond (see Table 1) indicate a high polarity of this bond. The relative polarity of the As=O bond in tertiary arsine oxides is higher than that of the As=S bond in the analogous sulphides, which can be accounted for by two factors: the stronger $p_\pi-d_\pi$ interaction between the sulphur and arsenic atoms and the smaller charge separation in the σ-bond as a consequence of the lower electronegativity of the sulphur atom[59].

Comparison of the dipole moments of the arsenyl and phosphoryl bonds (Tables 4 and 1) shows that higher values are characteristic of the As=O bond in the analogous compounds and that the difference Δμ increases with the number of electronegative substituents linked to the heteroatom.

The influence of the arsenyl group is reflected in the ^{1}H NMR spectra by a downfield shift of the proton signals of the substituents linked to the arsenic atom[20,25,26,62]. An analogous effect has also been observed for substituents linked to the phosphoryl group[63]. The arsenyl bond exerts a deshielding influence on both methyl and methylene protons (a displacement of the signals by 0.55–0.75 p.p.m.) and on phenyl protons (a displacement by approximately 0.35 p.p.m.). The regions where the proton-containing groups linked to the heteroatom in the tervalent state are manifested correspond to the electronegativities of the heteroatoms of[20] and are similar for arsenic and phosphorus compounds (Table 5). An increase of coordination number from three to four causes an appreciable alteration of the chemical shifts (Δδ, Table 5) for arsenic and phosphorus compounds and, as for the dipole moments (Δμ, Table 4), the difference increases with increase of the number of electronegative substituents (from 0.13 to 0.64 p.p.m.).

Table 4. Comparison of the dipole moments of the phosphoryl and arsenyl bonds: $\Delta\mu = \mu_{As=O} - \mu_{P=O}$.

Compound	$\mu_{P=O}$, D		Δμ, D
Me_3EO	4.3	[60,61]	0.9
$R_2(RO)EO$	1.6	[61]	2.2
$(RO)_3EO$	0.2	[61]	2.3

The increase can be accounted for in terms of the increasing role of $p_\pi-d_\pi$ interaction for phosphorus compounds with increase of the number of electronegative substituents at the phosphorus atom. It is known that, with increase of the positive charge on the atom (P or S), its 3*d* orbitals contract and favourable conditions are created for the overlap with the 2*p* orbitals of oxygen[64,65] (an increase in the multiplicity of the phosphoryl bond leads to a decrease of the dipole moment and of electron-attracting character in the bond to proton-containing substituents).

Table 5. The chemical shifts of the proton-containing groups linked to heteroatoms[20].

Compound	δ_{E-Me} (δ_{E-CH_2}), p.p.m.	Δδ*, p.p.m.	Compound	δ_{E-Me} (δ_{E-CH_2}), p.p.m.	Δδ*, p.p.m.
Me_3As	0.94	—	Me_3NO	3.32	−1.63
Me_3P	0.98	−0.04	Et_3AsO	1.31 (2.01)	—
Me_3N	2.1	−1.06	Et_3PO	1.16 (1.71)	—
$Me_2(MeO)As$	1.20	—	Et_3NO	1.31 (3.24)	—
$Me_2(MeO)P$	1.23	−0.03	$Me_2(MeO)AsO$	1.77	—
$Me(MeO)_2As$	1.19	—	$Me_2(MeO)PO$	1.40	0.37
$Me(MeO)_2P$	1.16	0.03	$Me(MeO)_2AsO$	2.00	—
Me_3AsO	1.69	—	$Me(MeO)_2PO$	1.36	0.64
Me_3PO	1.56	0.13			

*$\Delta\delta = \delta_{As-Me} - \delta_{E-Me}$.

If $\Delta'\delta = \delta_{OEMe} - \delta_{EMe}$ is adopted as characteristic of the change in the charge on the heteroatom, then the charge for different E varies in the sequence N > As > P ($\Delta'\delta$ = 1.2, 0.75, and 0.58 p.p.m. respectively).

X-Ray electronic spectroscopy appears to be extremely promising for the estimation of effective atomic charges in compounds and of the donor-accepter capacity of the ligands[66]. X-Ray spectroscopic methods have been used to investigate the $R_2S-R_2SO-R_2SO_2$ and $R_3NO-R_3PO-R_3AsO$ series[67,68]. X-Ray emission spectra of the sulphur atoms in Me_2SO and Me_2S indicate partial population of the 3*d*

orbital of the sulphur atom in the oxide as a result of $p_\pi-d_\pi$ interaction. The X-ray spectra of the oxygen in R_3EO (E = N, P, or As) also reveal $p_\pi-d_\pi$ interaction in R_3PO. The available data for R_3NO and R_3AsO are insufficient to rule out completely the occurrence of π-bonding in these compounds, but one may conclude that, even if it does occur, it is much weaker than in R_3PO.[67] The determination of the energy of the 1s level of oxygen in the compounds $(C_8H_{17})_3NO$, $(iso\text{-}C_5H_{11})_3PO$, and $(C_8H_{17})_3AsO$ yielded $E(O1s) = 531.3$, 532.2, and 530.0 eV respectively[68]. The energy of the 1s level of oxygen in R_3PO is a maximum, i.e. the negative charge on the oxygen atom in phosphine oxides is a minimum, the value of $E(O1s)$ in phosphine oxides and sulphoxides being similar [$E(O1s)$ = 532.1 eV for R_2SO].[68]

Summarising the investigations of the arsenyl bond, one must conclude that the nature of the arsenyl linkage can be represented by several structures differing in their multiplicity:

$$R_3\overset{\oplus}{A}s-\overset{\ominus}{O} \leftrightarrow R_3\overset{\delta+}{A}s \cdots \overset{\delta-}{O} \leftrightarrow R_3As{=}O.$$

The multiplicity is influenced by the nature of the substituents linked to the arsenic atom: electron-donating substituents decrease the multiplicity (a semipolar bond), while electron-accepting substituents increase it.

Problems associated with the nature of the arsenyl bond will also be considered in Section III in connection with the basicities of tertiary arsine oxides in water[70] and nitromethane[71]. Proton-containing solvents, including water, reduce the charge on the oxygen atom as a result of the formation of hydrogen bonds with the oxygen of the arsenyl group. In contrast to the behaviour in nitromethane, tertiary arsine oxides are therefore weak bases in water whose pK_a are independent of the length of the hydrocarbon group attached to the arsenic atom[70] (the levelling influence of water).

Thus the arsenyl bond is a complex labile linkage, which varies from a semipolar to a partially multiple bond.

