

Investigation in the Series of Substituted Butan- and Butenolides: XV.* Transformations of 4-Hydroxy-2-butenolide in Water Media at Various pH Values

N. K. Strizhov, V. V. Poskonin, L. A. Badovskaya, and E. P. Kupina

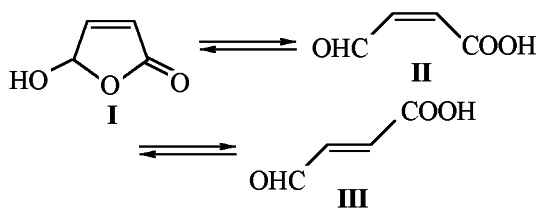
Kuban State Technological University, Krasnodar, 350072 Russia

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Abstract—The 4-hydroxy-2-butenolide was established by polarographic method to undergo in water solutions fast tautomeric and acid-base transformations. Depending on pH of the medium the compound is present either as a cyclic irreducible form (at pH 0–4) or in the open-chain (carbonyl-containing) reducible forms (at pH > 4 and < 0). It is presumed that in going from the basic to strongly acidic medium and backwards occur consecutive equilibrium transitions of four species: *cis*- β -formylacrylic acid anion (A^-), its neutral molecule (HA) existing as linear and cyclic tautomers, and protonated forms (H_2A^+ and H_3A^+). The formation mechanism thereof is considered.

The β -formylacrylic acid is among the main products in furan compounds oxidation by aqueous hydrogen peroxide in the presence of compounds of V and VI groups elements (V, Se, Cr) [2, 3]. This compound is known to exist as tautomeric and isomeric forms: cyclic substance [4-hydroxy-2-butenolide (I)], and acyclic *cis*- and *trans*-isomers II and III [4–8] (Scheme 1).

Scheme 1.



We reported formerly on isolation of *cis*- β -formylacrylic acid as lactone I from the mixture of furfural oxidation products [2]. However no published data was found on the behavior of its isomers I–III at different pH which were important for the control of butenolide preparation and for extending its application as a synthon. Only reports appeared on polarographic reduction of 5-ethoxy-2-(5H)-furanone and *trans*- β -formylacrylic acid in water solutions [7, 8]. In this connection we carried out a study of tauto-

meric and hydrolytic transitions of compound I in water media in a wide range of pH values by means of polarography.

We report in the present communication on results of transformation study and the structure of 4-hydroxy-2-butenolide (I) forms in water solution with pH in the range from 10 to –0.5. The discussion of results takes into account the assumption of [7, 8] on the polarographic activity of I–III forms.

We used in the study free of impurities butenolide I prepared by acid hydrolysis of 4-acetoxy-2-butenolide under mild conditions. The measurement of current intensity and of half-wave potential of reduction for different forms of compound I arising at its dissolution in water media at various pH values was carried out with a dropping mercury electrode at $25 \pm 0.2^\circ\text{C}$, the solution ionic strength 1.0 or $3.0 \text{ mol} \times \text{l}^{-1}$ ($\text{HClO}_4 + \text{NaClO}_4$), and initial concentration of compound I 4.0×10^{-3} – $4.0 \times 10^{-4} \text{ mol l}^{-1}$. As reference was used normal calomel electrode. The butenolide I solutions were subjected to measurement 1–5 min after preparation. The acidity of solutions was measured by titration with HClO_4 or NaOH . The initial reduction potential E_{in} was –0.2 V.

On adding butenolide I into weakly acidic, neutral, or basic solutions the reduction waves on polarograms depended on the pH value (Fig. 1). In the neutral solution were observed two waves. Therewith the half-wave potential of the first one ($E_{1/2}$, V)

* For communication XIV see [1].

