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Effect of Acid–Base Properties of the Medium on the Reactions in the 2-Furaldehyde–H_2O_2–H_2O System with and without $VOSO_4$

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Abstract—Data on the effect of acid-base properties of the medium in the pH range 0–9 on the intensity of transformation of 2-furaldehyde and the direction of the multi-stage reactions in the 2-furaldehyde–H_2O_2–H_2O system in the presence of $VOSO_4$ and without it are presented. Significant influence of the medium pH value on the reaction pathway in the system under investigation hase been found. Mechanism of these reactions considering the effect of acid-base properties of the medium has been suggested.

Key words: 2-furaldehyde, hydrogen peroxide, oxidation, vanadyl sulfate, mechanism

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We have found previously [1–3] that the reaction of 2-furaldehyde **I** with hydrogen peroxide in water medium without special catalysts proceeds through the formation of 2-furaldehyde hydroxyhydroperoxide **II** and its subsequent transformations (Scheme 1).

2-Furyl formiate **III** and a small amount of furoic acid **IV** were found in the reaction mixture. These substances are the products of of peroxide **II** rearrangement according to the Baeyer-Villiger mechanism [1, 2]. Through the intermediate 2-hydroxyfuran **V** a mixture of isomeric 2(5*H*)- and 2(3*H*)-furanones **VI**, **VII**, 5-hydroxy-2(5*H*)-furanone **VIII**, and such carbon acids as formic **IX**, β-formylpropionic **X,** succinic **XI**, *cis*- and *trans*-β-formylacrylic **XII**, **XIIa,** as well as maleic **XIII** and fumaric **XIV** acids is formed (Scheme 1). Lactol **VIII** and acid **XII** are tautomeric forms.

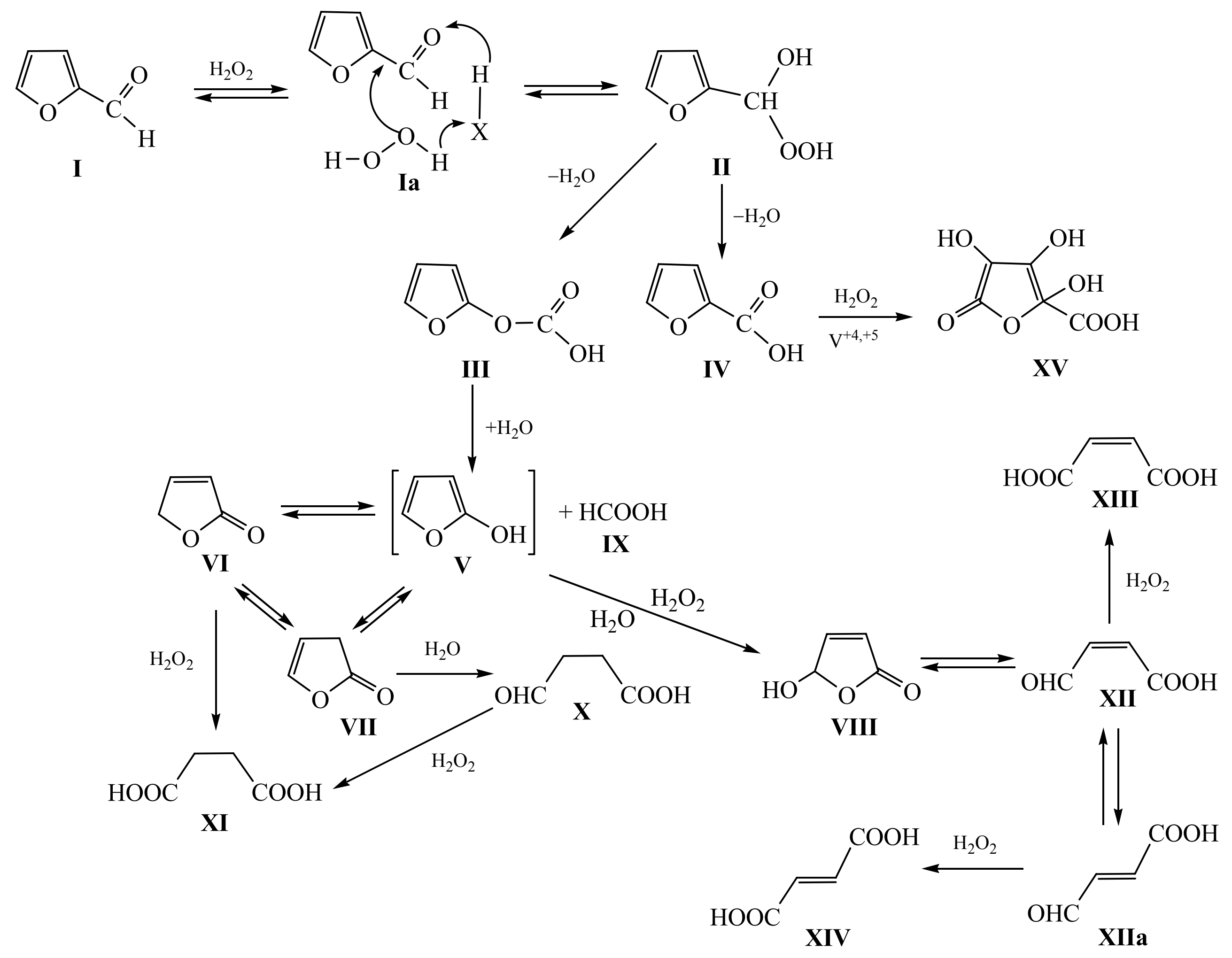
In the course of the reaction pH of the medium decreases to 1-2, and the acids formed play the role of catalysts of the processes taking place in the 2-furaldehyde–H_2O_2–H_2O system.

