Chemistry of Heterocyclic Compounds, Vol. 34, No. 7, 1998

CATALYTIC OXIDATION OF FURAN AND HYDROFURAN COMPOUNDS. 4.* OXIDATION OF FURFURAL BY HYDROGEN PEROXIDE IN THE PRESENCE OF SODIUM MOLYBDATE

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The oxidation of furfural by an aqueous solution of hydrogen peroxide in the presence of sodium molybdate was studied for the first time. Its final products are 2(5H)-furanone and also tartaric, malic, and succinic acids. The process takes place through the formation of peroxide and carbonyl compounds. Kinetic curves for the consumption of the reagents and the accumulation of the reaction products were obtained. In direction oxidation in this system differs substantially from the previously studied reactions of furfural with an aqueous solution of hydrogen peroxide without a catalyst and in the presence of selenium and vanadium compounds.

We have studied the oxidation of furfural by hydrogen peroxide in the presence of sodium molybdate in detail for the first time. The reactions of furfural with hydrogen peroxide under the conditions of autocatalysis by the acids that accumulate [2-7] and catalysis by compounds of selenium and vanadium [8, 9] were reported earlier. The authors of these papers isolated β-formylacrylic acid (I) or its esters [8, 9] and 2(5H)-furanone (II) and succinic acid (III) [6, 7] as the main products. It was assumed that oxidation took place either according to the classical Baeyer–Villiger mechanism [2, 7] or by hydroxylation [9], depending on the conditions. It was reported that compound (I), maleic acid (IV), and fumaric acid (V) and also a certain amount of malic acid (VI) were formed during the oxidation of furfural by a 5% solution of hydrogen peroxide in the presence of $NaHMoO_4$ [10]. The authors consider that the reaction in the presence of sodium hydromolybdate takes place similarly to the reaction in the furfural–hydrogen peroxide–selenium compound system.

As seen from the published literature, in papers on the peroxide oxidation of furfural [2-10] the possibility of using the peroxo complexes of molybdenum, which are easily formed in the aqueous hydrogen peroxide–molybdenum^{VI} system, has not been realized [11]. In the light of known data on the epoxidizing ability of such complexes [11-20] and in order to discover new synthetic possibilities in the reaction of furfural with hydrogen peroxide we studied its characteristics in the presence of sodium molybdate.

The oxidation of furfural was conducted at 60°C with a 30% aqueous solution of hydrogen peroxide in the presence of catalytic amounts of Na_2MoO_4 (Table 1, version 1). The pH of the initial reaction mixture was 5 on account of the stabilizer contained in the hydrogen peroxide. In the first 5-10 min its color changed from red-brown to lemon-yellow, which remained to the end of the process.

The end of the reaction was detected by the transformation of the initial reagents and the formation of the initial and final compounds by means of a set of analytical methods, i.e., chromatography with authentic samples (GLC, HPLC, TLC, and paper chromatography), polarography, and titrimetric analysis (for analysis of the acidic and peroxide compounds). Kinetic curves for the consumption of furfural and hydrogen peroxide and the accumulation of furanone (II) and acids were obtained (Fig. 1).

As seen from the obtained results (Table 1, version 1, and Fig. 1), the furanone (II) is mainly formed in the investigated system together with tartaric acid (VII), malic acid (VI), and succinic acid (III). A distinctive feature of the process

*For Communication 3, see [1].

Kubansk State Technological University, Krasnodar 350072, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 898-903, July, 1998. Original article submitted December 15, 1997; revision submitted March 2, 1998.

0009-3122/98/3407-0775$20.00

TABLE 1. Conditions and Results of the Various Versions of the Oxidation of Furfural by Hydrogen Peroxide in Water

Version	Catalyst	Molar ratios [fl]: $[H_2O_2]$:[Cat]*	Temperature, °C	Time for complete conversion of furfural, h	Concentration of H_2O_2 used for oxidation, %	Yield of main reaction products, *2					
						I	II	III	IV + V	VI	VII
1	Na_2MoO_4	1 : 3,5 : 0,05	60	2	30	<1	33	8	3	11	6
2*3	—	1 : 3	60	3	27...30	1	27	36	15	<1	—
3*4	$NaHSeO_3$	1 : 3 : 0,05	50	6	5	55	9	6	24	3	—

*fl = furfural; Cat = catalysis.