III. THE BASICITY AND PROTON-ACCEPTING CAPACITY OF ARSENYL COMPOUNDS IN THE FORMATION OF HYDROGEN BONDS

The ability of the arsenyl group to participate in complex formation with metal salts, hydrogen bonding, and acid-base interactions is the most important and most characteristic property of arsenyl compounds. The question of the possible classification of all these interactions of the donor–acceptor type and the role of charge transfer in these processes are controversial[72–75]. However, it has come to be assumed that the complexes of oxygen-containing extractants R_nEO with metal salts are formed via the mechanism of electron donor–electron acceptor interactions (EDA).[76] The classification of hydrogen-bonded complexes as EDA complexes has also been receiving increasing recognition[73,74]. Bent's view[77] that the formation of a hydrogen bond is the first stage in acid–base reactions with proton transfer has also been widely accepted[74,75].

Although there exists a view[73] that the pK_a cannot serve as a reliable measure of the electron-donating and electron-accepting molecules, nevertheless the basicity of compounds of the type R_nEO (E = N, P, As, S, or Se), which we shall call for brevity oxa-bases, is at present the best characteristic of the electron-donating capacity of oxygen, since the extracting capacity of these compounds varies in parallel with their basicity[67,75]. It has been shown[75] that the parameters characterising the hydrogen bond should characterise more adequately than the basicity (pK_a) the distribution of electron-density in the molecule in the ground state.

The constants characterising basicity and proton-accepting capacity in the formation of hydrogen bonds are thermodynamic data and cannot yield direct information about reaction mechanisms, but they do have a great advantage over kinetic data, because they can be used directly to compare the structures of the compounds[78].

Numerous studies have been devoted to the determination of the basicities of arsenyl compounds and other oxa-bases, but comparison of the pK_a obtained by different groups of investigators is difficult because of the lack of generally accepted standard methods; this applies particularly to titration in non-aqueous media. When arsenyl compounds are titrated, quaternary arsonium salts are formed ($R_3AsO + H^+ \rightarrow R_3AsOH^+$) and, although the arsenic atom is not involved in the protonation process, the multiplicity of the arsenic–oxygen bond changes[79].

The basicity of derivatives of tetracoordinate arsenic depends on the electronic effects of the substituents at the arsenic atom, which is also a consequence of the lability of the arsenyl bond. Different derivatives of tetracoordinate arsenic give rise to the following series based on the variation of basicity[71]:

$$RAs\begin{matrix}OR' \\ \| \\ O \\ NR''_2\end{matrix} > R_3AsO > R_2As(O)OR' \geqslant R_2As(O)OH >$$
$$> RAs(O)(OR')_2 \geqslant RAs(O)(OH)_2 > (RO)_3AsO \quad .$$

In this series the high basicity of the amidoesters of arsonic acids is due to the protonation of the nitrogen atom of the amido-group[71,78] and does not therefore indicate a high polarity of the arsenyl bond in these compounds.

Numerous correlation equations have now been found for the relation between the pK_a for the arsenyl compounds and the substituent constants σ, σ^+, σ^-,[81] σ^*, σ_I^{Ph}, and σ^{Ph} [49,71,82,83]. The use of σρ-analysis for organoarsenic compounds has been surveyed in a review[79] whose authors concluded that mainly the inductive effects of the substituents are transmitted via the arsenic atom.

The basicities of arsine sulphides and selenides are very much lower than those of arsine oxides[82,84], which, as mentioned above, corresponds to lower polarities of the As = S and As = Se bonds compared with As = O.

The comparison of the basicities and proton-accepting capacities in the formation of hydrogen bonds in the oxa-bases of Group VA and VIA elements incorporating similar functional groups E = O (E → O), responsible for the above properties of these compounds, is of very great interest. In contrast to non-oxidised compounds, examination of the oxa-bases of Group VA and VIA elements makes it possible to eliminate the influence of steric factors from the comparison. Thus analysis of numerous literature data on intermolecular hydrogen bonding involving compounds of Group VA and VIA elements shows that in the compounds R_2EO and R_3EO the influence of steric effects of the substituents is virtually absent, while in the compounds R_2E and R_3E it is large[85].

Hitherto mainly the problem of the involvement of compounds of the type R_2E and R_3E, where E are Group VA and VIA elements, in the formation of hydrogen bonds and acid–base interactions has been discussed in the literature[72,78,86,90]. It has been discovered for a large number of examples that the electron-donating capacities of the compounds R_2E and R_3E, where R is an alkyl substituent, diminish on passing to heavy elements: N > P > As > Sb and

O > S > Se > Te, the greatest differences being observed on passing from elements of the Second Period to those of the Third Period—from nitrogen to phosphorus and from oxygen to sulphur. Within any Period, for example, with increase of the number of the Group, the electron-donating capacity falls: N > O > F; P > S > Cl; As > Se > Br; Sb > Te > I. On passing to aromatic derivatives (R = Ar), complexes involving the π-system of the benzene ring as the proton acceptor appear; in this case there is a possibility of an inversion of the series based on the variation of the electron-donating capacity[86]. Thus the electron-donating capacity within a single Period decreases with increasing electronegativity of the heteroatoms, while within a single Group the electron-donating capacity increases as the electronegativity of the heteroatom increases; this gives rise to difficulties in the analysis of factors determining the electron-donating capacity of compounds.

The direction in which the electron-donating capacity changes within a single Period can be accounted for simply and logically—an increase of the electronegativity of the heteroatom leads to a greater difficulty of the abstraction of valence electrons; this is consistent with the increase of the ionisation potential and with decrease of the electron-donating capacity of the elements[78].

According to modern ideas, the electron-donating capacity of compounds is determined by two factors: the charge transfer from the *np* orbital of the atom E to the antibonding σ orbital of the A–H bond of the proton donor and the overlap of the 1s orbitals of the H atom with the *n* orbitals of the electron donor[72,86]. The increase of I hinders the charge transfer, which entails a decrease of the electron-donating capacity[72]. Since the ability of the orbitals to overlap decreases with increasing diffuseness of the orbitals of the donor *n* electrons, i.e. with increase of the principal quantum number *K*, the influence of the overlap within a single Period can be regarded as constant[86]. Within a single Group, an increase of the atomic number of the element entails a decrease of *I* and an increase of *K*, i.e. both factors (charge transfer and the overlap of the orbitals) exert an influence on the electron-donating capacity of the elements and there is a possibility of partial or complete cancelling of these effects[86].

The data for the basicities of the oxa-bases of Group VA and VIA element of the type R_nEO are presented below.

(1) Acid—H_2SO_4, comparison parameter—pK_a, solvent—water[87]:

$$\underset{4.65}{Me_3NO} > \underset{3.75}{Me_3AsO} > \underset{0.9}{Me_2SO} > \underset{-3.2}{Ph_2MePO} > \underset{-6.15}{PhMeCO}\ .$$

The basicity increases in the sequence N > As > P.