Main products of the reaction of 2-furaldehyde with hydrogen peroxide under the conditions of autocatalysis with acids which are formed in the course of the reaction (without controlling the pH of the medium) are 2(5*H*)-furanone **VI** and succinic acid **XI**. Their yields are comparable and reach 35–40% for each product [3]. The carbonyl group of 2-furaldehyde quantitatively converts to formic acid **IX**. The formation of compounds **VI**, **XI** is accompanied by small amounts of substances **VI**, **VIII**, **X**, and **XII–XIV**.

The addition of vanadyl sulfate to the 2-furaldehyde–H_2O_2–H_2O reaction system also leads to the formation of intermediate peroxides [4–5]. At the same time the conversion of 2-furaldehyde and hydrogen peroxide significantly accelerates, and the direction of oxidation turns to the side of prevailing formation of tautomeric forms of *cis*-β-formylacrylic acid **VIII**, **IX** with the total yield 30–40%. Lactone **VI** and acid **XI** are side products in this system. Depending on the reaction conditions their yields are 6–8 and 2–10% respectively. Yields of acids **XIII**, **XIV** do not exceed 5–9%.

The pH of the reaction medium in the presence of vanadyl sulfate during the oxidation decreases from 4 at the beginning to 1.5 units at the moment of complete conversion of 2-furaldehyde and hydrogen peroxide. The pH value at the beginning of the reaction is due to the hydrolysis of vanadyl sulfate in the reaction mixture, and the final pH value of the oxidate is caused by the formation of carbon acids **IX**, **XI–XIV.** Hence, a double catalysis of the process with the vanadium

Scheme 1.



compound and autocatalysis with the acids formed is observed in this reaction system.

As seen, the oxidation of 2-furaldehyde with hydrogen peroxide without controlling the oxidate pH value in the presence as well as without vanadyl sulfate proceeds through various directions and leads to the formation of the multi-component mixture of substances.

To determine the pH value effect on the processes taking place in the 2-furaldehyde–H_2O_2–H_2O system and to extend the synthetic possibilities the reaction mentioned we for the first time have studied these reactions under the conditions of controlled pH value of the reaction medium in the range 0.07–9.

It was established preliminary that no transormations of 2-furaldehyde in water without H_2O_2 take place in this pH range. Hydrogen peroxide in the absence of 2-furaldehyde and $VOSO_4$ is comparatively stable in the pH range 1–7 within 4 h, but it intensely decomposes at pH below 1 and above 7. In the presence of vanadyl sulfate decomposition of hydrogen peroxide takes place to a certain degree at any pH value, but the most intense reaction proceeds at pH below 1 and above 7.

