

**CATALYTIC OXIDATION REACTIONS
OF FURAN AND HYDROFURAN COMPOUNDS
9.* CHARACTERISTICS AND SYNTHETIC
POSSIBILITIES OF THE REACTION OF FURAN
WITH AQUEOUS HYDROGEN PEROXIDE
IN THE PRESENCE OF COMPOUNDS OF
NIOBIUM(II) AND (V)**

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The effect of the catalytic characteristics of compounds of niobium(II) and (V) on the duration and the composition of the products during the oxidation of furfural by aqueous hydrogen peroxide was studied. It was established that the process is intermediate in its main characteristics between reactions of the compounds taking place under the conditions of autocatalysis by the acids that are formed and in the presence of the vanadium compounds. The main product of the reaction is 2(5H)-furanone. A method is proposed for its production with yields of up to 60%.

Keywords: hydrogen peroxide, niobium(II) and (V) compounds, 2(5H)-furanone, furfural, oxidation.

Earlier we conducted a comprehensive investigation into the reactions of furfural (**1**) with aqueous hydrogen peroxide in the presence of compounds of vanadium(IV) and (V). It was established that the introduction of a vanadium catalyst into the furfural–H₂O₂ system in an acidic aqueous medium leads to a fundamental change in the mechanism and direction of the oxidation process that occurs in comparison with the reaction of these compounds taking place under the conditions of autocatalysis by the acids that are formed [2-5]. A distinguishing feature of the process is the formation of 5-hydroxy-2(5H)-furanone (**2**) as the main product [2, 3]; this made it possible to develop a rational method suitable for widespread use in the production of this previously difficult-to-obtain chemical compound [3, 6].

The results from the peroxide oxidation of the aldehyde **1** under the conditions of acid autocatalysis and in the presence of vanadium catalysts were compared with our results on the reactions of these compounds in the presence of compounds of group VI elements – chromium, molybdenum, and selenium. It was established that the type of catalyst has a substantial effect on the nature of oxidation of furfural and on the composition of

* For Communication 8, see [1].

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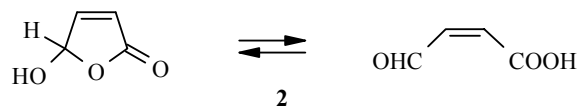
the obtained products: Whereas 2(5H)-furanone **3** and succinic acid **4** are mostly formed in the autocatalytic reaction, furanone **3** is formed in the presence of molybdenum compounds, furanone **3** and hydroxyfuranone **2** are formed in the presence of chromium compounds, and hydroxyfuranone **2** is formed in the presence of selenium compounds as also in the case of the vanadium catalysts [7-10].

These results served as the basis for a study of features of the oxidation of furfural in the H₂O₂-niobium compound system. The choice of niobium(II) and (V) compounds was based on the similarity in the structure of the electron shells in the V and Nb atoms (they are full electronic analogs) and also by some degree of similarity in the behavior of these compounds as catalysts in oxidation-reduction reactions involving organic compounds [11-14].

The main features of the oxidation of furfural in the presence of vanadium compounds ("V-catalytic reaction") are the substantial difference in the composition of the products and the significant acceleration of the reaction in comparison with the reaction taking place under the conditions of autocatalysis by the carboxylic acids ("H⁺-autocatalytic reaction") [2-4]. The "H⁺-autocatalytic" process also takes place in the presence of the vanadium catalysts, but in this case it is a side process.

In view of this the oxidation of furfural in the presence of the niobium(II) and (V) compounds Nb(OAc)₂ and Nb₂O₅ was conducted under the previously adopted conditions for "V-catalytic" and "H⁺-autocatalytic" reactions. The conditions and the results of the experiments are presented in Table 1.

During "H⁺-autocatalytic" oxidation (expt. 1) the predominating products from transformation of the aldehyde **1** under conditions comparable with the "V-catalytic" process were the furanone **3** and the acid **4**. [It is noteworthy that under the conditions with the optimum amount of H₂O₂ the ratio of the yields of products **3** and **4** were fundamentally different.] In the presence of V₂O₅ (expt. 2) the main product from the oxidation of furfural was the hydroxyfuranone **2** in two tautomeric forms.



