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Abstract

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On the Polarographic Behavior and Structure of Some Phosphorylated Aldehydes in Aqueous Solutions

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Only a few works have been devoted to the study of the behavior of organophosphorus compounds at the dropping mercury electrode. Ackerman, Jordan, and others ([1]) used polarography to demonstrate the structure of diethyl cyanophosphate. Zor ([2]) studied the capacitive effects caused by trialkyl phosphates and trialkyl phosphites on oscillopolarographic curves. The behavior of esters of phosphinic acids ([3]) at the dropping mercury electrode has also been studied.

In the present work, the polarographic reduction of phosphorylated aldehydes of the general formula

$$\begin{array}{c} \mathrm{R'} \\ \\ \mathrm{P-CH_2-CHO}, \\ \quad\quad\quad\| \\ \mathrm{R''} \quad \mathrm{O} \end{array}$$

was systematically studied for the first time, where $\mathrm{R'} = \mathrm{C_2H_5}, \mathrm{C_2H_5O}, \mathrm{C_6H_5}, n\text{-}\mathrm{CH_3}-\mathrm{C_6H_4}, n\text{-}\mathrm{C_2H_5}-\mathrm{C_6H_4}, n\text{-iso-}\mathrm{C_3H_7}-\mathrm{C_6H_4}, n\text{-Cl}-\mathrm{C_6H_4}; \mathrm{R''} = \mathrm{C_2H_5}, \mathrm{C_2H_5O}$, the synthesis of which has been described ([4,5]).

Their polarographic activity is due to the aldehyde group and not to the phosphoryl group, since such compounds as phosphonoacetals and diethylphosphinylacetic acid are not reduced at the dropping mercury electrode. When ethanol is added to solutions of the aldehydes, the magnitude of the limiting current gradually decreases, which apparently is associated with the formation of the corresponding acetals.

The polarographic study of the indicated compounds was carried out in aqueous solutions with concentrations $4.72 \cdot 10^{-3}$ and $6.65 \cdot 10^{-3}$ mol/l against the background of borate buffers and Britton–Robinson universal buffers at 20°. Polarograms were recorded on LP-55 polarographs of the Heyrovský system (capillary

characteristic $m = 2.02$ mg/sec, $t = 4$ sec with the circuit open, reference electrode–saturated calomel) and on a Polarecord E-261 (capillary characteristic $m = 1.65$ mg/sec, $t = 3.9$ sec, reference electrode–saturated silver chloride). The values of $E_{1/2}$ relative to the AgCl electrode differ from the values of $E_{1/2}$ relative to the S.C.E. by +46 mV.

When polarographed in aqueous solutions, the compounds studied give waves similar to those shown in Fig. 1, 1. Two regions are distinguished on the curves. The section of the curve at the base of the wave has the character of an adsorption prewave, which will be considered in detail below.

In the middle pH range, when the concentration of the substance in solution is increased to $7 \cdot 10^{-3}$ mol/l, the height of the reduction wave increases proportionally to the concentration. With increasing temperature, the total height of the wave of the compounds studied increases considerably. At the same time, a decrease in the height of the prewave is observed. Graphically, the dependence of the magnitude of the reduction current on temperature is expressed by a hyperbola. The value of the temperature coefficient is 4–5% per 1°. Consequently, the observed reduction currents–

the recovery of phosphorylated aldehydes have a kinetic character. Evidently, in aqueous solutions the aldehyde group is hydrated, and its dehydration, for example with increasing temperature, affects the magnitude of the reduction current. However, in the middle pH region the magnitude of the current is strictly proportional to the square root of the height of the mercury reservoir: the plot of the dependence $i_{\text{lim}} - \sqrt{h}$ passes through the origin. Thus the electroreduction current is determined by the equilibrium concentration of the free aldehyde form.