We established a significant influence of the reaction medium pH value on the intensity of 2-furaldehyde and hydrogen peroxide transformations in the presence of vanadyl sulfate as well as without it. In weak acidic media (pH 5–7) the process is slow, but it accelerates in more acidic and more basic media. Consumption of 2-furaldehyde and hydrogen peroxide are most intensive when the pH value is maintained below 3 or above 7. The effect of pH range 7–8 on the intensity of reagents consumption is more significant

Table 1. Effect of the medium pH value in the range 0–7.5 on the formation of furanone **VI** and carbon acids in the 2-furaldehyde–hydrogen peroxide–water system (exp. 1–9 in the Experimental)

Exp. no.	pH	2-Furaldehyde consumption[a]	Yields of oxidation products, % [b,c]			
			furanone **VI**	acid **IV**	acid **XI**	acid **XIII**
1	0	100	38	–	40	7
2	1	100	50	–	40	5
3	2	98	40	–	40	3
4	3	80	22	–	43	–
5	4	65	13	–	45	–
6	5	52	–	30	50	–
7	6	48	–	50	40	6
8	7	50	–	65	20	9
9	7.5	58	–	45	4	12

[a] Consumption in 4 h. [b] In final oxidates formic acid in the yield about 100%, a mixture of compounds **VIII**, **XII**, **XIIa**, **XIV**, and also malonic, oxalic, and malic acid in the total yield up to 15% are present. [c] With respect to consumed 2-furaldehyde.

Table 2. Composition of substances formed at the oxidation of 2-furaldehyde and the acid **VI** with hydrogen peroxide in the presence of vanadyl sulfate at various pH values of reaction medium

Exp. no.	pH[a]	Yields of oxidation products (see Scheme 1), %[a]					
		VIII + XII	**XIII + XIV**	**XI**	**IV**	**VI**	**XV**
Oxidation of 2-furaldehyde							
10	0–3	55	26	6	–	7	–
11	4–6	40	8	10	–	8	–
12	6.5–7	5	17	35	6	9	4
13	8–9	2	18	3	6	–	60
14	8–9[b]	–	29	3	13	–	39
Oxidation of furoic acid							
15	6.5–7	14	10	20	14[c]	1	1
16	8–9	4	22	8	2[c]	–	40

[a] pH ranges where the composition of products in the reaction mixtures is close are presented. [b] Experiment performed under analogous conditions without vanadyl sulfate. [c] Remaining amount of acid **IV**.

in the presence of vanadyl sulfate. At pH below 1 even in the absence of vanadyl sulfate 100% conversion of 2-furaldehyde is achieved within 1 h.

The significant effect of the medium pH value on the direction of reactions in the 2-furaldehyde–hydrogen peroxide–H_2O system in the presence or without vanadyl sulfate has been established for the first time (Tables 1, 2).

From Table 1 it follows that furanone **VI** is formed in the oxidation of 2-furaldehyde only at pH below 4, and in the largest amount only at pH about 1. At the same time acid **IV** is formed only in the processes taking place at pH above 4, and its highest yield is achieved in the reaction systems with pH about 7. These facts on the one hand open the way to optimization of methods of obtaining compounds **IV** and **VI**, and on the other hand show the effect of pH on the direction of rearrangement of peroxide **II** (Scheme 1). The obtained results show that at pH 0–3 the rearranegement of peroxide **II** into ester **III** and further to lactone **VI** prevails. At pH 6–7 the main product of peroxide **II** rearrangement is acid **IV**. Such effect of the acid-base properties of the medium on the direction of Baeyer–Villiger rearrangement is known also for the other hydroxyhydroperoxides [1].

Alongside with compounds **IV** and **VI** succinic **XI** and maleic **XIII** acids are also formed. They are the products of transformation of isomeric lactone **VII** and the tautomeric form of lactone **VI**, hydroxyfuran **V,** respectively (Scheme 1).

It may be due to the fact that during the pH increase from 4 to 7.5 the transformation of lactone **VI** to lactone **VII** and hydrolytic transformation of the latter to acid **X** is facilitated. The compound formed is oxidized to acid **XI** (Scheme 1). We proved it while studying the reactions of furanone **VI** with hydrogen peroxide in water media in the pH range 0–8 [6]. Maleic acid **XIII** is the side product of the reaction at these pH values. It shows that at the oxidation of 2-furaldehyde in the absence of vanadyl sulfate the reaction pathway leading to formation of hydroxyfuran **V** and then compounds **VIII** and **XII** is insignificant.

