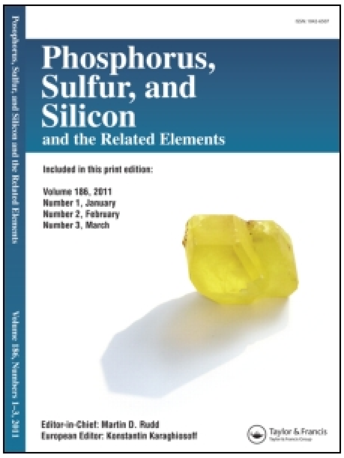

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POLAROGRAPHIC INVESTIGATIONS OF FUNCTIONALIZED ALKANEPHOSPHONIC ACIDS. PART II

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POLAROGRAPHIC INVESTIGATIONS OF FUNCTIONALIZED ALKANEPHOSPHONIC ACIDS. PART II

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Investigations on the polarographic activity of phosphonic acids are described. The electrochemical reduction of phosphorous acid and various phosphonic acids was studied in some details to discuss the scope and the limitation of this process. The possible course of the polarographical electroreduction of the phosphonic function is delineated.

Keywords: Electrochemical activity of phosphonic function; polarographic reduction of functionalized alkanephosphonic acids

INTRODUCTION

The functionalized alkanephosphonic acids belong to a class of compounds of significant analytical[1,2], bioorganic[3–5] and industrial[6,7] importance. For this reason an exploration of their physico-chemical properties attributed to the phosphonic function constitutes the problem of interest of organophosphorus, analytical and also synthetic chemistry.

For this reason it seems interesting to verify the very enigmatical problem of the electrochemical activity of the phosphonic function, especially its polarographic reduction.

Thus, the first report on the polarographic activity of the nitro substituted phenylphosphonic acid was presented by Kosolapov and Jenkins in 1957[8].

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*Corresponding author.

However, the first and still single report on the polarographic reduction of the phosphonic function was published by Tomilov and co-workers in 1975[9]. They observed that at the half-potential $E_{1/2} = -1.62$ V vs. SCE (aqueous solutions of potassium or lithium chloride as supporting electrolytes) or at $E_{1/2} = -1.96$ V vs. SCE (acetonitrile solution of tetraethylammonium chloride) the cathodic waves of phosphorous acid appeared. On the basis of this observation the occurrence of the polarographic reduction of the phosphonic function expressed by eq. 1 was postulated:

$$HP(O)(OH)_2 + 2H^+ + 2e \Rightarrow H_2P(O)(OH) + H_2O \qquad (1)$$

Occurrence of this electrochemical reaction in aqueous solutions would posses particular value (e.g. for the synthesis of polarographically active complexones or functionalized alkanephosphinous acids). Such a conversion, however, although possible in aprotic solvent[9] does not seem to occur in aqueous solutions on a mercury cathode.

The results indicating reluctance of the phosphonic function to the polarographic and generally electrochemical reduction in aqueous solutions are presented in this communication[10].

RESULTS AND DISCUSSION

The investigations of the electrochemical activity of the phosphonic acids were carried out in aqueous solutions and included:

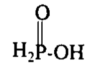
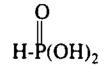
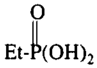
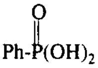
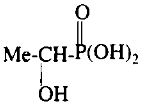
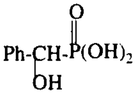
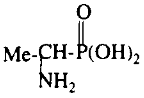
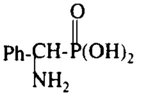
A. Polarographic and pulse-polarographic investigations on the reduction of the functionalized alkanephosphonic acids.
B. Electrochemical reductions of phosphorous acid (**2**) and phosphonic acids **3** and **7** on a mercury macrocathode.

The results of pulse-polarographic and polarographic reduction of phosphonic acids are summarised in Table I and II, respectively. The typical DP polarograms presenting the cathodic waves of polarographic reduction of hypophosphorous (**1**) and phosphorous (**2**) acids are shown on Fig. 1.

These results can be supplemented by the following experimental facts:

1. The potentials of cathodic peaks of phosphonic acids are slightly dependent on their molecular structure for majority of the compounds investigated.

TABLE I Results of the Pulse-Polarographic Reduction of Phosphoroorganic Acids[a]

