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The Structure and the Electron-donating Properties of Tertiary Arsine Oxides

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The complex-forming and physicochemical properties of tertiary arsine oxides are analysed in connection with the significant differences between them and the closest organophosphorus analogues. Attention is focused on the reactivities of organoarsenic ligands in complex-formation reactions with acids and metal salts. The specific features of the steric and electronic structures of arsine oxides and the mechanism of the transmission of the influences from groups via the arsenic atom to the reaction centre (the arsenyl oxygen) are discussed. Heterophase reactions in the extraction of acids and salts are considered within the framework of a single model of donor-acceptor processes in solution.
The bibliography includes 274 references.

CONTENTS

I. Introduction 454
II. The electronic structure of organoarsenic molecules 454
III. The basicity of arsenic-containing extractants in aqueous and non-aqueous solutions 456
IV. Electron-donating properties of tertiary arsine oxides 457
V. Complexes of tertiary arsine oxides with metal salts 458
VI. Extraction of protic acids and water 461
VII. Extraction of metal salts 464

I. INTRODUCTION

The chemistry of organoarsenic compounds (OAC) is now going through a period of new advance due to the appearance of realistic prospects for the practical utilisation of these derivatives in various branches of science and technology. At the same time, the development of this field is held back by the lack of review publications dealing with the numerous but extremely varied studies on the characteristics of the behaviour of the OAC in many important chemical reactions. This applies fully to the study of the properties of tertiary arsine oxides R_3AsO in reactions of the electron donor–electron acceptor (EDA) type in which the molecular complexes of R_3AsO with organic and inorganic Brønstedt and Lewis acids are formed. Such reactions constitute the basis of the complex formation processes in the homogeneous solutions and heterophase systems, where R_3AsO behave as strong ligands of the neutral type.

This valuable property of R_3AsO has for a long time attracted the attention of specialists in the field of coordination chemistry, who believe that the central problem is the search for relations between the electronic and steric structures of the substituents R at the arsenic atom and the reactivity of the R_3AsO in processes of the EDA type. The extensive experimental data accumulated hitherto have not so far been surveyed and arranged systematically, which limited the application of these compounds in complex formation and extraction processes. This review fills this gap and is devoted to the latest advances in the theory of the structure of the OAC and the applications of tertiary arsine oxides and ligands in the formation of EDA complexes.

Numerous methods of synthesising compounds of tetracoordinate arsenic have been described in detail in specialist publications and monographs[1-60].

II. THE ELECTRONIC STRUCTURE OF ORGANOARSENIC MOLECULES

The Group VB elements—nitrogen, phosphorus, arsenic, antimony, and bismuth—have similar structures of the outer electron shells, consisting of two *s* and three *p* levels. In tervalent compounds of these elements ER_3 three *p* bonds of the heteroatoms E with the groups R should therefore be at 90° angles relative to one another and the free electron pair should be of the pure *s* type. In reality the 2*s* orbital of the electron pair in nitrogen compounds is hybridised with the 2p orbitals, which leads to the formation of four equivalent hybrid sp^3 orbitals. For other Group VB elements, the hybridisation of the *s* and *p* levels is not observed, while the R–As–R valence angles are in the range from 91.8° in AsH_3 to 101° in AsF_3 and AsI_3 (for the majority of the derivatives, the angle is 96°)[61]. The valence angle hardly changes on oxidation of tertiary arsines to arsine oxides, i.e. on passing to the tetracoordinate state $R_3As^+-O^-$.[62]

One of the popular models of the arsenyl group involves the cooperative interaction between the arsenic and the oxygen in the $\geq As^+-O^-$ σ-bond and the $p_\pi-d_\pi$ conjugation of the unshared electron pairs of oxygen with the highest vacant 4*d* orbitals of arsenic. As a result of this, the $\geq As\ldots O$ bond acquires partial double bond character depending on the extent of the $p_\pi-d_\pi$ conjugation. This model has been confirmed in the study of the dipole moments of arsenyl compounds[63-65].

The study of a number of oxo-bases R_3NO, R_3PO, and R_3AsO ($R=C_8H_{17}$) by X-ray electron spectroscopy showed that[66] the spectra of R_3NO and R_3AsO are similar, while the spectrum of R_3PO differs significantly as a consequence of the $p_\pi-d_\pi$ interaction of the oxygen in the phosphoryl group with the 3*d* orbitals of the phosphorus atom. This permits the conclusion that, if the $p_\pi-d_\pi$ interaction actually occurs in the arsenyl group, its extent is small and at any rate significantly smaller than in phosphorus compounds. Comparison of the reactivities of compounds of the above series in the formation of charge-transfer complexes with molecular iodine in inert solvents leads to the same conclusion[67]. In this case the reaction constants, the interaction energy, and the degree of charge transfer are similar for R_3NO and R_3AsO, while the corresponding quantities for R_3PO are appreciably smaller.

In order to resolve this contradiction, most varied physicochemical methods, such as ^1H and ^{19}F nuclear resonance[68-71] ^{75}As [72-74] and ^{35}Cl [75] nuclear quadrupole resonance, photoelectron X-ray spectroscopy[76], and electron and vibrational

spectroscopy[77-80] have been used. However, unambiguous conclusions cannot be reached owing to the evident discrepancies between the results obtained by different methods. The solution of this problem was hindered also by the lack of reliable bond lengths and valence angles in arsenic compounds, which were determined accurately only very recently[81-84].

The first mention of the vibrational frequency of the arsenyl group was made in a study[85] where intense absorption maxima in the infrared spectra of tertiary arsine oxides (TAO) at 815 and 844 cm^{-1} were assigned to the AsO groups. The intense absorption bands in the range 815–910 cm^{-1} have also been assigned[86-89] to the As–O linkages. Having studied the infrared spectra of compounds of the type Ph_3MX (M = P, As, or Sb; X = O, Se, or S) in the range 400–3000 cm^{-1}, Jensen and Nielsen[90] determined the absorption frequencies of the As = O (881 cm^{-1}) of Ph–$As_{(as)}$ (474–479 cm^{-1}) groups. The infrared spectra of organoarsenic ligands (L) and complexes of the type ML_2X_2 (L = Ph_3AsO or Ph_2MeAsO; X = Cl or Br; M = bivalent metals ranging from Mn to Zn) have been investigated and discussed[91]. Having discovered that the stretching vibration frequencies ν(As–O) occur in the range 840–910 cm^{-1}, the authors[91] determined them experimentally in the range from 855 to 910 cm^{-1}. The earlier assignments of the intense absorption band in the spectra of triphenylarsine oxide[86-88,92] were confirmed in a study[93] of iso-substituted compounds.

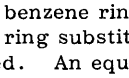
Deacon and Green[94] synthesised and investigated by infrared spectroscopy in the range 200–1650 cm^{-1} the complexes of triphenylarsine oxide with zinc, manganese, cobalt, and mercury ions (saturated solutions in chloroform) and obtained a satisfactory agreement with the results of other studies[90-93]. The absorption maximum at approximately 880 cm^{-1}, assigned to the stretching vibrations of the AsO bond, is resolved into a doublet with frequencies of 885 and 877 cm^{-1} in the spectrum of the solid specimen. A special method for the synthesis of virtually anhydrous complexes made it possible to isolate preparations giving rise to a weak peak in the region of 3300 cm^{-1}; the water absorption bands in the range 200–1650 cm^{-1} are entirely absent.

The infrared spectra of a large number of aromatic and aliphatic derivatives of tetracoordinate arsenic have been published[95]. All the spectra have been interpreted qualitatively and the influence of the vibrations of the benzene ring, the substituents at the arsenic atom, and the ring substituents on the ν(AsO) absorption bands was examined. An equation relating the stretching vibration frequencies of the M = X bonds to the bond order was derived for molecules of the type R_3M–X (where R = alkyl: M = P, As, or Sb; X = O, S, Se or Te), taking into account the molecular masses[96]. The force constants and bond orders have been calculated from the Raman and infrared spectra of the compounds $(CH_3)_3MO$ (where M = N, P, or As). According to the authors[95], there is extensive p_π–d_π interaction, which is particularly characteristic of the phosphorus and arsenic compounds[97], while according to other data[98], the extent of the interaction is small.

It is noteworthy that many studies on the vibrational spectroscopy of organic compounds of arsenic are to a large extent descriptive and in only some of them has an attempt been made to relate the spectroscopic data to the structures and properties of the compounds. Such comparisons were made for the first time in a number of investigations[77,79,99-102], whose authors were able to determine experimentally the characteristic spectroscopic features of the arsenyl group, to measure its vibrational frequencies for the class of compounds investigated, to find the relation between ν(AsO) and the nature of the substituents at the arsenic atom, and to investigate the influence of solvents on ν(AsO). However, the study of the vibrational frequencies does not yield complete information about the molecular structure. The characteristics of the structure of the electron shell are manifested most completely in the intensities (A) and polarisation of the spectral lines and bands.

The integral stretching vibration band intensity of the arsenyl group $A_{As=O}$ was first calculated[93] for triphenylarsine oxide. Subsequent careful determination of the $A_{As=O}$ for different TAO showed that the band has a high intensity comparable to the integral intensities of the bands due to the phosphoryl and carbonyl groups[100-102]. It has been noted[100] that, on passing from tertiary arsine oxides to arsonic acid esters, the integral intensity of the absorption band diminishes. This indicates an increase in the multiplicity and the strengthening of the AsO bond in the esters.

