

# Total reorganization energy and its components in processes of one-electron oxidation of phosphorus compounds in acetonitrile

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The ionization processes of phosphorus(III) and (IV) compounds oxidized in the potential range of 1.8–4.0 V vs. Ag/0.01 M AgNO<sub>3</sub> in MeCN were studied by chronovoltammetry on a Pt ultramicroelectrode in acetonitrile and by photoelectron spectroscopy in the gas phase. A relationship between the half-wave potential ( $E_{1/2}$ ) and vertical ionization potential ( $IP_v$ )  $E_{1/2} = 0.89IP_v - 6.27$  is fulfilled in a wide potential range from –0.37 to 3.98 V. The total reorganization energy of the system (1.45–2.50 V) and the energy of reorganization of the solvate shell (0.9–1.9 eV) were estimated.

**Key words:** electrochemical oxidation, ionization potential, phosphorus compounds, radical cation, reorganization, solvate shell, ultramicroelectrode.

Processes of adiabatic electron transfer to a polyatomic molecule or from a molecule in condensed media are accompanied by an internal reorganization of the molecule (a change in bond lengths and angles) (with the  $\Delta G_0^i$  energy) and reorganization of the solvate shell (with the  $\Delta G_0^s$  energy). The total reorganization energy ( $\Delta G_0^r = \Delta G_0^i + \Delta G_0^s$ ) defines<sup>1</sup> the kinetics of adiabatic electron transfer reactions at the standard potential  $E_0$ . We assumed<sup>2</sup> that the free activation energy ( $\Delta G_0^*$ ) is some fraction ( $\rho$ ) of the total reorganization energy

$$\Delta G_0^* = \rho \Delta G_0^r. \quad (1)$$

For electrochemical oxidation of neutral species, the total reorganization energy can be determined from the difference between the vertical ionization potential ( $IP_v$ ) and the standard redox potential ( $E_0$ ) measured in the absolute potential scale

$$\Delta G_0^r = nF(IP_v - E_0), \quad (2)$$

where  $IP_v$  is expressed in volts. Insertion of Eq. (2) into the kinetic equation gives the dependence of the electron transfer rate constant at the standard redox potential on the experimentally measured thermodynamic values

$$k_s = k_0 \exp[-\rho \Delta G_0^*/(RT)] = k_0 \exp[-\rho nF(IP_v - E_0)/(RT)], \quad (3)$$

and taking into account that

$$k = k_s \exp[\alpha nF(E - E_0)/(RT)]$$

we obtain the dependence that allows one to estimate the rate constant of the activation electron transfer at any electrode potential  $E$

$$k_E = k_0 \exp[-\rho nF(IP_v - E_0)/(RT)] \exp[\alpha nF(E - E_0)/(RT)]. \quad (4)$$

For reduction of neutral compounds, the electron affinity  $A$  is used in Eq. (4) instead of the ionization potential

$$k_E = k_0 \exp[-\rho nF(E_0 - A)/(RT)] \exp[-\alpha nF(E - E_0)/(RT)]. \quad (5)$$

The pre-exponential factor  $k_0 = 9.3 \text{ cm s}^{-1}$  and the proportionality coefficient  $\rho = 0.033$  were determined from the experimental  $k_s$ ,  $IP_v$ , and  $E_0$  values for the redox reactions  $\text{Li}^+_{\text{hydr}}/\text{Li}(\text{Hg})$  and  $\text{K}^+_{\text{hydr}}/\text{K}(\text{Hg})$  and accepting the potential of the hydrogen electrode to be +4.48 V in the absolute potential scale.<sup>3</sup> Thus, we derived the empirical equation that establishes a correlation between the electron transfer rate constant and the experimentally measured thermodynamic values. The dependences obtained can be used for various purposes, in particular, for the estimation of reorganization energies and rate constants  $k_s$  from experimentally measured  $IP_v$  and  $E_0$  values. In this connection, combined studies by photoelectron spectroscopy (PES) and voltammetry of ionization of organic compounds become very important.

In this report, we consider the organophosphorus compounds, their ionization and electrochemical oxidation potentials in acetonitrile, and reorganization energies on the basis of the previously obtained and new data on potentials of vertical and adiabatic ionization and electrochemical oxidation. *Ab initio* calculations, using the self-consistent reactive field method, of internal

reorganization and solvate shell reorganization energies were performed for phosphonous and phosphonic acids.

### Experimental

Anodic oxidation of the compounds was studied by chronovoltammetry in acetonitrile against 0.05 M Et<sub>4</sub>NBF<sub>4</sub> using a GWP 673 polarograph. A disk platinum ultramicroelectrode (UME) with a diameter of 10 μm sealed into glass served as the working electrode. A platinum wire was the auxiliary electrode, and Ag/0.01 M AgNO<sub>3</sub> in MeCN was the reference electrode. The solution was degassed with argon. The sweep rate was 0.1 V s<sup>-1</sup>. Acetonitrile was purified by triple fractional distillation above phosphorus anhydride with addition of potassium permanganate followed by distillation above potash. Tetraethylammonium tetrafluoroborate was purified by recrystallization from acetonitrile.

Ionization potentials were determined by PES. Photoelectron spectra were recorded on an ES-3201 instrument with a helium radiation source, and the calibration was performed by krypton lines.

