CATALYTIC OXIDATION OF FURAN AND HYDROFURAN COMPOUNDS.

2.* OXIDATION OF FURFURAL IN THE HYDROGEN PEROXIDE–VANADYL SULFATE–SODIUM ACETATE SYSTEM

V. V. Poskonin and L. A. Badovskaya

The characteristics of the oxidation of furfural in the hydrogen peroxide–$VOSO_4$–*sodium acetate system and the composition of the products were studied. The principal stages of the reaction occur at pH ~7. The direction of the reaction is very different from the process in an acidic medium, where β-formylacrylic and maleic acids are mainly formed. The main oxidation products in the acetate buffer solution in the presence of $VOSO_4$ are succinic and β-formylpropionic acids and 2(5H)-furanone; without the catalyst the main product is 2-furancarboxylic acid. A mechanism is proposed for the transformations of furfural in the investigated system.*

Earlier we presented the results from a study of the oxidation of furfural by hydrogen peroxide in the presence of compounds of $V^{IV,V}$ [2-4]. This reaction took place in an acidic medium at pH 4.0-5.5 at the beginning of the process and 1.0-1.5 or lower after the furfural had been completely consumed. Under the indicated conditions catalysis both by the vanadium ions and by the acids occurred. The main product here was 5-hydroxy-2(5H)-furanone (I) — the cyclic tautomer of cis-β-formylacrylic acid (II) [3, 5] (Scheme 1).

In addition, it was established [6-9] that additions of bases lead to a change in the direction of oxidation of furfural. Thus, at pH < 7, 2(5H)-furanone (II) and succinic acid (IV) were mainly obtained as a result of the reaction with hydrogen peroxide (without the vanadium catalyst), whereas in the presence of tertiary amines the main product was 2-furancarboxylic acid (V) (Scheme 1). The oxidation of furfural in the presence of the vanadium compounds and inorganic bases led to the formation mainly of 2-hydroxy-5-oxotetrahydrofuran-2-carboxylic acids (VI) [7].

Scheme 1

X, Y = OH, Cl
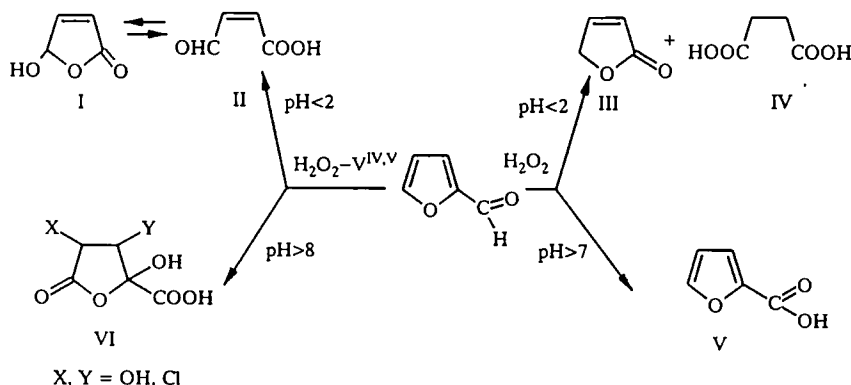
*For Communication 1, see [1].

TABLE 1. Results of the Oxidation of Furfural by Hydrogen Peroxide, Depending on the Presence or Absence of Sodium Acetate and the Vanadium Catalyst (60°C, furfural—hydrogen peroxide molar ratio 1:3.2)

| $VOSO_4$*	Sodium acetate*	Half-conversion time, h	Reaction time, days	Products (yield, %)							
				I + II	III	IV	V	VI	VII	XII	XIII
0,05	2,5	4,0	1	5	9	35	6	4	8	13	4
—	2,5	4,4	8	—	4	10	60	†	—	11	1
0,005	—	0,7	0,25	45	8	11	—	—	2	10	2
0,05 ‡	2,5	2,7	0,6	16	1	20	12	4	3	9	1

*Moles per mole of furfural.
†Traces.
‡2-Furancarboxylic acid (V) was used instead of furfural.