Here the total yield of the products **3** and **4** in the presence of V₂O₅ did not exceed 20%. Among the other products of the "V-catalytic reaction" maleic (**5**) and fumaric (**6**) acids were formed with the largest yield, and they accumulated in approximately the same amount in the absence of V₂O₅.

TABLE 1. The Results from the Oxidation of Furfural (FI) with Hydrogen Peroxide in the Presence of Various Catalysts at 60°C; [FI]:[H₂O₂] = 1:3.5; [FI]₀ = 1.2 mol/l

Experiment	Catalyst (Ct)	Amount of Ct, mol/mol FI	Half-conversion time of FI, τ _{1/2} , min	Full consumption time of H ₂ O ₂	Yield of products, %*			
					2	5+6	3	4
1	H ⁺ * ²	~2.8* ³	155	> 6 days	4 (7)	8 (11)	22 (40)	48 (20)
2	V ₂ O ₅	0.0025	39	6.5 h	36	11	6	12
3	Nb ₂ O ₅	0.025	55	~ 4 days	<1	12	29	17
4	Nb(OAc) ₂	0.05	60	~ 4 days	<1	8	34	14

* From theory. The yields of the products with the minimum amount of H₂O₂ needed for complete transformation of the furfural (2.2 mol/mol of substrate [4, 5]) are given in parentheses.

*² Carboxylic acids formed during oxidation, g-equiv/l.

*³ In the period after half-conversion of the furfural.

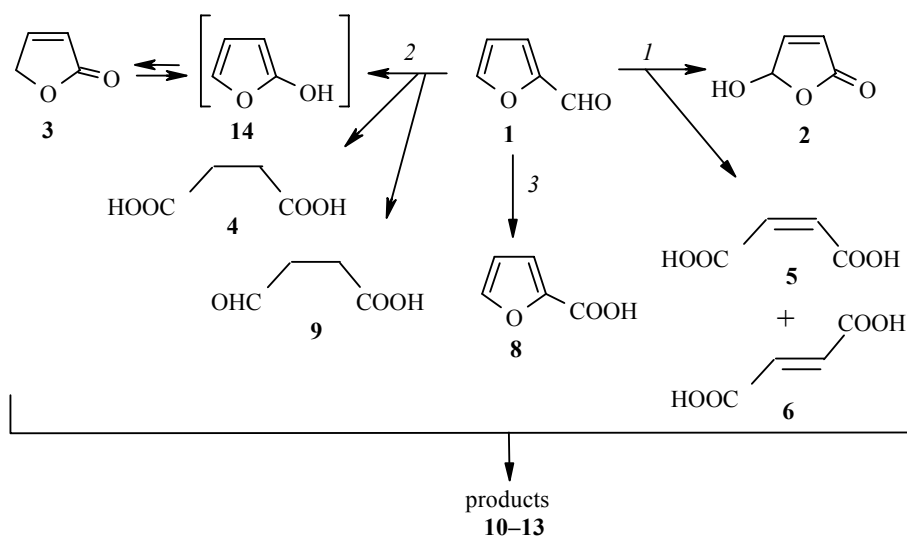
Replacement of the vanadium catalyst by the niobium(II) or (V) compound led to substantial retardation of the process and to a change in the quantitative composition of the products from oxidation of the furfural. In the presence of the same amounts of Nb₂O₅ or Nb(OAc)₂ as in the case of expt. 2 (2.5-5 mmol/mmol of furfural) the reaction went very slowly [$\tau_{1/2}$ for the aldehyde **1** was more than a few days]. With a tenfold increase in the content of the niobium catalysts (50 mmol/mmol of furfural) the duration of oxidation, determined by the moment of complete transformation of the H₂O₂, was approximately four days (expts. 3 and 4).