*2The calculation was made at the moment of complete consumption of the peroxy compounds.

*3Published data [6].

*4Published data [8].

TABLE 2. Comparison of the Results and Balance Calculation of the Oxidation of Furfural by an Aqueous Solution of Hydrogen Peroxide with the Addition of Na_2MoO_4 (version 1) and without the Addition of Catalysts (version 2) for Various Reaction Times*

Reaction time, min	Degree of transformation of furfural, %		Consumption of H_2O_2, g-eq/mole of consumed furfural		Yields of products		
					2(5H)-furanone, mole/mole of consumed furfural	acids, g-eq/mole of consumed furfural	
	version 1	version 2	version 1	version 2	version 1	version 1	version 2
6	25	3	4,3	2,7	0,07	0,79	1,71
18	50	33	2,8	3,1	0,18	1,04	1,14
40	70	50	3,0	4,0	0,29	1,46	1,65
60	80	61	2,6	4,8	0,30	1,62	1,71
125	97	96	2,4	4,7	0,32	1,84	2,00
240	~100	100	3,4	5,7	0,33	1,87	2,62

*For the conditions of versions 1 and 2, see Table 1.

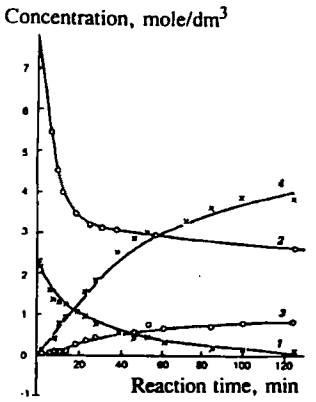
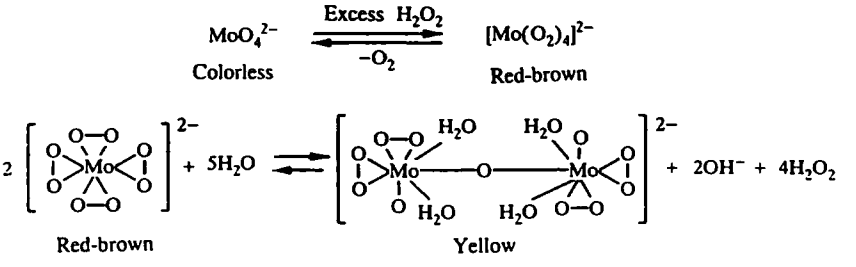


Fig. 1. Kinetic curves for the consumption of the reagents and the accumulation of the products from the oxidation of furfural in the hydrogen peroxide–sodium molybdate system at 60°C: 1) furfural; 2) hydrogen peroxide; 3) 2(5H)-furanone; 4) acids.

compared with oxidation without the addition of special catalysts (version 2) is the marked decrease of the yields of succinic (III) and maleic (IV) acids and also the formation of significant amounts of the hydroxy acids (VI) and (VII) (cf. versions 1 and 2, Table 1). The composition of the final products in version 1 also differs radically from the composition of the substances formed during the oxidation of furfural in the presence of selenium compounds (Table 1, version 3) [8, 10] and vanadium compounds [9].

It was established that during the oxidation of furfural in the hydrogen peroxide–sodium molybdate system the reaction mixture contains a series of compounds with an explicit or a latent carbonyl function capable of entering into reaction with 2,4-dinitrophenylhydrazine (DNPH). In the present work it was not possible to isolate these substances in the pure form and identify them. During treatment of samples of the oxidate, taken every 30 min over the whole process, with an acidic solution of DNPH the 2,4-dinitrophenylhydrazones were obtained. During chromatography on Silufol plates in the 3:1 chloroform–petroleum ether system they had the following R_f values: 0.04, 0.10, 0.22, 0.32, 0.43, 0.80. It is worth mentioning that compounds giving hydrazones with R_f 0.04, 0.10, and 0.22 are formed in the reaction mixture most vigorously in the first period of the reaction, but after complete consumption of the furfural their content is minimal. The substances whose R_f values are 0.32, 0.43, and 0.80 begin to accumulate in the oxidate only at the moment of 80% conversion of the substrate, while their maximum content is reached after complete decomposition of the peroxide compounds. The total content of these compounds calculated on the malonic monoaldehyde, which can be expected to form in the given reaction, amounts to 7% of the theoretical.