The vertical ionization potentials (*IP*<sub>v</sub>/eV) of the P<sup>III</sup> and P<sup>IV</sup> derivatives studied are presented below:

$\begin{array}{c} \text{Me} \\   \\ (\text{MeO})_2\text{P}-\text{CCH}_2\text{CMe} \\    \quad   \quad    \\ \text{O} \quad \text{Me} \quad \text{O} \end{array}$	9.23 ( <i>n</i> <sub>O</sub> ), 10.26, 10.45
BuOPCl <sub>2</sub>	10.08 ( <i>n</i> <sub>P</sub> ), 11.18 ( <i>n</i> <sub>O</sub> )
[CHF <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> O] <sub>3</sub> P	10.19 ( <i>n</i> <sub>P</sub> )
(BuO) <sub>3</sub> P	8.88 ( <i>n</i> <sub>P</sub> )

Nonempirical calculations were performed by the GAMESS program.<sup>4</sup> The conformational composition and electronic structure of H<sub>2</sub>POH and H<sub>2</sub>P(O)OH molecules were studied by the restricted Hartree–Fock method in the 6-31G\*\* basis set. Their radical cations were studied by the nonrestricted Hartree–Fock method. Energies of stable conformations were calculated by the perturbation theory at the MP2 level in the frozen framework approximation.

The electrostatic effect of a solvent on the electronic and spatial structures of the molecules and radical cations were studied in terms of the Kirkwood–Onsager model by the self-consistent reactive field method using a spherical cavity with a constant radius.<sup>5</sup> Radii of spherical cavities were determined by the formula  $r = (d_{AB} + r_A + r_B)/2$ , where  $d_{AB}$  is the distance between the most remote atoms A and B, and  $r_A$  and  $r_B$  are the van der Waals radii of atoms A and B, respectively.

### Results and Discussion

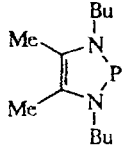
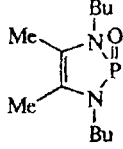
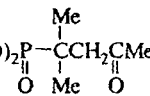

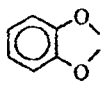
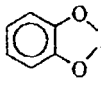

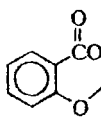
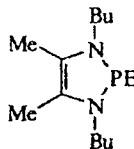
**Electrochemical oxidation in acetonitrile.** Electrochemical oxidation of phosphorus(III) organic derivatives has been under intense study during recent years. The mechanism of electrochemical transformations has been considered, and methods for synthesis of several new poorly accessible compounds have been proposed.<sup>6</sup> Diverse information on oxidation potentials of phosphines, phosphites, and other P<sup>III</sup> derivatives oxidized at potentials from 0.5 to 2.0 V is available in the literature. We were able to extend the potential region toward lower-anodic values (to

–0.37 V) in the study of the electrochemical oxidation of diazaphospholenes.<sup>7</sup> To reach general conclusions, it seemed reasonable to consider other phosphorus derivatives oxidized in a higher-anodic potential region. However, the electrochemical oxidation of phosphorus(III) compounds with strong electron-withdrawing substituents and compounds of four-coordinate phosphorus has not been described until recently. It is known<sup>6</sup> that these compounds are not oxidized in an accessible potential region.

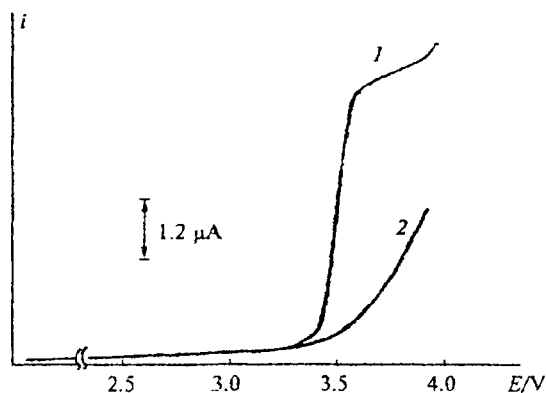
In acetonitrile, which is most widely used in electrochemical oxidation, potentials of up to +2.4 V relative to Ag/0.01 M AgNO<sub>3</sub> in MeCN are accessible for voltammetry on microelectrodes under classical conditions.<sup>8</sup> More anodic potentials are "closed" by the discharge current of the supporting electrolyte. Oxidation potentials of organophosphorus compounds with ionization potentials lower than 9.5 eV can be determined in this solvent against the background of tetrafluoroborate salts. At the same time, acetonitrile has an ionization potential of 12.21 eV, and the electrochemical oxidation of compounds with ionization potentials of up to ~11.5 eV can be studied in this solvent using ultramicroelectrodes characterized by low values of the ohmic voltage drop (*iR*) and fast charging of the double electric layer<sup>9</sup> in the absence of a supporting electrolyte at low depolarizer concentrations or under the conditions of suppression of oxidation currents of the supporting electrolyte at high depolarizer concentrations. The majority of organic compounds obey these requirements and, in particular, compounds of three- and four-coordinate phosphorus.

The chronovoltammograms (CVA) of compounds 1–21 (Table 1) on a Pt UME (the radius of the working electrode is 5 μm) under standard polarographic conditions (the concentration of depolarizer is ≤10<sup>-3</sup> mol L<sup>-1</sup>, that of the supporting electrolyte is 0.05 mol L<sup>-1</sup>, *T* = 22 °C) exhibit the oxidation waves of the aromatic P<sup>III</sup> and P<sup>IV</sup> derivatives only, which are oxidized in the potential region below +2.4 V. The aliphatic and alicyclic derivatives are not oxidized in this potential region. Their oxidation waves are not manifested when the temperature decreases to –40 °C, the concentration of the supporting salt decreases to 10<sup>-3</sup> mol L<sup>-1</sup>, or even in the absence of a supporting electrolyte. The distinct reproducible oxidation waves at superhigh anodic potentials can be detected only at a substantial increase in the depolarizer concentration in the presence of 0.05 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>. The more difficult the oxidation of the compound, the higher concentration is required for the suppression of oxidation currents of the supporting electrolyte and acetonitrile and for the detection of the oxidation wave of the depolarizer. For compounds oxidized in the 2.6–2.8 V potential region, distinct waves are detected already at a concentration of 0.01–0.05 mol L<sup>-1</sup>, whereas concentrations of ~1 mol L<sup>-1</sup> should be used for compounds with oxidation potentials of 3.5–4.0 V. The potential of +4.0 V is most likely the limit for this method of determination, since such high