(2) Acid—$HClO_4$, comparison parameter—pK_a, solvent—water[88]:

$$\underset{2.55}{Me_2SeO} > \underset{1.02}{C_5H_3Me_2NO} > \underset{1.01}{Ph_3AsO} > \underset{0.79}{C_5H_5NO} > \underset{0.54}{Ph_2SeO} > \underset{-2.10}{Ph_3PO} > \underset{-2.03}{(PhCH_2)_2SO} > \underset{-3.19}{Ph_2SO}$$

or $Ph_3AsO > C_5H_5NO > Ph_2SeO > Ph_3PO > Ph_2SO$. The basicity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(3) Acid—$HClO_4$, comparison parameter—ionisation constant K_i, solvent—acetic acid[88]:

$$\underset{4.60\cdot10^6}{Ph_3AsO} > \underset{2.73\cdot10^6}{C_5H_3Me_2NO} > \underset{4.18\cdot10^5}{Ph_2SeO} > \underset{2.82\cdot10^5}{C_5H_5NO} > \underset{2.72\cdot10^2}{Ph_2PO} > \underset{9.34}{Ph_2SO}; \underset{10^8}{Me_2SeO} > \underset{3.44\cdot10^3}{Me_3PO} > \underset{3.50\cdot10^2}{Me_2SO}\ .$$

The basicity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(4) Comparison parameter—pK_a, solvent—water#:[89]

$$\underset{6}{Me_2TeO} > \underset{5.36}{Me_3SbO} > \underset{4.65}{Me_3NO} > \underset{3.75}{Me_3AsO} > \underset{2.55}{Me_2SeO} > \underset{0}{Me_3PO} \simeq \underset{0}{Me_2SO}\ .$$

The basicity decreases in the sequences Sb > N > As > P, Te > Se > S, Te > Sb, and As > Se.

(5) Acid—$HClO_4$, comparison parameter—pK_a, solvent—nitromethane[84]:

$$\underset{12.76}{Ph_3SbO} \geqslant \underset{12.58}{Ph_3AsO};\ \underset{16.58}{Oct_3SbO} > \underset{16.18}{Oct_3AsO}\ .$$

The basicity decreases in the sequence Sb > As.

Data for the proton-accepting capacities in the formation of hydrogen bonds by the oxa-bases of Group VA and VIA elements of the type R_nEO are presented below.

(1) Proton donor—HSCN, comparison parameter—Δν, solvent—CCl_4:[88]

$$Oct_3PO > Me_3PO > Ph_3PO > Me_2SO > (PhCH_2)_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequence P > S.

(2) Proton donor—PhOD, comparison parameter—Δν, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > C_5H_3(Me)_2NO > Oct_3PO \geqslant Me_3PO > C_5H_5NO > Ph_3PO > Me_2SO > (PhCH_2)_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences As > N > P, Se > S, and P > S.

(3) Proton donor—methanol, comparison parameter—Δν, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > C_5H_3(Me)_2NO \simeq Oct_3PO > C_2H_5NO > Me_3PO > Ph_2SeO > Ph_3PO > (PhCH_2)_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(4) Proton donor—indole, comparison parameter—Δν, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > Oct_3PO > C_2H_5NO > Me_3PO > Ph_2SeO > Ph_3PO > C_5H_3(Me)_2NO > Me_2SO > (PhCH_2)_2SO > Ph_2SO.$$

The proton-accepting capacity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(5) Proton donor—PhN(Me)H, comparison parameter—Δν, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > Oct_3PO > C_5H_5NO > Me_3PO > C_5H_3(Me)_2NO \simeq Ph_2SeO \simeq Ph_3PO > Me_2SO > (PhCH_2)_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(6) Proton donor—HOOCPhX (X = 3-NO_2, 4-NO_2, or 3-Cl), comparison parameter—Δν, crystalline adducts[91]:

$$Ph_3AsO \simeq C_5H_5NO > Ph_3PO\ .$$

The proton-accepting capacity decreases in the sequence As ≅ N > P.

(7) Proton donor—phenol, comparison parameters—Δν, ΔH, and K_d^{298}, solvent—CCl_4:[92,93]:

$$R_3AsO > R_3PO;\ Oct_3AsO > Bu_3AsO > Ph_3AsO\ .$$

The proton-accepting capacity decreases in the sequence As > P.

(8) Donors—Ph_3COH and Ph_3COD, comparison parameters—Δν, crystalline adducts[94]:

$$Ph_3AsO > Ph_2SeO > Ph_2SO\ .$$

#The salts, for example, $R_nEO.HNO_3$, were titrated with alkali[89].

The proton-accepting capacity decreases in the sequences Se > S and As > Se.

(9) Proton donor—water, comparison parameter—$K_{298°}$, solvent—CCl_4:[95,96]

$$Alk_3AsO > Alk_3PO;\ Oct_3AsO > Ph(Oct)_2AsO > Bu_3AsO > Ph_2(Oct)AsO > Et_3AsO\ .$$

The proton-accepting capacity decreases in the sequence As > P.

(10) Proton donor—water, comparison parameters—$\Delta\nu$, E_H, and $\overline{K}$, solvent—CCl_4:[67]

$$Oct_3NO \simeq Oct_3AsO > iso\text{-}Am_3PO > Oct_2SO > (BuO)_3PO\ .$$

The proton-accepting capacity decreases in the sequences N ≅ As > P and P > S.

(11) Proton donor—CF_3COOH, comparison parameter—ΔH, solvent—CCl_4:[97]

$$Oct_3NO > Oct_3AsO > C_5H_5NO > Me(Bu)_2PO > Me_2SO > (BuO_3)PO\ .$$

The proton-accepting capacity decreases in the sequence N > As > P > S.

(12) Proton donor—CF_3COOH, comparison parameter—ΔH, solvent—benzene[98]:

$$Et_3AsO > Ph_3AsO > Et_3AsS\ .$$

(13) Proton donor—CCl_3COOH, comparison parameter—ΔH, solvent—CCl_4:[97]

$$Oct_3AsO > C_5H_5NO > Oct_3PO > (C_6H_{13})_2SO\ .$$

The proton-accepting capacity decreases in the sequence As > P > S.

(14) Proton donor—4-FC_6H_4OH, comparison parameter—ΔH, solvent—CCl_4:[99,100]

$$Me_3NO > Me_3PO \simeq C_5H_5NO > Me_2SO\ .$$

The proton-accepting capacity decreases in the sequence N > P > S.

(15) Proton donor—$CH_2ClCOOH$, comparison parameter—ΔH, solvent—CCl_4:[101]

$$Oct_3PO > Ph_2SeO > Ph_3PO > Me_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences P > S and Se > S.

