

ROLE OF WATER IN THE OXIDATION OF
FURFURAL WITH HYDROGEN PEROXIDE

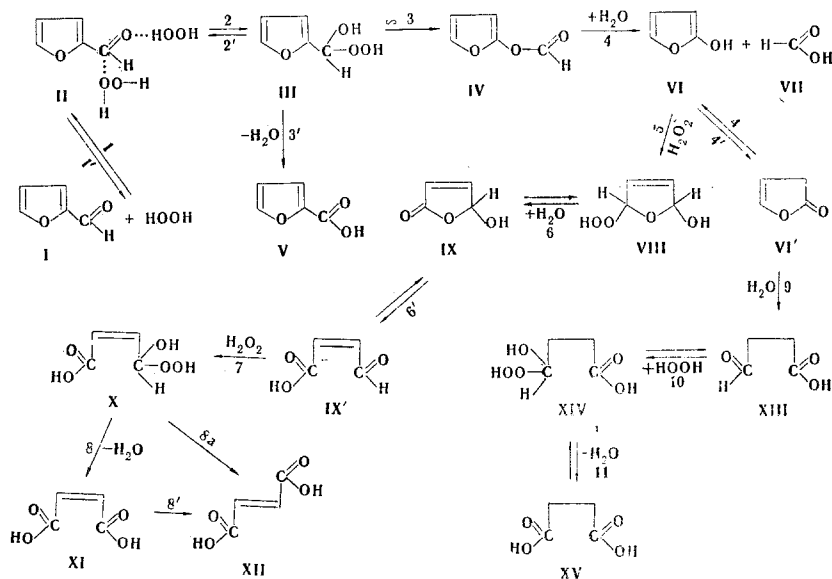
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The oxidation of furfural with hydrogen peroxide in water and in absolute ether containing small amounts of water was studied. It was found that water inhibits the formation of furfuryl hydroxyhydroperoxide but promotes the buildup of acids. The accumulated acids play a catalytic role in all stages of the process.

In conformity with the previously proposed mechanism for the oxidation of furfural with hydrogen peroxide [1] (see the scheme below), the water present in the reaction mixture may have a substantial effect on all of the stages of the process.

To ascertain the effect of water on the conversion of furfural, we oxidized it with hydrogen peroxide in water and in ether containing added water. It is apparent from a comparison of the reaction rates (Table 1 and Fig. 1) that an induction period of 60 min is observed in the oxidation of furfural in water. The reaction then proceeds vigorously ($k_1 < k_2$). In experiments with a small percentage of water present (oxidation in ether containing 0.83, 1.39, and 3.64% water), there is no induction period, and the reaction is retarded ($k_1 > k_2$) and approaches an equilibrium. We ascribed the difference in the reaction rates to the different conditions of the formation of the furfural-H₂O₂ complex (see II in the scheme below), which is then converted to furfuryl hydroxyhydroperoxide (III). The stability of the peroxide also depends on the medium. In the case of excess water, the carbonyl group of furfural is blocked by water molecules and, as it were, competition develops for the formation of hydrogen bonds with the carbonyl group among the water and H₂O₂ molecules. We assume that the furfural-H₂O complex should prevail under the conditions of excess



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TABLE 1

Solvent	$k \cdot 10^{-4}, \text{min}^{-1}$	
	k_1	k_2
Water	0,00	13,00
Ether contain. 0,83% H ₂ O	21,40	10,50
Ether contain. 1,39% H ₂ O	34,60	7,00
Ether contain. 3,64% H ₂ O	59,80	7,80

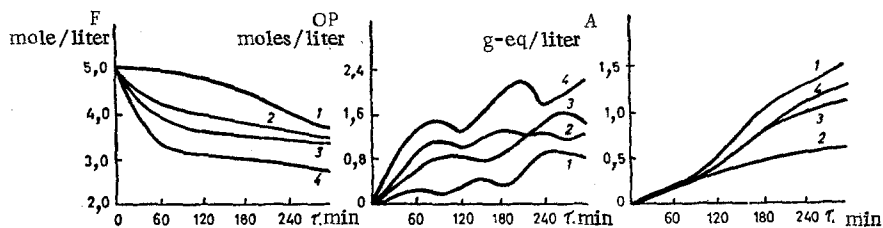


Fig. 1

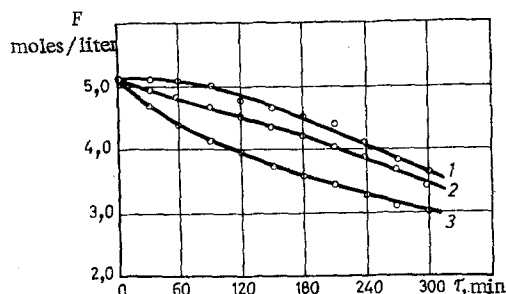


Fig. 2

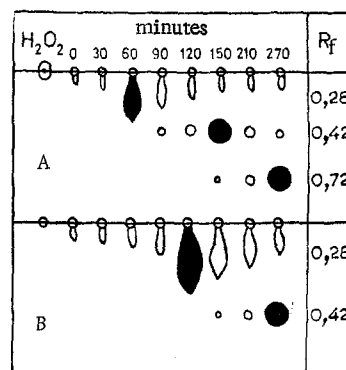


Fig. 3

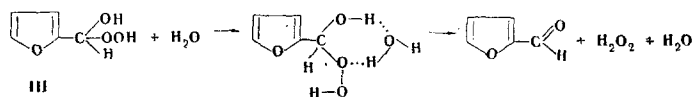
Fig. 1. Furfural consumption (F) and organic peroxide (OP) and acid (A) buildup in the oxidation of furfural with 50% hydrogen peroxide ($F:H_2O_2 = 1:2.2$, $22 \pm 0.5^\circ\text{C}$): 1) in water; 2-4) in ether containing water: 2) 0.83%; 3) 1.39%; 4) 3.64%.