**Table 1.** Ionization potentials ( $IP_v^1$ ) and electrochemical oxidation potentials ( $E_{1/2}^{ox}$ ) of organic phosphorus compounds

Compound	$IP_v^1$ /eV	$E_{1/2}^{ox}$ /V	$\Delta G_0^r$ eV	$\Delta G^s$	Compound	$IP_v^1$ /eV	$E_{1/2}^{ox}$ /V	$\Delta G_0^r$ eV	$\Delta G^s$
( <i>p</i> -TolO) <sub>3</sub> PO (1)		1.81			 (23)	6.43 <sup>17</sup>	-0.05	1.45	0.89
(PhO) <sub>3</sub> PO (2)		1.90			 (24)	6.86 <sup>17</sup>	0.33	1.50	1.01
(C <sub>6</sub> F <sub>5</sub> O) <sub>3</sub> P (3)		2.19			(Me <sub>2</sub> N) <sub>2</sub> POEt (25)	7.72 <sup>18</sup>	0.64 <sup>6</sup>	1.90	1.34
 (4)	9.23*	2.44	1.61	1.61	PPh <sub>3</sub> (26)	7.88 <sup>19</sup>	0.90 <sup>6</sup>	1.80	1.35
BuOPCl <sub>2</sub> (5)	10.26 10.08*	3.00 2.82	2.08 2.08	1.59 1.52	PEt <sub>3</sub> (27)	8.28 <sup>20</sup>	0.92 <sup>6</sup>	2.18	1.62
 (6)	10.20 <sup>11</sup>	2.83	2.19	1.63	Ph <sub>2</sub> PH (28)	8.29 <sup>19</sup>	0.86 <sup>6</sup>	2.25	1.69
(CHF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> O)P (7)	10.18 <sup>10</sup>	2.85	2.15	1.59	 (29)	8.45 <sup>13</sup>	1.29 <sup>13</sup>	1.98	1.42
[CHF <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> O] <sub>3</sub> P (8)	10.19*	2.89	2.12	1.56	(MeS) <sub>2</sub> PMe (30)	8.50 <sup>21</sup>	1.05 <sup>6</sup>	2.27	1.71
(CF <sub>3</sub> CH <sub>2</sub> O) <sub>3</sub> P (9)	10.37 <sup>10</sup>	2.93	2.26	1.70	 (31)	8.86 <sup>13</sup>	1.58 <sup>13</sup>	2.10	1.54
Bu <sub>3</sub> PO (10)		3.00			(BuO) <sub>3</sub> P (32)	8.88*	1.55 <sup>13</sup>	2.15	1.59
 (11)	10.74 <sup>13</sup>	3.15	2.41	1.85	Me <sub>3</sub> SiOP(OMe) <sub>2</sub> (33)	8.95 <sup>13</sup>	1.78 <sup>13</sup>	1.99	1.43
(BuO) <sub>3</sub> PO (12)	10.34 <sup>15</sup>	3.16	2.00	1.51	(MeO) <sub>3</sub> P (34)	9.18 <sup>22</sup>	1.66 <sup>13</sup>	2.34	1.78
(EtO) <sub>3</sub> PO (13)	10.54 <sup>14</sup>	3.24	2.12	1.63	 (35)	9.42 <sup>13</sup>	2.34 <sup>13</sup>	1.90	1.34
(MeO) <sub>3</sub> PO (14)	10.82 <sup>14</sup>	3.24	2.40	1.91					
[(CF <sub>3</sub> ) <sub>2</sub> CHO] <sub>3</sub> P (15)	10.71 <sup>10</sup>	3.37	2.16	1.60					
(MeO) <sub>2</sub> PHO (16)	11.10 <sup>12</sup>	3.57	2.35	1.86					
(EtO)P(O)Cl <sub>2</sub> (17)	11.46 <sup>14</sup>	3.98	2.30	1.81					
TGF (18)	9.57 <sup>16</sup>	2.71	1.68	1.68					
EtOEt (19)	9.53*	2.73	1.62	1.62					
MeC(O)Me (20)	9.69 <sup>16</sup>	3.04	1.47	1.47					
MeOH (21)	10.85 <sup>16</sup>	3.28	2.50	2.35					
 (22)	6.60 <sup>17</sup>	-0.37	1.94	1.38					

\* Data of this work.

**Fig. 1.** Chronovoltammogram of the oxidation of (MeO)<sub>2</sub>PHO (1 mol L<sup>-1</sup>) on a Pt UME (*r* = 5 μm) in MeCN against 0.05 M Et<sub>4</sub>NBF<sub>4</sub> (1) and supporting electrolyte curve (2).

concentrations of the depolarizer would have to be used to achieve higher potentials that the latter begins to act as the solvent, and we should consider the oxidation as not occurring in acetonitrile, but in a mixed solvent.