(16) Proton donor—$CHCl_2COOH$, comparison parameter—ΔH, solvent—CCl_4:[101]

$$Oct_3PO > Ph_2SeO > Ph_3PO > Me_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences P > S and Se > S.

(17) Proton donor—PhC ≡ CH, comparison parameter—$\Delta\nu$, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > Oct_3PO > Ph_2SeO > C_5H_3(Me)_2NO \simeq \simeq Me_3PO > Ph_3PO > C_5H_5NO \geqslant Et_2SO \geqslant Me_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences As > P > N, Se > S, As > Se, and P > S.

Evidently the sequences in which the basicity (pK_a) and the parameters characterising the hydrogen bond ($\Delta\nu$, ΔH, K, and E_H) vary are in most cases the same. It has been stated[88] that a simple relation between the pK_a and the parameters characterising the hydrogen bond holds for strong proton donors. For weak proton donors (for example, phenylacetylene), the pK_a and the parameters characterising the hydrogen bond do not always vary in parallel. Since the main bulk of the available experimental data on the involvement of the oxa-bases R_nEO in hydrogen bonding refer to strong proton donors, i.e., according to the classification adopted by Sergeev[102], these are moderately strong and strong hydrogen bonds, we observe a correspondence between the degree of protonation (i.e. the pK_a) and hydrogen bonding (i.e. $\Delta\nu$, ΔH, K, and E_H).

It is known that charge transfer from the donor to the acceptor molecule assumes an appreciable role in the formation of hydrogen-bonded complexes with strong and moderately strong hydrogen bonds[73,104]; on this basis, the above hydrogen-bonded complexes have been included in the general system for the classification of charge-transfer complexes, i.e. they can be regarded as EDA complexes.

The observed correspondence between the parameters characterising the basicity (pK_a) and the hydrogen bond ($\Delta\nu$, ΔH, E_H, and K) shows that these quantities characterise reliably the electron-donating capacity of the oxa-bases. The possibility of a correlation between the parameters of the hydrogen-bonded complexes and the pK_a has been questioned[73]. It was stated that such correspondence can refer only to a narrow range of analogous complexes, where the acid–base interaction proceeds up to the formation of solvated ions. Evidently, the oxa-bases, which are weak acceptors in ionisation (they are protonated in media with a high acidity[103]) and strong acceptors in hydrogen bonding[88], are precisely the type of compounds whose protonation leads to the formation of solvated ions.

It follows from the data presented that the electron-donating capacity of aliphatic derivatives Alk_nEO is always greater than that of aromatic derivatives Ar_nEO and that the replacement of alkyl groups by alkoxy-groups also entails a decrease of the electron-donating capacity of the oxa-bases. Comparison of the oxa-bases with substituents of the same type is therefore legitimate for the detection of the influence of E on the electron-donating capacity.

Analysis of the data presented permits the following conclusions. The first conclusion is the same as that reached in the analysis of the properties of the oxygen-free bases R_nE formed by Group VA–VIIIA-elements[72,78,86]: within any Period, the electron-donating capacity of the oxa-bases R_nEO decreases with increase of the number of the Group regardless of the Period under consideration. In all cases the basicity and proton-accepting capacity of phosphine oxides are greater than those of the sulphoxides and those of arsine oxides are greater than those of selenoxides. According to Nylen[89], the only exception is that Me_2TeO is somewhat more basic than Me_3SbO, but this requires an experimental test, since the author himself[89] believes that the pK_a for Me_2TeO has been determined only approximately.

There is a non-monotonic variation of the electron-donating capacities of the oxa-bases R_nEO within a single Group—the oxa-bases of the Second and Fourth Periods are stronger electron-donors than the oxa-bases of the Third Period (always $R_3NO > R_3PO$, $R_3AsO > R_3PO$, and $R_2SeO > R_2SO$); the oxa-bases of the Fifth Period are stronger electron donors than those of the Fourth Period ($R_3SbO \gtrsim R_3AsO$ and $R_2TeO > R_2SeO$).

Thus the following series based on the variation of the electron-donating capacities of the oxa-bases can be set up within Groups VA and VIA: Sb > As > P < N or Sb > As ≅ N > P and Te > Se > S. We may note that the electron-donating capacities of arsine and amine oxides are similar, so that, according to the data presented above, they frequently change places (this finding is also evidence in support of the semipolar nature of the arsenyl bond in arsine oxides). Consequently, partial inversion of the series based on the variation of the electron-donating capacity found for the non-oxidised bases R_nE has been observed for the oxa-bases R_nEO: N > P > As > Sb and O > S > Se > Te.[72,78]

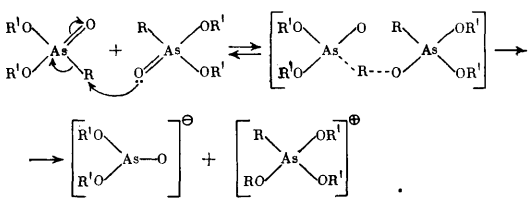
The observed characteristics of the variation of the electron-donating capacities of the oxa-bases R_nEO, where E are Group VA and VIA elements, on the whole agree with the known type of variation of the electronegativities and

the ionisation potentials *I* of these elements: with increase of the number of the Group and with decrease of the atomic number of the element within the Group (i.e. from left to right and from below upwards in the Periodic System), the electronegativity and *I* increase, which should naturally entail a decrease of the electron-donating capacity. The nitrogen atom is an exception in this instance.

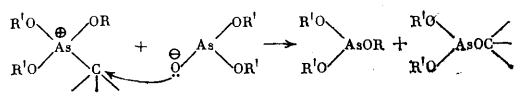
As stated above, the overlap of the 1*s* orbitals of the hydrogen atom with the *n* orbitals of the donor plays an appreciable role in the formation of hydrogen bonds in addition to the charge transfer from the *np* orbital of the donor to the antibonding orbital of the A–H acceptor. When the oxa-bases R_nEO are involved in the formation of hydrogen bonds, the 1*s* orbitals of hydrogen always overlap with the *n* orbitals of oxygen, i.e. the second factor may be regarded as constant. The influence of E on the electron-donating properties of the oxa-bases, which is transmitted via the oxygen atom, evidently reduces to an influence on the charge transfer from the oxygen atom (donor) to the acceptor molecule.