Hypotheses concerning the fractional AsO bond order in TAO have been put forward in several investigations. Thus, having calculated the force constants and the stretching vibration frequencies of the As–O and As = O bonds (770 and 964 cm^{-1} respectively), an experimental stretching vibration frequency of approximately 880 cm^{-1} was obtained on the basis of the study of the vibrational spectra[91,103]. The AsO bond order calculated from the formulae of Gordy and Siebert proved to be 1.5.[97] In the calculation of the stretching vibration frequency, Shagidullin et al.[99] introduced a correction for the ionic shortening of the bond. The experimental AsO bond length in Ph_3AsO is 1.66 Å,[104] which is intermediate between the values calculated from the Shomaker–Stevenson formula for single and double bonds (1.74 and 1.58 Å respectively). The authors[104] also suggested that the multiplicity of the AsO bond can change under the influence of the electronic properties of substituents by virtue of the polarisation of the d_π–p_π linkage. On the basis of the equation relating the stretching vibration frequency of the AsO bond to the overall electronegativity of the substituent R at the arsenic atom, it has been concluded that the bond under consideration is more polar than the PO bond[104].

On the basis of calculations of the parameters of the correlation of the stretching vibration frequency shift and the known reaction constants of the substituents and taking into account data indicating that the ν(As = O) vibrations are highly characteristic, Shagidullin and Lamanova[100] concluded that the substituent X is conjugated with the As = O group in the chain X––As = O. Since the conjugation has a significant influence on the parameters of the electronic transitions in molecules, such effects should be manifested in the ultraviolet spectra of the test compounds. There are no systematic literature data of this kind and it is only known that the unshared electron pair of the central atom in the phenyl derivatives of Group VB element interacts weakly with the π orbitals of the benzene ring[105-107], and, when the central atom does not have such electrons, there is no resonance interaction at all[108].

The overall electronic effect of the arsenyl groups is electronegative and in aromatic derivatives they behave as *meta*-directing substituents[69,109], i.e. as electron acceptors in relation to the benzene ring. If account is taken of the fact that the electronegativity of the arsenic atom is lower than that of the carbon atom (2.10 and 2.60 according to Pauling[110]), then the most acceptable hypothesis which will explain the above effect may be that of p_π–d_π conjugation. Furthermore, it has been found that[69,109], the shifts of the p absorption band caused by substituents in the series of arsines and their oxides are analogous to the shifts for the corresponding derivatives of aromatic ketones. Since the keto-group is a typical *meta*-directing substituent, the results can be regarded as additional confirmation of the above hypothesis.

Comparison of the frequencies $\nu(As=O)$ with the additivity constants of the substituting groups obtained for organophosphorus compounds showed[111,112] that a linear relation between $\nu(As=O)$ and $\Sigma\chi$ (where χ is the constant of the phosphoryl shift) holds also for organoarsenic derivatives within the limits investigated. This confirms the analogy, noted previously, between the structures and properties of phosphorus and arsenic and also shows that the interactions of the PO and AsO bonds of the substituents are of the same type. The σ constants of arsenic-containing substituents can be found in Lobanov's thesis[113] and in all cases where substituents exhibit electron-accepting properties.

However, despite the fact that the amount of information which can be used for theoretical and semiempirical descriptions of compounds of the type R_3AsO is considerable[114], it is still insufficient for an unambiguous solution of the problem of the multiplicity of the As=O bond in organic compounds of arsenic. In conclusion of the discussion of the results of studies on the electronic structure of compounds of tetracoordinate arsenic, we may note that many most important problems in the chemistry of arsenic have still not been solved. Thus there have been virtually no quantum-mechanical calculations on the structures of arsenic compounds and the amount of double bond character in the arsinyl group and its dependence on the nature of the substituents at the arsenic atom has not been finally established, there are few data on the transmission properties of arsenic in different valence states, and the amount of information on its stereochemistry is insufficient[115-123]. The lack of these data complicates the specific synthesis of new organoarsenic preparations and retards their introduction into various branches of science and technology. In this connection one may hope that, as the theory of the structure of arsenic compounds develops, new fields of practical applications of this interesting class of organoelemental derivatives will be discovered.

III. THE BASICITY OF ARSENIC-CONTAINING EXTRACTANTS IN AQUEOUS AND NON-AQUEOUS SOLUTIONS

The adducts of tertiary arsine oxides with protic acids have been known for a long time. Stable complexes with nitric acid[124,125], chloroacetic acids[126,127], perchloric acid[128], and hydrogen halides[126,128] have been described. The first data concerning the basicity of TAO were obtained in 1941, when Nylen[129] determined the acid dissociation constants of the conjugate acids of trimethylarsine oxide ($pK_a=3.75$) and triethylarsine oxide ($pK_a=3.71$) in water at 20 °C. A wider set of TAO was investigated by Chernokal'skii et al.[130], who determined the basicities of a series of *para*-substituted aryldiethylarsine oxides having the general formula $p\text{-}XC_6H_4As(O)(C_2H_5)_2$ with a variable electronic structure of the substituent X. It was noted that all the TAO investigated are weak bases in water and that their basicity depends on the structure of the Group X. While the length of the hydrocarbon chains of the groups X has almost no influence on the basicity, there is a linear relation between the pK_a of the TAO and the Hammett constants. Analysis of the relations obtained enabled the authors to conclude that the tetracoordinate arsenic atom is capable of transmitting inductive and resonance effects but is a weaker conductor than carbon.

In order to refine the relations between the nucleophilicity of trialkylarsine oxides and their basicity, the pK_a of a series of TAO were determined in water[131]. It was found that oxides of the type Alk_3AsO are moderately strong bases in aqueous solutions, their thermodynamic protonation constants pK_a^T being in the range 3.59–4.03 depending on the structure of the alkyl groups. The lengths of the hydrocarbon groups in the range from $Alk=CH_3$ to $Alk=C_4H_9$ has almost no influence on the basicity, while their steric structure does have an influence. Using a series of oxides of *para*-substituted 10-aryl-5,10-dihydrophenarsazines, the influence of substituents in the *para*-position of the benzene ring on the basicity of the arsinyl oxygen was investigated[132] with the aid of $\sigma\rho$ analysis. The test oxides proved to be fairly weak bases, as shown by the absence of a sharp potential jump at the neutralisation point, with low values of pK_a^T even on titration in aqueous alcoholic media. The observed low reaction constant ρ confirms the earlier conclusion[130] that the electronic conductivity of arsenic is smaller than that of the elements in the Second Period. However, the data[132] concerning the relation between the structure of the compounds and their basicity cannot be regarded as correct for a number of reasons, the principal of which are the low basicity of the majority of the TAO in aqueous solutions, the inadequate accuracy of the measurement of pK_a^T under these conditions, and the short range of variation of ΔpK_a^T as the structure of the groups attached to arsenic is varied. The study of the basicity of the TAO in differentiating organic solvents, among which nitromethane and acetic anhydride are outstanding, is much more promising from this point of view[133].

In the study of the acid–base properties of organoelemental bases in non-aqueous media, the high basicity of the TAO in nitromethane and acetonitrile was noted[134,135]. These observations were fully confirmed in the determination of the basicity ($pK_{B,HX}$) of the oxo-bases in acetic anhydride by the spectrophotometric method and on comparing their electron-donating capacities in the formation of intermolecular hydrogen bonds with thiocyanic acid, deuterophenol, methanol, indole, methylaniline, and phenylacetylene[136]. The results show that triphenylarsine oxide (TPAO) becomes a fairly strong base on non-aqueous solutions, whose strength approaches that of tertiary amines such as triethylamine and trioctylamine.

The rules governing the formation of the basicity of the organoelemental oxo-bases R_nXO with X = S, Se, N, P, or As have been established in a series of studies[136-138]. Particular attention was devoted to the search for relations between the polar effects of the substituents and the basicity or the extracting capacity of the oxo-bases and also to the study of the distribution of the oxides between different phases as the H_2SO_4 concentration in the two-phase system is varied. The constants K_a were determined by Arnett's method. The results of the study showed that the extraction capacity of the oxo-bases is determined to a large extent by their basicity, which is influenced by the nature of the element X in the group XO and by the type of the substituent R. Among both aliphatic and aromatic derivatives, the strongest bases proved to be the oxides of arsenic, antimony, and selenium.

Potentiometric titration of the oxides of substituted aryldihydrophenarsazines in a mixture of acetic acid and acetic anhydride showed[139] that this medium does not have a differentiating effect on the basicities of the test compounds. More hopeful results are obtained when the basicities of the TAO of the type $XC_6H_4As(O)(C_2H_5)_2$ in acetic anhydride and nitromethane are compared[140]. The authors established that acetic anhydride exhibits a differentiating effect and that the pK_a of arsine oxides vary markedly as a function of the structure of the substituents X in the benzene ring. The mixture of nitromethane and acetic anhydride[141], which permits the titration of a wide variety of compounds of tetracoordinate arsenic, possesses such properties.

