REACTION OF FURAN COMPOUNDS WITH HYDROGEN PEROXIDE IN THE PRESENCE OF VANADIUM CATALYSTS

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The reactions of furan and a number of its derivatives (furfural, furan-2-carboxylic acid, 2-furfuryl alcohol, and others), in systems containing H_2O_2 and vanadium compounds, proceed through a mechanism of radical hydroxylation of the furan ring with the formation of 5-hydroxy-2(5H)-furanone and maleic acid. The total yield and ratio of the synthesized compounds depend on the reaction conditions.

The oxidation of furan oxo compounds by peroxide has been studied extensively in aqueous solutions of hydrogen peroxide without any added catalyst [1]. The main products of this reaction are 2(5H)-furanone, 2(3H)-furanone, succinic acid, and formic acid [1]. The acids that are formed play the role of autocatalysts of the oxidative and hydrolytic reactions that are taking place. The oxidation of furfural proceeds through a stage of formation of furan hydroxyperoxides [1] and 2-formyloxyfuran [3]. As a result of oxidative and hydrolytic conversions of 2-formyloxyfuran and 2(3H)-furanone, dibasic acids and γ-oxoacids are formed as byproducts: maleic, fumaric, β-formylacrylic, β-formylpropinic, and other acids. Experimental data indicate that this reaction proceeds mainly through a nonradical (ion—molecular) mechanism [1].

Certain reaction schemes include attack of the reagent through the diene system of the substrate. For example, a mechanism proposed in [4] for the reaction of furan with H_2O_2 in sulfuric acid medium postulates the formation of an intermediate ozonide. The process of furfural oxidation by H_2O_2 in the presence of acids has been described in [5] as a combination of reactions of radical hydroxylation of the ring and an ionic reaction of ring opening. These schemes, the same as the mechanism of radical hydroxylation of the furan ring that was given in [6], have not obtained any experimental support.

Thus far there have been no systematic studies of the peroxide oxidation of furan compounds in the presence of metal-containing catalysts. The reaction of furfural with H_2O_2 in the presence of $FeSO_4$, in the opinion of Cross et al. [7], leads to the formation of hydroxyfurfural and hydroxypyromucic acid; however, their structure was not subsequently confirmed. Proposed schemes for the hydroxylation of furfural [8] and furan [9] in the presence of H_2O_2 and OSO_4 were presented without any study of the mechanism.

The reaction of furfural with aqueous H_2O_2 in the presence of compounds of Group VI elements (Se, Mo, W), yielding mainly β-formylacrylic acid, proceeds through an ionic-molecular mechanism without any significant participation of hydroxyl radicals [10].

We have undertaken a study of furfural oxidation in the H_2O_2/V_2O_5 system [11]. The V_2O_5 was chosen because of the known high activity, high selectivity, low toxicity, and ready availability of vanadium catalysts in general [12]. This process goes forward with the formation of β-formylacrylic acid as the main product; however, under the accepted conditions (high concentration of H_2O_2 and large quantities of catalysts), the reaction is highly exothermic and difficult to control.

Here we are presenting new results from an investigation of this reaction for certain furan compounds (furan, furfural, 5-nitrofurfural, 5-bromofurfural, furan-2-carboxylic acid, and 2-furfuryl alcohol).

Oxidation of these substrates yields primarily 5-hydroxy-2(5H)-furanone (I), the cyclic form of β-formylacrylic acid (Table 1). Byproducts of the reaction are maleic acid (II), and also 2(5H)-furanone (IV), which was detected in all cases other than the oxidation of furan-2-carboxylic acid. In the oxidation of 5-nitro- and 5-bromofurfural, the main products are compounds II and III. The preferential formation of the acid III from 5-

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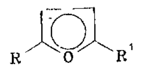
TABLE 1. Results from Reactions of Furans  with 10% H_2O_2 (T_{reac} 50°C, substrate:catalyst mole ratio 1:0.005)