IV. THE NUCLEOPHILIC PROPERTIES OF ARSENYL COMPOUNDS

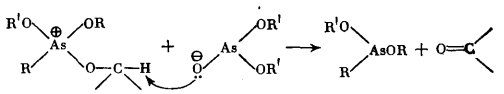
Many reactions are now known in which the nucleophilic properties of arsenyl compounds in relation not only to the proton but also to the carbon atom are manifested. An example of such reactions is the thermal transformations of arsonic and arsinic acids and arsine oxides. The mechanisms of these fairly complex reactions have been analysed in detail[19]. The pyrolysis of arsenyl compounds apparently begins with the nucleophilic attack by the oxygen of the arsenyl Group on the α-carbon atom attached to the arsenic atom:



Further attack by the anion on the α-carbon atom of the cation leads to isomerisation products:

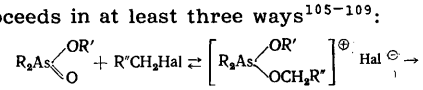


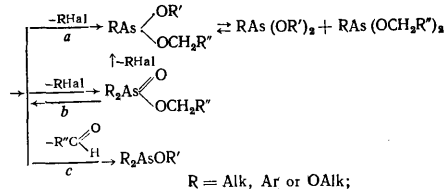
while the reaction involving the hydrogen at the α-carbon atom of the cation leads to the formation of reduction products and aldehydes:



Isomerisation predominates for arsonic acid esters, while reduction predominates for arsine oxides[19].

Together with thermal transformations, the interaction of arsenyl compounds with electrophiles has been studied. The interaction of arsonic and arsinic acid esters with alkyl halides proceeds in at least three ways[105–109]:





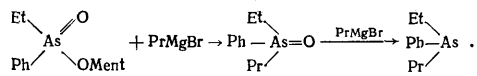
(1)

R = Alk, Ar or OAlk;
R′ = Alk; R″ = Alk or Ar .

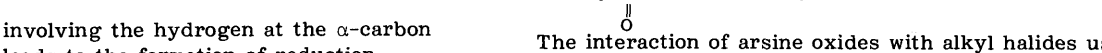
Nucleophilic attack by the oxygen of the arsenyl group on the α-carbon atom of the alkyl halide leads to the formation of an alkoxyarsonium salt, further reactions of which are determined by the nature of the reactants and the reaction conditions. In the presence of an aliphatic carbon atom linked to arsenic (alkylarsonic and dialkylarsinic acid esters) the attack by the nucleophile is directed to the α-carbon atom of the alkoxyarsonium cation; as a result, a retro-Arbuzov rearrangement of the initial esters takes place (pathway *a*) with formation of a new alkyl halide. The esters of alkyl alkylarsonous and arsenous acids formed under these conditions are usually symmetrised. If the alkyl halide produced in this reaction (RHal) is more reactive than the initial halide ($R''CH_2Hal$), then RHal will subsequently participate in the reaction preferentially and isomerisation products will predominate among the reaction products.

Pathway *b*, i.e. attack by the nucleophile on the α-carbon atom of the calkoxy-group of the alkoxyarsonium cation as a result of which the arsenyl group is regenerated, is characteristic of aromatic derivatives (esters of arylarsonic and diarylarsinic acids). The pathway in which the nucleophile abstracts a proton from the α-carbon atom of the alkoxy-group (α-elimination), which results in the formation of an aldehyde and the product of the reduction of the initial ester, obtains for the same compounds under more severe conditions (on increase of reaction temperature to 180–195 °C).

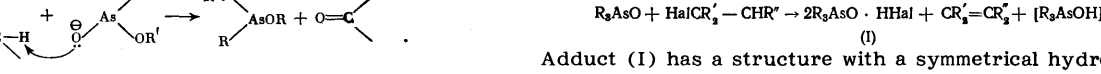
The menthyl esters of alkylarylarsinic acids react with alkylmagnesium halides with inversion of the configuration and for a molar reactant ratio of 1 : 1 a tertiary arsine oxide is formed, while for a ratio of 1 : 2 reduction to the corresponding arsine takes place[110]:



The reduction of quinquevalent arsenic acid esters is also observed in their reactions with mercaptans, which entails an exchange of the alkoxy-group of the ester for the mercapto-group[111]:



The interaction of arsine oxides with alkyl halides usually leads to the dehydrohalogenation of the alkyl halide by the oxide with formation of 2 : 1 adducts (I), olefins, and hydroxyarsonium salts[70,112–115]:



(I)

Adduct (I) has a structure with a symmetrical hydrogen bond between the oxygen atoms and an ionic or covalent bond between the hydrogen atom and the halogen: $[R_3AsO...H...OAsR_3]^{\oplus}\ Hal^{\ominus}$.[116] Analogous products have also been isolated in the reaction of triphenylarsine oxides with monohalogenoacetate esters, chloroacetone, and chloroacetonitrile[117].

If the arsenic atom is linked to even one aliphatic carbon atom, then, together with the reactions indicated above, the retro-Arbuzov rearrangement of the arsine oxides

(yield from 7 to 75%) takes place, as for arsonic and arsinic esters[118–122]:

$$R_3AsO + R'Hal \rightarrow R_3AsOR' .$$

The mechanism of the reaction of arsine oxides with alkyl halides has been studied in many investigations[19,70,123–127] and, although there are certain discrepancies in the treatment of the individual stages of the reaction by different workers, there is no doubt about the first reaction stage—the nucleophilic attack by the oxygen of the arsenyl group on the α-carbon atom of the alkyl halide, leading to the formation of an alkoxyarsonium salt:

$$R_3AsO + HalCR'_2 - CHR''_2 \rightarrow [R_3AsOCR'_2 - CHR''_2]^{\oplus}Hal^{\ominus}.$$

Further reactions of the alkoxyarsonium salt are also determined by the nature of the reactants and the reaction conditions:

$$[R_3AsOCR'_2 - CHR''_2]^{\oplus}Hal^{\ominus} \rightarrow \begin{cases} \xrightarrow{a} R_3AsOCR'_2 - CHR''_2 + RHal \\ \xrightarrow[b]{+R_3AsO} CR'_2 = CR''_2 + [HOAsR_3]^{\oplus}Hal^{\ominus} \rightarrow 2R_3AsO \cdot HHal . \end{cases}$$

The retro-Arbuzov rearrangement (*a*) takes place when the nucleophile attacks the α-carbon atom of the alkoxyarsonium salt, as for arsonic and arsinic acid esters. Pathway (*b*), involving the abstraction of a proton from the β-carbon atom of the alkoxy-group of the arsonium cation by another arsine oxide molecule, obtains only for arsine oxides. Evidently, as a consequence of the higher basicity of arsine oxides compared with other compounds of tetracoordinate arsenic, they are capable of competing with another nucleophile present in the reaction sphere, namely the halide anion. The large size of the nucleophile (arsine oxide) apparently precludes α-elimination accompanied by the formation of aldehydes (as for arsonic and arsinic acid esters), as a result of which β-elimination, leading to the formation of an olefin, takes place.