The CVA of the oxidation of (MeO)<sub>2</sub>PHO (Fig. 1) exhibits one oxidation wave with the pronounced limiting current. The slope of the wave ( $dE/d\log[i/(i_{lim} - i)] = 80$  mV) corresponds to the reversible electron transfer (some increase is related to the voltage drop) and indicates the absence of a substantial *iR* contribution to the measured potentials even at high concentrations of the depolarizer. This conclusion is consistent with the results of studying the dependence of the parameters of the reduction waves of (PhO)<sub>3</sub>PO on the concentration of the depolarizer on the amalgamated Pt UME (radius 5 μm). The potential of the half-wave ( $E_{1/2}$ ) and the slope of the wave deviate only insignificantly from the true value at high concentrations of the depolarizer

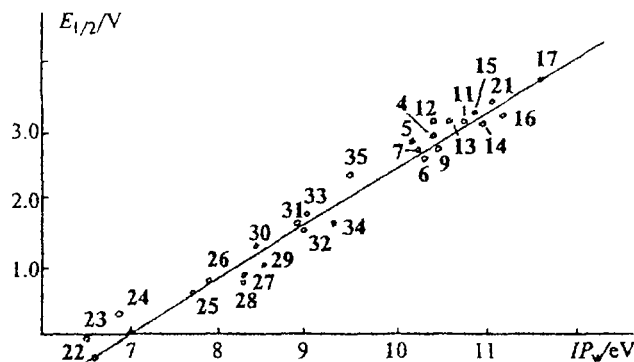
**Table 2.** Electrochemical parameters of reduction waves for triphenyl phosphate in DMF against 0.1 M Et<sub>4</sub>NClO<sub>4</sub> on Pt/Hg UME

<i>C</i> /mol L <sup>-1</sup>	$-E_{1/2}$ /V	$i_{lim}$ /nA	$\frac{dE}{d\log[i(i_{lim} - i)]}$ /mV	$\frac{i_{lim}}{C} \cdot 10^{-3}$ /nA L mol <sup>-1</sup>
$1.4 \cdot 10^{-3}$	3.06	16.8	70	12.0
$2.5 \cdot 10^{-3}$	3.06	30.8	75	12.1
$5.2 \cdot 10^{-3}$	3.05	51.0	65	9.9
$1.1 \cdot 10^{-2}$	3.05	89.0	60	8.5
$2.4 \cdot 10^{-2}$	3.05	176	70	7.3
$4.9 \cdot 10^{-2}$	3.05	356	70	7.3
0.1	3.07	640	70	6.4
0.2	3.06	1120	80	5.6
0.5	3.07	2160	85	4.3

(Table 2). Therefore, the experimentally measured  $E_{1/2}$  values on UME are true at superhigh depolarizer concentrations and have the same sense as potentials measured under classical electrochemical conditions.

The obtained values of  $E_{1/2}$  are presented in Table 1. It is noteworthy that the oxidation potentials of aromatic and aliphatic phosphorus derivatives differ substantially. In the series of both fluorinated phosphites (3, 7–9, and 15) and phosphates (1, 2, and 12–14), the aromatic derivatives are much more easily oxidized than the aliphatic derivatives, although the corresponding phosphines are oxidized almost at the same potentials.<sup>6</sup> The F atom in P<sup>III</sup> compounds manifests much stronger electron-withdrawing properties than the Cl atom (6 and 11). Fluorinated trialkyl phosphites (7–9, 15) are oxidized at potentials 1.3–2.0 V more positive than the oxidation potentials of the corresponding nonfluorinated phosphites. Trialkyl phosphites (12–14) are oxidized in the same potential region. The CVA curves of dimethylphosphite (4) exhibit two oxidation waves ( $E_{1/2}^1 = 2.44$  V,  $E_{1/2}^2 = 3.00$  V), the first of which corresponds to the oxidation of the ketone part of the molecule, and the second wave corresponds to the oxidation of the fragment with the phosphoryl group. This follows from a lower value of the oxidation potential of acetone (20) than that of dimethyl phosphite (16). The successive substitution of two alkoxyl groups in dimethyl phosphite by alkyl groups results in a potential shift of ~0.4 V per each group, thus facilitating the oxidation process. This influence is much stronger than in the corresponding P<sup>III</sup> compounds, which indicates a higher contribution of alkyl groups to the energy of HOMO in molecules of P<sup>IV</sup> compounds.

**Ionization and oxidation potentials.** The half-wave potentials of the compounds under study are compared to the ionization potentials (see Table 1). For dimethylphosphite, the second ionization and oxidation potentials were used, which corresponds to the ionization of the fragment with the phosphoryl group. Although  $E_{1/2}^2$  corresponds to the oxidation of the phosphoryl group of the molecule with the already oxidized ketone group, it



**Fig. 2.** Dependence of the oxidation potentials ( $E_{1/2}$ ) on the ionization potentials ( $IP_v$ ) for organophosphorus compounds.

can be attributed, most likely, to the starting molecule, because these two fragments are sufficiently remote from each other, and their oxidation can be considered, in the first approximation, as mutually independent.

We have previously studied<sup>13</sup> the ratio between the ionization and oxidation potentials in the series of P<sup>III</sup> derivatives with ionization and oxidation regions of about 9.42 eV and 2.34 V, respectively. In this work, for the combined consideration of the P<sup>III</sup> and P<sup>IV</sup> derivatives, the region of the ionization and oxidation potentials has been extended considerably.

