

Kinetics and Mechanism of the Furan Peroxide Formation in the Reaction of Furfural with Hydrogen Peroxide in the Presence or Absence of Sodium Molybdate*

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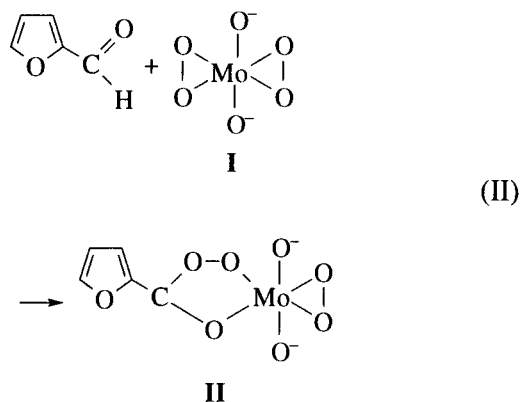
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Abstract—The kinetics of the initial stage of the furfural reaction with hydrogen peroxide was studied in water in the presence of Na_2MoO_4 and in *n*-butanol without a catalyst. The mechanisms of furfural conversion in the $\text{Na}_2\text{MoO}_4\text{-H}_2\text{O}_2$ system and oxidation by hydrogen peroxide in the absence of sodium molybdate are discussed. Based on kinetic studies, the mechanism of furan peroxide formation is proposed.

INTRODUCTION

Earlier, we performed the first reaction between furfural and hydrogen peroxide in the presence of sodium molybdate in catalytic amounts [1]. At a molar ratio of these reagents of 1 : 3.5 : 0.05, the conversion of the furan substrate for 2 h reached 97% at 60°C and resulted in 2(5H)-furanone and a number of carbonyl compounds and acids. The accumulation of these products became noticeable only after some time after the reaction start. At the same time, a number of organic peroxides, one of which incorporated Mo(VI), appeared in the reaction mixture already during the first minutes. We failed to isolate these intermediates [2].

Using the above data and available information on the formation of molybdenum peroxy compounds in the Mo(VI)– H_2O_2 system [3], their high oxidizing ability [4], and their ability to react with carbonyl compounds [5], we proposed a scheme for the formation of intermediate peroxide products in the reaction (Scheme 1). According to this scheme, the interaction of Na_2MoO_4 with hydrogen peroxide that occurred according to equation (I) and resulted in diperoxymolybdate I stable in acidic solutions was the first and last stage of the process under examination. In our opinion, compound I formed coordination bonds with the carbonyl group of furfural and gave peroxy compound II.



Scheme 1

The hydroxylation and epoxidation of the furan ring during its interaction with molybdenum peroxy complex I seem highly improbable because of a lower electron density on the furfural ring conjugated with the carbonyl group.

EXPERIMENTAL

Kinetic Study of the Furfural Reaction with Hydrogen Peroxide in the Presence of Sodium Molybdate

The kinetics of the reaction was studied in a reactor equipped with a stirrer, a reflux condenser, and a sampler at $60 \pm 0.2^\circ\text{C}$. Temperature was maintained with a thermostat. Dilute solutions of reagents were used to monitor the initial stage of the reaction.

The consumption of furfural was determined spectrophotometrically. Hydrogen peroxide was taken in large excess. The reaction rate orders were determined by maintaining the concentrations of two reactants con-

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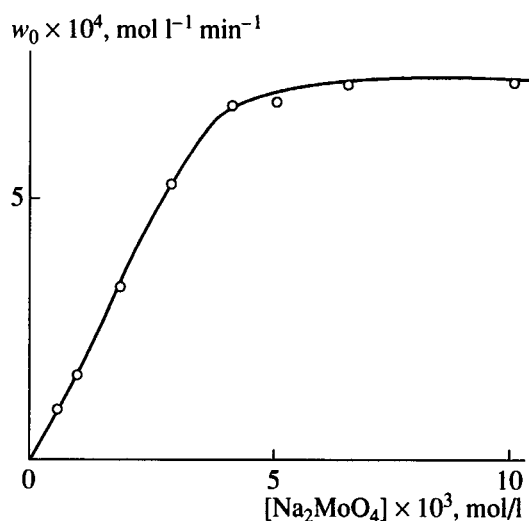


Fig. 1. Dependence of the initial reaction rate on the initial concentration of the catalyst (60°C, [H₂O₂]₀ = 2.13 mol/l, [FI]₀ = 0.1 mol/l).

stant and varying the concentration of the third reactant. The concentrations of furfural, hydrogen peroxide, and sodium molybdate varied from 0.3 to 0.25, from 1.07 to 2.66, and from 0.0005 to 0.01 mol/l, respectively.