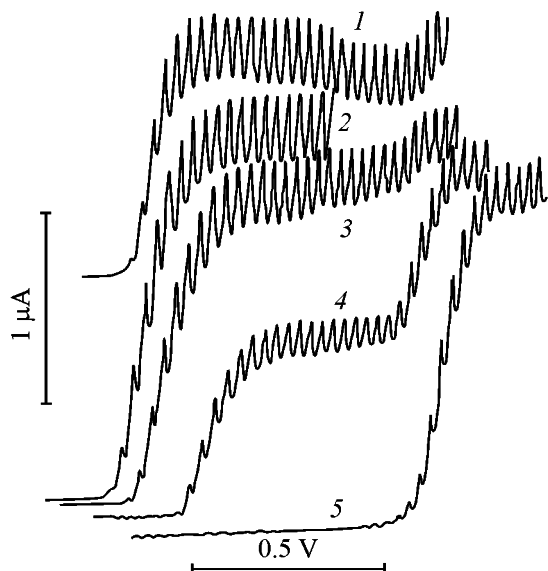


Fig. 1. Reduction waves of butenolide **I** (4×10^{-3} M) in solutions of HClO_4 and NaOH of ionic strength 1.0 M ($\text{NaClO}_4 + \text{HClO}_4$ or NaOH), $E_{\text{in}} -0.2$ V: (1) 4×10^{-3} M HClO_4 , (2) 4×10^{-4} M HClO_4 , (3) no additives, (4) 0.9×10^{-3} M NaOH , (5) 2.7×10^{-3} M NaOH .

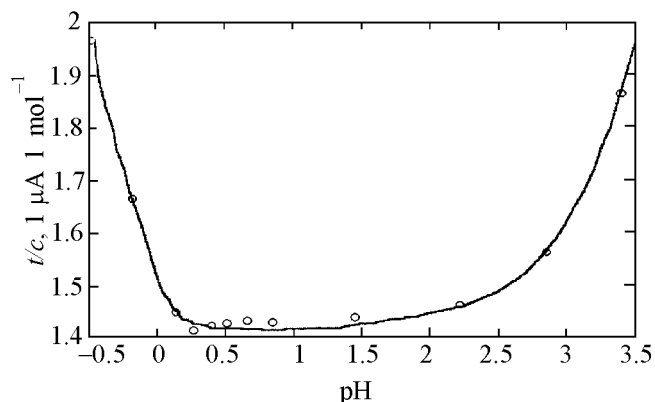
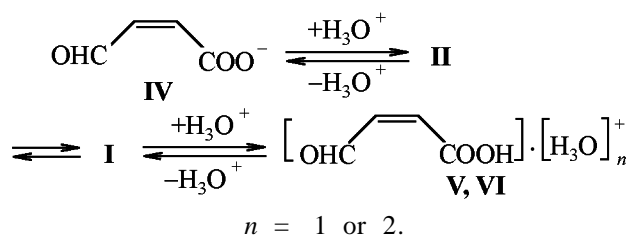


Fig. 2. Effective limiting current intensity for the first reduction wave of the molecular form **II** of butenolide **I** (i/c) as a function of pH ($-\log c_{\text{HClO}_4}$).

Scheme 2.



previously described in [7] depended on pH of the medium according to equation $E'_{1/2} = -0.386 \text{ V} + 0.059 \text{ pH}$ (curves 1–4), and the potential of the second wave $E'_{1/2}$ equal to -1.12 V was independent of proton concentration (curves 3–5).

As NaOH was added to the butenolide **I** solution the first wave decreased and the second wave grew (curve 4). On addition of 0.70–0.75 mol of the base per 1 mol of compound **I** the first wave totally disappeared, and the height of the second remained constant at further alkalization (curve 5). At successive addition of HClO_4 to the initial butenolide **I** solution till $\text{pH} \sim 1$ the first wave started to grow (curve 2) and then decreased (curve 1). This result suggesting the kinetic character of the wave was already reported in [7] at polarographic measurements on the solutions of 5-ethoxy-2(5H)-furanone. The latter is known to provide isomers of the β -formylacrylic acid on hydrolysis [5].

These data and also those presented in the table and on Fig. 2 show that at $\text{pH} > 1$ the current intensity (i_{eff}) depends on pH as has been observed in [4].

We demonstrated that behavior of butenolide **I** in more acidic media ($\text{pH} < 1$) in the range from $\text{pH} 1$ to -0.5 is characterized by the dependence of i_{eff} on pH that grew with rising acidity and did not attain any limiting value (Fig. 2). This fact evidences formation in the strongly acidic solutions of previously unknown reducible species of compound **I**.