The determination of the basicity of weak bases in nitromethane by potentiometric titration with perchloric acid became possible after the improvements proposed in a number of investigations[142-144]. The study of the protonation of the oxides of organic derivatives of Group VB elements (nitrogen, phosphorus, and arsenic) by the above procedure made it possible for the first time to determine the pK_a in nitromethane for the derivatives investigated[145]:

$(C_8H_{17})_3PO$	9.72
$(C_8H_{17})_3NO$	16.85
$(C_8H_{17})_3AsO$	16.14

It was found that the protonation reaction proceeds in steps:

$$2R_3EO + H^+ \overset{K_{a_1}}{\rightleftarrows} R_3EO \ldots \overset{+}{H} \ldots OER_3;$$

$$R_3EO \ldots \overset{+}{H} \ldots OER_3 + H^+ \overset{K_{a_2}}{\rightleftarrows} 2R_3\overset{+}{E}OH.$$

On the titration curve, this is manifested by two distinct potential jumps corresponding to 50% ($E^{I}_{0-50\%}$) and 100% ($E^{II}_{50-100\%}$) neutralisation. The use of *N,N'*-diphenylguanidine as the reference standard ($pK_a = 17.2$) made it possible to adjust the observed half-neutralisation potentials $E^{I}_{1/2}$ and $E^{II}_{1/2}$ to the basicity constant scale of the test compounds in nitromethane, which permits in its turn the calculation of the overall basicity constants of the compounds and the equilibrium association constants of the bases in solution ($\lg K_{ass}$). Comparison of the pK_a obtained shows that trioctylphosphine oxide is a weaker base than the corresponding nitrogen and arsenic oxides whose basicities are similar.

Developing this concept further, Laskorin and coworkers determined the pK_a for a series of tertiary arsine oxides and sulphides in nitromethane[146,147]. It follows from the results that the basicity of arsine oxides in both water and nitromethane increases with increasing length of the hydrocarbon group R at the arsenic atom. The pK_a values in water and in nitromethane are linearly related which suggests that the mechanism of the protonation of arsine oxides in water and in non-aqueous neutral solvents is the same. It is noteworthy that the Ka of arsine oxides in nitromethane are higher than in aqueous solutions approximately by a factor of 10^{11} and that trialkylarsine oxides behave in this solvent as organic bases whose strength is not inferior to that of trialkylamines. The replacement of arsenyl oxygen by sulphur on passing from TAO to a trialkylarsine sulphides $R_3As(S)$ reduces the basicity of these compounds approximately by a factor of 10^9 compared with the corresponding arsine oxides. This confirms the adopted mechanism of the protonation of arsenyl compounds at the oxide oxygen, where the pK_a of arsine oxides constitute a relative measure of the electron density at the oxygen of the arsenyl group. The latter has been confirmed also by the linear relations between the pK_a and the σ constants of the substituents at the arsenic atom for a series of aliphatic-aromatic TAO (Table 1). The best correlations are achieved when the σ^{ph} and σ^* constants are used, the slopes of the resulting relations for the TAO being close to the slopes ρ for tertiary phosphine oxides[149]:

$$pK_a = 3.08 - 1.608\Sigma\sigma^{ph}; \quad r = 0.993, \quad n = 30$$
$$pK_a = 8.26 - 1.570\Sigma\sigma^*, \quad r = 0.980, \quad n = 30.$$

This demonstrates the similarity of the mechanisms of the transmission of the electronic influences via the phosphorus and arsenic atoms and eliminates the need for the introduction of specific arsenic substituent σ constants. A similar confirmation was obtained also in the study of the nucleophilicity of the TAO in the reactions with alkyl halides[150-172], where the rate of formation of the complexes is correlated with the constants σ^{ph}.

IV. ELECTRON-DONATING PROPERTIES OF TERTIARY ARSINE OXIDES

The electron-donating properties of the oxo-bases R_nEO (E = N, P, As, or Sb) are determined by the presence of the unshared (lone) electron pairs (LEP) of the oxide oxygen in the upper, energetically low-lying, non-bonding orbital. The first ionisation potentials I_D of these compounds, which determines their electron-donating capacities, refer to the removal of an electron from the molecular orbital (MO), the p_π orbitals of the oxygen atom making the dominant contribution.

Table 1. Parameters of the correlations between the acid dissociation constants of the conjugate acids of arsine oxides and the reaction of constants of substituents: $pK_a = pK_{a_0} - \rho\Sigma\sigma_i$.

σ_i	pK_{a_0}	ρ	r	s	n
σ *para.*	12.654	4.94	0.923	0.44	5
σ ph*	9.619	1.742	0.964	0.33	10
σ ph'*	8.932	1.835	0.982	0.23	7
σ^*	15.145	1.534	0.958	0.35	9
σ_I ph*	12.996	0.807	0.941	0.42	10
σ_I ph'*	16.629	0.718	0.989	0.17	8

* σ^{ph}, $\sigma^{ph'}$, σ_I^{ph}, and $\sigma_I^{ph'}$ were taken from Laskorin and coworkers[146,147].

The energies of formation $\Delta H°$ of the donor–acceptor bond (DA bond), the overlap integrals of the interacting atoms DA, and the ionisation potentials of the compounds I_D can serve as measures of the electron density at the donor atom whose LEP are involved in the formation of the donor–acceptor bond. Comparison of these data[173] with the pK_a values shows that none of the above parameters is correlated with the basicity of the compound. The absence of a linear relation between the basicity and the effective charge on the oxygen of the oxide group (δ_O) should be noted particularly, which conflicts with the widely held conviction that the two parameters are equivalent.

Consequently the electron-donating properties of the molecules cannot be characterised with the aid of the basicity of the compounds but require special consideration. Comparison of the enthalpies of formation of the DA complexes between the bases of the type of oxo-bases (B) and acceptors (A) leaves no doubt that there is no direct relation between the quantity δ_O and $\Delta H°_{AD}$. Many investigators believe that the enthalpy of formation of DA complexes is the most suitable parameter for the description of the electron-donating capacity of compounds in processes of the EDA type. Such processes may include the formation of intermolecular hydrogen bonds (IRHB). The most well-founded method of estimating the electron-donating capacity of molecules in the formation of IRHB involves the determination of the thermodynamic parameters of the formation of hydrogen-bonded complexes with a standard acid—phenol in solution in carbon tetrachloride. Bearing in mind that the entropy of this reaction is virtually constant, one may conclude that the change of Gibbs free energy in the series of compounds investigated is caused by the change in the energy of the DA bond formed. Thus the enthalpy $\Delta H°$ is a quantitative characteristic of the electron-donating properties of the TAO in processes of the donor–acceptor type (Table 2).

It has been established[176] that aliphatic arsenic oxides form solid 1:1 complexes with phenol, which have been isolated and recrystallised from appropriate solvents. After the interaction of TAO with catechol, complexes were isolated and their structure was investigated by X-ray diffraction; the strength of the hydrogen bond in these complexes is so great that they sublime without decomposition[177,178]. The products of the interaction of TPAO with aromatic amines and with acid amides are stable 1:1 adducts. Their structure has been established by infrared spectroscopy; they are molecular compounds with an $R_3AsO...H_2NR^1$ hydrogen bond[179]. Complexes with a similar composition are formed when TAO are mixed with toluene-*p*-sulphonamide : $R_3AsO...H_2NSO_2C_6H_4.CH_3$.[180] Much attention has been devoted to the study of complexes of TAO with hydrogen peroxide, which are formed when arsenic oxides are produced by the oxidation of tervalent arsenic derivatives. Infrared spectroscopic data established that the adducts of H_2O_2 with TPAO and triphenylphosphine oxide (TPPO) have similar structures and have a component ratio of 1:2; the components are linked via a hydrogen bond[181]. The presence of a strong TPAO...HO–OH hydrogen bond, much stronger than in the complex with phosphine oxide, has been demonstrated by a study of the infrared spectra of the solution of TPAO in methanol in the presence of an excess of H_2O_2.[51] The adducts of hydrogen peroxide with TAO are therefore formed quantitatively simply on mixing arsenic oxides in solution in toluene with 30% hydrogen peroxide[1].

Table 2. Thermodynamic parameters of the complex formation reactions between tertiary oxides and phenol in solution in carbon tetrachloride[174,175].

Compound	$-\Delta H^\circ$ (ΔA)	$-\Delta H_f^\circ$	K°_{298}	$-\Delta G^\circ_{298}$	$-\Delta S^\circ$
	kJ	kJ	litre mol^{-1}	kJ mol^{-1}	kJ K^{-1}
$(C_6H_5)_3AsO$	—	—	352	14.5	—
$(C_6H_5)_2As(O)C_8H_{17}$	33.4	29.7	3030	19.8	56.0
$C_6H_5As(O)(C_8H_{17})_2$	31.8	33.6	7960	22.2	47.0
$(C_8H_{17})_3AsO$	35.0	36.0	7840	22.7	47.6
$(C_2H_5)_3AsO$	35.7	—	2518	19.4	59.5
$(C_4H_9)_3AsO$	28.4	—	7142	21.8	44.7
$(C_{12}H_{25})_3AsO$	32.4	—	10000	22.7	44.6
$(C_{16}H_{33})_3AsO$	31.0	—	19596	24.4	37.9
$(cyclo\text{-}C_6H_{11})_3AsO$	35.5	38.3	20000	24.5	41.5
$(C_4H_9CH(C_2H_5)CH_2)_3AsO$	31.5	—	7062	21.9	46.7

Among the other molecular complexes of TAO, mention should be made of the adducts with sulphur trioxide formed in the absence of atmospheric moisture[182], the complexes with iodocyanogen, which exist in solution in two different forms[183], and molecular compounds with iodine[67,184,185]. The last compounds are the most important, since the energy of their formation and their physicochemical properties were studied in detail by Mulliken[186] in connection with the development of the theory of charge-transfer complexes. The energy of the DA bond in the complexes of TAO with molecular iodine depends on the structure of the group attached to the arsenic atom and varies within wide limits[67,184].