The qualitative and quantitative compositions of the products from oxidation of furfural in expts. 3 and 4 differed little. Thus, in both cases the main reaction product was the furanone **3**. The yield of the acid **4** decreased significantly compared with the "H⁺-autocatalytic reaction" while the main product of "V-catalytic" oxidation hydroxyfuranone **2** accumulated by a very small amount. Other characteristic products of the "H⁺-autocatalytic" and "V-catalytic" reactions were detected in the furfural-H₂O₂-niobium catalyst system by GLC and polarography: C₁-C₄-carboxylic acid – formic acid (**7**), 2-furancarboxylic acid (**8**), β -formylpropionic acid (**9**), malic acid (**10**), tartaric acid (**11**), malonic acid (**12**), and oxalic acid (**13**).

Under these conditions the acid **7** accumulates at the rate of 120-130% of the initial aldehyde **1**. The results obtained during study of the "H⁺-autocatalytic" and "V-catalytic" reactions make it possible to assume that the acid **7** is formed as a result of oxidative cleavage of the C-C bonds between the furan ring and the substituent (in the molecule of the intermediately formed furfural hydroxyhydroperoxide) and, partly, between the aldehyde group and the hydrocarbon chain (in the molecules of the aliphatic carbonyl-containing intermediates). The overall yield of the acids **8-13** in the reactions under discussion (expts. 3 and 4) did not exceed 20%.

From the presented results it is seen that the type of niobium catalyst does not have a significant effect on the duration of the process and the yields of its main products under the adopted conditions.

With regard to our earlier ideas about the mechanism of the oxidation of furfural in the aqueous H₂O₂-vanadium catalyst system it can be supposed that the reaction of the aldehyde **1** with hydrogen peroxide in the presence of niobium(II) and (V) compounds also evolves in two competing directions *1* and *2*:



Whereas the "V-catalytic" reaction takes place mainly along path *1* the path *2*, characteristic of "H⁺-autocatalytic" oxidation, mostly develops in the presence of the niobium catalysts. At the same time the overall yield of the products from more extensive oxidation **8-13** in the presence of niobium compounds is much more perceptible than in the "H⁺-autocatalytic" process and is comparable with their total yield in the presence of V₂O₅.

In order to detect the possible formation and participation of furan and furancarboxylic acid **8** at the early stages of the reaction certain features of the oxidation of these furan compounds in the "H₂O₂–niobium compound" system were studied. The obtained data were compared with the results from the oxidation of furfural under the same conditions. In contrast to the "V-catalytic reaction" furan is not formed during the oxidation of furfural in the presence of the niobium compounds and is hardly oxidized at all under the employed conditions. At the same time the oxidation of the acid **8** in the "H₂O₂–niobium compound" system hardly differs at all in duration and in the composition of the products from the reaction involving furfural. These results make it possible to state that furan is not formed in the presence of the niobium compounds, whereas the acid **8** is apparently one of the key intermediate products. It can therefore be assumed that path 3 in the oxidation of furfural in the presence of the niobium compounds is substantially more significant than in the "V-catalytic" and "H⁺-autocatalytic" reactions.

Additional information on the reaction was obtained by comparing the consumption rates of the reagents and the formation of the products from the oxidation of furfural in the presence of V and Nb compounds and also without the metal-containing catalyst. These results were obtained under identical conditions chosen in such a way that the process occurred under thermal control in all cases – with 1:3.5:0.01 molar ratios of furfural, H₂O₂, and transition metal compound and an initial substrate concentration of 1.2 M at 60°C. The catalysts were NaVO₃ and Nb(OAc)₂, which were chosen as the most suitable according to the solubility of the compounds in water. The reaction was monitored by the consumption of the initial reagents and also by the accumulation and consumption of the products from the oxidation of furfural – organic peroxides as the main initial intermediates, furanone **3**, and carboxylic acids.

The results of the investigation show that the reactions have a series of common features. Thus, at the very beginning of the reaction in all cases a brief period of rapid consumption of furfural, leading to the accumulation of organic peroxides, was observed. Then, in all cases it was replaced by an induction period, which appeared in the form of a marked reduction in the rate of consumption of the furfural and the further accumulation of peroxides. The length of the induction period depended on the type of catalyst and increased in the order: V < Nb < H⁺.

After the induction period the rapid accumulation of organic peroxides was again observed, and they were then gradually used up. In all the experiments after the consumption of approximately 50% of the furfural the accumulation of furanone **3** and carboxylic acids was observed. As a result of this all the studied reactions after the induction period took place at pH < 2.