Kinetic Study of Furfural Reaction with Hydrogen Peroxide in the Absence of Sodium Molybdate

To determine the reaction rate order with respect to furfural, we carried out a set of experiments using different initial concentrations of the substrate and an excess concentration of H₂O₂ to neglect its change. H₂O₂ and *n*-butanol of 99.0–99.5% purity were used as solvents. The solutions of furfural (0.14, 0.4, and 0.8 mol/l) and H₂O₂ (4 mol/l) in *n*-butanol were prepared separately using gravimetry. Thermally stable glass ampules (8–10) were filled with 1-ml portions of reagent and substrate solutions, cooled with an ice-sodium chloride mixture, sealed, and placed into the thermostat. The reaction was stopped by the rapid cooling of an ampule with icy water. After opening the ampule, 1 ml of the reaction mixture was withdrawn, diluted with butanol, and analyzed by spectrophotometry.

To determine the reaction rate order with respect to hydrogen peroxide, furfural (FI) was oxidized at a constant initial concentration ([FI]₀) of 0.4 mol/l and at concentrations of H₂O₂ of 2, 4, 6, and 8 mol/l.

RESULTS AND DISCUSSION

We studied the kinetics of the oxidation of furfural with hydrogen peroxide in the presence of sodium molybdate to verify Scheme 1.

To determine the reaction rate orders with respect to reagents, we either significantly diluted H₂O₂ or took it in excess with respect to furfural. The experiments were carried out in the presence of catalytic amounts of Na₂MoO₄. Under the reaction conditions, the initial pH of the reaction solution was 5 because of an acidic stabilizer present in H₂O₂. The value of pH remained unchanged during the entire process. The reaction did not occur under these conditions in the absence of sodium molybdate additives.

Starting from the first minutes of the furfural oxidation with hydrogen peroxide in the presence of Na₂MoO₄, a Mo(VI)-containing organic peroxide was formed in the reaction mixture; it was the only reaction product at the initial stage. For this reason, we managed to study only the kinetics of the formation of furan peroxide II in the complex furfural–H₂O₂–Na₂MoO₄ system.

The reaction rate order was determined by differentiation with respect to initial reaction rates (*w*₀) at different concentrations of reagents [6]. It turned out that the initial rate of the reaction under consideration linearly depends on the furfural concentration and does not depend on the hydrogen peroxide concentration. The facts that the slope of the log *w*₀–log [FI]₀ line was 1 and that the initial reaction rate was independent of the initial concentration of H₂O₂ pointed to the first and zero orders of the reaction rate with respect to furfural and hydrogen peroxide, respectively.

At the same time, the dependence of the initial rate on the concentration of sodium molybdate was linear only at its concentrations equal to or lower than 0.005 mol/l (Fig. 1).

The slope of the linear portion of the line was 1; that is, the reaction rate had the first order with respect to the catalyst.

Usually, the zero order of the reaction rate with respect to H₂O₂ and the first order with respect to molybdenum compound that is present in the reaction mixture in catalytic amounts are explained by the participation of these compounds in the formation of peroxy compounds of Mo(VI), which further act as oxidants. The formation of the furfural–peroxymolybdic acid complex was proven spectroscopically [7].