Kuzovnikova *et al.* [7, 8] suggested for the polarographic activity of 5-ethoxy-2(5H)-furanone that a reduction mechanism of forming therefrom at $\text{pH} 4\text{--}6$ *cis*- β -formylacrylic acid (**II**) involved $\text{C}=\text{C}$ bond. However nonlinear dependence of i_{eff} on pH and the direction of the $E_{1/2}$ shift at the change in the acidity that we have observed in the study of compound **I** correspond to the behavior of the majority of the previously investigated aldehydes and ketones [9]. Thus it is presumable that the reduction of butenolide **I** occurs at the aldehyde $\text{C}=\text{O}$ groups of its open-chain forms arising in water solutions. This assumption is supported by the fact of one-electron reduction of these forms as we have established along the known methods [10], whereas the $\text{C}=\text{C}$ bond (e.g., in ethylene, maleic and fumaric acids, etc.) is reduced along the two-electron mechanism [10].

On Scheme 2 and in the table are presented the main forms of butenolide **I** that according to this study and [7, 8] arise in its water solutions at various pH. Their presumable structures are considered below.

Main existing forms of butenolide **I** and hydrolysis products of 5-ethoxy-2(5*H*)-furanone at various pH values

Presumed structure	Polarographic activity	Registration conditions and polarographic characteristics of the first wave					
		base		pH		$E_{1/2}$, V	
		1 ^a	2 ^a	1 ^a	2 ^a	1 ^a	2 ^a
IV	+	NaClO ₄ + NaOH	Universal buffer	> 6	6–8	0.7–1.0	0.7–0.8
II	+	NaClO ₄ or NaClO ₄ + HClO ₄	0.1 M HCl + 1 M KCl	4–6	3–6	0.6–0.7	0.5–0.7
I	–	NaClO ₄ + HClO ₄	1 M HCl	0–4	< 3	0.4–0.6	~0.35–0.5
V	+	same	–	< 0.5	–	< 0.4	–

^a 1, data of this study; 2, data from [7, 8].

The dependence of i_{eff} on pH (Figs. 1–3) suggests that in the electrode process at different pH take part at least four forms of compound **I**; therewith three of them, namely **II**, **IV**, and **V** and/or **VI** are polarographically active. The behavior features we revealed permit stating the following: (a) the reduction of species **I**, **IV**, and **V**, **VI** involves an aldehyde group C=O; (b) compound **I** in a water solution with no addition of acids or bases exists mainly as acyclic tautomer **II** that on variation of the medium acidity undergoes a number of transitions detected by polarography.

The decrease in the current intensity at growing pH was ascribed in [7] to the decrease in the concentration of the molecular form of *cis*- β -formylacrylic acid **II** due to its transformation into anion **IV** characterized by another reduction potential. Our data support this assumption. As shown above (Fig. 1) the decrease in the current intensity of the first wave is accompanied by appearance at more negative potentials of the second wave. Its current intensity grows with pH to attain finally the value of the limiting current intensity of reduction of *trans*- β -formylacrylic acid **III**.

As the neutral solution of butenolide **I** existing nearly totally in the form of acyclic tautomer **II** is acidified till pH > 0.5 a transformation into irreducible form occurs that has been previously regarded as lactol **I** [7]. Thus our data on polarographic activity of butenolide **I** species in water solutions at pH > 0.5 are in general consistent with the results of [4, 5] (see the table). In both case in the basic, neutral, and weakly acidic media were observed the reducible forms **IV** and **II**, and at pH from 3–4 to ~0.5 was present irreducible form **I**.

However as seen from Fig. 2 at further acidification of the solution in question, namely at pH < 0.5, occurs a sharp increase in the current intensity of the first wave evidencing the transformation of irreducible species **I** into polarographically active product of presumable structure **V** and/or **VI** (Scheme 2).

Thus we found a definite range of solution pH ($0 < \text{pH} < 4$) where occurred significant accumulation of the cyclic form of *cis*- β -formylacrylic acid (**I**): up to 30–60% to the overall amount of its speciations (depending on its initial concentration and the ionic strength of the medium) (Figs. 2 and 3). Note that the degree of transition of molecule **II** into irreducible form **I** directly depends on the ionic strength of the solution.

