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Polarographic Study of Reactions in the System 2-Furaldehyde–Hydrogen Peroxide–$NaVO_3$

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Abstract—The oxidation of 2-furaldehyde to β-formylacrylic acid in 0.1 N $HClO_4$ containing hydrogen peroxide and sodium vanadate was studied by polarography using a dropping mercury electrode. The conversion of 2-furaldehyde and the yield of the products were found to depend on the reactant ratio. A mechanism was proposed which includes preliminary complex formation between the reactants.

We previously showed [1] that the reaction of 2-furaldehyde (**I**) with hydrogen peroxide in the presence of vanadium(IV) or vanadium(V) compounds at pH < 7 yields mainly *cis*-β-formylacrylic acid (**II**) which was isolated as the corresponding cyclic tautomer, 5-hydroxyfuran-2(5*H*)-one (**III**) [2] (Scheme 1). Another product of 2-furaldehyde oxidation in the same system was maleic acid (**IV**). Appreciable amounts of *cis*-β-formylacrylic acid as tautomeric mixture **II**+**III** and acid **IV** accumulate in the reaction mixture even in the initial period, and their yields can vary over a wide range depending on the reaction conditions.

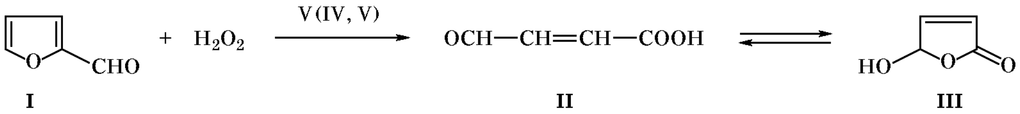
With the goal of elucidating fine details of the mechanism of oxidation of 2-furaldehyde (**I**) to give products **II**+**III** and **IV** we performed polarographic study of the reaction in the system 2-furaldehyde–hydrogen peroxide–$NaVO_3$. The reaction was carried out directly in a polarographic cell under conditions differing from those reported for preparative syntheses [1]: The reactant concentrations were fairly small, and their ratio was varied over a wide range.

Compounds **I**, **II**, and **IV** are known to be polarographically active; the limiting diffusion current for **I** and **II** depends on the pH value in a definite pH range [3–5]. Therefore, the oxidation was carried out at a constant ionic strength in 0.1 N $HClO_4$; i.e., in the pH range where variation of proton concentration due to accumulation of acid products did not affect the limiting currents for reduction of 2-furaldehyde and *cis*-β-formylacrylic acid.

Preliminary experiments showed that in 0.1 N perchloric acid 2-furaldehyde and $NaVO_3$, taken separately, are reduced at comparable potentials, giving clearly defined waves (Fig. 1, plots *2* and *3*). Mixing of solutions containing equimolar amounts of 2-furaldehyde and $NaVO_3$ gives rise to two new waves which are strongly displaced toward the negative region (Fig. 1, plot *1*). These findings suggest formation of an intermediate complex of vanadium(V) with 2-furaldehyde. According to our data [6], the complex has the composition ML_2 (**V**) and is fairly stable: its stability constant β_2 is 5.2×10^5 l/mol.

Hydrogen peroxide is also readily reduced under the above conditions (Fig. 2, plots *2* and *5*). Addition of hydrogen peroxide to a solution of compound **I** leads to a considerable variation of the general reduction pattern. With insufficient H_2O_2, a joint wave is formed (Fig. 2, plot *4*), whose shape resembles the reduction wave of pure 2-furaldehyde; however, it is reversible to a lesser extent, and the limiting current is lower than that corresponding to the initial wave of compound **I** (Fig. 2, plot *3*) which was observed before addition of hydrogen peroxide. These data

Scheme 1.



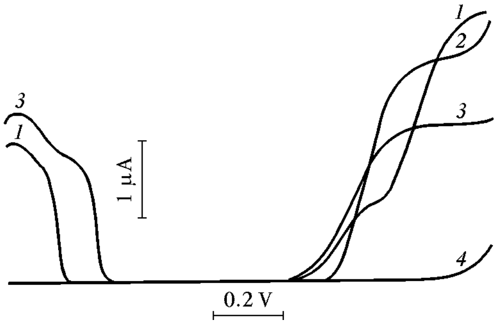


Fig. 1. Polarographic curves for (*1*) a mixture of 2-furaldehyde and $NaVO_3$; (*2*) 2-furaldehyde, $c = 5 \times 10^{-3}$ M; (*3*) $NaVO_3$, $c = 5 \times 10^{-3}$ mol/l; and (*4*) 0.1 N $HClO_4$ (supporting electrolyte).