It is seen from the presented results that the peroxide oxidation of furfural in the presence of niobium compounds is similar to the "H⁺-autocatalytic" reaction in its general duration and direction (in both cases the main product is the furanone **3**). The reaction also has features in common with the "V-catalytic" process: a) Both reactions take place almost entirely along paths involving removal of the substituent from the heterocycle; b) In both cases the processes of oxidation of the formyl substituent and the furan ring of the substrate are supplemented by stages with more drastic oxidation leading to the carboxylic acids **8-13**.

At the same time the process occurring in the presence of niobium compounds differs from the "H⁺-autocatalytic" and "V-catalytic" reactions in the character and rate of accumulation of the products from oxidation of furfural and also in their quantitative composition. The reaction took place most quickly in the presence of NaVO₃; after a brief induction period the process developed extremely vigorously, and it was complete after only 2 h. The reaction catalyzed by niobium(V) acetate was the slowest. Here the furfural was completely transformed after reaction for 5 h, whereas the H₂O₂ residue and the accumulated organic peroxides were used up quite slowly. Here lies the specific similarity between the given process and the "H⁺-autocatalytic" reaction.

The $\tau_{1/2}$ value of furfural in the investigated processes increased in the order V(V) < Nb(V) \ll H⁺, which corresponds to the order of decrease of the oxidation–reduction potentials of these cations in one- and two-electron reactions in acidic media [15-17].

The obtained results make it possible to suppose that the niobium catalysts accelerate the formation of 2-hydroxyfuran **14** as key intermediate product. In the presence of the vanadium compounds the intermediate **14** is apparently oxidized to the hydroxyfuranone **2** by the peroxy complexes of this metal more quickly than it isomerizes to the more stable furanone **3**. In the presence of the peroxy complexes of niobium, which have appreciably lower oxidizing power than the peroxy compounds of vanadium, the isomerization of the furan **14** clearly takes place more quickly than its oxidation.

In connection with the preferred accumulation of the furanone **3** in the furfural–aqueous hydrogen peroxide–niobium compound system further research was directed toward determination of the optimum conditions for the production of the given product.

2(5H)-Furanone (**3**) is an important intermediate in the synthesis of heterocyclic compounds and the components of biologically active compositions for comprehensive applications [5, 18]. The most convenient method for its production with a yield of up to 40% is based on the reaction of furfural with aqueous hydrogen peroxide [5, 19, 20]. Due to these researches the furanone **3** became an accessible compound, but the problem of increasing its yield remained urgent. Modified versions of the method only led to a small increase in the yield of the product [21].

We proposed a new method for the production of the lactone **3** with yields of up to 55-60%. The method is based on the fact that in the presence of niobium compounds furfural is oxidized significantly more quickly than its oxidation products. This made it possible to achieve its almost complete transformation in the presence of a minimal amount of hydrogen peroxide. The optimum molar ratios of furfural, H₂O₂, and niobium(II) acetate, sufficient for 95-98% conversion of the aldehyde **1**, amount to 1:1.1:0.005. In the new method for the production of the furanone **3** the process is simpler (reduced consumption of the reagents, lower process temperature) and the yield of the required product is higher.

The structure of the synthesized lactone **3** was confirmed by spectral data, which agreed with the published data [5, 20, 21]. In the IR spectrum two strong absorption bands for the lactone C=O bond attached to the unsaturated group were observed at 1740 and 1780 cm⁻¹, and there were also bands in the region of 1030-1170 cm⁻¹ indicating the presence of the C–O–C group. In the ¹H NMR spectrum there were two doublet signals (6.13 and 7.86 ppm) corresponding to the *cis* protons at the C=C bond and a triplet at 4.96 ppm due to the resonance of the two protons at the C-5 atom of the furanone **3**.

Thus, the use of niobium compounds as catalysts for the peroxide oxidation of furfural makes it possible to obtain the product **3** with appreciably higher yields than by the familiar methods.