Fig. 2. Kinetic curves of furfural consumption during oxidation with 50% H_2O_2 in ether containing 0.83% H_2O ($F:H_2O_2 = 1:2.2$, $22 \pm 0.5^\circ\text{C}$). The experimental points were found by spectrophotometry during dilution of a sample of the oxidate: 1) with water; 2) with ethanol; 3) with dioxane.

Fig. 3. Thin-layer chromatogram of peroxides formed in the oxidation of furfural with 50% H_2O_2 ($F:H_2O_2 = 1:2.2$, $22 \pm 0.5^\circ\text{C}$): A) in water; B) in ether containing 0.83% H_2O .

water. This hinders the approach of H_2O_2 to the furfural molecule and the formation of III; in the absence of water, the intermediate polar furfural- H_2O_2 complex (II) prevails.

In addition, reverse reaction 1', involving the conversion of III to furfural, is facilitated in the presence of water:



Reaction 3 is accelerated when a sufficiently high concentration of III is reached. The above reasoning is confirmed by a comparison of the kinetic curves of furfural consumption, which were obtained by recording the UV spectra of samples of the oxidate in various solvents. We set out to establish whether the solvent

used for dilution affects the spectrophotometrically determined furfural content. For this, in the oxidation of furfural with H_2O_2 in ether containing 0.83% H_2O , three samples of equal volume were selected from the oxidate after 30 min and subjected to spectrophotometry in three solvents - water, ethanol, and dioxane. It was found that the furfural content differs and is a maximum when the samples are dissolved in water as compared with dissolving them in ethanol and - especially - dioxane (Fig. 2), since water decomposes the furfuryl hydroxyhydroperoxide (III) that is formed in the course of the reaction and shifts the equilibrium to favor the starting furfural (reaction 1'). The aprotic dioxane is incapable of polarizing the -O-O- bond in peroxide III, and the rate of reverse reaction 1' is therefore insignificant in it. Thus the furfural content determined in the spectrophotometry of samples of the oxidate dissolved in dioxane is close to the true value, but the value obtained in water is too high.

The results and the reasoning presented above are in agreement with the kinetics of peroxide and acid buildup (Fig. 1) in the oxidation of furfural in various solvents. The maximum amount of III is formed in the oxidation of furfural in media with a small percentage of water, in which the peroxide and acid buildup proceeds through complex II sufficiently intensively, and the hydrolyzing action of water is minimal (Fig. 1). The thin-layer chromatogram of the intermediate peroxides in the oxidation of furfural in water and in ether containing 0.83% H_2O confirms the kinetic studies (Fig. 3). In the oxidation of furfural in water, the buildup of III (R_f 0.28) in the course of 60 min prevails over its decomposition. Decomposition proceeds primarily via reaction 1' to furfural. This is attested to by the insignificant percentage of products of its subsequent transformations (IV-VII) (Fig. 1). Peroxide III buildup reaches a maximum after 60 min, and its conversion via reaction 3 becomes appreciable. Transformations 3-9 proceed rather intensively, as confirmed by the buildup of peroxides VIII (R_f 0.42), X, and XIV (R_f 0.72), and acids VII, IX', XI, XII, and XV (Fig. 1, curve 3). In the oxidation of furfural in ether containing 0.83% H_2O , the conversion of peroxide III (R_f 0.28) via reactions 1' and 3 is retarded as compared with its oxidation in water.

It is apparent that water inhibits the formation of peroxide III from furfural but accelerates its conversion via reactions 3-9 by promoting acid buildup. The maximum amounts of acids are formed in the oxidation of furfural in water (Fig. 1). The accumulated acids begin to play a catalytic role in all stages of the process. This explains the fact that in the oxidation of furfural in water, after the induction period is surmounted, the process takes place more intensively than in the oxidation with an insignificant percentage of H_2O ($k_2 > k_1$ in water).

EXPERIMENTAL

A 1-mole (82 ml) sample of vacuum furfural (d^{25} 1.1562, n^{25} 1.5235) was introduced into a three-necked flask equipped with two reflux condensers and a stirrer and situated in a thermostat (22°). A solution of 2.2 moles (113 ml) of 50% H_2O_2 in water or an appropriate solvent was then added with vigorous stirring. The reaction was carried out for 5 h until 50-60% of the furfural had been consumed. Samples were taken after 30 min. The furfural content was determined by spectrophotometry [3] in the UV region with an SF-4 spectrometer, while the hydrogen peroxide and organic peroxides were determined by cerimetric and iodometric titration [4]; the acids were determined by titration with 0.1 N KOH. To establish the nature of the organic peroxides, samples of the oxidate were chromatographed in a thin layer of silical gel/gypsum with elution with ethanol-toluene (3:20). The developer was starch-saturated KI solution-glacial acetic acid (5:2:3). The nature of the peroxides was established by means of additional development of the chromatograms with 2,4-dinitrophenylhydrazine; this reagent is characteristic only for hydroxyhydroperoxides [5].

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