The oxidation ( $E_{1/2}^{ox}$ ) and vertical ionization potentials are related by the linear correlation (Fig. 2) described by the regression equation

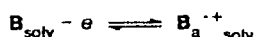
$$E_{1/2}^{ox} = 0.89IP_v^1 - 6.27 \quad (r = 0.997, s = 0.17, n = 25). \quad (6)$$

This correlation covers a wide region of oxidation potentials (to  $\Delta E_{1/2}^{ox} = 4.35$  V) and is valid for compounds with different reaction centers (an unshared electron pair (UEP) of the P or O atom of the phosphoryl group) that are reversibly or irreversibly oxidized. Fulfillment of the linear correlation between  $E_{1/2}^{ox}$  and  $IP_v^1$  indicates first of all that the same highest occupied molecular orbital is the reaction center during electrochemical oxidation and photoionization. In both cases, the electron transfer results in the radical cation. Although radical cations were directly detected in the electrochemical experiment with compounds 22–24 only, their formation during the electrochemical oxidation in MeCN is doubtless, because the existence of these species for several P<sup>III</sup> compounds and oxygen-containing compounds 18–21 has reliably been detected by ESR at a low temperature.<sup>6,23</sup> In addition, the linear character of Eq. (6) implies either the correlation of energies of processes accompanying the electron transfer in the solution with the ionization potentials, or their insignificant contribution to the  $E_{1/2}^{ox}$  value. The observed deviations from the linear dependence are low (the maximum deviation amounts to 0.23 V for compound 12) and can be explained by the influence of

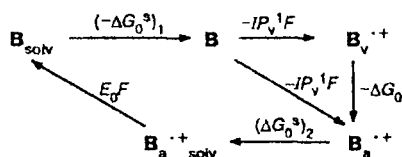
various factors (reorganization of the molecule, subsequent chemical and electrochemical reactions, steric and heterogeneous factors) on the  $E_{1/2}^{\text{ox}}$  value.

Comparison of the obtained dependence with similar dependences described in the literature for series of various organic compounds (the range of oxidation potentials varied from 0.34 to 3.28 V)<sup>24</sup> and bielemental organic compounds<sup>25</sup> suggests that the value of the angular coefficient ( $\sim 0.90$ ) is almost the same in all cases. Probably, the same factors affect the experimental values of the angular coefficients in the reaction series mentioned.

A relation between  $E_{1/2}^{\text{ox}}$  and  $IP_v^1$  for the electrode reaction



can be obtained from the thermochemical cycle



$$E_0 F = FIP_v^1 - \Delta G_0^s - \Delta G_0^i = FIP_v^1 - \Delta G_0^r,$$

where  $\Delta G_0^s = (\Delta G_0^s)_2 - (\Delta G_0^s)_1$  is the reorganization energy of the solvate shell, and  $\Delta G_0^i = F(IP_v^1 - IP_a^1)$  is the reorganization energy of the molecule during adiabatic electron transfer. For reversible reactions,  $E_{1/2} = E_0 - RT/F \ln(f^+ D/fD^+)$ , where  $f$ ,  $f^+$  and  $D$ ,  $D^+$  are the activity and diffusion coefficients of the molecule and radical cation, respectively. They differ insignificantly for the molecule and radical cation; therefore,  $E_{1/2} = E_0$ . For irreversible reactions, an additional factor appears, which is due to the occurrence of subsequent chemical or electrochemical reactions

$$E_{1/2} = E_0 - f(k).$$

In the general case, the effect of ion pair formation should also be taken into account; however, in this work, we used bulky perchlorate and tetrafluoroborate anions that do not tend to considerably associate; therefore, we did not consider this factor.

When  $E_{1/2}$  and  $IP$  are measured in volts, and the reorganization energy is measured in electron-volts, the Faraday number ( $F$ ) can be omitted for simplicity, because numerical values in these measurement units coincide. Then the relation between  $E_{1/2}$  and  $IP$  takes the following form:

$$E_{1/2}^{\text{rev}} = IP_v^1 - \Delta G_0^s - \Delta G_0^i = IP_a^1 - \Delta G_0^s,$$

$$E_{1/2}^{\text{irrev}} = IP_v^1 - \Delta G_0^s - \Delta G_0^i - f(k) = IP_a^1 - \Delta G_0^s - f(k).$$

It is noteworthy that  $E_{1/2}$  values in these equations are presented in the absolute scale of potentials, and

$E_{1/2}$  were experimentally measured relative to  $\text{Ag}/0.01 \text{ M AgNO}_3$ . The potential of the reference electrode used is equal to +0.55 V relative to the hydrogen electrode, whose potential (according to the last data of Trasatti<sup>3</sup>) amounts to +4.48 V in the absolute potential scale. Therefore, to obtain  $E_{1/2}^{\text{abs}}$  in the absolute potential scale, 5.03 V should be added to the experimentally measured values, i.e.,

$$E_{1/2}^{\text{abs}} = E_{1/2}^{\text{ox}} + 5.03.$$

The difference  $IP_v^1 - E_{1/2}^{\text{abs}}$  for the compounds studied is equal to 2.0–2.6 V (see Table 1). Compounds 22–24 are reversibly oxidized, and this difference for them is equal to the total reorganization energy of the system

$$\Delta G_0^r = IP_v^1 - E_{1/2}^{\text{abs}}.$$

The electrochemical oxidation of trimesitylphosphine occurs reversibly,<sup>26</sup> and it can be assumed that in the case of triphenylphosphine, the contribution of subsequent chemical reactions to the  $E_{1/2}^{\text{abs}}$  value is also insignificant. The difference between  $IP_v^1$  and  $E_{1/2}^{\text{abs}}$  is equal to 1.95 V and also corresponds to the total energy of internal reorganization of the molecule and reorganization of the solvate shell. For the remaining compounds that are irreversibly oxidized, the  $IP_v^1 - E_{1/2}^{\text{abs}}$  difference is determined by the factors of reorganization and subsequent transformations of radical cations. Let us consider possible contributions of each factor.