Note that in the processes without vanadyl sulfate at pH 0–7.5 succinic acid **XI** is one of the main products. At pH below 5 it is formed together with lactone **VI**, and at higher pH values, along with acid **IV** (Table 1).

Note also that in acidic and close to neutral media in the presence and in the absence of vanadyl sulfate a significant difference in the yields of main products of oxidation, and hence in the direction of the processes taking place is observed (Tables 1, 2).

In the systems with pH below 3 containing no vanadyl sulfate furanone **VI** and the acid **XI** are the main reaction products. In the presence of vanadyl sulfate *cis*-formylacrylic acid existing as a mixture of tautomeric forms **VIII** and **XII** prevails among the oxidation products (Table 2). In the absence of vanadyl sulfate their total yield is no more than 4%.

At pH 6–7 the main oxidation product of 2-furaldehyde in the presence of vanadyl sulfate is acid **XI**, while in its absence the acid **IV** is formed. It is characteristic that in any other studied reaction conditions in the presence of vanadyl sulfate acid **IV** is not the main product.

A common specific feature of processes in the 2-furaldehyde–hydrogen peroxide–H_2O–vanadyl sulfate system in all the pH range under consideration as compared to the process without vanadyl sulfate is the formation of noticeable amounts of oxalic and malonic acids and carbon dioxide as well as increased yield of formic acid. It may be the result of oxidative cleavage of molecules of the main reaction products in the presence of $VOSO_4$.

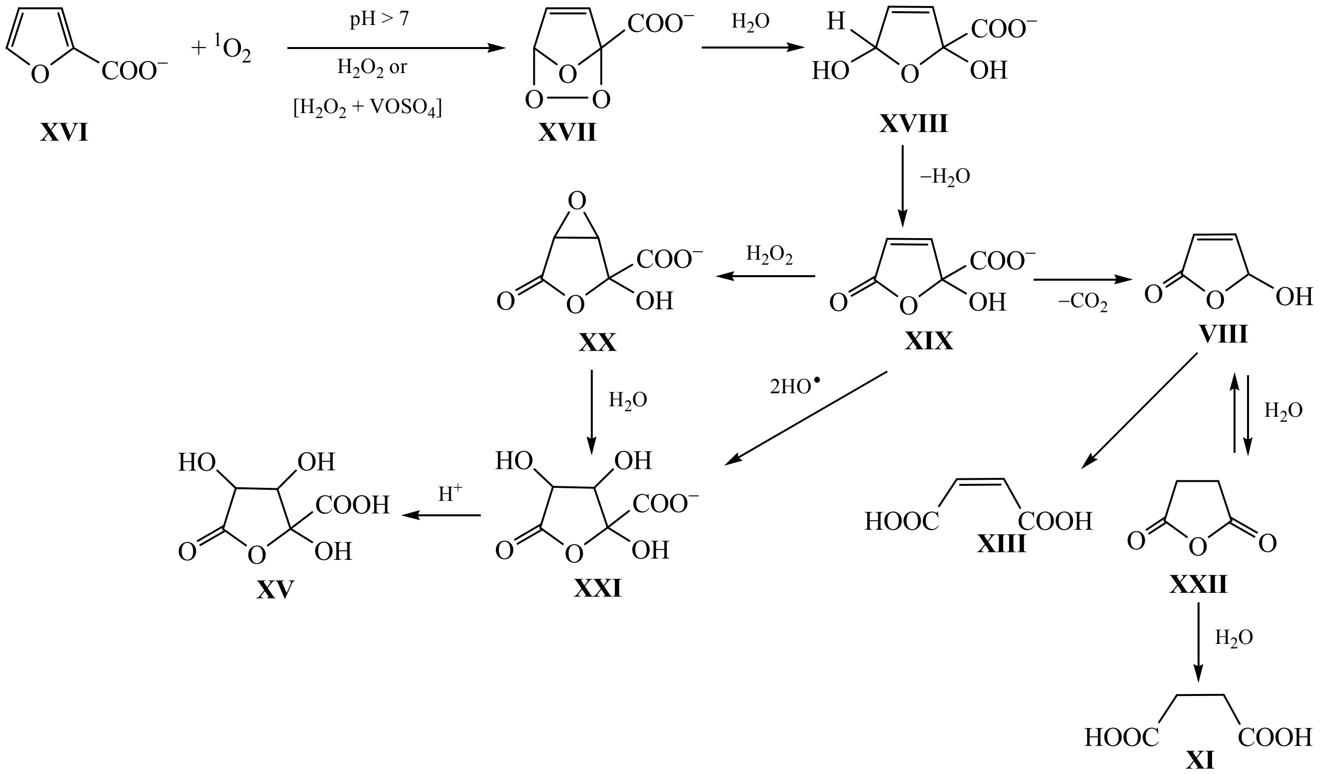
It is noticeable that in the reaction of 2-furaldehyde with hydrogen peroxide in the presence of vanadyl sulfate in the conditions under consideration content of furanone **VI** among the final reaction products is insignificant. It may be explained by its quantitative transformation to the acid **XI** (Scheme 1) which is significantly activated in the presence of vanadyl sulfate [5].