In the reaction of trialkylarsine oxides with acid halides, there is a rearrangement analogous to the retro-Arbuzov rearrangement (yield 95%):[120]

$$Pr_3AsO + CH_3COCl \rightarrow Pr_3AsOCCH_3 .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

However, the reactions of triphenylarsine oxide with acetyl bromide and chloride result in the formation of dihalogenoarsoranes[128,129]:

$$Ph_3AsO + CH_3COHal_2 \rightarrow Ph_3AsHal_2 + (CH_3CO)_2O .$$

Such substitution also takes place in the reaction of triphenylarsine oxide with phosgene[130]:

$$Ph_3AsY + COCl_2 \rightarrow Ph_3AsCl_2 + COY ;$$
$$Y = O \text{ or } S$$

and with arsenic trichloride[131].

Depending on the structure, arsine oxides react with hydrogen halides in different ways[132–135]:

$$\underset{(I)}{R_3AsO} + HX \rightleftarrows R_3AsO \ldots \underset{(II)}{HX} \rightarrow \underset{(II)}{[R_3AsOH]^{\oplus}X^{\ominus}} \rightleftarrows \underset{(III)}{R_3AsX_2} + H_2O .$$

The reaction of tertiary arsine oxides, having a comparatively low basicity, for example, the derivatives of dihydrophenarsazine, stops at the first stage involving the formation of hydrogen-bonded adducts (with partial proton transfer[134]). Complete proton transfer to the oxygen of the arsenyl group leads to the formation of a salt-like product (II) [113,133,135,136], which can be dehydrated in the presence of an excess of hydrogen halides with formation of dihalogenoarsorane (III).[132,133].

Summarising the entire complex range of reactions occurring when oxygen-containing compounds of tetracoordinate arsenic interact with electrophiles, one can distinguish four principal pathways: the retro-Arbuzov rearrangement (*a*) characteristic of arsenyl compounds having at least one C_{aliph}–As bond; the protonation of the oxygen of the arsenyl group with formation of a hydroxyarsonium salt (*b*), which can undergo further reactions; the exchange reaction (*c*), which can lead not only to the formation of new arsenyl compounds but also to the regeneration of the initial reactants; the reduction of the initial arsenyl compounds (*d*), which usually occurs at elevated temperatures:

$$R_3AsO + R'X \begin{cases} \xrightarrow{a} R_2AsOR' \\ \xrightarrow{b} [R_3AsOH]X \rightarrow \begin{cases} \xrightarrow{+R'X} R_3AsX_2 \\ \xrightarrow{+R_3AsO} 2R_3AsO \cdot HX ; \end{cases} \\ \underset{c}{\rightleftarrows} R_2AsOR' + RX \\ \qquad\quad \| \\ \qquad\quad O \\ \xrightarrow{d} R_3As \end{cases}$$

R = Ar, Alk or OAlk; R′ = HAlk, CH_2COR, CH_2CCN, CH_2CCH_3, AlkMg, CCl_2COOH or $AsCl_2$; X = Hal .

In all these reactions the primary step is nucleophilic attack by the oxygen of the arsenyl group on the electrophile, leading to the formation of alkoxyarsonium salts.

Thus onion salts play the main role in the reactions of compounds of tetracoordinate arsenic with electrophiles. Analogous onion salts are also formed in the reactions of other oxa-bases R_nEO with electrophiles. In the reactions of phosphoryl compounds with alkyl halides, quasi-phosphonium salts are formed[137]:

$$\underset{\|}{R_2POR'} + R''Hal \rightarrow [R_2P(OR')(OR'')]^{\oplus}Hal^{\ominus} \rightarrow \underset{\|}{R_2POR''} + R'Hal , \qquad (2)$$
$$O \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad O$$

in the reactions of amine oxides the products are alkoxyammonium salts[138]:

$$R'CH_2Hal + R_3NO \rightarrow [R_3NOCH_2R']^{\oplus}Hal^{\ominus} \rightarrow R'C\begin{matrix} O \\ \diagdown \\ \diagup \\ H \end{matrix} + R_3N , \qquad (3)$$

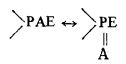
and in the reactions of sulphide oxides the products are alkoxysulphonium salts $[R_2SOR']^{\oplus}Hal^{\ominus}$.[65]

Alkoxyarsonium salts are extremely reactive, so that attempts to obtain them by alkylating arsine oxides did not lead to the desired result at −75 °C even when the halide anion was replaced by the less reactive perchlorate and tetrafluoroborate anions[139]. Instead of alkoxyarsonium salts, the adduct of the arsine oxide with the corresponding acid, $2R_3AsO.HX$, was always isolated.

Alkoxyarsonium salts have been obtained by the reaction of tertiary arsines with t-butyl hypohalites at temperatures in the range between −5° and −10 °C [140,141] and by the reaction of methyl dimethylarsinite with methyl iodide[142]. A whole series of products, usually observed in the pyrolysis of arsine oxides[19], were isolated in the thermal decomposition of alkoxyarsonium salts[140]. In addition t-butyl halide and arsine oxide were isolated, which constitutes indirect evidence for the possibility of an exchange reaction when arsine oxides interact with alkyl halides, giving rise to the regeneration of the arsenyl group (this corresponds to pathway *b* in scheme 1), which indicates that processes of the same type occur in the interaction of compounds of tetracoordinate arsenic (arsine oxides and arsonic and arsinic acid esters) with alkyl halides.

Trimethylmethoxyarsonium iodide interacts instantaneously with arsine oxide, forming the usual adduct $2Me_3AsO.HI$,[142] which confirms the hypothesis[124-126] that the rate-limiting stage of the reaction of arsine oxides with alkyl halides is the formation of alkoxyarsonium salts. The report[143] of the synthesis of an alkoxyarsonium salt from tripropylarsine oxide and ethyl bromide on refluxing the components in benzene is evidently erroneous.

A rearrangement of the type of the retro-Arbuzov rearrangement, which is common for arsenyl compounds, is not characteristic of phosphoryl compounds, for which the bond equilibrium



is displaced towards the tetracoordination form for E = H or C and A = O or S; only for E = P is there a possibility of the existence of both tautomeric forms[144].

The possibility of the retro-Arbuzov rearrangement is determined by the mode of nucleophilic attack on the alkoxy-onium cation $[C_{aliph}-E-OC]^{\oplus}$. When E = As, the nucleophile attacks preferentially the α-carbon atom at the arsenic atom, whereas for E = P the attack by the nucleophile is directed to the α-carbon atom of the alkoxy-group. This finding can be explained as follows. Firstly, the strength of the $C_{aliph}-As$ bond is much lower than the strength of the $C_{aliph}-P$ bond in analogous compounds (by 40.2 kJ mol^{-1} and more).[69,145] Secondly the arsonium cation should be stabilised preferentially via an inductive mechanism: $C \to C \to As^{\oplus} \leftarrow O \leftarrow C$. The $p_\pi-d_\pi$ interaction of the oxygen and arsenic atoms is then weak or absent, while in the stabilisation of the alkoxyphosphonium cation $p_\pi-d_\pi$ conjugation should play a significant role and should therefore lead to considerable positive polarisation of the α-carbon atom of the alkoxy-group, which facilitates in its turn nucleophilic attack on this atom.