Experiment	R	R^1	Catalyst	Substrate: H_2O_2 mole ratio	t, h*	Yield, %			
						I	II	III	IV
1**	H	H	V_2O_5	1:3,2	24	45	25	3	15
2	CH_2OH	H	V_2O_5	1:3,2	6,5	50	27	3	10
3	COOH	H	V_2O_5	1:3,2	8,0	50	22	6	—
4	CHO	H	V_2O_5	1:3,2	6,0	55	25	2	8
5	CHO	H	$FeSO_4$	1:3,5	7,0	42	30	—	4
6	CHO	H	SeO_2	1:3,0	8,0	50	25	5	8
7	CHO	NO_2	V_2O_5	1:3,2	8,0	10	60		15
8	CHO	Br	V_2O_5	1:3,2	12,0	10	Trace	40	15

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*Time for complete conversion of substrate.

**At 20°C.

TABLE 2. Influence of Catalyst and Added Inhibitors on Yield of Compound I in Reaction of Furfural with 10% H_2O_2 (T_{reac} 50°C, mole ratio H_2O_2:catalyst:inhibitor:furfural 3.2:0.005:0.005:1)

Catalyst	Inhibitor	t, h*	Yield, %	Catalyst	Inhibitor	t, h*	Yield, %
V_2O_5	—	6,0	55	$(NH_4)_2\cdot(dipy)_2\times H_2V_2O_{11}$	—	4,0	35
$VOSO_4$	—	6,0	55	Vanadium 2-hydroxy-naphthoate	—	3,5	65
VO	—	7,5	50	V_2O_5	Pyrocatechol	12,0	70
$VO(acac)_2$	—	6,0	64	V_2O_5	Hydroquinone	12,0	68
$VO(phen)_2$	—	6,0	60	V_2O_5	Pyrogallol	24	70
				V_2O_5	Naphthylamine	24	60

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*t is the time for complete conversion of furfural.

TABLE 3. Rate of Catalytic Oxidation of Furfural by 30% H_2O_2 as a Function of Type and Quantity of Inhibitor of Radical Chain Reactions (T_{reac} 50°C, mole ratio furfural:H_2O_2:V_2O_5 1:30:0.1)

Inhibitor	V_2O_5: inhibitor mole ratio	$W\cdot10^4$, moles·liter^{-1}·sec^{-1}	Inhibitor	V_2O_5: inhibitor, mole ratio	$W\cdot10^4$ moles·liter^{-1}·sec^{-1}*
—	—	1,11	Pyrogallol	1:1	0,76
Hydroquinone	1:1	0,40	β-naphthylamine	1:1	0,20
Hydroquinone	1:3	0,49			

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*Rate of furfural conversion.

bromofurfural can be explained by isomerization of the intermediate acid II under the influence of the bromide anion that has been split out [13].

In the oxidation of furfural, its 5-derivatives, and 2-furfuryl alcohol, formic acid is formed (80-95%); and in the oxidation of furan-2-carboxylic acid, CO_2 is evolved. In the oxidation of furan, neither formic acid nor CO_2 can be detected.

2(3H)-Furanone and succinic acid were not detected in any of the experiments.

The type of vanadium catalyst does not affect the direction of furfural oxidation, but it does influence the ratio of products and correspondingly the yield of compound I, which is higher in the presence of complexes of vanadium with acetylacetone, 1,10-phenanthroline, or 2-hydroxynaphthoic acid, in comparison with the product yield in the presence of V_2O_5 or $VOSO_4$ (Table 2).