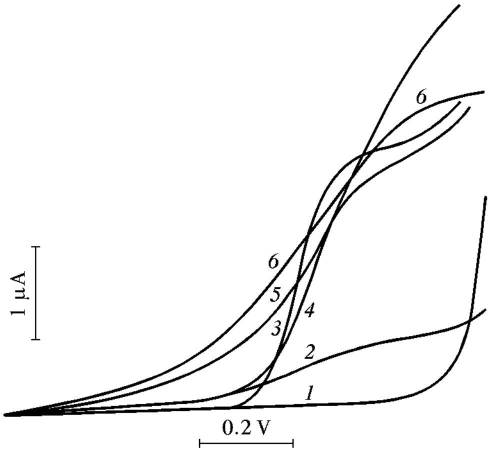


Fig. 2. Polarographic curves for (*1*) 0.1 N $HClO_4$ (supporting electrolyte); (*2*) 0.1 N $HClO_4$ containing 4.84×10^{-4} mol/l of H_2O_2; (*3*) 0.1 N $HClO_4$ containing 5×10^{-3} mol/l of 2-furaldehyde; (*4*) 0.1 N $HClO_4$ containing 4.84×10^{-4} mol/l of H_2O_2 and 5×10^{-3} mol/l of 2-furaldehyde; (*5*) 0.1 N $HClO_4$ containing 4.84×10^{-3} mol/l of H_2O_2; and (*6*) 0.1 N $HClO_4$ containing 4.84×10^{-3} mol/l of H_2O_2 and 5×10^{-3} mol/l of 2-furaldehyde.

indicate fast formation of a primary reaction product by 2-furaldehyde and hydrogen peroxide; such product may be known 2-furaldehyde hydroxyhydroperoxide (**VI**) [7]. On addition of an equimolar amount of H_2O_2 a single wave is observed with a different shape (Fig. 2, plot *6*), indicating a considerable interaction between the reactants; however, in the absence of vanadium compound, this interaction does not result in appreciable formation of products **II**–**IV** over a period of 7 days.

Addition of $NaVO_3$ to a mixture of compound **I** and H_2O_2 strongly accelerates the process. Figure 3 shows that even on mixing the components (2-furaldehyde–hydrogen peroxide–$NaVO_3$) a new wave system appears on the polarogram, which indicates complex formation between the reactants. The wave shapes almost do not depend on the order of mixing of the components, but they change during the process together with the magnitudes.

Unlike binary systems 2-furaldehyde–H_2O_2 and 2-furaldehyde–$NaVO_3$, the transformations of 2-furaldehyde and hydrogen peroxide in the presence of $NaVO_3$ are fairly fast. As in preparative experiments [1], these transformations lead to predominant formation of tautomeric mixture **II** + **III** (Fig. 4). On the other hand, the yield of acid **IV** as a result of further oxidation is quite small, and it almost does not depend on the conditions. The limiting currents for compounds **I** and **II** + **III** are very similar (provided that their concentrations are also similar) and are twice as low as the limiting current for reduction of the ethylene bond in maleic and fumaric acids. This means that the reduction involves aldehyde groups.

Unfortunately, the presence of hydrogen peroxide made it impossible to monitor the reaction kinetics, for clearly defined waves of products **II** + **III** and **IV** were obscured by the wave of H_2O_2, so that they could be measured only after complete transformation of hydrogen peroxide (Fig. 3, curve *4*). Our attempts to terminate the process at an intermediate stage by adding compounds reacting with H_2O_2 were unsuccessful. Such compounds as SO_2, hydrazine, and hydroxylamine, which promote fast decomposition of hydrogen peroxide, either were reduced in the range of potentials to be measured or reacted with 2-furaldehyde and its oxidation products. Taking into account that the wave of compound **I** was observed during the reaction only in the presence of excess substrate with respect to H_2O_2, our further study included two series of experiments. In the first series of experiments solutions with constant concentrations of 2-furaldehyde and $NaVO_3$ and variable concentration of hydrogen peroxide (0–4 mol per mole of **I**) in 0.1 N $HClO_4$ were prepared and were left to stand until hydrogen peroxide was consumed completely. In the second experiment series, the concentration of sodium vanadate was varied in the range from 0 to 0.4 mol per mole of 2-furaldehyde, the concentrations of **I** and H_2O_2 being constant. Polarograms of these solutions were measured when the reactions were complete. Figures 4 and 5 show the dependences of 2-furaldehyde consumption and yields of products **II** +**III** and **IV** on the concentration of H_2O_2.