It is seen from Scheme 1 that the reaction of furfural with hydrogen peroxide both with and without the vanadium catalyst takes place with elimination of the carbonyl group (in the form of formic acid) and the formation of products containing four carbon atoms. In basic media it takes place without cleavage of the C—C bond between the furan ring and the substituent, leading preferentially to acids with five carbon atoms. These data demonstrate the important role of the acidity (basicity) of the medium as a factor determining the direction of oxidation.

In a continuation of research into features of the peroxide oxidation of furfural in various ranges of pH and also to discover new synthetic possibilities for the process we studied the transformations of the compound in the H_2O_2—$VOSO_4$ system while regulating the pH of the reaction medium with sodium acetate. (The conditions and the results of the experiments are given in Table 1.) Here almost complete transformation of the furfural was achieved. The process continued until all the hydrogen peroxide had been used (monitored by GLC and TLC). The yields of the products were determined by GLC and polarography and also by preparative methods. For quantitative analysis of the mixtures of products we used PMR, GLC, and IR spectroscopy.

A scheme of the transformations of furfural was formulated on the basis of the obtained data (Scheme 2). This is discussed further in parallel with the experimental results.
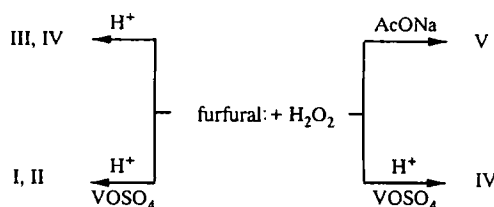

Scheme 2
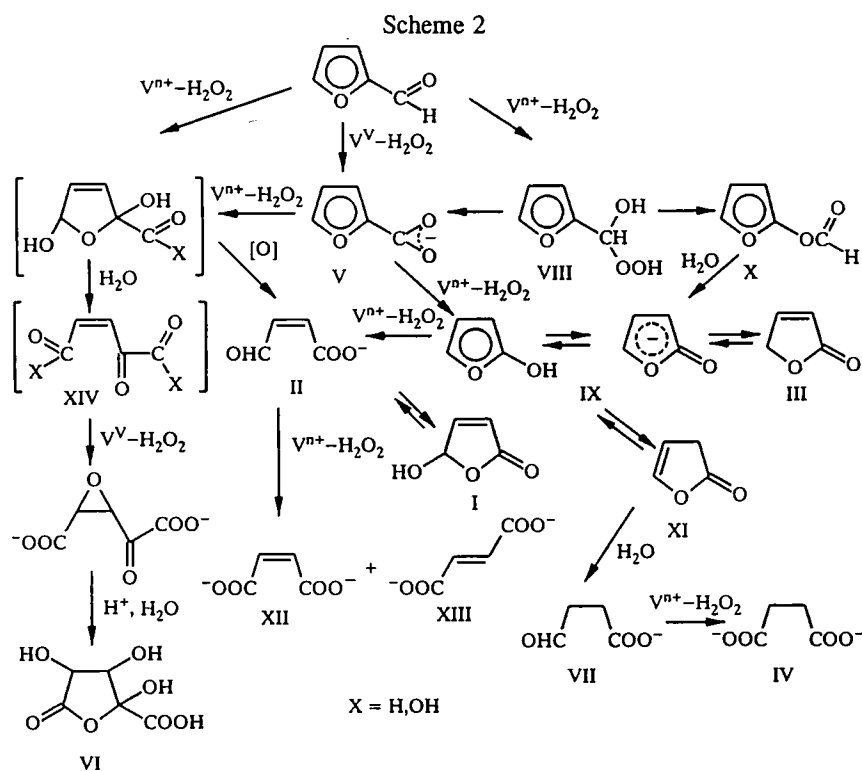
In the presence of 2.5 moles of sodium acetate to one mole of furfural, the main transformation of the latter (by 75-80%) occurred at a pH value close to 7 (not lower than 6.5). Only at the end of the reaction did it decrease somewhat (to ~5.5) as a result of the accumulation of relatively strong acids (maleic, malonic, and oxalic). Thus, the mixture of sodium acetate and the acidic products probably has sufficient buffer capacity to continue the reaction in a medium close to neutral. With successive decrease in the amount of acetate the pH of the reaction medium decreased more rapidly to 2 and lower, i.e., the reaction took place mainly in an acidic medium.