The comparison of data presented in Tables 1 and 2 shows that the influence of the medium pH on the composition of products, and hence on the direction of oxidation in the 2-furaldehyde–hydrogen peroxide–H_2O system is more significant than in the presence of vanadyl sulfate. This means that the main role in this system at pH 0–7.5 belongs to vanadyl sulfate catalyst while the contribution of acid–base catalysis is less significant. The preferred formation of tautomeric forms **VIII**, **XII** and acid **XIII** in the presence of vanadyl sulfate may be due to the activation of oxidation with hydrogen peroxide first of hydroxyfuran **V** and then of tautomers **VIII, XII** into acid **XIII** (Scheme 1). The preferred oxidation of acids **VIII, XII** to acid **XIII** we established previously [2, 5]. In its turn it favors the shift of equilibrium transformations of compounds **V, VI, VII** to the isomer **V**.

It turned out unexpectedly that at pH 8–9 the compositions of oxidation products in the systems containing vanadyl sulfate and without it differ insifnificantly. They are in striking contrast with the com-position of oxidation products at pH 0–7.5 (Tables 1, 2). It permits a conclusion that in the processes at pH 8–9 the main factor determining the direction of oxidation is the high basicity of the medium. Most probably in this case the same active particles leading to similar oxidation products in the presence or without vanadyl sulfate are formed from H_2O_2.

One more peculiarity of oxidation processes of 2-furaldehyde with hydrogen peroxide in highly acidic media in the presence as well as in the absence of

Scheme 2.



vanadyl sulfate is the preferred formation of 3,4,5-trihydroxy-5-carboxy-2(3*H*,5*H*)-furanone **XV**. Its yield significantly increases in the presence of vanadium catalyst. We first obtained and described lactone **XV** in [7].

The lack of acid **IV** among the products of 2-furaldehyde oxidation with hydrogen peroxide in the presence of vanadyl sulfate at pH 0–6 requires to be explanated. It is characteristic that at pH 6.5–9 it forms only in insignificant amounts (Table 2). At the same time in the absence of vanadyl sulfate acid **IV** is present in the reaction mixtures obtained in the media with pH 4–9. Its maximum yield is achieved at pH about 7, and then its content decreases (Tables 1, 2).

Note that at pH 8–9 in the reactions in the presence as well as in the absence of vanadyl sulfate carboxylactone **XV** is mainly formed (Table 2). Apparently acid **IV** is transformed to lactone **XV** at these pH values. Taking this fact in consideration we carried out the oxidation of the acid **IV** with hydrogen peroxide in the media with definite pH values varying from 6.5 to 9 (Table 2). It occurred that the compositions of the products in the presence as well as in the absence of vanadyl sulfate are similar, but the process in the presence of vanadyl sulfate proceeds significantly faster. At pH 6.5–7 insignificant amounts of lactone **XV**, tautomeric forms of acids **VII,XII**, acids **XIII** and **XI** with the prevalence of the latter are formed. At pH 8–9 the main products of acid **IV** oxidation are carboxylactone **XV** and acid **XIII**.

The results presented permit to explain formation of carboxylactone **XV** in the reactions of 2-furaldehyde oxidation with hydrogen peroxide at pH 8–9 by the transformations of a salt of acid **IV** according to Scheme 2.