It was found by titrimetric and chromatographic methods that peroxide products were present in the investigated reaction. Their accumulation passes through a maximum 20 min after the beginning of the reaction. The content of the peroxide products then decreases gradually, and they are absent from the final reaction mixture. According to TLC of samples of the oxidate on Silufol plates in various solvent systems, five peroxide compounds are formed during the reaction of furfural with hydrogen peroxide in the presence of sodium molybdate. They include a peroxide compound of molybdenum. During the chromatography of samples of the reaction mixture (TLC, 2:1 acetone–chloroform) it remains at the start and corresponds to a model peroxo complex of molybdenum, which is formed in accordance with published data [16] and can be transformed according to the following scheme:



Study of the qualitative composition of the discovered peroxides showed that three of them with R_f 0.08, 0.30, and 0.49 (in the 2:1 chloroform–acetone system) are shown up on the chromatogram by solutions of potassium iodide or 2,4-dinitrophenylhydrazine. Such behavior is typical of the peroxides formed by carbonyl compounds. One of these peroxides (R_f 0.08) contains molybdenum^{VI}, detected by a qualitative reaction [21]. We suppose that this peroxide is the product from the reaction of furfural with the peroxo compound of molybdenum.

The kinetic curves of the process (Fig. 1) show that full conversion of the furfural takes 2 h, while full conversion of the hydrogen peroxide, taken in excess, takes 7 h. Here most of the furfural (~80%) enters into reaction in the first hour of the reaction (Fig. 1, curve 1). In this time up to 60% of the hydrogen peroxide is consumed (Fig. 1, curve 2), most of the furanone (II) is formed (curve 3), and the acidity of the medium is greatly increased (curve 4). The active period of the process in the presence of sodium molybdate is over in the first hour, after which only the acidity of the medium continues to increase, and to a considerably larger degree than the substrate is consumed. The further formation of the acids probably results from the transformation of the intermediate products. It is noticeable that the content of the furanone (II) in the oxidate only increases to a small degree after 1 h of the reaction.

Comparison of the degree of conversion of furfural and the consumption of hydrogen peroxide in identical time intervals for the reaction with and without the presence of sodium molybdate (Table 2, versions 1 and 2 respectively) shows that the oxidation process takes place more vigorously in the first case particularly in the initial period; the $\tau_{1/4}$ value of furfural is reduced by a factor of four, while the amount of hydrogen peroxide consumed in the initial period is increased. At the same time a balancing calculation showed (Table 2) that a much greater accumulation of the acids per mole of reacted furfural is characteristic of the reaction without the addition of the catalysts.

Thus, the obtained data make it possible to single out certain features and relationships in the reaction of furfural with hydrogen peroxide in the presence of sodium molybdate. In all probability organic peroxide compounds and substances containing an explicit or a latent carbonyl function can be regarded as the main intermediate products of this reaction. The detection of molybdenum-containing peroxides in the intermediate products and also the characteristic change in the color of the reaction mixture in the course of oxidation make it possible to consider that the role of the principal oxidizing agents in the reaction is fulfilled by the peroxo complexes of molybdenum; the OH^- ions, formed during the hydrolysis of the tetraperoxomolybdate, can also participate in this process. The oxidation of the substrate takes place more vigorously in the presence of sodium molybdate than in the case of the uncatalyzed reaction. During catalysis by sodium molybdate, in contrast to oxidation in the presence of selenium compounds, a significant amount of the furanone (II), exceeding its yield in the noncatalytic reaction, is formed. A significant feature of the investigated process is the formation of tartaric and malic acids among the main products.

EXPERIMENTAL

Procedure for the Oxidation of Furfural. To a 50-ml three-necked flask, immersed in a water bath at 60°C, we added with vigorous stirring 3 ml (36 mmole) of furfural and 0.44 g (1.8 mmole) of sodium molybdate. After 5 min we added 12.9 ml (126 mmole) of 30% hydrogen peroxide. The oxidation was continued with vigorous stirring at 60°C until the initial reagents had been completely transformed. The reaction was monitored by the consumption of furfural and hydrogen peroxide and the accumulation of acids.