As follows from Fig. 4, the conversion of 2-furaldehyde (**I**) and the yield of *cis*-β-formylacrylic acid (**II** + **III**) depend on the amount of hydrogen peroxide added (curves *3* and *4*). With a large deficit of the oxidant, the yield of **II + III** is close to quantitative (calculated on the reacted 2-furaldehyde, the fraction of **I** consumed for formation of complex with vanadium ions, acid **IV**, and a small amount of unidentified polarographically inactive product **VII** being subtracted; curve *5*). When the ratio H_2O_2–2-furaldehyde is close to 0.2, the yield of **II + III** falls down to 75–80%. On further raising the concentration of hydrogen peroxide, the consumption of 2-furaldehyde and accumulation of acid **II + III** are accompanied by oxidation of the latter at an appreciable rate. As a result, the yield of **II + III** (calculated on the reacted 2-furaldehyde) notably decreases as excess of H_2O_2 increases. With a threefold excess of H_2O_2, 2-furaldehyde (**I**) is oxidized comletely, and in the presence of 4 equiv of H_2O_2, product **II + III** also disappears.

Figure 5 shows that at the initial parts of plots *1′–6′* the conversion of **I** is proportional to the catalyst concentration; in the range of $NaVO_3$ concentrations about 0.04–0.2 mol per mole of 2-furaldehyde, the conversion of **I** slightly decreases; and it sharply increases as the concentration of $NaVO_3$ further rises. Therefore, plots *1′–6′* are third-order curves. The yield of *cis*-β-formylacrylic acid (**II + III**) (plots *1–6*) increases as the concentration of sodium vanadate changes from 0 to 0.2 mol per mole of 2-furaldehyde. On further raising the $NaVO_3$ concentration, the yield of **II + III** falls down to zero due to its oxidation to polarographically inactive saturated acids.

Our results led us to presume that 2-furaldehyde, hydrogen peroxide, and sodium vanadate, taken at a ratio close to 5 : 1 : 1, form a stable intermediate complex which ensures selective oxidation of **I** to β-formylacrylic acid (**II + III**) with a small admixture of acid **IV**. Increased amount of $NaVO_3$ is likely to promote wasteful decomposition of H_2O_2 and more intense oxidation of **II + III**. Raising the concentration

Scheme 2.

$$VO_3^- + H^+ \rightleftharpoons HVO_3 \qquad (1)$$

$$HVO_3 + H^+ \rightleftharpoons VO_2^+ + H_2O \qquad (2)$$

$$VO_2^+ + \mathbf{I} \rightleftharpoons \text{Complex } \mathbf{V} \qquad (3)$$

$$VO_2^+ + H_2O_2 \rightleftharpoons VO(O_2)^+ \ (\mathbf{VIII}) \qquad (4)$$

$$VO_2^+ + 2H_2O_2 \rightleftharpoons VO(O_2)^- \ (\mathbf{IX}) \qquad (5)$$

$$\mathbf{I} + \mathbf{VIII} \longrightarrow \mathbf{X} \longrightarrow (\mathbf{II} + \mathbf{III}) + \mathbf{IV} \qquad (6)$$

$$\mathbf{V} + H_2O_2 \longrightarrow (\mathbf{II} + \mathbf{III}) + \mathbf{IV} \qquad (7)$$

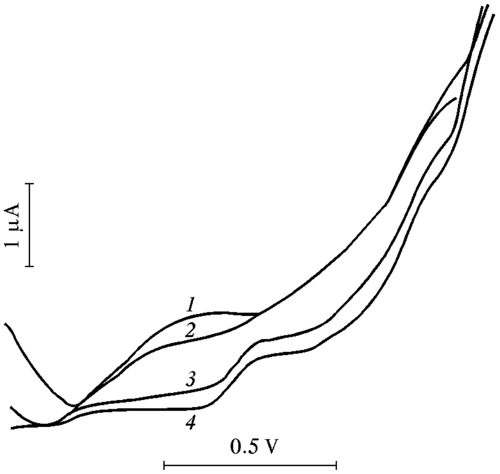


Fig. 3. Polarographic curves for (*1*) 0.1 N $HClO_4$ containing 4.8×10^{-3} mol/l of H_2O_2 and 5×10^{-3} mol/l of $NaVO_3$; (*2*) 0.1 N $HClO_4$ containing 4.8×10^{-3} mol/l of H_2O_2, 5×10^{-3} mol/l of $NaVO_3$, and 5×10^{-3} mol/l of 2-furaldehyde 3 min after mixing the components; (*3*) the same as *2* 1 h after mixing; and (*4*) the same as *2* after complete consumption of H_2O_2.