In the molecule of salt **XVI** the electron density distribution significantly differs from that in 2-furaldehyde. The anionic substituent significantly increases the electron density in the furan ring. It distorts its aromaticity and favors the reactions of the furan ring as the diene system. As known [8–10], at pH > 7 an active decomposition of hydrogen peroxide molecules takes place. It leads to the formation of a set of active particles, among them of $HO^•$, $HOO^•$, HO_2^-, O_2^{2-}, and singlet oxygen ${}^1O_2$. In the presence of vanadyl sulfate this process is activated to form peroxocomplexes of VO_5^- type as well as peroxocomplexes containing a larger number of peroxoligands [11–13].

These vanadium compounds are significantly more active oxidants than H_2O_2, and their decomposition leads to intense formation of singlet oxygen $^1O_2$. A lot of reactions reactions of furan compounds with singlet oxygen are known [14]. The lifetime of singlet oxygen is sufficient for its entering the reaction with substances present in the reaction mixture. These facts permit the suggestion of the formation of ozonides **XVII** and their trans-formation to compounds **XVIII, XIX** during the reaction of the acid **IV** with hydrogen peroxide in basic media. In the course of our studies of the reaction of the acid **IV** with hydrogen peroxide in basic media the formation of several peroxo-compounds was established chromatographically, but we failed to reveal their structure. Analogous trans-formations and their products were found in the studies of photochemical reactions of furan compounds with molecular oxygen [15, 16].

Our results [7] permit to suggest that unsaturated carboxylactone **XIX** is epoxized to lactone **XX**. The latter by hydrolysis converts to compound **XXI** which at acidifying the reaction medium forms lactone **XV** (Scheme 2). The formation of compound **XXI** may be regarded also as the result of hydroxylation of double bond of lactone **XIX** with hydroxyl radicals formed from hydrogen peroxide. This pathway of acid **IV** reaction with hydrogen peroxide leading to lactone **XV** prevails at pH > 7. The directions leading to the acids **XI, XIII** are developed in parallel. Most probably they form through the stage of decarboxylation of lactone **XIX** giving lactol **VIII** followed by its subsequent oxidation to acid **XIII**, and also by isomerization to acid **XI**. Recently we have found such isomerization, and its dependence on the pH of the medium was established [17]. It was found also that the preferred product of oxidation of compounds **VIII**, **XII**, and **XIIa** is acid **XIII** [2, 5].

Results we have obtained show that pH of the medium in the 2-furaldehyde–H_2O_2–water and the 2-fural-dehyde–H_2O_2–$VOSO_4$–water systems significantly influences the rate and the direction of transformations of substances in these systems.

The established rules of the influence of the medium pH value on the reactions in these systems is the basis for optimization of methods for the syntheses of lactones **VI**, **VII**, **VIII**, **XV**, and acids **IV**, **X**–**XII** (Scheme 1). On the other hand, the obtained results extend our knowledge on the mechanism and the effect of acid–base properties of the reaction medium on the majority of stages of multiple-directed reactions in the reaction systems under study. The acids protonate the carbonyl oxygen of 2-furaldehyde increasing the electrophilicity of the carbonyl carbon atom in the reactions with hydrogen peroxide. Analogous effect produces the complex formation of 2-furaldehyde with $VOSO_4$. Bases favor the increase in the nucleophilicity of hydrogen peroxide in its reactions with the carbonyl group of 2-furaldehyde and also the formation of HOO^- nucleophilic species from hydrogen peroxide. Due to that the rate of oxidation of 2-furaldehyde increases in the presence of acids as well as of bases. Acids protonate the peroxide bond oxygen in peroxide **II** favoring its cleavage and the formation of intermediate through which proceeds the Baeyer-Villiger rearrangement of the peroxide including the transfer of furyl radical and the formation of hydroxyfuran formiate **III**. The latter in the presence of acids as well as of bases readily hydrolyses to form hydroxyfuran **V** (Scheme 1).

As known [1], the rearranegement of hydroxy-hydroperoxides to carboxylic acids facilitates in basic media. It is also observed in the reaction under study where at pH > 6 among the compounds forming at the oxidation of furoic acid **VI** or the products of its transformation prevail (Tables 1, 2; Schemes 1 and 2).