In contrast to the reactions of compounds of tetra-coordinate arsenic with electrophiles described above, the reaction of trialkyl arsenates, which have the smallest basicity among arsenyl compounds[71], with electrophiles such as arsenic trihalides and phosphorus trichloride takes place with the retention of the arsenyl group and the formation of tetra-alkyl meta-arsenates[146,147]:

$$2\,(RO)_3AsO + 2AsHal_3 \to (ROAsO_2)_2 + 2RHal + 2ROAsHal_2\ .$$

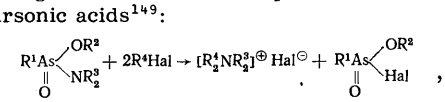
The interaction of trialkyl arsenates with phosphorus trichloride is also complicated by an oxidation-reduction reaction in which trialkyl arsenate behaves as an oxidant:

$$(RO)_3AsO + PCl_3 \to (RO)_3PO + AsCl_3\ .$$

A similar oxidation-reduction reaction has also been observed in the interaction of arsine oxides and tertiary phosphines[148]:

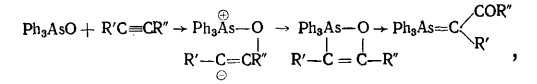
$$R_3AsO + R_3P \to R_3PO + R_3As\ .$$

In the reactions of amidoesters of arsonic acids with electrophiles (alkyl halides and halogenoesters) a competition might have been expected between the two nucleophilic centres of the amidoester molecule—the oxygen atom of the arsenyl group and the nitrogen atom of the amido-group. However, the study of the products of these reactions showed that the nitrogen atom is the nucleophilic centre in the amido-esters of arsonic acids[149]:



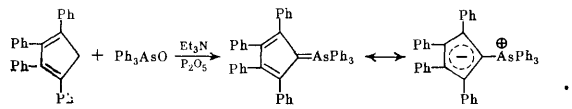
which also agrees with the conclusion that these derivatives are protonated at the nitrogen atom[71,80].

The nucleophilic reactivity of arsenyl compounds in relation to an unsaturated carbon atom is manifested, for example, in the reactions of triphenylarsine oxide with highly electrophilic reagents such as activated acetylenes (dicyanoacetylene and others).[148] It has been suggested that the reaction proceeds via the formation of a zwitterion:

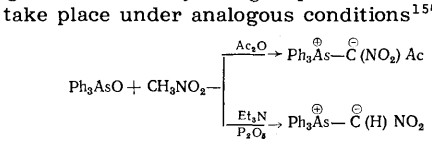


and that the ylid formed as a result of the reaction is resonance-stabilised. Triphenylphosphine oxide is less reactive in this kind of reaction because it reacts only with dicyanoacetylene and at a higher temperature than triphenylarsine oxide[148].

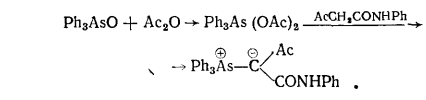
The condensation of triphenylarsine oxide with substituted cyclopentadienes, which takes place in acetic anhydride[150,151] or in triethylamine in the presence of phosphorus pentoxide[152,153], also leads to ylids:



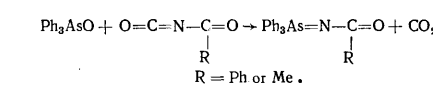
The reactions of tertiary arsine oxides with compounds containing activated methylene groups and also with nitro-methane take place under analogous conditions[154]:



The role of acetic anhydride in these reactions reduces to the formation of the intermediate diacetoxyarsorane[153-155], which can subsequently react with compounds containing activated methylene groups, giving rise to the corresponding ylids[155]:

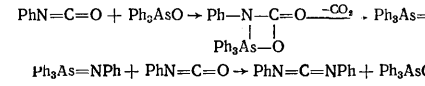


The reactions of stabilised isocyanates with triphenylarsine oxide also lead to the formation of arsine imides[156]:



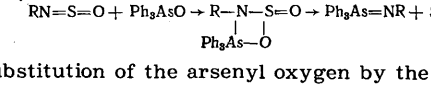
The benzoyl- and acetyl-arsine imides formed under these conditions are also resonance-stabilised.

The interaction of triphenylarsine oxide with phenyl isocyanate leads to the formation of diphenylcarbodi-imide[157]:

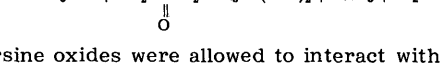


However, under mild conditions the reaction stops at the first stage, involving the formation of arsine imide[158].

N-Sulphinamides react analogously with triphenylarsine oxide[58,159]:



The substitution of the arsenyl oxygen by the isocyanate group takes place in the reactions of tertiary arsine oxides with urea[160,161]:



When arsine oxides were allowed to interact with diols in

benzene with azeotropic distillation of the water formed, cyclic esters of pentacoordinate arsenic—dioxa-arsolanes—were obtained[162]:

$$R_3AsO + \begin{matrix} HO \\ HO \end{matrix} \xrightarrow{-H_2O} R_3As\begin{matrix} O \\ O \end{matrix}$$

Under analogous conditions, phosphine oxides do not form the corresponding dioxaphospholanes. The interaction of stibine oxides with diols also results in the formation of dioxastibolanes[163].

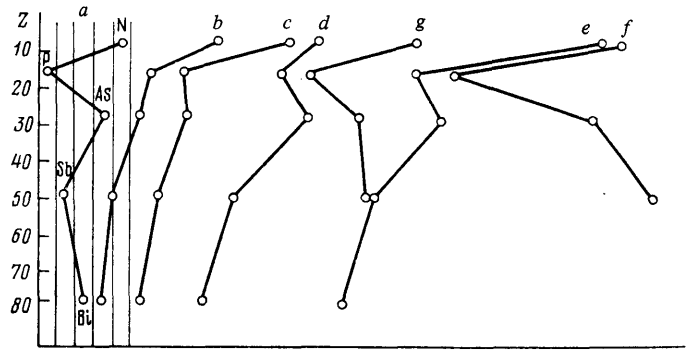
Nucleophilic addition to the carbonyl group is a general reaction for carbonyl-containing compounds; in particular, ketones interact with α-glycols to form quantitatively the corresponding cyclic ketals[164]. By analogy with carbonyl compounds, for which the mechanism of reactions involving nucleophilic addition to the carbonyl group has been studied in detail[165,166], it has been suggested that the mechanism of the reactions of arsine oxides with diols is based on proton transfer from the diols to the oxygen of the arsenyl group with formation of a new arsenic–oxygen bond and subsequent dehydration of the intermediate formed[162].