**Subsequent chemical or electrochemical reactions.** The half-wave potential  $E_{1/2}$  corresponds to the potential at which the current is equal to half the limiting diffusion current, which corresponds (with the retarded electron transfer) to the electron transfer rate constant  $k_e = 2-4 \cdot 10^{-3} \text{ cm s}^{-1}$  (chronovoltammetry on micro- and ultramicroelectrodes,  $V = 0.1 \text{ V s}^{-1}$ ). The experimentally measured standard rate constant for highly conjugated systems is the following<sup>27</sup>:  $k_s \leq 1 \text{ cm s}^{-1}$ . The transfer coefficient  $\alpha$  is usually equal to 0.5. Calculation by the equation of electrochemical kinetics using these data shows that the maximum deviation of  $E_{1/2}$  from  $E_0$  due to subsequent chemical and electrochemical reactions is equal to  $\sim 0.3 \text{ V}$ . This estimate agrees with the independent data of Parker<sup>28</sup> for EC processes followed by chemical reaction of the first (287 mV) and second (127 mV) orders. Taking into account that retarded transfer takes place in several cases (for example, with compound 16), and  $k_s$  for these compounds is somewhat lower, we can suggest that the deviations of  $E_{1/2}$  from  $E_0$  are considerably lower than 0.3 V. Apparently, in the series studied, the contribution of the subsequent chemical and electrochemical reactions to the  $IP_v^1 - E_{1/2}^{\text{abs}}$  difference is low ( $\leq 12\%$ ).

For all compounds oxidized irreversibly, the  $E_{1/2} - E_0$  difference is accepted to be equal to 0.15 V, and the

values of the total reorganization energy (1.45–2.50 eV, see Table 1) were determined from the formula

$$\Delta G_0^r = IP_v^1 - E_{1/2}^{abs} - 0.15.$$

**Internal reorganization of a molecule.** Analysis of the published data<sup>29,30</sup> shows that the P<sup>III</sup> and P<sup>IV</sup> compounds undergo a noticeable spatial reorganization in adiabatic ionization–oxidation reactions. The internal reorganization energy of reacting species, according to the experimental values of vertical and adiabatic ionization potentials, is almost independent of the nature of substituents and amounts to  $0.56 \pm 0.02$  eV for the P<sup>III</sup> compounds and  $0.49 \pm 0.02$  eV for the P<sup>IV</sup> compounds. We used these  $\Delta G_0^i$  values for studying the P<sup>III</sup> and P<sup>IV</sup> compounds. Note that the factor of internal reorganization contributes noticeably ( $\leq 30\%$ ) to the  $IP_v^1 - E_{1/2}^{abs}$  difference. Molecules of compounds 22–24, 26 contain the conjugated  $n-\pi$ -system and obey the rule of "minimum change in structure."<sup>31</sup> Nevertheless, in this case, the internal reorganization energy is sufficiently high and has the same value as those for other P<sup>III</sup> compounds.

**Reorganization of the solvate shell.** The reorganization energy of the solvate shell  $\Delta G_0^s$  is defined as the  $\Delta G_0^r - \Delta G_0^i$  difference. The analysis presented shows that the difference in potentials of vertical ionization and electrochemical oxidation of the compounds studied is mainly due to the reorganization of the solvate shell. The  $\Delta G_0^s$  values obtained are presented in Table 1. As can be seen, the free energy of solvation of radical cations is 0.9–1.9 eV higher than the similar value for the starting compounds. If the contribution of various ignored factors is accepted as compensated, we can obtain a formal correlation between the reorganization energy of the solvate shell and the ionization potential  $\Delta G_0^s = 0.11IP_v^1 + 0.57$ , and  $\Delta G_0^s$  increases by 0.4 eV as the ionization potential increases by 5 V.

The application of the known<sup>32</sup> Mairanovskii anti-bate rule to the processes considered implies an increase in the rates of subsequent chemical reactions and, hence, in the shift of  $E_{1/2}$  relative to  $E_0$  with an increase in the oxidation or ionization potential. This should result in a decrease in the angular coefficient of the dependence of  $IP_v^1$  on  $E_{1/2}^{abs}$  without distortion of the linear dependence itself. The aforesaid implies that the maximum value of the reorganization of the solvate shell is equal to 2.0 eV, and the real angular coefficient of the dependence of  $\Delta G_0^s$  on  $IP_v^1$  can be somewhat lower. The dependence of the reorganization energy of the solvate shell on the ionization potential, as well as the occurrence of subsequent chemical reactions, affects the experimental value of the angular coefficient of the dependence of  $E_{1/2}$  on  $IP_v^1$ .

Another regularity is also noteworthy. In the series of structurally similar compounds, the reorganization energy of the solvate shell decreases as the species sizes increase. This is valid for the series of trialkyl phosphites (7, 9, 15, and 35), halophosphites (6, 11, and 31), and trialkyl phosphates (12–14). This dependence is characteristic of

the nonspecific (electrostatic) solvation of charged species in polar media. Probably, the regularity observed indicates that in the series of compounds indicated, the differences in reorganization energies of the solvate shell are due to the distinctions in the electrostatic solvation of the radical cations. These distinctions are so high that they align, to a considerable extent, the changes in  $IP_v^1$  and, as a consequence, in this series of compounds,  $E_{1/2}$  is less sensitive to the nature of the substituent.

Thus, the  $\Delta G_0^s$  value can be presented as a function of the ionization potential and the species size. The last parameter, which is only slightly noticeable during the variation of  $IP_v^1$  in a wide range, becomes more noticeable in the analysis of narrow series of structurally similar compounds.