Nr	*Compound (structure)*	*Concentration (mol × l^{-1})*	*pH*	E_p *(V)*
1	 $H_2\overset{O}{\overset{\|}{P}}\text{-}OH$	5×10^{-4}	3.40	1.48
2	 $H\text{-}\overset{O}{\overset{\|}{P}}(OH)_2$	5×10^{-4}	3.50	1.48
		1×10^{-3}	3.10	1.47
		1×10^{-3}	5.10[b]	-
3	 $Et\text{-}\overset{O}{\overset{\|}{P}}(OH)_2$	4×10^{-4}	4.88	1.69
			5.70[c]	-
4	 $Ph\text{-}\overset{O}{\overset{\|}{P}}(OH)_2$	4×10^{-4}	4.78	1.69
			5.70[c]	-
5	 $Me\text{-}\underset{OH}{CH}\text{-}\overset{O}{\overset{\|}{P}}(OH)_2$	4×10^{-4}	4.78	1.69
			5.70[c]	-
6	 $Ph\text{-}\underset{OH}{CH}\text{-}\overset{O}{\overset{\|}{P}}(OH)_2$	4×10^{-4}	4.78	1.69
			5.70[c]	-
7	 $Me\text{-}\underset{NH_2}{CH}\text{-}\overset{O}{\overset{\|}{P}}(OH)_2$	4×10^{-4}	4.88	1.69
			5.70[c]	-
8	 $Ph\text{-}\underset{NH_2}{CH}\text{-}\overset{O}{\overset{\|}{P}}(OH)_2$	4×10^{-4}	4.84	1.69
			5.70[c]	-

a—Conditions: Ag/AgCl, KCl (sat.) as a reference electrode; 0.1 M KCl as a supporting electrolyte; drop duration t = 2s; amplitude ΔE = 20 mV.

b—Titrated with 0.2 M NaOH to corresponding value of pH.

c—As a supporting electrolyte used acetate buffer at pH = 5.70, [c (AcONa + NaOH) = 0.2 M].

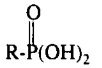
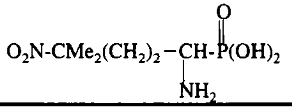
2. The intensities of the reduction currents are proportional to the pH of the solutions of phosphonic acids (dependent on the pK value) with descending tendency with an increase of pH. These reduction waves practically disappear at pH > 5.5.
3. Almost identical cathodic peaks are obtained for solutions of hypophosphorous (**1**) and phosphorous (**2**) acids (Fig. 1). The peaks obtained for phosphonic acids **3–8** were in satisfactory accordance with them.
4. The similar cathodic peaks are observed in the polarograms of supporting electrolytes without phosphonic acids but acidified to pH < 5.

5. The additional electroreduction waves appeared only for phosphonic acids containing auxiliary polarographically active functions, as the nitro group (Table II). These waves exhibited strong dependence on the solution pH illustrating the pH influence on the mechanism of electroreduction of the nitro function.

This evidence has been supported by experiments based on the semipreparative electrochemical reductions of phosphorous acid (**2**) and phosphonic acids **3** and **7** on a mercury macrocathode (see experimental). The reaction progress have been monitored by NMR. Thus, the ^{31}P-NMR spectrum of the electrolyzate solution (catholyte) of electrochemical "reduction" of phosphorous acid (**2**) is presented in Fig. 2. The spectrum does not indicate the presence of hypophosphorous acid (**1**). In similar experiments of the electroreduction of ethanephosphonic acid (**3**) or phosphonoalanine (**7**) only starting substrates in their catholytes were detected. In the last case over 90% of unchanged amino acid was recovered from the catholyte.

On the basis of these experimental facts, we conclude that during polarographic reduction of aqueous solutions of phosphorous and/or phosphonic acids (−1.7 V vs. SCE, a mercury cathode) the phosphorous atom does not undergo electroreduction.

TABLE II Results of the polarographic reduction of the polarographically active phosphoroorganic acids[a]

Nr	*Compound (structure)*	*Concentration (mol × l⁻¹)*	*pH*	*E*$_{1/2}$^{a} *(V)*	*Lit.*
9–12	 $\mathrm{R{-}\overset{\overset{O}{\|}}{P}(OH)_2}$				
9	R: o-nitrophenyl	2.0 × 10^{-3}	2.3	0.21	[8]
			6.9	0.55	
			10.0	0.73 & 0.91	
10	R: m-nitrophenyl	2.0 × 10^{-3}	2.3	0.23	[8]
			6.9	0.64	
			10.0	0.77	
11	R: p-nitrophenyl	2.0 × 10^{-3}	2.3	0.24	[8]
			6.9	0.63	
			10.0	0.75 & 1.48	
12	R: p-nitrobenzyl	2.0 × 10^{-3}	2.3	0.25	[8]
			6.9	0.56	
			10.0	0.78	
13	 $\mathrm{O_2N{-}CMe_2(CH_2)_2{-}\underset{NH_2}{CH}{-}\overset{\overset{O}{\|}}{P}(OH)_2}$	2.5 × 10^{-3}	3.0	0.86	
			4.4[b]	0.84 & 1.12;	

[a]Conditions: SCE as a reference electrode, 0.1 M KCl as a supporting electrolyte, drop duration t = 2s.
[b]Titrated with a 0.2 M NaOH to the corresponding value of pH.