The examples examined show that the TAO are some of the strongest electron donors and form stable molecular complexes with molecules having a deficiency of electron density at one of the atoms or vacant orbitals. The wide variety of the possible products of such processes is still far from exhausted; presumably further development of this field will open up new prospects for the theoretical and practical employment of organoarsenic compounds.

V. COMPLEXES OF TERTIARY ARSINE OXIDES WITH METAL SALTS

The complex-forming properties of arsenic oxides in relation to metal ions have been known for a long time and tertiary arsine oxides are therefore widely used as ligands in coordination chemistry. The properties of TPAO, from which numerous complexes of different structure and stoichiometry have been obtained, have been investigated in greatest detail. The structure of the complexes of metal salts with triphenylarsine oxide has been studied in fair detail by Goodgame and Cotton[86]. On mixing alcoholic solutions of copper(II) salts with a solution of TPAO, the complexes $[Cu(TPAO)_2Cl_2]$ and $[Cu(TPAO)_2Br_2]$ were obtained. It has been suggested on the basis of the reflection and absorption spectra of these complexes in the visible and infrared regions, X-ray diffraction patterns of the powders, and a comparison of the results of the available data for complex nickel[187], cobalt[188,189], and manganese(II)[87] salts that the complexes synthesised have a tetrahedral configuration.

The enthalpies of solution of the complex $[Cu(MePh_2AsO)_4.ClO_4]ClO_4$ in 0.02M solution of ethylenediamine in dimethylformamide have been measured calorimetrically at 25 °C. Measurements have also been made of the enthalpies of solution of $MePh_2AsO$ and water in the above solvent. The enthalpies of formation of the solid complexes and the reactants in the condensed state have been calculated. Furthermore, calculations have been made of the dissociation energies of the gaseous complex ions and the stabilisation energies of the metal ions in the crystal field[190]. The possibility of synthesising complexes with transition metals by direct precipitation from acetone solution has been investigated[191]. The complexes $CuCl_2(TPAO)_2$ and $CoCl_2(TPAO)_2$ obtained have been identified by elemental analysis. The compounds have been compared with their analogues synthesised by the available literature methods. The synthetic procedures, compositions, and infrared spectra of the complexes of TPAO, trimethylarsine oxide (TMAO), and trioctylarsine oxide (TOAO) with copper have been described[88,192,193].

The complexes of cobalt(II) salts with TPAO and the bidentate compound $Ph_2As(O)(CH_2)_n(O)AsPh_2$ (henceforth designated by L) have been isolated. It has been established that the TPAO forms complexes with a tetrahedral structure in perchlorate solutions and with a distorted octahedral structure in nitrate solutions. The reaction of the dioxide with cobalt(II) gives rise to complexes of the type $LCo(NO_3)_2$ (I), $[L_2(H_2O)_2Co](ClO_4)_2$ (II), and $[L_2Co](ClO_4)_2.2H_2O$ (III). The crystal structures of the complexes have been determined by magnetic and spectrophotometric analysis. It has been suggested[194] that complexes (I) and (II) have the octahedral structure and complex (III) the tetrahedral structure[194]. Somewhat earlier the cobalt complexes were obtained also by other workers[195]. The ligands employed were trimethyl- and tribenzyl-arsine oxides. The cobalt complexes with various TAO have also been examined in a number of other studies[88,192,193,196–198].

Studies of the infrared spectra of the complexes of TPAO with bivalent metal salts of the type ML_2X_2 (where X = Cl, or Br; M = Mn, Fe, Co, Ni, Cu, or Zn), showed that the stretching vibration frequencies of the AsO bonds occur in the range 840–910 cm^{-1}.[88] The authors believe that the coordination of the oxide to the metal salts increases the $\nu(As=O)$ frequency as a result of the superposition of the arsenic–oxygen

and metal–oxygen bond vibrations, which alter only slightly the position of ν(As=O) in the spectrum. In the spectra of similar complexes with methyldiphenylarsine oxide ν(As=O) is at 875 cm^{-1} and there is a shoulder at 866 cm^{-1} as a result of the superposition of the vibrations of the methyl group and the stretching vibrations of the AsO bond.

Phillips and Tyree[193] obtained a whole series of coordination compounds of TPAO with chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), zinc(II), mercury(II), tin(IV), antimony(III), and antimony(V) salts. In their studies on the infrared spectra of these compounds, the authors concluded that the arsenic–oxygen bond has some double bond character as a result of the p_π–d_π overlap of the occupied *d* orbitals of oxygen with the vacant *d* orbitals of arsenic. The coordination of the oxide to electron acceptors reduces the electron density of the π orbital and diminishes at the same time the bond multiplicity and the ν(As=O) frequency.

Generally speaking the ν(As=O) frequency tends to decrease on complex formation, which indicates a decrease of the bond order; the spectra shift on complex formation can be fairly significant. Thus the shift in the spectrum of the complex $HgCl_2$.TPAO reaches 70 cm^{-1}.[92] The change in the ν(As=O) vibrational frequency on complex formation with manganese salts, where the shifts can be both bathochromic[88] and hypsochromic[87,88], is an exception.

The complexes of zinc salts with TPAO and TMAO have been investigated[87,88,189,192,193,196]. The complex $Ni(TPAO)_4.(ClO_4)_2$ was first synthesised in 1971 [199] and was found to have three different isomers. The magnetic moments of all the isomers were determined, chemical analysis was carried out, and the melting points, electronic absorption spectra, and reflection spectra were measured. The results of the study of the nickel complexes with different TAO have been published[17,87,88,189,192,193]. The complexes of molybdenum(V) with TAO,[200] obtained by methods proposed previously[22,201], have been investigated by EPR. Compounds analogous to those already described[22,201] are formed in solution. Analysis of the EPR spectra led the authors to propose two possible structures of the molybdenum complex with a *cis*- and *trans*-disposition of the arsenic-containing ligands in the coordination sphere. The molybdenum(V) complexes of triphenylarsine oxide were also examined in another study[202].

The interaction of $UO_2(CH_3COO)_2.2H_2O$ with TPAO on refluxing in ethanol led to the isolation of the complexes $UO_2TPAO.nC_2H_5OH$.[203] The presence of the 860 cm^{-1} band in the infrared spectra of the complexes confirmed that the formation of complexes with UO_2^{2+} involves the oxygen of the AsO group. Bearing in mind the high melting point and low solubility of the complex in organic solvents, a polymeric structure was proposed for it with bridging oxygen atoms. The synthesis of the monomeric complexes $UO_2(CH_3.COO)_2.L_2$ and $UO_2[(C_2H_5)_2NCS]_2.L$ and the dimeric complex $[UO_2(CH_3COO)_2.L_2]_2$, where L=TPAO, has been described in a series of communications[204–208]. X-Ray diffraction studies have been made on the compounds obtained, their lattice parameters have been calculated, their molecular weights and molar conductances have been determined, and their infrared spectra have been measured. It has been established that the uranium atoms in the monodentate complex occupy positions at the centres of symmetry of the crystal lattice. The structural parameters of the dimeric complex have been determined by X-ray diffraction and it has been established that uranium(VI) has a coordination number of 7 and that dimerisation takes place via bridging acetate groups.

The complexes of $[UO_2(C_4H_2S_2N)_2]^{2-}$ with TPPO and TPAO have been synthesised and identified by elemental analysis and on the basis of their physicochemical characteristics (colour, melting points, electrical conductivities, and infrared spectra)[209]. It was established that TPAO is a more powerful donor and that the U–O bond in its complex is therefore weakened to the maximum extent. The infrared spectra (in the range 200–500 cm^{-1}) of the complexes $UO_2X_2L_2$ (L=TPAO or TPPO; X=Cl, Br, NO_3, or NCS) have been studied in detail[210]. Comparison with the spectra of the caesium and rubidium complexes[210] enabled the author to carry out new or corrected assignments of the absorption bands. Thus the intense band in the range 247–265 cm^{-1} was assigned to the O–U–O deformation vibrations instead of the metal–nitrate stretching vibration proposed previously. The U–O stretching vibration frequencies in the complexes were found to lie in the range 435–440 cm^{-1}, which indicates unambiguously a stronger bond in the complex with TPAO compared with TPPO. The infrared spectra of TPAO with uranyl nitrate and uranyl chloride have been investigated. In all the cases studied the asymmetric stretching vibration frequency of the AsO group decreases. The values of ν(As=O) have been published for the complex $UO_2(NO_3)_2.2TPAO$, namely 868 cm^{-1} [211] and 862–870,[212,213] while the frequency found for the complex $UO_2Cl_2.2TPAO$ was found to be 848 cm^{-1}.[212] The symmetrical stretching vibration frequency of the U–O group is observed in all cases in the range 910–925 cm^{-1}.