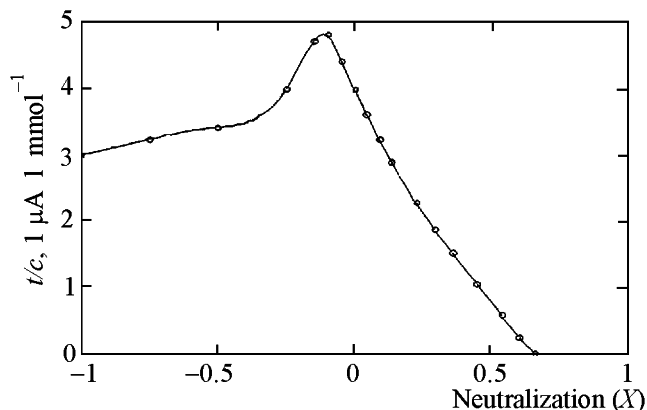


Fig. 3. Effective limiting current intensity i/c of acid **II** as a function of neutralization degree of acid **II**: $c_{\text{of acid II}} = 4.0 \text{ mmol l}^{-1}$; $c_{\text{NaClO}_4} + c_{\text{HClO}_4} = 1.0 \text{ mol l}^{-1}$; at $X < 0$ $X = c_{\text{HClO}_4}/c_{\text{of acid II}}$; at $X > 0$ $X = c_{\text{NaOH}}/c_{\text{of acid II}}$.

Additional information on butenolide **I** transformations and on the forms arising therefrom we obtained by titration of its water solutions in the polarographic cell with solutions of HClO_4 or NaOH . The experiment was carried out with no buffer; the solution contained predominantly molecular form **II**, and the acidity was adjusted by adding various amounts of acid or base solutions. The results of the experiment describing the variation of current intensity for the first wave depending on the neutralization degree of the open-chain molecular form **II** ($X = c_{\text{NaOH}}/c_{\text{of acid II}}$) and on the degree of its acidification ($-X = c_{\text{HClO}_4}/c_{\text{of acid II}}$) are given as a curve on Fig. 3. As seen, the pattern of molecule **II** behavior at small pH variations is different at acidification or neutralization. Thus in the presence of a small amount of HClO_4 the content of acyclic form **II** reaches the maximum (the current intensity of its reduction attains that of reduction of *trans*-isomer **III**). At further acidification to pH ~ 1 its content starts to decrease. At the same time on adding only ~ 0.7 mol of NaOH per 1 mol of acid **II** its concentration falls to zero. The data on Fig. 3 suggest the following. In the water solution without HClO_4 or NaOH butenolide **I** nearly completely is present as molecular acyclic form **II**. As the acidity of the medium grows HA molecule **II** goes through a maximum of its content and then affords polarographically inert species that on further acidification is transformed into protonated forms H_2A^+ (**V**) and/or H_3A^+ (**VI**).

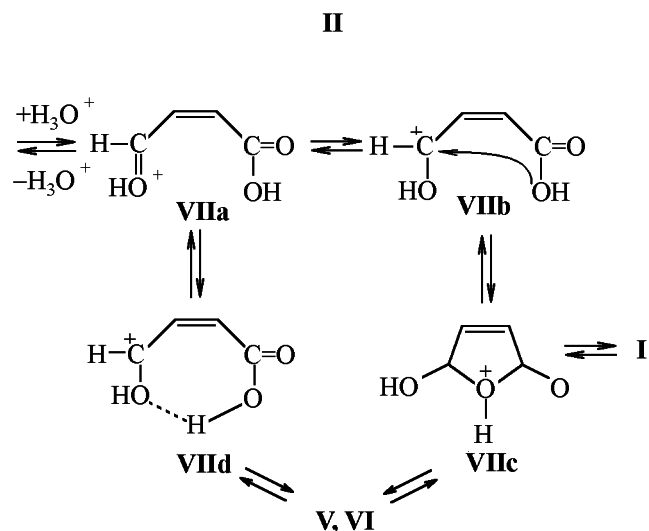
It was remarkable that the above interconversions of butenolide **I** and its forms **II**, **IV**, and **V**, **VI** within all the pH range under study occurred virtually instantaneously (the time of equilibration tends to zero) and reversibly (the curves obtained by direct and reversed titration of the neutral compound **I** solution coincided). This fact indicates the absence of significant energy barrier to the transitions. The experimental value of the activation energy for the reversible conversion of acid **II** into the irreducible form **I** amounts to 14 kcal mol^{-1} . The value was obtained by measuring the current intensity in the minimum point on the curve (Fig. 3) as a function of the temperature. The calculated value of the heat evolution in this stage has a close figure ($\Delta H -23 \text{ kcal mol}^{-1}$) [10].