Fig. 1 Fig. 2

Fig. 1. Polarograms of phenylethoxyphosphinylacetic aldehyde: 1 –pH 7.0; 2 –pH 11.1; Polarrecord E-261

Fig. 2. Dependence of the half-wave potential and wave height on pH for phenylethoxyphosphinylacetic aldehyde; concentration $6.65 \cdot 10^{-3}$ mol/l

In turn, the position of the equilibrium aldehyde form–hydrated form depends on the pH of the solution, which apparently explains the decrease in the reduction current when the pH is increased to 5.5 (Fig. 2). As a result of microcoulometric measurements it was found that, upon reduction of one molecule in a neutral medium, about 1.6 electrons are consumed. However, the number of electrons calculated from the Ilkovič equation and going into the reduction, for example of phenylethoxyphosphinylacetic aldehyde under the same conditions (with a diffusion coefficient value of $5.5 \cdot 10^{-6}$ cm^2/sec), proved to be equal to 0.22. From comparison of the limiting reduction currents of several phosphorylated aldehydes in a neutral medium with the limiting currents of compounds for which the number of electrons participating in their polarographic reduction is known, a value of 0.23–0.25 electron was obtained. Thus, these data show that

in neutral solutions about 11-12% of the total concentration of the substances studied is the polarographically active aldehyde form, if the latter is assumed to be reduced by a two-electron mechanism.

In the region where $E_{1/2}$ is almost independent of pH, the waves of the compounds studied are characterized by identical semilogarithmic dependences

$$\lg \frac{i}{i_{\text{lim}} - i} = f(E),$$

whose plots have the form of a broken line. Its first segment corresponds to an αn value equal to 0.42; the second to a value of 1.3. When the drop time of the electrode was varied within the range 0.25-5.5 sec, the $E_{1/2}$ value of the substances studied in the middle pH region remained practically constant, i.e., the process of their polarographic reduction was as if reversible. On passing from buffered solutions to unbuffered ones, $E_{1/2}$ of the substances shifts slightly toward negative potentials. However, the form of the logarithmic

of the graph, $\lg \frac{i}{i_{\text{lim}} - i} = f(E)$, does not change in this case. It also does not change when the temperature is raised, for example to 50°.

According to A. N. Frumkin' s theory of retarded discharge ([6]), the influence of the indifferent electrolyte on $E_{1/2}$ should be determined mainly by the change in the ψ'-potential. It was found that increasing the concentration of potassium chloride in the solution led to a shift of $E_{1/2}$ toward positive potentials. For phenylethoxyphosphinylacetic aldehyde, the value

$$\frac{\Delta E_{1/2}}{\Delta \lg C_{\text{salt}}}$$

is about 60 mV. Under the same conditions the value of the ψ-potential decreases by almost 60 mV ([6,7]), i.e., the shift of $E_{1/2}$ with increasing KCl concentration is indeed associated with a change in the ψ'-potential.

As follows from Fig. 2, on going to alkaline solutions $E_{1/2}$ shifts toward negative potentials. The potential of the prewave changes only slightly in this case, as a result of which a distinct separation of these waves is observed for alkaline solutions (Figs. 1, 2).

Fig. 3. Phenylethoxyphosphinylacetic aldehyde, pH 11.1; dependence of the height of the adsorption wave on the pressure on the dropping mercury electrode and on concentration; upper graph: dependence of $E_{1/2}$ on concentration

Fig. 4. Plot of the dependence of $E_{1/2}$ on $\Sigma\sigma$ of substituents according to Hammett. The values of σ for the n-tolyl and n-Cl-phenyl groups were calculated from data ([10])

Fig. 3. Phenylethoxyphosphinylacetic aldehyde, pH 11.1; dependence of the height of the adsorption wave on the pressure on the dropping mercury electrode and on concentration; upper graph: dependence of $E_{1/2}$ on concentration

Figure 1: Fig. 3. Phenylethoxyphosphinylacetic aldehyde, pH 11.1; dependence of the height of the adsorption wave on the pressure on the dropping mercury electrode and on concentration; upper graph: dependence of $E_{1/2}$ on concentration

Fig. 4. Plot of the dependence of $E_{1/2}$ on $\Sigma\sigma$ of substituents according to Hammett. The values of σ for the n-tolyl and n-Cl-phenyl groups were calculated from data ([10])