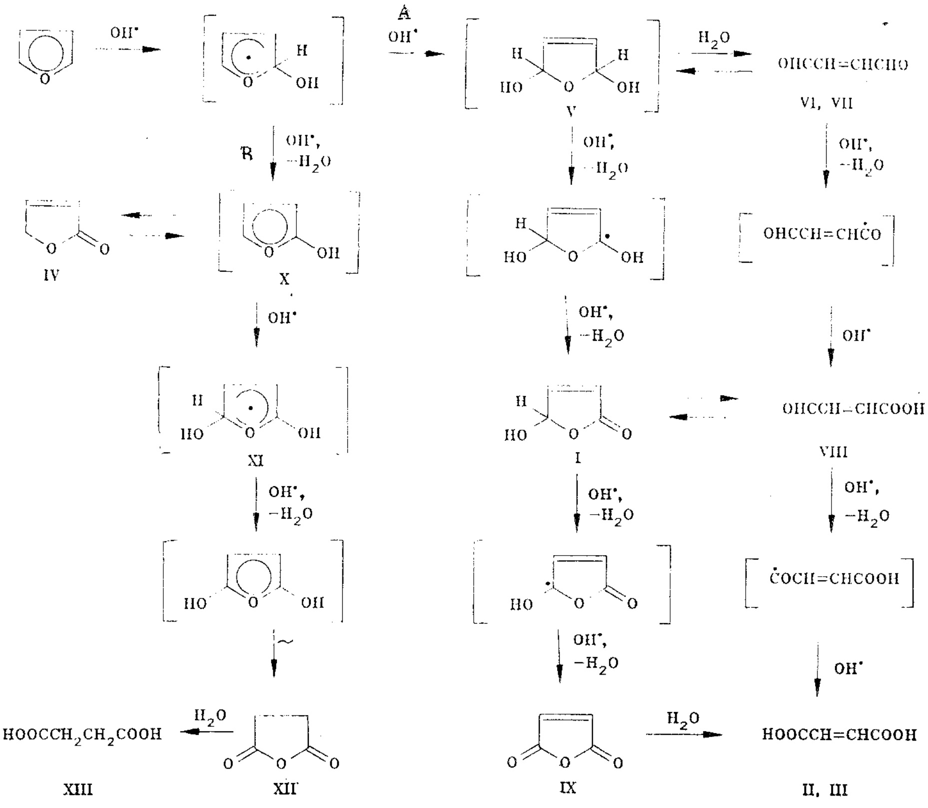
In the presence of polyhydric phenols that act as inhibitors of radical chain processes, when taken in equimolar quantity relative to the catalyst, the yield of compound I is increased by 13-15% (compare Tables 1 and 2). In the presence of β-naphthylamine, the yield of the hydroxyhydrofuranone I is slightly higher. At the same time, additions of these compounds give a severalfold reduction of the furfural conversion rate (Table 3). This indicates the possibility that at least some of the individual stages of the reaction proceed through a homolytic mechanism.

The oxidation of furfural in the presence of V_2O_5, SeO_2 (ionic-molecular process [14]), or $FeSO_4$ (radical process [15]) leads to the formation of exactly the same products. It is known that vanadium compounds can catalyze both homolytic and heterolytic reactions involving hydroperoxides [16]. In order to elucidate the mechanism of the chemical conversions of furfural in a system including H_2O_2 and a vanadium compound, it was necessary to bring in additional data.

It was established by means of ÉPR that a mixture of C-radicals is formed in the furfural/H_2O_2/H_2O/$VOSO_4$ system.

A competing-acceptor method was used to study the possibility of radical hydroxylation of furfural in the presence of H_2O_2 and $VOSO_4$. As a model trap for hydroxyl radicals we used ethanol. The rate constant of ethanol oxidation in the experiments with $VOSO_4$ was found to be on the same order of magnitude as in the presence of $FeSO_4$, which is a known generator of hydroxyl radicals from H_2O_2.* This is evidence of active formation of hydroxyl radicals in the H_2O_2/$VOSO_4$ system. Next, in experiments using 2-propanol (reference acceptor) and furfural as competing acceptors of hydroxyl radicals, high reactivity was demonstrated for the furan substrate with respect to the indicated radicals obtained in the H_2O_2/$VOSO_4$ system.

On the basis of these results, we believe that the formation of the products I and II goes through a stage of interaction of the furan ring with OH· radicals that are formed in the H_2O_2/vanadium catalyst system. Interaction of the furan ring with the OH· radical was postulated in [15, 17] for the H_2O_2/$FeSO_4$ system.



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*These studies were performed at the L. V. Pisarzhevskii Institute of Physical Chemistry, Ukrainian Academy of Sciences, in cooperation with N. A. Vysotskaya, Doctor of Chemical Sciences.