Recent conductimetric and potentiometric studies in anhydrous media demonstrated yet again[214,215] that the ligands containing AsO exhibit a greater capacity for the substitution of chloride ions in the coordination sphere of the uranium atom in UCl_4 than their analogues with the PO linkage. It has been shown by X-ray crystallography that the crystal structure of the complex $UCl_4.2TPPO$ varies as a function of the type of the phosphine oxide substituent[215]. By analogy, the authors decided to investigate the structure of the complex of an arsine oxide with UCl_4. They decided to determine whether or not the strong interaction of the oxygen with uranium leads to a decrease of the U–O bond length. The first compound in the test series was the complex of UCl_4 with triethylarsine oxide. The resulting molecule proved to be centrally symmetrical with four chlorine atoms located in the same plane as uranium and two oxide ligands coordinated to the uranium atom in the *trans*-positions, which leads to the distortion of the tetragonally octahedral arrangement. The bond lengths and the angles are similar to those found previously, but it was discovered that the increase in the length of the UCl bond in the complex with arsine oxide is accompanied by actual shortening of the U–O bond. All the measurements demonstrated convincingly that the interaction with U–O in the example investigated is much stronger than those observed in a wide variety of complexes of phosphine oxides with UCl_4.

The complex of triphenylarsine oxide with $Pu(NO_3)_4$, having the composition $Pu(NO_3)_4.2TPAO$, has been studied in detail[216]. The above communication gives the method of synthesis and infrared spectroscopic data in the range from 200 to 4000 cm^{-1}. It has been established that on complex formation the asymetric stretching vibration frequency of the AsO bond decreases, which is consistent with data obtained previously in the study of the formation of complexes of uranyl nitrate with TPA.[211–213]. As a rule the ν(As=O) frequency is not split on complex formation and in the spectrum of a plutonium complex of TAO there is an intense single band at 850 cm^{-1}. The spectrum of the complex in the visible region indicates the presence of only tetravalent plutonium, although its coordination number is 10. High coordination numbers of the thorium(IV) and thorium(III) complexes had been found previously by X-ray diffraction, amounting to 11 and 12 respectively[217].

Comparison of the frequencies of the nitrato-groups in the plutonium complex with those found earlier for $UO_2(NO_3)_2$. .2TPPO [218] showed that the agreement between them is satisfactory. Bullick[211] assigned the bands at 1515, 1282, 1028, 1032, and 809 cm^{-1} to nitrato-groups, which is fully consistent with data obtained for the plutonium(IV) complex of triphenylarsine oxide[216], where the nitrato-group exhibits bidentate coordination. The 420 cm^{-1} band, observed in the plutonium complex of TPPO, is absent from the spectrum of the TPAO complex. However, a band at 377 cm^{-1} appears in the spectrum of the latter complex, which the authors[216] assigned to the asymetric stretching vibration of the Pu–O bond in the plutonium–oxygen–arsenic group. This assignment is in good agreement with the results of an earlier study of the complexes $MCl_2(TPAO)_2$, where M = Mn, Fe, or Co.[88]

By mixing boiling alcoholic solutions of TPAO and salts of the type $M(NO_3)_3$ (in different molar proportions), where M(III) represents lanthanide elements and yttrium, crystalline complexes of different compositions were obtained[219]. The authors suggested that the alcohol molecule in the complex is coordinated to the M atom and that the complex is a polymer containing NO_3 bridging groups. Infrared spectroscopic data led to the conclusion that the TPAO–M bond is much more stable than the analogous bond in the complexes with triphenylphosphine oxide. A considerable thermal stability of the complexes with the organoarsenic compound compared to the analogous complex with TPPO was noted.

Complexes of lanthanum(III), neodymium(III), and samarium(III) oxides with ethyldiphenylarsine oxide (L) have been synthesised[220]. The complexes isolated were investigated by elemental, magnetic and spectrophotometric analyses. It was established that they are consistent with the fundamental formula $Ln_2Cl_6L_3.xH_2O$ ($x = 0–2$). The high melting points and limited solubilities of the majority of the organic diluents indicate the polymeric nature of the complexes.

More than 25 complexes of the type SnX_4L_2 (where X = Cl, Br, or I; L = TPPO or TPAO) have now been obtained[221]. All the complexes synthesised have been characterised by their infrared spectra and it has been established that in the above series only the *trans*-isomers are produced, with the exception of bidentate structures. A strengthening of the Sn–O bond has been noted and the authors[221] believe that this is caused by the smaller electronegativity of arsenic, the higher polarisability of TPAO, and the smaller contribution of π-bonding in AsO. The tin complexes of triphenylarsine oxide have also been investigated in other studies[193,222–224]. Apart from tin halides, the TAO also react with organotin compounds to form singly- and doubly-charged cationic complexes[225,226], whose structure has been investigated by infrared and ^1H NMR spectroscopy.

It is noteworthy that there is no literature data for the complexes of TAO with alkali metal cations. The complexes $SbCl_3$.2TPAO, $SbCl_3$.2TPPO, $BiCl_3$.2TPAO, and $BiCl_3$.2TPPO have been synthesised and their vibrational spectra investigated in the range 30–1700 cm^{-1}. The structural effects have been examined in terms of the principle of the correspondence between the ν(P=O) and ν(As=O) frequency shifts and the Lewis acidity and basicity of the ligands and the coordination numbers have been calculated. It was established that the difference between AsO and PO is as expected, i.e. TPAO is a stronger base, which is confirmed also by the difference between the metal–oxygen stretching vibration frequencies. A polymeric structure, characteristic also of complexes of heavier elements[227,228], has been proposed for the above complexes. The study of the complex $HAuCl_4$.2TPPO established that the phosphine oxide molecules are not coordinated directly to the metal atom but form a bond with a proton of the chloroauric acid. The complex $[H(TPAO)_2]$. .$AuCl_4$, whose structure is close to that of the complex examined above, was synthesised by an analogous procedure and investigated[229].

The determination of the heats of complex formation made it possible to set up a series based on the electron-donating capacities of different ligands in relation to antimony pentachloride ($Ph_2SeO \cong Ph_3AsO > Me_3PO > Me_2SO$) and tin tetrachloride ($Ph_2SeO \cong Ph_3AsO > Me_3^1PO > Ph_3PO$).[230] The most probable cause of the change in the electron-donating activity is the decrease in the above series of the negative charge on the oxygen atom of the ligand molecule and hence an increase of the multiplicity of the EO bond. The example quoted shows that TPAO is in both cases a fairly powerful ligand, i.e. a compound with a considerable charge at the oxygen atom and a relatively small multiplicity of the bond between the arsenic and oxygen atoms.

Complexes of the type $M(O–O)F_3(TPAO)_2$, where M = Nb or Ta, have been synthesised by a standard method[231]. They are sparingly soluble in organic solvents. The molar conductances indicate a molecular structure of the complexes, which were characterised by the results of elemental, X-ray diffraction, and spectroscopic analyses[231]. The interaction of niobium and tantalum pentachlorides with TPAO led to the formation of complexes with a polymeric structure[232].

Several complexes of manganese(II) salts with TPAO and TPPO are now known, but their stability in air and at room temperature is limited, which significantly hinders their investigation[233]. Our knowledge about their stoichiometry and magnetic and spectroscopic properties is therefore extremely incomplete. The ligands mentioned above have high dipole moments, which in some cases favours the stabilisation of the transition metal complexes, as, for example, in the case of manganese(III) salts. In this connection, synthetic procedures, the results of elemental analyses, and the spectroscopic and magnetic properties of the complexes $Mn(TPPO)_3Cl_3$ and $Mn(TPAO)Cl_3$ have been described. The complexes synthesised are stable in most solvents. Data have been published[233] on their molar conductances in acetone and nitromethane and on their infrared spectra in the range 250–4000 cm^{-1}. The manganese compounds have also been investigated in other studies[87,88,189,192,193].

The reversible and irreversible reactions of iron(III) with the organic bases TPPO and TPAO have been investigated[234] and the equilibrium constants for the formation of 1:1 complexes of TPAO have been determined. It was established that the formation reaction of the complex is a first-order process. The spectra of the adducts have an absorption maximum in the region of 510 nm (TPAO) and 480 nm (TPPO). Complexes of TPAO with iron(II) [235] and mercury(II) [236] salts have been obtained. It has been established that the compounds synthesised have a tetrahedral structure. The iron(II) and iron(III) complexes with trimethyl- and triphenylarsine oxides have been investigated[88,192,193,236].

Rhenium complexes have been described[237,238]. Studies have been made of the complexes of BF_3 with sulphoxides and amine, phosphine, and arsine oxides of the type $R_nXO.BF_3$ (R = Me or Et).[239] The ^1H, ^{11}B, and ^{19}F NMR spectra (at different temperatures) and the ^{31}P NMR spectra have been measured[239]. Data have been published on the complex-forming properties of tribenzylarsine oxide[240].

In conclusion of the discussion of the numerous studies on the complexes of TAO with different metals, one should note that the bond in the complexes investigated is in all cases stronger than in the analogous complexes with organophosphorus compounds. This property of TAO has been used widely in coordination chemistry for the synthesis of new

complexes, which extends our ideas concerning complex formation in aqueous and non-aqueous solutions.