The acidity of the medium also influences mutual tautomeric and isomeric transformations of compounds **V**, **VI**, **VII**, and **VIII**, **XII** (Scheme 1) as well as the oxidative and hydrolytic transformations of compounds **VIII**, **XII** and lactones **VI**, **VII** as well as the oxidation processes of compounds **IV**, **V**, **X, XII** and lactones **VI**, **VII** (Scheme 1).

Hence, in the oxidation of 2-furaldehyde with hydrogen peroxide the acid-base properties of the reaction medium play significant role at all stages of the process and determine its direction.

EXPERIMENTAL

All compounds used were of “pure” or “chemically pure” grade. 2-Furaldehyde was preliminary distilled in a vacuum.

Reactions were carried out under temperature control and intense stirring. Every 20–40 min samples were taken, and the content of 2-furaldehyde, hydrogen peroxide, organic peroxides, general acidity, pH of the medium, and also the content of acids **IV**, **IX**–**XIV**, lactol **VIII**, and lactones **VI**, **VII**, **XV** was evaluated. General acidity was evaluated by the acid-base titration. pH value was determined by means of pH-meter. Content of hydrogen peroxide and organic peroxides in the case of their joint presence was evaluated according to the procedure [18]. The content of 2-furaldehyde and acid **IV** in oxidates was evaluated spectrophotometrically using the calibrating curves at 278 and 245 nm in water solutions. The content and concentration of unsaturated carboxylic acids was evaluated polarographically using a mercury dropping electrode [19–21] and chromatographically [22]. Evaluation of acids was also carried out by known and previously described methods of acid-base [1], iodometric, and cerimetric titration [3, 21], polarography with a dropping mercury electrode [21], pH-metering [3, 23], UV spectroscopy in the range 230–300 nm [3, 4], TLC, paper chromatography, GLC [1, 22, 25], and chromatomass spectrometry. Yields of all compounds are presented with respect to reacted 2-furaldehyde.

General procedure of performing the experiments. A three-necked flask equipped with a stirrer and a reflux condenser placed in a thermostat was charged with desired amounts of 2-furaldehyde, 30% hydrogen peroxide solution, and buffer solutions for creating a definite pH value of the medium. The desired pH value in the range 0–7.5 was maintained by addition of definite amount of phosphoric acid and various amounts of potassium hydroxide. Constant value of ionic power was maintained by addition of corresponding amount of potassium chloride. To obtain pH 8–9 the starting reaction mixture was treated with 1.25 mol of sodium carbonate per 1 mol of 2-furaldehyde. In some cases vanadyl sulfate was added to starting oxidate as a catalyst.

Reactions of 2-furaldehyde with hydrogen peroxide at pH 0.07–7.5 without the vanadyl sulfate (Table 1, exp. 1–9). Reactions were carried out during 4 h at 60°C and the ten-fold molar excess of hydrogen peroxide with respect to 2-furaldehyde. The starting concentration of the latter was 0.5 mol/L. In the experiments 0.05 mol of 2-furaldehyde and 100 mL of the corresponding buffer solution containing 0.5 mol of hydrogen peroxide were used.

Reaction of 2-furaldehyde with hydrogen peroxide at pH 8–9 without the addition of vanadyl sulfate (Table 2, exp. 14). The process was carried out at 60°C and 1 : 5 2-furaldehyde–H_2O_2 molar ratio.

Reactions of 2-furaldehyde with hydrogen peroxide in the presence of vanadyl sulfate at pH 0.07–7.5 (Table 2, exp. 10–12). Experiments were carried out at 60°C, 2-furaldehyde–hydrogen peroxide–$VOSO_4$ molar ratio 1 : 3.2 : 0.005, and starting concentration of 2-furaldehyde 1.2 mol/L.

Oxidation of 2-furaldehyde with hydrogen peroxide at pH 8-9 in the presence of $VOSO_4$ (Table 2, exp. 13). Reaction was carried out at 60°C, 2-furaldehyde–H_2O_2–vanadyl sulfate molar ratio 1 : 5 : 0.005.

Oxidation of the acid IV with hydrogen peroxide at pH 6.5–9 (exp. 15, 16). Reaction conditions are analogous to that of the exp. 12, 13, but instead of 2-furaldehyde acid **IV** is used.

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