**Quantum-chemical study.** The quantum-chemical calculations for phosphonous and phosphonic acids give an insight into reorganization processes of three- and four-coordinate phosphorus compounds during adiabatic electron transfer in the gas phase and in acetonitrile ( $\epsilon = 36$ , Tables 3 and 4). The nonempirical calculations of the molecules by the restricted Hartree–Fock method at the HF/6-31G\*\* level and of the radical cations by the nonrestricted Hartree–Fock method at the UHF/6-31G\*\* level indicate the existence of two stable conformations (*cis* and *trans*). For both molecules and radical cations, the *cis*-conformation is preferable. The relative energies of the *trans*-conformation are presented in Table 5.

The geometric parameters and indices of the electronic structures of the *cis*- and *trans*-conformations are sufficiently close. The adiabatic electron transfer in the gas phase results in a change in all geometric parameters of the  $H_2POH$  and  $H_2P(O)OH$  molecules (see Table 3). The  $H_2POH^{+\cdot}$  and  $H_2P(O)OH^{+\cdot}$  radical cations, as compared to the starting molecules, exhibit shortening of the P–O bond, an increase in the POH bond angle, and a decrease in the pyramidal character of the coordination polyhedron of phosphorus. A considerable elongation of the P=O bond is observed in the  $H_2P(O)OH^{+\cdot}$  radical cation. The flattening of the molecule is a substantial factor that defines the spatial reorganization energy of the molecule. A change in the angle of internal rotation about the P–O bond ( $n_pPOH$ ) is the characteristic feature of the structure of the most stable *cis*-conformation of the  $H_2POH^{+\cdot}$  radical cation. In the *cis*-conformation of the molecule, this angle is equal to  $0^\circ$  (the unshared pairs  $n_p$  and  $n_o$  are orthogonal), and in the radical cation, it is  $\sim 60^\circ$ . A change in the corresponding torsion angle is not observed in the *cis*- and *trans*-conformations of the  $H_2P(O)OH^{+\cdot}$  radical cation and in the *trans*-conformation of the  $H_2POH^{+\cdot}$  radical cation.

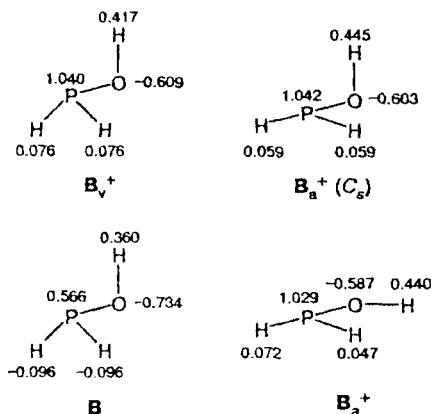
To describe the spatial reorganization of the  $H_2POH^{+\cdot}$  radical cation in more detail, in addition to the vertical and adiabatic states, we also calculated the structure of symmetry  $C_s$ , in which the  $n_pPOH$  angle was accepted to be  $0^\circ$  and the remaining parameters were optimized. The change in energy due to the inter-

**Table 3.** Results of quantum-chemical calculations of geometric parameters of  $\text{H}_2\text{POH}$ ,  $\text{H}_2\text{P(O)OH}$  (HF/6-31G\*\* level), and their radical cations (UHF/6-31G\*\* level) in the gas phase and in an acetonitrile solution ( $\epsilon = 36$ )

Particle (conformation)	Phase	Bond length/Å				Bond angle/deg			
		P—O	P=O'	P—H	O—H	OPO'	OPH	POH	$n_{\text{pPOH}}$
$\text{H}_2\text{POH}$ ( <i>cis</i> )	Gas	1.648		1.404	0.943		99.5	111.2	0.0
	Solution	1.644		1.408	0.942		99.0	111.6	10.0
$\text{H}_2\text{POH}$ ( <i>trans</i> )	Gas	1.641		1.411	0.944		101.3	115.8	180.0
	Solution	1.641		1.411	0.944		101.3	115.8	180.0
$\text{H}_2\text{POH}^{\cdot+}$ ( <i>cis</i> )	Gas	1.550		1.381	0.953		109.6	123.5	65.5
	Solution	1.560		1.384	0.952		108.2	123.7	62.5
$\text{H}_2\text{POH}^{\cdot+}$ ( <i>trans</i> )	Gas	1.545		1.386	0.954		113.5	126.4	179.0
	Solution	1.545		1.386	0.954		113.5	126.4	179.0
$\text{H}_2\text{P(O)OH}$ ( <i>cis</i> )	Gas	1.596	1.457	1.388	0.947	115.4	102.0	113.1	0.2
	Solution	1.586	1.466	1.383	0.949	114.1	104.4	111.4	0.1
$\text{H}_2\text{P(O)OH}$ ( <i>trans</i> )	Gas	1.594	1.454	1.392	0.945	114.5	103.3	117.4	180.0
	Solution	1.594	1.454	1.392	0.945	114.5	103.3	117.4	180.0
$\text{H}_2\text{P(O)OH}^{\cdot+}$ ( <i>cis</i> )	Gas	1.535	1.591	1.377	0.953	115.0	109.6	126.5	0.2
	Solution	1.537	1.599	1.376	0.953	113.5	110.2	125.4	0.0
$\text{H}_2\text{P(O)OH}^{\cdot+}$ ( <i>trans</i> )	Gas	1.536	1.587	1.379	0.952	109.4	112.4	126.8	180.0
	Solution	1.536	1.587	1.379	0.952	109.4	112.4	126.8	180.0