Figure 2: Fig. 4. Plot of the dependence of $E_{1/2}$ on $\Sigma\sigma$ of substituents according to Hammett. The values of σ for the n-tolyl and n-Cl-phenyl groups were calculated from data ([10])

The height of the prewave is directly proportional to the pressure on the dropping mercury, and with increasing concentration of the substance it rapidly reaches its limiting value. The value of $E_{1/2}$ of the prewave, as the concentration of the substance is increased, shifts toward negative potentials along a curve characteristic of adsorption processes. Thus, the data obtained, whose graphical representation is given in Fig. 3, make it possible to conclude that the prewave considered has an adsorption character. Using the known equations ([8]), we calculated the area occupied by a molecule of phenylethoxyphosphinylacetic aldehyde in the adsorbed state. For a solution with pH 11.1 the value of i_{ads} was 0.62 μA, and from this the area corresponding to one molecule of the substance is about 100 Å^2.

In alkaline solutions, with increasing concentration of HO^- ions, the wave height of the compounds studied decreases (Fig. 2).

However, if acid is added to such a solution, the reverse dependence is observed on the polarograms: the wave height increases. This phenomenon is most probably associated with the presence of tautomeric equilibrium in the solutions:

$$\begin{array}{ccc} & & O \\ & & \| \\ \backslash & & \\ \text{P} - \text{CH}_2 - \text{C} & \rightleftarrows & \text{P} - \text{CH} = \text{CH} \\ / \; \| & & / \; \| \quad | \\ O & & O \ldots \text{HO} \end{array}$$

In alkalis the equilibrium is shifted toward the enol, which is present in solution in an anionic, polarographically nonreducible form. The possibility of the

existence of an enol form is confirmed by spectral study of the phosphorylated aldehydes. In the IR spectra of the individual substances, absorption bands appear in the region 1729-1742 and 2736 cm^{-1}, characteristic of the aldehyde group [9]. In the IR spectra of solutions of the same aldehydes in chloroform, in addition to these bands, there are absorption bands at 1623-1638 cm^{-1}, caused by stretching vibrations of the C=C bond, and a broad absorption band of the hydroxyl group, apparently perturbed by a hydrogen bond, in the region 3405-3417 cm^{-1} [9]. The presence of the enol form in solution is also confirmed by the positive reaction of phosphorylated aldehydes with an aqueous solution of ferric chloride (intense red-violet coloration).

Table 1

Substituents	Substituents	i (at pH 7.0, conc. $4.72 \cdot 10^{-3}$ mol/l), µA	$-E_{1/2}$ (vs. SCE, pH 7.0), V	$\frac{\Delta E_{1/2}}{\Delta pH}$ (for pH 6.5-8.5), V/pH
R′	R″			
n-Cl–C_6H_4	C_2H_5O	2.73	1.44	0.005
C_6H_5	C_2H_5O	2.75	1.47	0.006
n-CH_3–C_6H_4	C_2H_5O	2.55	1.48	0.008
n-C_2H_5–C_6H_4	C_2H_5O	2.75	1.48	0.008
n-iso-C_3H_7–C_6H_4	C_2H_5O	2.54	1.48	0.005
C_2H_5	C_2H_5	2.54	1.54	0.010
C_2H_5	C_2H_5O	2.73	1.56	0.008
C_2H_5O	C_2H_5O	2.50	1.60	0.008

The material presented above and the data of Table 1 show that reduction of the aldehyde group proceeds by a single mechanism.

For a quantitative assessment of the influence of substituents at the phosphorus atom on the reactivity of the aldehyde group, we applied the principle of linearity of free energy. It was found that a satisfactory correlation of the $E_{1/2}$ values (Table 1) and $\sum\sigma$ of the substituents is observed only when the values of the Hammett total constants are used (Fig. 4), whereas if the substituent constants according to Taft and Kabachnik are used, no such regularity is manifested. Apparently, steric hindrances are absent in this case [11].

The positive value of the reaction constant of polarographic reduction–ρ', equal to +0.52 V, indicates that the potential-determining stage of the process consists in the addition of an electron to the molecule of the phosphorylated aldehyde.

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Note: Figure translations are in progress. See original paper for figures.