VI. EXTRACTION OF PROTIC ACIDS AND WATER

The greatest number of studies in this field are associated with the extraction of nitric acid. The ability of trialkylarsine oxides or their hydrates to interact with dilute nitric acid in an alcoholic medium has been pointed out in a number of studies[30,241,242]. As a result of such interaction, it has been possible to obtain crystalline salt-like adducts [Alk_3.AsOH]NO_3. The adducts of nitric acid with alkylarylarsine oxides[14,29,30,121] and trialkylarsine oxides[30,57,89,243] are also known.

Numerous X-ray diffraction, infrared spectroscopic, and spectrometric data for the adducts of acids with TAO established two possible structures of the latter in the solid state:

(a) $R_3AsO...HX$—structure presupposing the presence of a hydrogen bond;

(b) $[R_3AsOH]^+X^-$—ionic structure.

The structure of the 1:1 adducts of TAO with acids depends in each specific case on numerous factors, the principal of which are the nature of the acid anion and the strength of the base.

In a study of the electrical conductivity of the adducts of triphenylarsine oxide with nitric acid in acetonitrile it was established[243] that the adduct partly ionises under the influence of the solvent. In addition, the interaction of Rh_3AsO or its hydrate with concentrated HNO_3 yielded triphenylarsine dinitrate $Ph_3As(NO_3)_2$. The compound is extremely hygroscopic and readily hydrolyses in the presence of traces of moisture. A crystalline complex of triphenylarsine oxide with nitric acid precipitates from a solution of triphenylarsine dinitrate in acetone treated with petroleum ether. A detailed study of the extraction of nitric acid has been carried out[244] and the authors showed that the interaction of the acid and the organic base takes place in steps and reduces to a gradual substitution of the water molecules in the structure of the hydrated extractant. Thus at a HNO_3 concentration of 0.1–1.0M the product is a 1:1 adduct with coextraction of water. With increase of the acid concentration, the acid : reagent ratio increases with a corresponding decrease of the water : acid ratio.

It has been suggested[244] that the complex has the composition $R_3AsO.XHNO_3.YH_2O$ with variable values of X and Y depending on the concentration of nitric acid in the aqueous phase and of the extractant in the organic phase. The nature of the associated species formed by water and nitric acid with the organic base has been studied in detail[245,246]. The extraction of HNO_3 into solutions of triphenylarsine oxide in dichloroethane has been studied by both partition and infrared spectroscopic methods. The fractions of free, hydrated, and protonated oxide were determined as logarithmic functions of the ionic activity of nitric acid in the aqueous phase, which was calculated from the corresponding (adjusted to the equilibrium activity of water in the aqueous phase) hydration constants, the protonation constant, and the ionic activity of nitric acid. It was noted that in the case of trioctylphosphine and triphenylarsine oxides the concentration of free oxide (relative to triphenylphosphine and tribenzylphosphine oxides) is too low to be taken into account.

The determination of the energetic characteristics of the hydration of neutral arsenyl compounds is necessary both from the point of view of understanding and a quantitative description of the extraction processes and for the establishment of the electron-donating capacities of these derivatives using water as the reference electron acceptor[247]. For this purpose, the standard enthalpies ΔH°, entropies ΔS°, free energies ΔG°_{298}, and equilibrium constants K^θ of the process[248]:

$$R_3As(X) + H{-}O{-}H \rightleftarrows R_3As(X)\ldots HOH \quad (X{=}O,\ S)$$

were determined in CCl_4 solution by infrared spectroscopy.

When water is added to solutions of TAO in CCl_4, a narrow intense band at 3700 cm^{-1} (ν_S) and a broad diffuse band at 3280–3300 cm^{-1} (ν_{AS}) appear in the infrared spectra, their intensity increasing with increasing concentration of water in the solution. At the same time the stretching vibration frequency of the arsenyl group $\nu(As=O)$ shifts from 890 cm^{-1} to 875 cm^{-1}, which implies that the complex $R_3AsO...H_2O$ is formed under the experimental conditions via an intermolecular hydrogen bond between the water protons and the unshared pairs of the oxygen atom of the arsenyl group.

The calculated hydration constants of arsine oxides are significantly higher than those obtained for phosphine oxides[247]. Contrary to expectation, the replacement of alkyl groups at the arsenic atom by aryl group has little effect on the hydration constants, which decrease only slightly in the sequence trioctylarsine oxide > dioctylphenylarsine oxide > octyldiphenylarsine oxide. The sequence of hydration constants for arsine oxides is fully consistent with the reactivity series calculated on the basis of the complex formation reaction with phenol. The hydration of arsine oxides in solution in CCl_4 is an isoenthalpic reaction, like their complex formation reaction with phenol[174].

In contrast to arsine oxides, arsine sulphides $R_3As=S$ are weaker bases and the constants for the formation of their complexes with water are lower. In solution in CCl_4 it is impossible to determine the hydration constants of these compounds owing to the low concentration of the hydrated form even under the conditions of the complete saturation of the organic solution with water. The equilibrium constant for the process changes little with the length and structure of the groups at the arsenic atom and these changes are wholly determined by entropic factors. In contrast to this, the thermodynamic characteristics of the hydration reaction of phosphoryl compounds depends significantly on the nature of the substituents at the phosphorus atom[249]. Thus the changes in the reactivity of the organophosphorus and organoarsenic extractants in the hydration reaction are due to different causes, which must be taken into account in determining the relation between the electronic structure of these compounds and their reactivity.

The infrared spectra of organic solutions of TPPO and TPAO saturated with nitric acid (equilibrated with an aqueous HNO_3 solution) have two fundamental features[245,246]: (a) with increase of the activity of nitric acid, the intensity of the characteristic absorption bands of the monohydrate falls; (b) the PO and AsO stretching vibrations are displaced towards lower frequencies. The latter data yield reliable information about the nature of the bond between nitric acid and the phosphoryl or arsenyl oxygen in the protonated form. More detailed information about the nature of the bond in the complex $TPAO.HNO_3$ was obtained with the aid of the infrared spectra of the organic phase equilibrated with 2M acid and also the infrared spectra of the solid deposit $TPAO.HNO_3$ in an emulsion with hexachlorobutadiene[246]. The considerable (~100 cm^{-1}) splitting of the ν_3 band due to the antisymmetric vibration of the nitrate ion at 1380 cm^{-1} indicates the interaction of the nitrate ion with the cation. The authors attribute it to a protonated structure of the type $TPAO...H^{\delta+}{-}NO_3^{\delta-}$ with incomplete transfer of the proton. The possible structure of the mixed associated species can be represented

in the following form on the basis of the analysis of the infrared spectra:

$$\begin{matrix} \text{TPAO}\ldots\text{H} \\ \text{TPAO}\ldots\text{H} \end{matrix}\!\!>\!\text{O}\ldots\text{H}^{\delta+}\!-\!\text{NO}_3^{\delta-}\ .$$

The hypothesis of the partial proton transfer from the acid to the oxygen atom of water was subsequently confirmed by the absence of bands due to the H_3O^+ ion in the spectrum of the mixed associated species. Analogous results had been obtained earlier[244]. According to Rozen and Nikolotova's data[250], the complex TPAO.HNO_3, where nitric acid fully displaces water from the organic phase, is extracted into the latter. Similar conclusions were reached in the study of the infrared spectra of solutions of trioxylarsine oxide in CCl_4 after contact with water and nitric acid[251]. The decrease of the intensity of the absorption bands due to the stretching vibrations of free and bound water at 3695 and 3350 cm^{-1} and the $\nu(As=O)$ band at 890 cm^{-1} indicates the displacement of nitric acid by water from the organic phase and the formation of the monosolvate $R_3AsO.HNO_3$.

When the benzene ring is replaced by the octyl group under comparable conditions, the HNO_3 extraction constant increases by a factor of almost 7 in the sequence of $Ph_3AsO < Ph_2As(O)Oct_2 < PhAs(O)Oct_2 < Oct_3AsO$.[251] The extraction constant also increases with increasing length of the group R on passing from aliphatic to alicyclic substituents (Table 3). The extraction capacity of arsine oxides is linearly related to their reactivity in processes of the donor–acceptor type, which confirms in its turn the qualitative conclusions concerning the decisive role of the basicity of arsine oxides in the liquid extraction of inorganic acids and salts. At the same time there are no grounds for isolating trialkylarsine oxides in a separate group of extractants, extracting nitric acid via special mechanisms different from that of extraction by TPAO. It is most probable that one is dealing with a purely quantitative increase of the extraction constant as a result of the replacement of aryl groups by alkyl groups. In this case arsine oxides are full analogues of phosphine oxides for which such properties are well known.

Table 3. Effective constants for the extraction of nitric acid from aqueous solutions by solutions of arsine oxides in carbon tetrachloride[251].

Extractant	$\bar{K}_{HNO_3}$	Extractant	$\bar{K}_{HNO_3}$
$(C_6H_5)_3AsO$	2 220*	$(C_8H_{17})_3AsO$	16 020
$(C_6H_5)_2As(O)C_8H_{17}$	7 630	$(C_9H_{19})_3AsO$	21 390
$C_6H_5As(O)(C_8H_{17})_2$	10 910	(cyclo-$C_6H_{11})_3AsO$	37 250

* In dichloroethane.