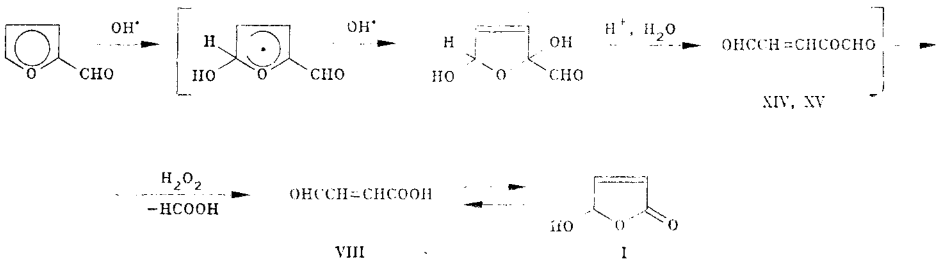
We have investigated the reaction mechanism in catalytic hydroxylation of furan in the presence of H_2O_2 and $VOSO_4$. Radical hydroxylation of furan is theoretically possible along the directions A and B as indicated in the following scheme. Direction A consists of a set of consecutive reactions of addition of OH· radicals to the furan ring through an A_R mechanism, leading to the formation of the dihydrofuran structure V. Direction B is made up of reactions of replacement of hydrogen atoms in ring position 2 (or 2 and 5) by OH· radicals through an S_R mechanism.

We have isolated and characterized intermediate products of this reaction in the form of 2,4-dinitrophenylhydrazones of the dialdehydes of maleic (VI) and fumaric (VII) acids. This fact indicates that the reaction proceeds mainly through a stage of formation of the diacetal V, i.e., along direction A. 5-Hydroxy-2(5H)-furanone (I) may be formed by hydroxylation of compound V and also by oxidation of the dialdehydes VI and VII. The latter path is obviously preferred, since the diacetal V is readily hydrolyzed under the reaction conditions to form the more stable products VI and VII. The formation of maleic acid (II) from the acyclic form of β-formylacrylic acid (VIII) is more probable than its formation from the lactone I, since maleic anhydride (IX), the formation of which would be extremely probable in the latter case, has not been detected in the reaction mixture.

The formation of a small quantity of the lactone IV in the catalytic oxidation of furan indicates that direction B is also possible. Formation of the adduct XI from compound X is improbable, since compound IV in the H_2O_2/H_2O/vanadium catalyst system is not oxidized, and succinic anhydride XII and succinic acid XIII are not formed in this reaction.

The lactone IV is also formed in the uncatalyzed reaction of furan with H_2O_2, so that we cannot eliminate the possibility of partial oxidation of the substrate to compound IV in the presence of vanadium ions through a nonradical mechanism.

It was noted above that in the oxidation of furfural in the H_2O_2/vanadium catalyst system, formic acid is formed in almost quantitative yield, while neither furan-2-carboxylic acid nor CO_2 could be detected. The same as in the reaction of furan with H_2O_2, in this case also we found intermediate dicarbonyl compounds in the form of their 2,4-dinitrophenylhydrazones, with values of R_f that are similar to those for the dialdehydes VI and VII. We believe that the basic relationships in the reaction mechanism for the furan/H_2O_2/vanadium catalyst system remain the same in the oxidation of furfural.



According to the above scheme, the process of forming hydroxyhydrofuranone I from furfural proceeds through a stage of intermediate dialdehydes XIV and XV, structurally analogous to the dialdehydes VI and VII.

It was also established chromatographically that the oxidation of 2-furfuryl alcohol in the H_2O_2/vanadium catalyst system results in the formation of the dialdehydes VI and VII and also other carbonyl-containing compounds with structures that have not been established. These data are consistent with the conclusions drawn in [15, 17] regarding the special behavior of 2-furfuryl alcohol in the reaction of radical hydroxylation.

In the catalytic hydroxylation of furan-2-carboxylic acid, CO_2 is formed; and in the mixture of 2,4-dinitrophenylhydrazones in the products of its oxidation, an unknown hydrazone has been detected. We believe that furan-2-carboxylic acid in the H_2O_2/vanadium catalyst system is oxidized through a mechanism similar to that in the hydroxylation of furfural.