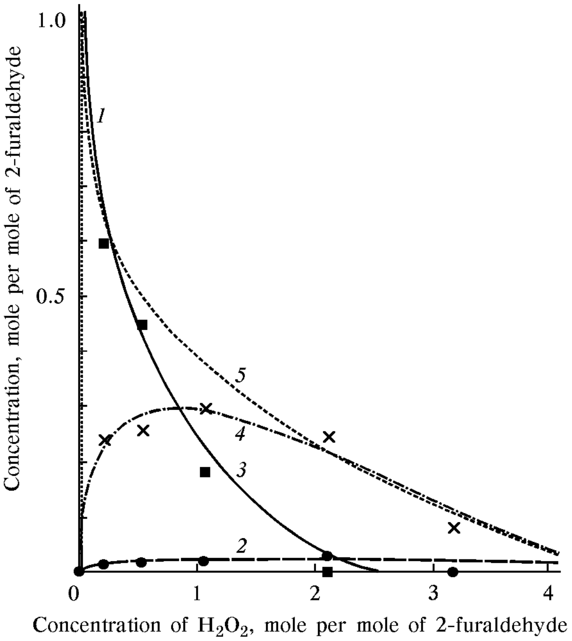


Fig. 4. Effect of hydrogen peroxide concentration on the conversion of 2-furaldehyde (**I**) and the yields of polarographically detectable products: (*1*) unidentified product; (*2*) acid **IV**; (*3*) 2-furaldehyde (**I**); (*4*) β-formylacrylic acid (**II + III**); and (*5*) ratio of the yield of **II + III** and the amount of oxidized 2-furaldehyde. Reaction conditions: 0.1 N $HClO_4$; initial concentrations, M: 2-furaldehyde, 5×10^{-3}; $NaVO_3$, 5.4×10^{-4}; H_2O_2, 0–0.02.

of hydrogen peroxide increases not only the degree of oxidation of **II** + **III** but also the contribution of concurrent transformation of 2-furaldehyde to succinic acid and 2,5-dihydro-2-furanone [1, 6].

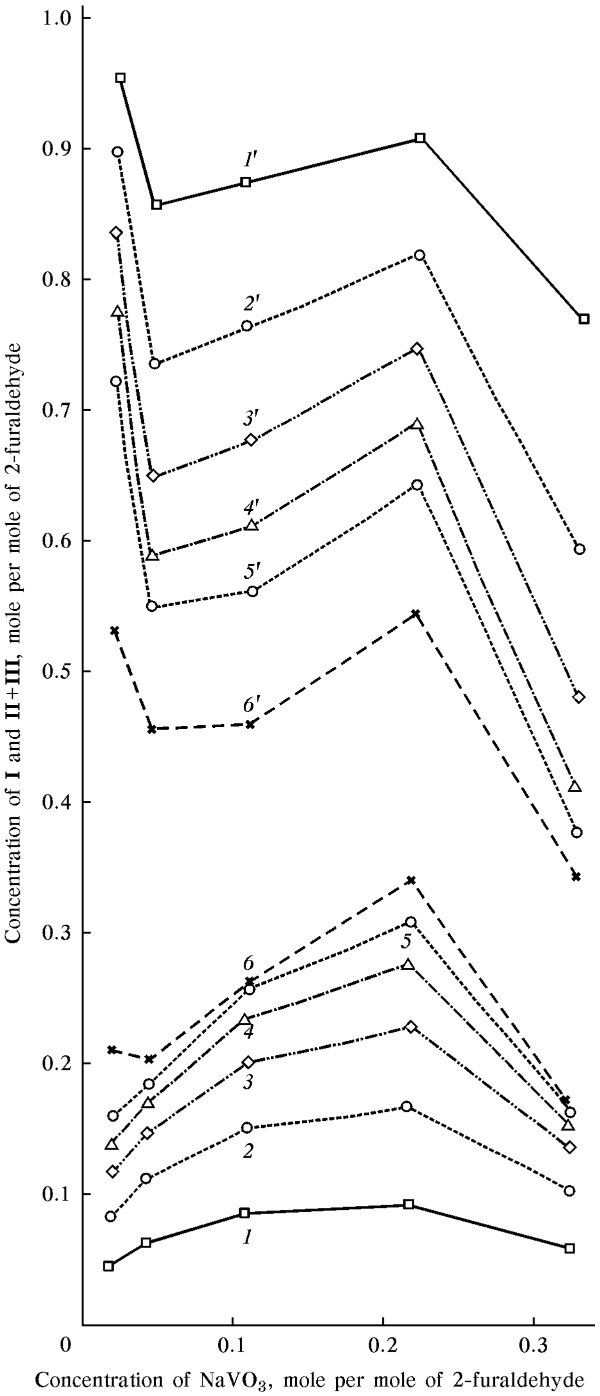
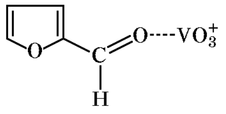