V. THE PROBLEM OF ANALOGY IN GROUP VA OF THE PERIODIC SYSTEM

Examination of certain physicochemical and chemical properties of arsenyl compounds and their comparison with those of the oxa-bases R_3EO, where E is a Group VA element makes it possible to put forward certain considerations concerning the problem of analogy in Group VA. This problem is closely related to the more general problem of the analogy of the elements within any Group. Examination of the properties of organoelemental compounds on the basis of the properties of the elements and hence of their positions in the Periodic System is extremely important, because it provides a guideline which enables one to become orientated in the enormously wide variety of organoelemental compounds and their properties. It has been mentioned in a number of studies[167–170] that the simplified formulation of the Periodic System, widely used at the present time, in which the elements of the main subgroups are arranged in vertical columns, had led to some 'fetishisation' of the properties of these elements and to the widespread delusion that there is a gradual and smooth increase of the changes in the properties of the elements and their compounds.

Without attempting to consider the historical aspects of the development of various formulations of the Periodic System, we shall confine ourselves to mentioning studies in which the problem of analogy in Group VA was directly involved. Evidently one should mention that in the form of the Periodic System proposed by Mendeleev the elements of the Second Period are displaced relative to the heavier elements, which emphasises their special role. In the pyramidal form of the Periodic System proposed by Nekrasov[171] the elements of the Second and Third Periods are isolated. From the standpoint of Nekrasov's ideas concerning complete and incomplete electronic analogues, nitrogen and phosphorus and also arsenic, antimony, and bismuth are complete electronic analogues, while phosphorus and arsenic are incomplete analogues. This modification of the Periodic System takes into account the electronic structures not only of neutral atoms but also of all the characteristic valence states of the elements.

Subsequent studies in which the problems of the analogy of the elements of the Periodic System were developed and new forms of the Periodic System were proposed, reflecting finer differences between analogous elements, were based on the allowance for the structural and energetic characteristics not only of the outer electron shells of atoms but also of the two electron shells immediately preceeding the outer shell[167–170]. On the basis of the analysis of the energetic characteristics of the atoms (ionisation potentials, electron affinities, orbital radii, etc.), Godovikov[169,170] proposed an improved form of the Periodic System. Two variants of the subdivision of the elements into small subgroups were proposed for Group VA: first variant: VA1(N), VA2(P, As, Sb), VA3(Bi); it agrees well with the analysis of the properties of the oxygen compounds of the elements; second variant: VA1(N), VA2(P), VA3(As, Sb), VA4(Bi); it agrees with the properties of the sulphides.



Dependence of certain parameters of Group VA elements and their compounds on the atomic number Z of the element in the Periodic System: *a*) the arrangement of analogous Group VA elements in the matrix form of the Periodic System[167]; *b*) the first ionisation potentials of the elements[169]; *c*) the change Δr(Å) in the difference between the orbital radius of the atom and the radius of its occupied electron shell immediately preceding the outer shell in analogous elements[169]; *d*) electron affinity[69]; *e*) electronegativity[172]; *f*) pK_a for R_3EO;[89] *g*) E=O bond energy in R_3EO.[58,69].

A similar approach to the construction of the Periodic System with displacements was used by Grigorovich[167,168], who proposed a matrix form of the Periodic System, which provides for the subdivision of the main subgroups of Groups II–VII into five items (see Figure, a). This subdivision is based on the variation of the structures of the inner electron shells and the variation of the binding of the outer electrons to the nucleus. Although the matrix form of the Periodic System has not received its due recognition among chemists, nevertheless it reflects most clearly the non-monotonic, frequently zigzag, variation of the physical properties of the elements of the subgroup. This finding is also emphasised in Godovikov's studies[169,170]. The Figure presents plots of the variation of certain properties of Group VA elements and their compounds, illustrating the above postulate. The non-monotonic variation within a subgroup of fundamental properties of the elements such as electronegativities, ionisation potentials, electron affinities, orbital radii, etc., leads to a non-monotonic, frequently zigzag, variation of the physicochemical properties of organoelemental compounds (such as the E=O bond energy and pK_a). This type of variation of the physical and

physicochemical parameters of organoelemental compounds should evidently affect also the variation of their chemical properties.

Analysis of the arrangement of analogous elements within a subgroup, proposed in the matrix form of the Periodic System, explains the similarity of many physicochemical and chemical properties of nitrogen and arsenic compounds which are more likely to be regarded as an anomaly when the usual Periodic System is employed. The similarity of the physicochemical characteristics of the AsO and NO groups as well as of the electron-donating capacities of the oxa-bases R_3NO and R_3AsO was mentioned above. Such similarity has also been observed on comparing the chemical behaviour of the oxa-bases of nitrogen and arsenic, for example, their capacities for the tautomeric transformation

$$R_3EO \rightarrow R_2EOR,$$
$$E = N \text{ or } As.$$

In the N, P, As triad in the matrix form of the Periodic System the phosphorus atom is displaced to the extreme left-hand position (*a*) due to the strong shielding effect of the s^2p^6 electrons, which is greater than that of the $s^2p^6d^{10}$ electrons of arsenic and s^2 electrons of nitrogen. This is evidently also responsible for the specificity of the properties of many phosphorus compounds. The arsenic atom in the matrix form of the Periodic System occupies an intermediate position with some displacement towards nitrogen (see Figure, *a*). This intermediate position of arsenic is reflected in the reactions of the compounds R_3EO with alkyl halides. Comparison of arsenyl compounds in these reactions [scheme (1)] with phosphoryl compounds [scheme (2)] and amine oxides [scheme (3)] shows that arsenyl compounds undergo transformations which are characteristic also of amine oxides—an oxidation-reduction reaction [scheme (1), pathway *a*]—and of phosphoryl compounds—an exchange reaction [scheme (1), pathway *b*].

In the search for similarity, one must not forget the uniqueness of each element of the subgroup. The advantage of the matrix form of the Periodic System also consists in the fact that it reflects not only the similarities but also the differences between the properties of analogous elements caused by the differences between the structures of their inner shells, while the structures of the outer shells are similar.

The problem of the analogy of the elements and their compounds is one of the exciting problems in chemistry. The present review is in essence limited solely to the indication of the new possibilities of the analysis of this problem, which have arisen in connection with the development of new improved formulations of the Periodic System.

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