nal rotation about the P—O bond ( $1.5 \text{ kcal mol}^{-1}$ ) is an insignificant portion of the reorganization energy of the radical cation (see Table 4). According to the results of calculations at the HF/6-31G\*\* level, the reorganization energies of the *cis*- and *trans*-conformations of the  $\text{H}_2\text{P(O)OH}^{\cdot+}$  radical cation are 18.9 and  $19.8 \text{ kcal mol}^{-1}$ , respectively. Correction of the correlation energy by the perturbation theory of the second order MP2/6-31G\*\* results in an insignificant decrease in the reorganization energies of the  $\text{H}_2\text{POH}^{\cdot+}$  radical cation by 2.9 and  $1.6 \text{ kcal mol}^{-1}$  for the *cis*- and *trans*-conformations, respectively. The effective charges on

atoms of the  $\text{H}_2\text{POH}$  molecule and radical cation in different states are presented below:

**Table 4.** Ionization potentials and energies of HOMO, internal reorganization, solvation, and reorganization of the solvate shell in acetonitrile for phosphonous and phosphonic acids calculated at the HF/6-31G\*\* level

Molecule (conformation)	$-\epsilon$	$IP_a$	$IP_v$	$\Delta E_i$	$E_s$	$\Delta E_s$
		eV		kcal mol <sup>-1</sup>		
$\text{H}_2\text{POH}$ ( <i>cis</i> )	9.98	8.12	8.96	19.5	0.3	58.6
$\text{H}_2\text{POH}$ ( <i>trans</i> )	10.20	8.25	9.14	20.5		
$\text{H}_2\text{P(O)OH}$ ( <i>cis</i> )	12.13	8.82	9.64	18.9	2.3	57.8
$\text{H}_2\text{P(O)OH}$ ( <i>trans</i> )	12.06	8.68	9.54	19.8		

**Table 5.** Relative energies of the *trans*-conformation calculated by different quantum-chemical methods

Compound	$E/\text{kcal mol}^{-1}$	
	HF/6-31G**	MP2/6-31G**
$\text{H}_2\text{POH}$	0.12	0.57
$[\text{H}_2\text{POH}]_v^{\cdot+}$	4.30	6.90
$[\text{H}_2\text{POH}]_s^{\cdot+}$	3.14	4.54
$\text{H}_2\text{P(O)OH}$	4.84	4.67
$[\text{H}_2\text{P(O)OH}]_v^{\cdot+}$	2.44	
$[\text{H}_2\text{P(O)OH}]_s^{\cdot+}$	1.56	

**Table 6.** Calculated values of standard rate constants ( $k_s$ )

Compound	$k_s/\text{cm s}^{-1}$	Compound	$k_s/\text{cm s}^{-1}$
4	0.45	21	0.15
5	0.24	22	0.30
6	0.20	23	0.50
7	0.20	24	0.49
9	0.18	25	0.30
11	0.14	26	0.30
12	0.20	27	0.18
13	0.20	28	0.16
14	0.15	29	0.22
15	0.20	30	0.16
16	0.16	31	0.20
17	0.16	32	0.19
18	0.39	33	0.24
19	0.40	34	0.14
20	0.44	35	0.26

Note. For electrooxidation of organophosphorus compounds in acetonitrile on the Pt electrode ( $T = 25^\circ\text{C}$ ,  $0.05 \text{ M Et}_4\text{NBF}_4$  as the background).

During the electron transfer, the maximum change in the charge density occurs directly on the P atom. The internal rotation about the P—O bond makes the maximum contribution to the rearrangement of the electronic structure of the radical cation on going from the vertical to adiabatic state.

The electrostatic effect of the solvent on the electronic and spatial structure of the molecules and radical cations was studied by the self-consistent reactive field method using a spherical cavity with a constant radius.<sup>5</sup> The radii of spherical cavities of the structures studied are close and equal to 2.71–2.83 Å. The values calculated by the SCRF HF/6-31G\*\* method of the solvation energy of the *cis*-conformers of the molecules studied and the reorganization energy of the solvate shell are presented in Table 4. The presence of the solvent results in the elongation of the P=O bond in the molecule and radical cation and, to this or another extent, in a change in the values of all geometric parameters (see Table 3).

Comparison of the data in Tables 2–4 shows that the theoretical values of energies of internal reorganization and reorganization of the solvate shell are close for the P<sup>III</sup> and P<sup>IV</sup> derivatives studied and exceed not very substantially the experimental values.

**Kinetics of electron transfer reactions.** The kinetics of electron transfer reactions is determined by the internal reorganization energy of the molecule and the reorganization of the solvate shell (see above), *i.e.*, the total reorganization energy  $\Delta G_0^\ddagger$ . The  $k_s$  values (Table 6) were calculated by Eq. (3).

The  $k_s$  values obtained have the same order as in the case of other organic compounds. The one-electron transfer involving molecules of organic P<sup>III</sup> and P<sup>IV</sup> derivatives in acetonitrile (oxidized in a wide potential region with substantial internal reorganization of the molecule) is characterized by a sufficiently high rate and corresponds to the reversibility criterion in stationary electrochemical methods.<sup>33</sup>

It should be mentioned in conclusion that the combined study by PES and voltammetry of ionization—oxidation of various substrates can help in solving other important problems. On the one hand, based on the electrochemical oxidation potentials, using the regression equation (6), we can calculate the ionization potentials of the P<sup>III</sup> and P<sup>IV</sup> compounds for which these values are unknown or can hardly be measured. On the other hand, if the solvation energies of the compounds studied are known, the free energy of solvation of the radical cations, including unstable, can be determined.

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