It is seen from the results presented in Table 1 that sodium acetate retards the oxidation of furfural, and most noticeably in the presence of the vanadium catalyst. Without the $VOSO_4$ the half-conversion time ($\tau_{1/2}$) of furfural with the addition of sodium acetate is increased by only 5%, whereas in the presence of 0.05-0.005 mole of this catalyst per mole of furfural it is increased by 5.7-6.3 times. In view of the $\tau_{1/2}$ values of furfural, determined for the acetate oxidates with and without the addition of $VOSO_4$, it can be said that the vanadium catalyst catalyzes oxidation in the same way at pH ~7 as in the acidic medium, but not to such a significant degree. This agrees with data in [10] on the decrease in the catalytic activity of vanadium ions during the decomposition of hydrogen peroxide by a chain and oxidation−reduction mechanism in a medium close to neutral.

Another factor that retards the oxidation of furfural in the presence of sodium acetate is the deficiency of protons, which as mentioned catalyze a series of key stages in the process. Moreover, the increase in the ionic strength of the solution on account of the introduction of a fairly large amount of acetate is also clearly one of the reasons for the observed retardation.

Unlike the $\tau_{1/2}$ values, the total duration of the reaction of furfural with hydrogen peroxide, which corresponds to the time for the complete transformation of both reagents, at pH ~7 depends to a much greater degree on the addition of the catalyst — the introduction of 5 mole % of $VOSO_4$ leads to an eightfold reduction in the reaction time. This may be due to the high catalytic activity of the vanadium ions at the stages involving oxidation of the carboxylic acids that form and their ionized forms [11, 12].

The presented data indicate that the oxidation of furfural changes in nature with increase in the pH values from 1.0-1.5 to 6.5-7.0, and this leads to the most important result of the process at pH ~7 — a change in its direction both with and without the presence of $VOSO_4$. In the absence of the vanadium ions the main product from the oxidation of furfural in an acetate solution, as in an amine medium, is 2-furancarboxylic acid (V) (yield 60%). In the acidic medium, as mentioned, 2(5H)-furanone (III) and succinic acid (IV) are mostly formed with yields of 40 and 20%, respectively [8]. In the presence of $VOSO_4$ the composition of the products changes substantially. Whereas the main product in the acidic medium is β-formylacrylic acid (I + II) (yield 45%), the main product at pH ~7 is succinic acid (IV) (yield 35%). The foregoing can be illustrated by the following scheme:

$$
\begin{array}{ccccc}
\text{III, IV} & \xleftarrow{\ H^+\ } & & \xrightarrow{\ AcONa\ } & \text{V} \\
 & & \text{furfural} + H_2O_2 & & \\
\text{I, II} & \xleftarrow[\ VOSO_4\ ]{\ H^+\ } & & \xrightarrow[\ VOSO_4\ ]{\ H^+\ } & \text{IV}
\end{array}
$$

It is noticeable that the yields of the furanone (III) and β-formylpropionic acid (VII), which is an intermediate product in the formation of the acid (V), are increased appreciably in the presence of $VOSO_4$. It was established [8, 13] that, in the absence of the acetate, the products (III, IV, VII) are formed as a result of a Baeyer−Villiger rearrangement of the key intermediate — furfural hydroxyhydroperoxide (VIII). Its formation in the course of the oxidation of furfural in a medium close to neutral was detected by TLC. We suppose that the reaction under discussion at pH ~7 also takes place through the intermediate (VIII). However, with decrease in the acidity of the medium the direction of its rearrangement changes from preferential migration not of the furyl group but of a hydride ion, leading to the acid (V) (Scheme 2).

In the absence of the vanadium ions the oxidizing ability of the system is probably insufficient for further transformation of the acid (V). At the same time in the presence of $VOSO_4$ it is oxidized approximately 1.5 times more quickly than furfural (Table 1), while the qualitative composition of the products remains the same as before, including compounds (III, IV, VII) (total yield 24%). The acid (V) is oxidized by the $V^{(V)}$ ions by a mechanism of oxidative decarboxylation [11, 12], presumably including synchronous attack on the furyl substituent by the hydrogen peroxide or its activated form. The product of such a transformation is 2-hydroxyfuran (IX), formed in the acidic medium according to the path peroxide (VIII)

→ 2-formyloxyfuran (X) → product (IX). Compound (IX) soon changes into the more stable tautomeric lactone forms (III) and (XI), the last of which leads to compounds (VII) and (IV).