Fig. 5. Plots (*1′–6′*) of the conversion of 2-furaldehyde and (*1–6*) the yield of acid **II** + **III** versus concentrations of $NaVO_3$ and hydrogen peroxide. Concentration of H_2O_2, mole per mole of 2-furaldehyde: (*1, 1′*) 0.05; (*2, 2′*) 0.1; (*3, 3′*) 0.15; (*4, 4′*) 0.2; (*5, 5′*) 0.25; (*6, 6′*) 0.5.

On the basis of the above experimental data, we propose a mechanism for the oxidation of 2-furaldehyde with hydrogen peroxide in the presence of sodium vanadate, shown in Scheme 2.

It is known that at pH < 2 vanadium(V) ions exist mainly as hydrated VO_2^+ cations [8] which are capable of coordinating 2-furaldehyde molecules [9] [see Eqs. (1)–(3) in Scheme 2]. On addition of hydrogen peroxide peroxo compounds of quinquevalent vanadium are quickly formed [Eqs. (4) and (5)]; their structure depends on the concentration of H_2O_2. When the amount of the latter is insufficient with respect to $NaVO_3$, monoperoxo complex $VO(O_2)^+$ (**VIII**) is mainly formed in acid medium; at a H_2O_2/V(V) ratio of greater than 2, diperoxo complex $VO(O_2)_2^-$ (**IX**) is obtained [10]. Our previous results in combination with published data [9, 11, 12] led us to presume that under optimal conditions, i.e., at a **I**–H_2O_2–$NaVO_3$ ratio of about 5 : 1 : 1, the formation of intermediate **VIII** is responsible for highest efficiency and selectivity of the process. The predominant formation of **VIII** is also indicated by a weak red color of the reaction mixtures (λ_{max} 450 nm) [13]. The reaction of 2-furaldehyde with intermediate **VIII** gives complex **X** whose possible structure is shown below. Complex **X** decomposes into products **II**–**IV** through intermediate formation of organic peroxides [14] [Eq. (6)].



X

Complex **V** reacts with hydrogen peroxide to give a peroxo complex which cannot be distinguished from intermediate **X** by polarography. That complex also decomposes with formation of products **II**–**IV**. The low yield of maleic acid **IV** and its weak dependence on the yield of **II** + **III** suggests that in the system under study acid **IV** is formed via concurrent transformation of 2-furaldehyde rather than as a result of oxidation of β-formylacrylic acid (**II** + **III**). This assumption is consistent with the other data [14, 15].

EXPERIMENTAL

Polarographic studies were performed in a cell placed in a temperature-controlled unit. The potentials were measured with the aid of a dropping mercury electrode relative to a standard calomel electrode. The polarograms were recorded using a PLS-1 electronic polarograph. Experiments were carried out in 0.1 N $HClO_4$ with an initial 2-furaldehyde concentration c_{init} of $(1.8–5.0)\times10^{-3}$ M at 25±0.2°C; the capillary parameters were as follows: m = 2.01 mg/s, t_1 = 3.41 s. Dissolved oxygen was removed by purging with nitrogen.

The initial concentration of hydrogen peroxide was varied from 0 to 4 mol per mole of 2-furaldehyde, and of $NaVO_3$, from 0 to 0.4 mol per mole of **I**. Solutions of $HClO_4$, H_2O_2, and $NaVO_3$ were prepared from chemically pure reagents using distilled water. Pure *cis*-β-formylacrylic acid was synthesized by the procedure reported in [2]. Products **II**–**IV** were identified by adding standard solutions of authentic samples to the polarographic cell prior to the end of the reaction.

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