Our proposed reaction schemes explain the inhibiting effect of polyhydric phenols on the process of catalytic hydroxylation of furfural. On the other hand, the presence of these inhibitors does not change the yield of compound IV, while the ratio I:II is increased. This suggests that the polyhydric phenols also inhibit the stage of oxidation of β-formylacrylic acid (VIII). Also, we do not exclude the possibility that the product I is bound into a complex with the polyhydric phenol, resulting in a decrease in the content of the acyclic form VII and hence the content of the acid III. The polyhydric phenols may also tend to increase the yield of compound I by retarding the formation of tars from the reaction components.

EXPERIMENTAL

The course of the reaction was monitored by UV spectroscopy in a Specord Vis instrument and by TLU on Silufol plate (chromatographic system chloroform; 3:1 chloroform/acetone; 2:1 acetone/chloroform; developers — acidified aqueous solutions of $KMnO_4$ and 2,4-dinitrophenylhydrazine, caustic solution of Bromphenol Blue, iodine vapor) and was evaporated at reduced pressure.* The mixture of oxidation products was separated in a column with silica gel, using chloroform as the eluent. The 5-hydroxy-2(5H)-furanone that was isolated from the chromatographic fractions and recrystallized from chloroform and hexane melted at 56-57°C (mp 57-58°C according to [18], 55°C according to [19]); R_f 0.47 (in 3:1 chloroform/acetone system). PMR spectrum, δ, ppm (in $CDCl_3$): 5.44 bs (1H, OH); 6.20 dd (1H, 3-H, J = 1.2 Hz); 6.24 dd (1H, 5-H; J = 1.2 Hz); 7.32 dd (1H, 4-H; J = 6.0, J = 1.2 Hz). IR spectrum, ν, cm^{-1} (in $CDCl_3$): 3350, 1780, 1750, 1620. Mass spectrum, m/z (intensities relative to maximum peak, %): 43 (8.1), 44 (10.0), 45 (18.6), 46 (4.3), 53 (10.5), 54 (37.1), 55 (100.0), 56 (22.9), 71 (13.3), 82 (5.7), 83 (5.2), 99 (7.6), 100 (M^+, 7.1).

Formic acid was determined quantitatively by GLC in a Tsvet-4.67 instrument with a katharometer detector, solid phase a mixture of 20% bis(ethylhexyl) sebacate and 5% sebacic acid supported on Celite 545, 30-50 μm. The chromatographic conditions were as follows: $t_c = 130°C$, $t_i = 180°C$, I = 100 A, r = 1, V_l = 720 mm/h, carrier gas hydrogen, R = 120 ml/min.

Catalytic Oxidation of Furans. The furan substrate, catalyst (mole ratio 1:0.005, and 10% H_2O_2 (3.3-3.5 moles per mole of substrate) were stirred at 50°C (in the case of furan itself, at 20°C) until the furan compound was completely converted. The inhibitors were introduced into the reaction mixture at a concentration of 0.005 mole per mole of substrate.

2,4-Dinitrophenylhydrazones of Intermediate Oxidation Products. To samples of the oxidized products, a solution of 2,4-dinitrophenylhydrazine in HCl was added. After 15 min, the precipitate was filtered off, washed with ice water and alcohol, dried, and deposited on plates in the form of a solution in ethyl acetate. The plates were chromatographed in systems consisting of chloroform and petroleum ether (3:1) and ethyl acetate and benzene (1:5). The hydrazones were identified on the basis of the color of the spots, the values of R_f of the product and the reference spot, and the values of the ratio of R_f of furfural to R_f of the product and reference spots. These results were compared with the data of [20].

The rate constants for the reaction of the OH· radicals (generated in the H_2O_2/vanadium catalyst system) with furfural were determined in accordance with [21-23]. As radical traps we used thymine and 2-propanol. The reaction was performed at pH 2; the substrate consumption was followed by means of UV spectroscopy in a Specord -vis instrument.

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