CATALYTIC OXIDATION OF FURAN AND HYDROFURAN COMPOUNDS.

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

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The characteristics of the oxidation of furfural in the hydrogen peroxide–VOSO₄–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 VOSO₄ 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 VIV,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

*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)

<table>
<thead>
<tr>
<th>voso₄</th>
<th>Sodium acetate*</th>
<th>Half-conversion time, h</th>
<th>Reaction time, days</th>
<th>Products (yield, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>2.5</td>
<td>4.0</td>
<td>1</td>
<td>5 9 35 6 4 8 13 4</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>4.4</td>
<td>8</td>
<td>4 10 60 †</td>
</tr>
<tr>
<td>0.005</td>
<td>—</td>
<td>0.7</td>
<td>0.25</td>
<td>45 8 11 —</td>
</tr>
<tr>
<td>0.05†</td>
<td>2.5</td>
<td>2.7</td>
<td>0.6</td>
<td>16 1 20 12 4 3 9 1</td>
</tr>
</tbody>
</table>

*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 H₂O₂—VOSO₄ 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.