EXPERIMENTAL

The IR spectrum of the furanone **3** was obtained on a Specord 40M spectrometer (Germany) in vaseline oil in the region of 800-3800 cm⁻¹ (NaCl and KBr prisms). The scanning rate was 10 min, resolving power 1 cm⁻¹, and photometric accuracy ±2%. The ¹H NMR spectrum of the obtained product was recorded in carbon tetrachloride on a Bruker WM-200 instrument (250 MHz) with TMS as internal standard. Thin-layer chromatographs of the reaction mixtures and the lactone **3** were obtained on Silufol UV-254 plates in chloroform or in the 3:1 chloroform–acetone system with development by acidified solutions of KMnO₄ and 2,4-dinitrophenylhydrazine, an alcohol solution of bromophenol blue, and iodine vapor. Gas-liquid chromatography was used to determine the contents of furfural, furanone **3**, and the carboxylic acids **2**, **4-6**, and **8-13** (as the ethyl esters) in the reaction mixtures. Analysis of the reaction mixtures and the esterification products was realized on a Chrom-4 instrument (Czech) with a flame-ionization detector and a glass column (300×0.3 cm). The carrier gas was nitrogen, and the flow rate 30 ml/min. Polarography was used to determine the yields of the acids **2** and **5-7** in the reaction mixtures. The reaction solutions (0.5-2 ml) obtained in expts. 1-4 were dissolved in the supporting electrolyte (0.1 M HClO₄), made up to 50 ml, and stirred. The samples

were analyzed after 24 h on an LP-70 polarograph in a thermostated cell with a dropping mercury electrode ($m = 1.59$ mg/s, $t = 3.66$ s at potential -1.0 and 25 ± 0.2 °C) with a normal calomel electrode. Half-wave reduction potentials: Compound **2** – 0.38-0.40; compounds **5** and **6** – 0.67; compound **7** – 1.3 V.

The concentrations of the substances in the tests were determined against calibration curves. The total content of the acids in the reaction mixtures obtained by the oxidation of furfural in expts. 1-4 was determined by titration. To a 0.5 ml sample of the oxidate we added 4.5 ml of distilled water. The solutions were titrated with 0.01 or 0.1 N solutions of NaOH, depending on the concentration of protons, in the presence of an alcohol solution of phenolphthalein.

The content of peroxides in the reaction mixtures was determined by the usual methods by cerimetric titration of the H₂O₂ and iodometric determination of the total amount of peroxides [5]. The content of organic peroxides was determined from the difference in the obtained data.

The furfural was oxidized by the following methods.

Experiment 1. To a mixture of water (30.3 ml) and hydrogen peroxide (14.7 ml, 0.192 mol) with weight fraction 38.5% we added of the distilled furfural (5.0 ml, 0.060 mol). The mixture was stirred at 60°C until the H₂O₂ and organic peroxides were completely transformed.

Experiments 2-4. The experiments were carried out by the same procedure as for expt. 1 except that the corresponding catalyst was first added to the reaction flask – V₂O₅ ($1.5 \cdot 10^{-4}$ mol) or Nb₂O₅ ($1.5 \cdot 10^{-3}$ mol), or Nb(OAc)₂ ($3 \cdot 10^{-3}$ mol).

Synthesis of 2(5H)-Furanone (3). A mixture of furfural (33.4 ml, 0.3 mol), Nb(OAc)₂·4H₂O (0.57 g, $1.5 \cdot 10^{-3}$ mol), water (133 ml), and an aqueous solution of H₂O₂ (30.7 ml, 0.3 mol) with weight fraction 38.5% was stirred at 60°C for 3.5 days until the peroxides were completely transformed. The product **3** was extracted with ether, washed with NaHCO₃ solution, dried with Na₂SO₄, and evaporated. The residue was distilled at reduced pressure, and 16.1 g (64%) of 2(5H)-furanone (**3**) was obtained; bp 90-93 °C (13 mm Hg), (bp 90-92 °C (12-13 mm Hg) [19]); n_D^{20} 1.4650 (n_D^{20} 1.4650 [19]). The ¹H NMR spectrum agreed with the previously obtained spectrum [19]. Found, %: C 57.14; H 4.79. C₄H₄O₂. Calculated, %: C 57.33; H 4.96.

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