Thus, it is clear that at pH ~7 the furfural is converted into the products (III, IV, VII) not only by the normal mechanism for an acidic medium [through the intermediate product (IX)] but also through the acid (V). We explain the preferential formation of the acid (IV) during the oxidation of furfural and the product (V) in the acetate medium in the following way. Whereas the 2(5H)-furanone (III) is fairly stable at pH ~7 in the absence of $VOSO_4$, with the introduction of vanadium ions it is easily oxidized, forming compounds (VII) and (IV). Under the conditions of the oxidation of furfural the degree of transformation of the lactone (III) in 24 h amounts to 92% [78% of the acid (IV) and 2-3% of the acid (VII) are formed]. It can be supposed that the vanadium ions lead to ready oxidation of the carbonyl group of the product (VII) with the formation of compound (IV). As a result the dynamic equilibrium that exists between the tautomers (III, IX, XI) is displaced toward the latter, leading to rapid decomposition of the lactone (III).

In view of the partial polymerization of styrene in the hydrogen peroxide$-VOSO_4-$sodium acetate system the content of β-formylacrylic (I + II), maleic (XII), and fumaric (XIII) acids in the products from oxidation of the furanone (III) (0.5, 9, and 1% respectively) indicates the formation of free radicals capable of reacting with the furan ring [14] and makes it possible to speak of hydroxylation of the intermediate 2-hydroxyfuran (IX) at pH ~7. However, in contrast to the acidic medium, the process does not predominate, and this may be due to decrease in the rate of homolytic decomposition of the hydrogen peroxide in the presence of the vanadium ions at high pH values [10].

Apart from the indicated products 5-oxo-2-hydroxytetrahydro-2-furancarboxylic acids (VI), which we obtained during the oxidation of furfural in the presence of certain bases, were found in the investigated reaction [7]. The formation of compounds (VI) in the acetate buffer solution indicates that even at pH ~7 the reaction begins to develop along a path involving nucleophilic epoxidation of the intermediates (XIV), which contain an electron-deficient C=C bond, by the perhydroxyl anion activated by the V^V ions.

X = H, O⁻
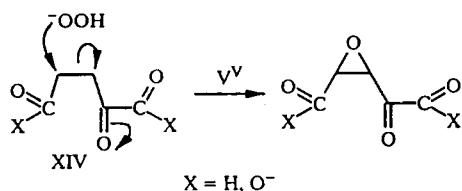
Under the conditions of the investigated reaction the yield of the acids (VI) amounts to only 4%. However, the contribution from this path increases with increase in the basicity of the medium [7].

Thus, the introduction of sodium acetate into the furfural$-$hydrogen peroxide$-VOSO_4$ system makes it possible to change the direction of the process compared with oxidation both in an acidic medium and at pH ~7 in the absence of the vanadium catalyst. Whereas its course at pH 1.0-1.5 is determined by the high hydroxylating activity of the hydrogen peroxide$-V^{IV,V}$ system and the catalytic action of the acids that form, in the presence of sodium acetate under conditions with a proton deficiency the main direction of the process involves the formation of the peroxide (VIII) and the acid (V) and their transformation into the products (III, IV, VII). The action of the vanadium ions on the system at pH ~7 is clearly due to their display of Lewis acidity, which partly compensates for the proton deficiency, and also to their high oxidation potential, which promotes ready oxidation of the products (III, V, VII). In addition, in a medium close to neutral the nucleophilicity of the oxidant is increased, and this enables the epoxidation of the electron-deficient C=C bonds of the intermediate products (XIV). The obtained data supplement theories about the features and mechanism of the peroxide oxidation of furfural in various ranges of pH and confirm the significance of the acidity (basicity) as one of the factors determining the direction of the process.

EXPERIMENTAL

The IR spectra were recorded in Vaseline oil on a UR-20 spectrometer. The PMR spectra were recorded on a Tesla BS-467A instrument at 60 MHz for solutions in acetone-d_6, deuterochloroform, methylene-d_2 chloride, and deuterotrifluoroacetic acid with HMDS and tert-butyl alcohol as internal standards.