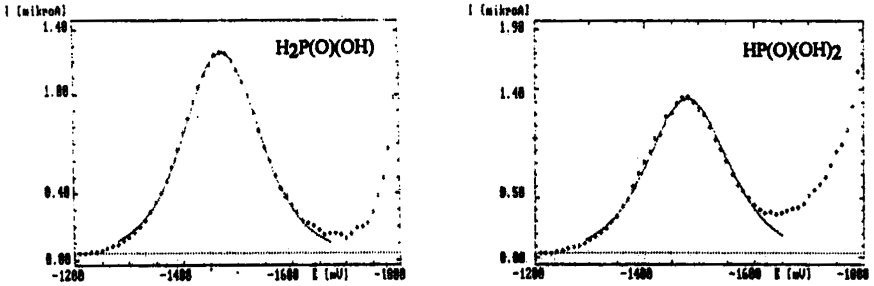


FIGURE 1 DP polarograms for phosphorous acid and hypophosphorous acid. (Conditions are given in Table I)

The observed cathodic peaks of hypophosphorous acids (1) and/or phosphonic acids **3–7** (Table I), are presumably caused by the electrochemical reduction of hydrogen ion irrespective of its origin.

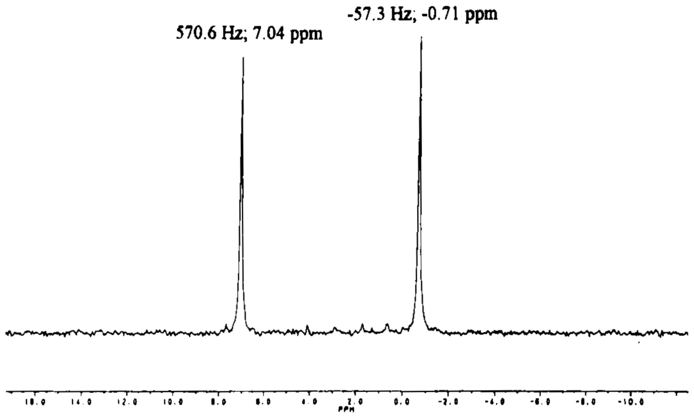


FIGURE 2 ^{31}P-NMR spectrum (decoupler off) of the catholyte solution, contained the products of electrochemical reduction of phosphorous acids (**2**). The corresponding spectrum of hypophosphorous acid exhibited triplet at about 5.6 ppm, 12.5 ppm and 19.4 ppm, $J_{P\text{-}H}$ = 559 Hz. (The proton decoupled ^{31}P-NMR spectrum of the catholyte solution showed a single peak at about 3.2 ppm). The spectra were recorded at 20°C on a Brucker AC 200 spectrometer operating at 81.01 MHz for ^{31}P.

EXPERIMENTAL

Materials

Sodium hypophosphite (**1a**), phosphorous acid (**2**), were purchased from Aldrich (Milwaukee, USA). Other functionalized alkanephosphonic acids were prepared in accordance with published procedures comprised in Ref. 11. All phosphoroorganic compounds were homogenous according to ^{31}P-NMR and/or ^{1}H-NMR spectral analysis. Other materials were obtained from commercial suppliers and used without purification, unless otherwise stated.

Solutions

All reagents were used as 1×10^{-2} M stock solution. For their preparation doubly distilled water was used. The samples were flushed with argon for 10 min. to remove dissolved oxygen before the DP polarograms were recorded.

Hypophosphorous acid (**1**) was prepared instantly before use (experiments) by passing a solution of sodium hypophosphite (**1a**) through an ion-exchanger column charged with Amberlite resin IR-120 in H^+ form. The concentration of hypophosphorous acid (**1**), phosphorous acid (**2**) and ethanephosphonic acid (**3**) were determined by means of potentiometric titration with the standard solution of sodium hydroxide.

Instrumentation and Measurements

Pulse polarographic measurements were carried out in a tri-electrode system: a dropping mercury electrode (DME) as a cathode, a platinum electrode as an anode and a silver–silver chloride electrode as a reference electrode. The mercury drop at the DME was dislodged by a magnetic hammer after a required time (t = 2 sec), the pulse amplitude $\Delta E = 20$ mV. Polarographic analyser (EMU) (IChF, Wroclaw, Poland) operated by computer IBM PC was employed.

An electrolyzer, type EP-4 (Mera-Elwro, Poland) (mercury as a macrocathode, a platinium electrode as an anode and a saturated calomel electrode as a reference electrode) co-working with voltameter was used.

Electrochemical reductions of phosphonic acids were carried out in aqueous solutions on a mercury macrocathode. Conditions applied: Macrocathode polarized to -1.7 V vs. SCE, concentration of the electroreduced compounds ca. 5×10^{-2} M of **2**, **3** or **7** in 0.1 M aq. HCl, electrolysis time 8h, stirring.

A pH-meter, type N 517 (Mera-Elwro, Poland) connected with a glass combinated electrode, type TC 220 (Tacussel, France) was used. ^{31}P-NMR spectra were recorded on a Brucker AC 200 spectrometer operating at 81.01 MHz.

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