Low energy values characterizing this process and the polarographic inertness of the form accumulating at pH 0–4 are inconsistent with the structure of *trans*-isomer **III**.

The results obtained and literature data on the ring-chain tautomerism of β -acylacrylic acids [6] are

in general consistent with the previously reported suggestion [7, 11, 12] that the irreducible form existing at pH 0–4 is lactol **I**. At the same time the unusual form of the curve on Fig. 2 and the dependence of the current intensity of reduction on the ionic strength of the medium and the reasoning given further suggest that in the above mentioned pH range may also exist the other polarographically inactive forms of the *cis*- β -formylacrylic acid (Scheme 3).

Scheme 3.



In principle on acidifying the weakly acidic solution containing mainly molecular species **II** may arise several monoprotonated forms with presumable structures **VIIa–c**. Polarographically inactive intermediates **VIIb** and **VIIc** may contribute to the decrease in current intensity of reduction in the pH range 0–4. However their concentration as also that of lactone **I** should be dependent on the medium acidity. Actually it is not observed (at pH 0–2.5 i_{eff} is virtually independent of pH). Thus the accumulation of these species is insignificant. Therefore it is presumable that in this pH range alongside the cyclic structure **I** exists one more irreducible form of the *cis*- β -formylacrylic acid that may be represented as acid **VIIId** with an intramolecular hydrogen bond.

At pH < 0 the proton concentration becomes apparently sufficient for decyclization of structures **I** and **VIIId** to afford reducible species **V**, **VI** (biprotonated molecule **VI** is polarographically indistinguishable from adduct **V**).

In consideration of spatial models of *cis*- β -acylacrylic acids it was previously presumed that their

open-chain structures could exist only in the energetically unfavorable noncoplanar form preventing full-fledged conjugation of the π -bonds [6]. We carried out a formal computation by the software PCModel of the structural and energy parameters of molecular form **II** and of hypothetical biprotonated structure **VI**. The calculation confirmed that theoretically the most stable conformation of molecular form **II** is nonplanar molecule of *cis*- β -formylacrylic acid that arises apparently as a result of mutual repulsion of two C=O groups. The simulation with the use of the above software of two hydroxonium ions addition to molecule **II** resulted in an analogous nonplanar structure **VI**, therewith according to the calculated model each H_3O^+ ion is located at one oxo group and does not form a hydrogen bond with the carbonyl. These data suggest that biprotonated form **VI** may be regarded as a complex of molecular form **II** with two hydroxonium ions.

EXPERIMENTAL

Procedure for preparation of 4-hydroxy-2-butenolide (I). To 0.1 mol (14.2 g) of pure 4-acetoxy-2-butenolide obtained along procedure [2] was added 100 ml of bidistilled water and 3 ml of 35% HCl, the mixture was stirred for 6–10 h at 40–50°C till complete hydrolysis of the initial butenolide, the reaction mixture was evaporated at reduced pressure, dried in air, the reaction product was extracted with anhydrous ethyl ether, and dried with Na_2SO_4 . On evaporating the solvent we obtained 0.095 mol (9.5 g) of 4-hydroxy-2-butenolide (**I**) as yellow oily substance that slowly crystallized. The physico-chemical characteristics of the compound were in agreement with the published data [2].

The method of polarographic investigation. The base electrolytes were prepared from HClO_4 , NaClO_4 , and NaOH of the "chemically pure" grade with the use of bidistilled water. Polarographic measurements were performed on PLS-1 instrument. The characteristics of the dropping mercury electrode were as follows: m 2.01 mg s^{-1} , t_1 3.41 s. Butenolide **I** was charged into the polarographic cell as a solution in the base electrolyte of concentration 4.0×10^{-3} – 4.0×10^{-4} mol l^{-1} . The cell was maintained at temperature $25 \pm 0.2^\circ\text{C}$ and was flushed with nitrogen to remove oxygen. In experiments where was

measured the dependence of current intensity of reduction on the neutralization degree 20 ml of base electrolyte with appropriate pH value was charged into the polarographic cell then the temperature was brought to the desired value, the cell was flushed with nitrogen, the solution of compound **I** was charged with a microsyringe, and the mixing was performed by the nitrogen flow. The polarograms were recorded at definite time intervals till the current no more grew due to reduction of the polarographically active forms.

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