The results of kinetic studies of the reaction between furfural and H₂O₂ in the presence of Na₂MoO₄ were treated using the Michaelis scheme for enzymatic reactions [8]:



Taking into account that [Mo]₀ = [Mo]_{free} + [I] and $K = [\text{I}]/([\text{H}_2\text{O}_2][\text{Mo}]_{\text{free}})$, i.e., $[\text{I}] = K[\text{H}_2\text{O}_2][\text{Mo}]_{\text{free}}$, we obtain $[\text{Mo}]_{\text{free}} = [\text{Mo}]_0/(1 + K[\text{H}_2\text{O}_2])$. Knowing the

orders of the reaction rate with respect to single reagents, we can write that the initial rate of furfural oxidation is $w_0 = k[\text{F}][\text{I}]$; i.e., $w_0 = k[\text{F}][\text{H}_2\text{O}_2][\text{Mo}]_0/(1 + K[\text{H}_2\text{O}_2])$.

Because we studied the kinetics of the reaction in a large excess of hydrogen peroxide, the initial rate of the reaction can be written as follows:

$$w_0 = k[\text{F}][\text{Mo}]_0/K.$$

The maximum reaction rate (w_{max}) of $3.92 \times 10^3 \text{ mol l}^{-1} \text{ min}^{-1}$ and the Michaelis constant (K_M) equal to 0.306 l/mol were found from the Lineweaver–Burk plot (Fig. 2).

To verify our assumptions on the mechanism of the reaction under consideration and the role of the catalyst in it, we studied the kinetics of the furfural oxidation with hydrogen peroxide in the absence of any catalytic additives. *n*-Butanol, in which the rate of furfural oxidation is rather high, was used as a solvent. This allowed us to perform the experiment at a low initial concentration of the substrate. As in the presence of sodium molybdate, in its absence, the oxidation of furfural proceeded via the formation of intermediate peroxy compounds. However, in this case, furfural α -oxyhydroperoxide (III) and furfural α,α' -dioxyhydroperoxide (IV) were formed [9]. The oxidation of furfural performed in nonaqueous medium made it possible to stop the reaction at the stage of the formation of substances III and IV and to study the kinetics of their formation. An error in the determination of rate constants was at most 5%.

Semilogarithmic anamorphoses presented in Fig. 3 indicate that the reaction rate was of pseudo-first order with respect to furfural.

This is confirmed by the fact that the time of furfural half-conversion ($\tau_{1/2}$) and reaction rate constants found from the slope of semilogarithmic anamorphoses were independent of the initial rate of the substrate (see the table). To determine the partial reaction rate order with respect to hydrogen peroxide, we considered the dependence of the apparent rate constant for the consumption of furfural on the concentration of H_2O_2 (Fig. 4).¹

It is seen that the straight line plotted on logarithmic coordinates fits the experimental points. The slope of the line equals two, which corresponded to the second order of the reaction rate with respect to hydrogen peroxide. Thus, the reaction of furfural with H_2O_2 at the stage of the formation of organic peroxy compounds follows the overall third-order rate law.

It is known [10] that the third order of the reactions of nucleophilic addition to the carbonyl group to which the process under study can be assigned was observed when the addition of a nucleophile occurred synchro-

¹ The apparent rate constant for the reaction of the pseudo-first order with respect to furfural was used in the construction of the curve in Fig. 4, because the true constant is independent of the initial concentration of H_2O_2 .

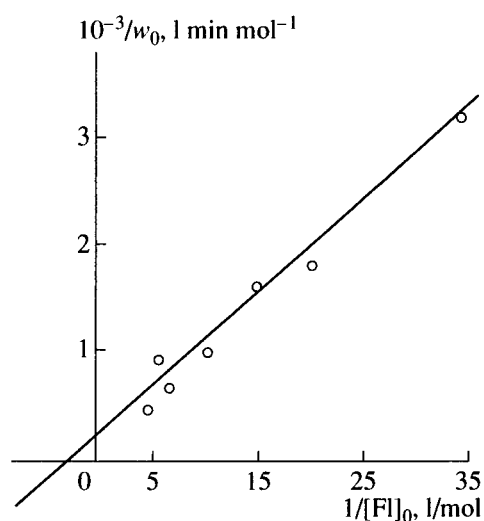


Fig. 2. Dependence of $1/w_0$ on $1/[\text{F}]_0$ for the reaction of furfural with an aqueous solution of H_2O_2 in the presence of sodium molybdate (60°C , $[\text{H}_2\text{O}_2]_0 = 2.13 \text{ mol/l}$, $[\text{Na}_2\text{MoO}_4]_0 = 4.5 \times 10^{-3} \text{ mol/l}$).