Thin-layer chromatography of the reaction mixtures was conducted on Silufol UV-254 plates in the following systems: Chloroform; 3:1 chloroform$-$acetone; 2:1 acetone$-$chloroform; 20:3 toluene$-$ethanol. The chromatograms were developed

with acidified solutions of potassium permanganate and 2,4-dinitrophenylhydrazine, an alcohol solution of bromophenol blue, and iodine vapor. The peroxide (VIII) (a marker for TLC) was obtained by the method described in [15].

Gas-liquid chromatography of the reaction mixture was carried out on a Chrom-4 instrument with a flame-ionization detector and a glass column (300 × 0.3 cm). The carrier gas was nitrogen, and the flow rate was 30 ml/min. The furfural, 2(5H)-furanone (III), and the carboxylic acids that form as esters were determined quantitatively on polymethylphenylsiloxane oil (PMFS-4) deposited at the rate of 15% on Chromaton N-AW DMCS; column temperature 150°C, evaporator temperature 220°C, detector temperature 220°C.

The yields of the acids (I + II) and (XII) were determined by polarography [8]. The analyses were performed on an LP-70 instrument in a thermostated cell with a dropping mercury electrode (m = 1.59 mg/sec, t_1 = 3.66 sec, at −1.0 V) at 25 ± 0.2°C; the reference electrode was a normal calomel electrode. The supporting electrolytes were 0.1 N solutions of perchloric acid and a phosphate buffer mixture (pH 7.4).

Procedure for the Oxidation of Furfural. To a mixture of 0.815 g (0.005 mole) of $VOSO_4$ and 20.5 g (0.25 mole) of sodium acetate we added 8.3 ml (0.1 mole) of furfural and 75 ml (0.32 mole) of 12% hydrogen peroxide solution. The reaction mixture was stirred at 60°C until the peroxide had completely decomposed.

Similar procedures were used in the absence of the catalyst and sodium acetate and also when the furfural was replaced by the acid (V).

REFERENCES

1.   V. V. Poskonin, L. V. Povarova, and L. A. Badovskaya, Khim. Geterotsikl. Soedin., No. 5, 633 (1996).
2.   V. V. Poskonin and L. A. Badovskaya, Khim. Geterotsikl. Soedin., No. 11, 1462 (1991).
3.   V. V. Poskonin, L. A. Badovskaya, S. P. Gavrilova, and V. G. Kul'nevich, Zh. Org. Khim., 25, 1701 (1989).
4.   V. V. Poskonin and L. A. Badovskaya, Chemistry and Technology of Furan Compounds [in Russian], Izd. Krasnodar. Politekhn. In-ta., Krasnodar (1987), p. 38.
5.   V. V. Poskonin and L. A. Vadovskaya, Russian Patent No. 1,715,806; Byull. Izobret., No. 4 (1992).
6.   V. V. Poskonin, Thesis for Candidate of Chemical Sciences [in Russian], Krasnodar (1990).
7.   V. V. Poskonin and L. A. Badovskaya, Zh. Org. Khim., 30, 1001 (1994).
8.   L. A. Badovskaya, Thesis for Doctor of Chemical Sciences [in Russian], Krasnodar (1982).
9.   H. Baba, Reports Scient. Res. Inst., 33, 168 (1957).
10. G. A. Bogdanov, G. K. Yurchenko, V. I. Frolov, and N. A. Vorob'eva, Zh. Fiz. Khim., 49, 1873 (1975).
11. P. Bonchev, Complexation and Catalytic Activity [Russian translation], Mir, Moscow (1975).
12. Yu. A. Serguchev and I. P. Beletskaya, Usp. Khim., 49, 2257 (1980).
13. V. V. Poskonin and L. A. Badovskaya, Organic Peroxides and Homolytic Reactions with Their Participation [in Russian], Izd. Volgograd. Politekhn. In-ta., Volgograd (1989), p. 19.
14. T. Shiga and A. Isomoto, J. Phys. Chem., 73, 1139 (1969).
15. L. A. Badovskaya, G. D. Krapivin, T. Ya. Kaklyugina, V. G. Kul'nevich, and G. F. Muzychenko, Zh. Org. Khim., 11, 2446 (1975).