The results obtained demonstrate a sharp (by a factor of 10^3) increase of the extraction capacity of arsine oxides compared with their organophosphorus analogues. This phenomenon is difficult to account for, particularly since some workers have adopted the concept of the p_π–d_π conjugation of the unshared electron pairs of the arsenyl oxygen with the vacant 4d orbitals of the arsenic atom. In this case the entire difference between the organophosphorus and organoarsenic compounds reduces to a slight difference between the electronegativities of the phosphorus and arsenic atoms (2.19 and 2.18) and the longer bond lengths for arsenic owing to the greater radius of the latter ($r_P = 1.10$ Å, $r_{As} = 1.21$ Å), while the hybridisation is virtually the same.

These differences do not explain the considerably greater basicity and reactivity of the arsenyl compounds and also the different energy and force constant of the $\geqslant$As–O bond. The model of the arsenyl group with the coordinate bond $\geqslant As^+-O^-$ and only slight conjugation of the arsenyl oxygen with arsenic is more justified. In this case TAO are more likely to be analogues of *N*-oxides than phosphine oxides, which is manifested when the reactivities of these classes of compounds are compared.

Bearing in mind that one of the causes of the increase of the reactivity of the compound R_3EO is the size of the atom E, a number of workers[252–256] attempted to classify the changes in extraction capacity in the series R_3NO–R_3PO–R_3AsO–R_3SbO ($r_N = 0.75$ Å, $r_P = 1.11$ Å, $r_{As} = 1.24$ Å, $r_{Sb} = 1.41$ Å). The increasing basicity of oxygen when phosphorus is replaced by arsenic is caused, in their view, by the decrease of the energy of the element–oxygen bond, as shown by the infrared spectroscopic data for the oxides of the trialkyl derivatives of Group VB elements: $\nu(P=O) = 1170$ cm^{-1} and $\nu(As=O) = 884$ cm^{-1}. The force constant for AsO is smaller by a factor of 1.47 than for PO. The bond energy is reduced as a consequence of the increase of the interatomic distance and also apparently owing to the difficulty of the interaction of the 2p electrons of oxygen with a vacant 4d orbitals of arsenic. Furthermore, the changes in extraction capacity in the series $R_2CO < R_2SO < R_3PO < R_3AsO < R_3SbO$ is explained also by the different electronegativities of the elements, which decreases in the above series of extractants as a consequence of the variation of the amount of ionic character of the element–oxygen bond, the degree of covalence, and bond strength.

The structure of the groups R at the arsenic atom has a significant influence on the partition of nitric acid between water and organic phases. The claim[252] that the mechanism of the extraction of nitric acid changes abruptly on passing from aryl to alkyl organic derivatives of tetracoordinate arsenic is problematical. The authors put forward the variant[252] in which the increase of the basicity of the compound leads to the replacement of the hydrogen bond by proton transfer. Incidentally, in the last study by the same investigators[257], devoted to the formation of complexes by nitric acid with phosphine, arsine, and amine oxides, a linear relation was established between the degree of extraction of nitric acid and the number of phenyl substituents in the molecules of TAO, which disproves an abrupt alteration of the properties in the given reaction series.

Noting the appreciable progress in the study of the extraction of nitric acid by TAO achieved by Rozen et al.[257], we may remark that their conclusions[257] and those of the present authors[251] are quite identical although the two groups of investigators base them on different extraction mechanisms (solvate and ionic respectively). It is extremely probable that the properties of nitric acid extracts in the systems investigated depend significantly on the experimental conditions such as temperature, the type of diluent employed, and the concentrations of the extractant and acid. One can claim with much justification that the extraction of nitric acid by dilute solutions (<0.01M) of TAO in CCl_4 at 25 °C and an HNO_3 concentration <0.01M proceeds via the solvate mechanism. This is supported by the internally consistent linear relations between the free energy of the extraction of HNO_3 and the analogous quantities for donor–acceptor processes[258].

The parallel variation of the free energies of all the reactions considered with the structure of the groups attached to the arsenic atom for a constant reaction centre (arsenyl oxygen) shows that there is no doubt that the donor–acceptor

processes involving TAO obey linear free energy relations (Table 4). For the reactions of arsenyl compounds with acids in organic solvents, the best results have been obtained using the constants σ^*, which ensure high correlation coefficients r for low values of s. The use of the resonance constant σ_R and the overall constants σ, describing the joint inductive and resonance influence of the substituents on the reaction centre, proved successful only for Kabachnik's overall constants σ^{ph} introduced for substituents attached directly to the phosphorus atom.

Table 4. Relation between the free energies (kJ mol^{-1}) of donor–acceptor processes and the reaction constants of substituents: $-\Delta G_i = \Delta G_0 + \rho\Sigma\sigma_i$.

ΔG_i	σ_i	ΔG_0	ρ	r	s	n
$-\Delta G^0_{HNO_3}$	σ^*	23.65	−0.5494	0.94	0.1824	5
$-\Delta G^0_{HNO_3}$	σ^Φ	13.73	−0.7779	0.96	0.1499	5
$-\Delta G^0_{H+(CH_3NO_2)}$	σ^*	6.72	−0.0643	0.97	0.0124	9
$-\Delta G^0_{H+(CH_3NO_2)}$	σ^Φ	5.76	−0.0751	0.96	0.0145	10
$-\Delta G^0_{H+(H_2O)}$	σ^*	3.06	−0.1546	0.99	0.0182	6
$-\Delta G^0_{H+(H_2O)}$	σ^Φ	0.78	−0.1861	0.95	0.3122	6

Thus, within the limits of the series of compounds investigated, the description of the reactivity of arsenyl compounds in processes of the EDA type does not require the introduction of new constants for substituents attached directly to the arsenic atom and one can employ the tabulated σ^* and σ^{ph} constants. The above correlation analysis also permits the conclusion that the mechanism of the transmission of electronic influences in the molecules of organoarsenic compounds is predominantly inductive. At any rate, the resonance interaction between the benzene ring and the arsenic atom observed by physicochemical methods in aromatic arsine oxides does not have an appreciable influence on the reactivity of the organoarsenic compounds. The correlation of the electron-donating capacity of arsine oxides with the overall constants σ^{ph} does not conflict with the inductive model of the transmission of the electronic influences in the molecules of organoarsenic compounds[259], since according to some investigators[258] the inductive component predominates in σ^{ph}.

It is noteworthy that no less attention has been devoted to the study of the products of the interaction of TAO with hydrogen halides than to the extraction with nitric acid. However, the proposed extraction system with HCl has still been relatively little investigated. The model of the extraction with HCl is analogous to that proposed previously for nitric acid, i.e. with increase of the concentration of the acid its molecules displace water molecules combined with the organic base[244]. The infrared spectra of the solid adduct of hydrochloric acid with TPAO have been investigated and the authors observed a complex high-intensity absorption in the range 2000–2750 cm^{-1}, which is a feature of the hydroxy-group involved in a strong hydrogen bond [57]. The behaviour of the adduct in acetonitrile made it possible to classify it as a weak electrolyte.

The oxides of 10-alkyl(aryl)-5,10-dihydrophenarsazines react with HCl in an aqueous alcoholic medium or boiling benzene and give rise to a 1:1 adduct[260]. According to the authors, the structure of the adduct presupposing the presence of a hydrogen bond without proton transfer is the most probable. A detailed study of the HBr and HI systems showed that the extraction behaviour of the two acids is similar[244]. Thus, at an initial concentration of the aqueous acid of 0.1–2.0 M they give rise to 1:1 adducts. The coextraction of one mole of water for each mole of the acid is observed also below the concentration indicated. The tertiary arsine oxide–HBr and HI systems have also been studied in other investigations[57,89,260]. Special experiments[261] demonstrated the possibility of isolating tertiary arsine dihalides as a result of the interaction investigated. It was found that, in the presence of a sufficient excess of the acid, the dihalides become the main reaction products, which is only possible when their resistance to hydrolysis is fairly high.

Among all the acids investigated, perchloric acid exhibited the most distinctive extraction characteristics[244]. Saturation is attained at an acid concentration of 0.1 M and the resulting adduct has the composition $R_3AsO : HClO_4 = 1:1$. It has also been established that each mole of water is coextracted with a mole of perchloric acid entering the organic phase. The interaction of perchloric acid with TPAO has been studied in detail[57]. The compound obtained contained the triphenyloxyarsonium cation, since the high measured conductivity in acetonitrile (λ, cm^2 equiv.$^{-1}$ Ω^{-1} > 100) showed that the compound has an ionic structure. It is known that chloroacetic acids can be arranged in the sequence monochloroacetic acid < dichloroacetic acid < trichloroacetic acid in terms of their strength. Spectroscopic study of the products of the interaction of TAO and the acids in proportions of 1:1 showed that the infrared spectra of the solid adducts can be divided into three types[89,134,262].

1. The infrared spectrum of the adduct of the base with the weak monochloroacetic acid contains three main bands in the range 1800–3000 cm^{-1}. The intensity of these bands changes in accordance with the strength of the acid or the base. A weak hydrogen bond is characteristic of such adducts.

2. The bases investigated form adducts with the strong trichloroacetic acid, whose spectrum does not contain bands characterising the hydroxy-group but there is a broad and intense band in the region of low frequencies. The $\nu(As=O)$ band shifts towards lower frequencies. The spectrum is analogous to those of substances with symmetrical hydrogen bonds without proton transfer to the oxygen of the base. According to the above investigators, the strongest hydrogen bond is characteristic of such adducts. It has also been established that a change in the state of the substance does not entail considerable changes in the spectrum. Analogous results were also obtained by Abalonin et al.[260].