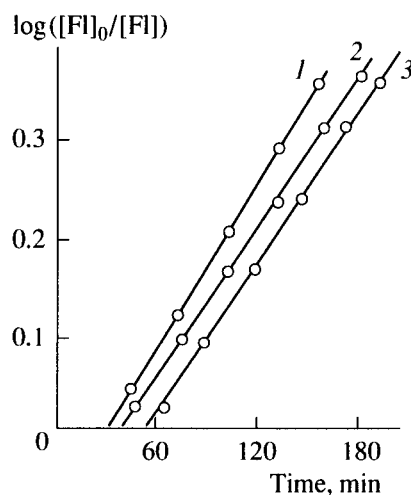


Fig. 3. Semilogarithmic dependence of the $[\text{F}]_0/[\text{F}]$ ratio on the reaction time at the initial concentrations of furfural of (1) 0.8, (2) 0.4, and (3) 0.14 mol/l.

nously with the proton transfer. Knowing the reaction rate orders with respect to single reagents, we propose the following scheme (Scheme 2) for the oxidation of

Rate constants for the oxidation of furfural with hydrogen peroxide and times of the half-conversion of the substrate ($[\text{H}_2\text{O}_2] = 4 \text{ mol/l}$, 60°C)

$[\text{F}]$, mol/l	$k \times 10^3$, $\text{l}^2 \text{ mol}^{-2} \text{ min}^{-1}$	$\tau_{1/2}$, min
0.80	0.39	150
0.40	0.33	158
0.14	0.36	163

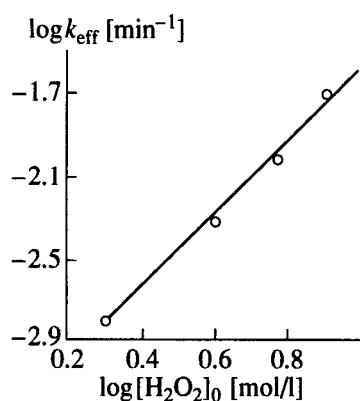
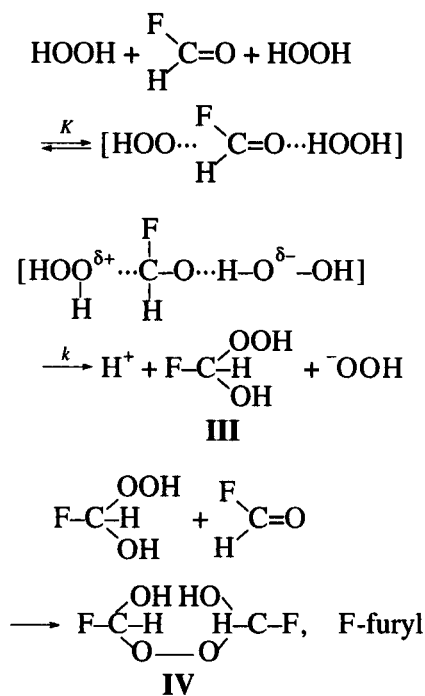


Fig. 4. Logarithmic dependence of the apparent rate constant for the oxidation of furfural with hydrogen peroxide on the concentration of H₂O₂ (60°C, [Ff]₀ = 0.4 mol/l).

furfural with hydrogen peroxide:



Scheme 2

The following equation corresponding to the third-order reaction follows from this scheme:

$$-d[\text{Ff}]/dt = 2kK[\text{Ff}][\text{H}_2\text{O}_2]^2.$$

This equation agrees well with the results of kinetic studies.

Comparison of the data obtained shows that the presence of the catalyst (sodium molybdate) in the reaction mixture results in a change in the reaction rate order with respect to hydrogen peroxide. This can be explained by stronger oxidizing properties of peroxy-molybdenum compounds as compared to H₂O₂ [4] and also by their higher coordination ability due to a large positive charge on the molybdenum atom.

The obtained kinetic data agree with the proposed scheme for the reaction of furfural with hydrogen peroxide in the presence of sodium molybdate.

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