Analysis of the Acidic Products. The total amount of acids formed during the reaction was determined by titration. To a 0.5-ml sample of the oxidate we added 4.5 ml of distilled water, and we then titrated the solution with a 0.1 N aqueous solution of sodium hydroxide in the presence of an alcohol solution of phenolphthalein. For qualitative determination of the composition of the acids we used paper chromatography [22]. The mobile phase was *n*-butanol–formic acid–water (9:1:4 by volume). The developers were acidified aqueous solutions of potassium permanganate and 2,4-dinitrophenylhydrazine, an alkaline solution of bromophenol blue, and iodine vapor.

For analysis of the mixture of carboxylic acids we used modified HPLC on an HPP 4001 instrument fitted with an RIDK-101 refractometric detector with two series-connected glass columns (150 × 3.3 mm) filled with Separon SGX C-18 enriched solid phase with particle size 5 μm. The analysis was conducted at 20°C at a pressure of 0.8 MPa in the column. The flow rate of the mobile phase (0.6% aqueous acetic acid) was 0.3 cm^3/min. The sample size was 6 μl. The analysis took 10 min. The yields of tartaric, malic, and succinic acids were determined by this method. The retention times of the acids in the

analyzed sample were 10.25, 11.16. and 14.33 min respectively. The emergence times of authentic samples of these acids are 10.25, 11.00, and 14.12 min.

The yields of maleic and fumaric acids and also the overall yield of all the forms of β-formylacrylic acid were determined on an LP-70 polarograph in a thermostated cell with a dropping mercury electrode (m = 1.59 mg/sec, t = 3.66 sec at −1.0 V) at 25 ± 0.2°C. The reference electrode was a normal calomel electrode. The supporting electrolyte was a 0.1 M solution of perchloric acid. The $E_{1/2}$ values for compounds (I) and (IV + V) were −0.38 to −0.40 and −0.67 V respectively.

Analysis of the Reaction Products by GLC. This method was used to monitor the consumption of furfural and the accumulation of 2(5H)-furanone (II) and also to determine the acidic products (in the form of their ethyl esters). The reaction mixtures and the products obtained after their esterification were analyzed on a Chrom-4 instrument with a flame-ionization detector and a glass column (300 × 0.3 cm), containing polymethylphenylsiloxane oil (PMPS-4) at the rate of 15% on Chromaton N-AW DMCS. The samples were chromatographed at a column temperature of 150°C, evaporator temperature 220°C, and detector temperature 220°C. The carrier gas was nitrogen, and the flow rate was 30 ml/min. The retention times of furfural and 2-(5H)-furanone were 1.39 and 2.7 min respectively. The retention times of the ethyl esters of the carboxylic acids had the following values: oxalic 2.16, malonic 3.17, succinic 5.22, maleic 5.73, malic 9.25, tartaric 15.33 min.

The ethyl esters of the acids were obtained in the following way. About 80% of the water was removed from a sample of the oxidate by evaporation under vacuum. Ethanol (10 ml), chloroform (30 ml), and hydrochloric acid (0.1 ml) as catalyst were then added to the obtained concentrate, and the mixture was boiled for 7 h in a flask with a Dean and Stark tube (80°C). A model mixture of tartaric, malic, succinic, maleic, malonic, fumaric, and pyromucic acids was esterified similarly in the presence of sodium molybdate (to eliminate its possible effect on the result of the analysis). The acids whose esters were used as reference standards for the model mixture were also esterified individually.

Production and Chromatography of the 2,4-Dinitrophenylhydrazones of the Oxidation Products. To 0.1-ml samples of the oxidate, taken at various stages of the reaction, we added 5 ml of a hydrochloric acid solution of 2,4-dinitrophenylhydrazine. The precipitate was filtered off, washed with water and alcohol, and dried. A solution of the precipitate in ethyl acetate was applied to Silufol plates and chromatographed in the 3:1 chloroform–petroleum ether system.

Analysis of the Peroxide Compounds. Samples of the oxidate, taken during the reaction, were analyzed by the familiar method [23] by cerimetric titration with hydrogen peroxide and iodometric titration of the total peroxides. The organic peroxides were determined by difference. The peroxide compounds contained in the reaction mixture were also analyzed by TLC on Silufol plates using the chloroform, 3:1 chloroform–acetone, 2:1 acetone–chloroform, and 20:1 toluene–ethanol systems. The developers were an acidified aqueous solution of 2,4-dinitrophenylhydrazine, an alkaline solution of bromophenol blue, iodine vapor, and a solution of potassium iodide.

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