3. The spectrum of the adducts of dichloroacetic acid with TPA changes with the state of the substance[262]. The authors regard this as an intermediate spectrum between the two spectra discussed above. The study of the infrared spectrum of the adducts of dichloroacetic acid with trimethylarsine oxide demonstrated a strong hydrogen bond with proton transfer[262]. A triplet at 1720, 1655, and 1580 cm^{-1} in the region of the band of the antisymmetric vibrations of the CO_2 group was isolated in the spectrum. The addition proton bands at 1720 and 1580 cm^{-1} disappear on deuteration.

The ability of tertiary arsine oxides to interact with picric acid with formation of a crystalline salt is frequently used to isolate them[29,263–265]. It has been established that methylenebis(diphenylarsine) oxide reacts with picric, styphnic, and picrolonic acids, forming the corresponding hydroxypicrates, hydroxystyphnates, and hydroxypicrolonates[16].

The data considered in this Section show that the interaction of TPAO with protic acids (Brønsted acids) is a complicated process whose mechanism is determined by the type of

acid considered. Changes in the structures of the groups attached to the arsenic atom have little influence on the extraction capacity of the compounds, causing purely quantitative alterations within the limits of a single extraction mechanism. On the other hand, a change in the type of acid extracted frequently alters the nature of the interaction of the acid with the extractant from complexes with a weak hydrogen bond to the formation of purely ionic structures. This property of organoarsenic extractants must be carefully taken into account in the study of the extraction of metal salts from acid aqueous solutions.

VII. EXTRACTION OF METAL SALTS

The study of the complex-forming capacity of different classes of organoarsenic compounds led to the discovery of certain effective extractants among them. Thus in a series of studies Rozen and coworkers[250,252-256] investigated the influence of the structure of the reaction centre on the extraction and compared the extraction capacities of trioctylphosphine, triphenylarsine, and trioctylarsine oxides. They established that the reaction capacities of the organophosphorus and organoarsenic oxides are approximately described by a common equation, the maximum extraction capacity being virtually obtained for arsine oxides. It was noted that, in contrast to the extraction with R_3PO, inorganic acids cannot displace metals from the organic phase containing aromatic arsine oxides[250,252-256].

The extraction of metal anions of the type ReO_4^- and TeO_4^- from a 1M solution of hydrochloric acid has been studied. The extraction constants obtained differentiate appreciably the organoarsenic compounds from their phosphorus-containing analogues. The authors[252-256] see the cause of this finding in the different capacities of the oxides for protonation due to the nature of the PO and AsO bonds[137].

The possibility of the extraction of more than 40 elements by trioctylarsine oxide was tested by activation analysis and a detailed study was made of the extraction of iron(III), zinc(II), cadmium(II), hafnium(IV), and zinc(IV).[266] The authors' determination for the equilibrium constants for the formation of the zinc and cadmium halide complexes are of great importance for the estimation of the reactivity of the extractant. At the same time it was established that the extraction of hafnium and zirconium differs appreciably from the extraction of the above elements by phosphine oxides. The principal difference consists in the exceptional stability of the ion $(Oct_3AsOH)^+$, formed with the increase of the acid concentration, whose presence in solution sharply reduces the degree of extraction of metal ions[266].

In order to elucidate the nature of the interaction between the extracted metal and trioctylarsine oxide, a study was made by vibrational spectroscopy of the composition of the extracts formed in the extraction of molybdenum(VI) from sulphuric acid solutions. It was shown that trioctylarsine oxide effectively extracts molybdenum(VI) from sulphuric, hydrochloric, and nitric acid solutions. Regardless of the type of acid, the maximum extraction is observed in the pH range 2–3. It has been established[267] that molybdenum(VI) is extracted from sulphate solutions in the form of molybdenum-containing acids. The above data are fully consistent with the results of the study of the extraction of $CoCl_2$ by R_3NO, R_3AsO, and R_3PO solutions in benzene and CCl_4.[66] The effective constant for the extraction of cobalt decreases by five orders of magnitude, regardless of the solvent, on passing from R_3NO, to R_3AsO, and R_3PO.

The possibility of the quantitative extraction of uranyl nitrate was first investigated by Pietch and Nagl[268]. In the study of a solution of TPAO in chloroform they showed that uranyl ions are fully extracted from nitric acid solutions at pH 2–3. The addition of $NaNO_3$ or $Ca(NO_3)_2$ increases the partition coefficient and extends the limits of effective extraction. The use of EDTA in the process permits the selective extraction of uranium[269]. A study was published later in which methods for the selective extraction of iron(III), in particular in the presence of uranium(VI), were considered at a hydrochloric acid concentration ≥ 8 M.[270]

Among the transuranium elements (M^{3+}), a study has been made of the extraction of americium(III), curium(III), and promethium(III) into cyclohexane solutions of trioctylarsine oxide from aqueous solutions with a variable content of nitric acid and lithium nitrate[271]. The similarity of the dependences of the partition coefficients of M^{3+} on the concentrations of HNO_3 and $LiNO_3$ at constant concentrations of trilaurylamine and trioctylarsine oxide as extractants led the authors to the conclusion that the compound extracted is the complex $TOAO.HNO_3$. It has also been established that, in the case investigated, the extraction properties of trioctylarsine oxide differ significantly from those of its phosphorus-containing analogue. In extraction with a mixture of trilaurylamine and trioctylarsine oxide a synergistic effect is observed, its magnitude depending little on the ratio of the extractants and the nature of M^{3+}. When the organoarsenic compound in the above mixture is replaced by the analogous phosphorus-containing ligand, both synergistic and antisynergistic effects are observed.

The extraction of actinides with TAO has been studied in greatest detail[272] in relation to the partition of trace amounts of uranium, plutonium, and neptunium in different oxidation states between aqueous nitric acid solutions and solutions of aliphatic and aromatic arsine oxides in dichloroethane. On the basis of the linear relations between $\overline{K}_{HNO_3}$ and the constants for the extraction of the actinides (An) by trialkylarsine oxides, one should expect in the given reaction series a parallel increase of $\overline{K}_{An}$ with a sharp increase of the extraction constants owing to the transition to an ion-exchange process mechanism. It has been shown[272] that all the tertiary arsine oxides investigated are powerful extractants of transuranium elements and have values of $\overline{K}_{An}$ ranging from 10^8 to 10^{11} depending on the type of ion extracted, its oxidation state, and the structure of the extractant investigated. The extraction constants of the actinides increase in the sequence $Pu(IV) < Np(IV) < Np(VI) < U(VI) < Pu(VI)$, reaching 10^{11} mol^2 litre^{-2} in the extraction of plutonium(VI).

These values exceed by more than three orders of magnitude the constants for the extraction of the actinides by the isomeric phosphine oxides and are among some of the highest of all those known at the present time. The sequences corresponding to the extractability of metals by phosphine oxides and arsine oxides are the same, which is an argument in support of a single mechanism of the extraction of the actinides by the organoelemental extractants R_3EO with E = P or As. The fact that, regardless of the degree of oxidation, the partition coefficients K_D and extraction constants $\overline{K}_{An}$ of all the actinides investigated decrease on substitution of the phenyl groups in the arsine oxide molecule by octyl substituents merits special attention[273].

The quantitative relations between the basicities of a number of TAO with aromatic and aliphatic substituents at the arsenic atom and the constants for the extraction of the actinides from aqueous nitric acid solutions have been investigated[274]. The linear relation between $\overline{K}_{HNO_3}$ and pK_a implies that the partition of protic acids between aqueous and organic phases under standard conditions for the given

series of compounds is determined by the basicity of the arsenyl oxygen and hence can serve as a measure of its electron-donating capacity. On passing from protic to aprotic metal salts, the linear relations between the pK_a of the compounds and the extraction constants persist, but the increase of the basicity of the TAO (in contrast to their phosphorus-containing analogues) is accompanied by a decrease of the extraction capacity in relation to all the actinides investigated.

The attempt to describe the extraction of the actinides in terms of indices of the electron-donating capacity ($K_{HOC_6H_5}$ and ΔH_T°) proved less successful, since the correlation parameters of these equations were somewhat impaired. It has also been established[274] that the values of $\overline{K}$ for HNO_3 and the actinides are linked by linear relations, but, in contrast to the organophosphorus extractants, they vary in opposition, i.e., after the successive substitution of the aryl groups R by alkyl groups, the extraction capacity of R_3AsO increases in the extraction of protic acids and decreases in the extraction of the actinides.

Thus arsenic compounds have specific features which distinguish them from organophosphorus derivatives and are related to the specific features of the electronic and steric structures. Both these factors can give rise to the observed effect, but, in the absence of non-empirical quantum-chemical calculations for arsenic compounds and thermodynamic parameters of the extraction equilibria involving organoarsenic derivatives, one cannot at the present time give preference to any one of the possible explanations. However, the results obtained leave no doubt that the use of organoarsenic extractants in the far-reaching elimination of radioactive and toxic elements from aqueous solutions is promising. It may be hoped that, with expansion of studies using TAO, other applications of this interesting class of organoelemental compounds will be discovered in both analytical and coordination chemistry and in hydrometallurgical sorption-extraction processes.

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