INFLUENCE OF THE REACTION CONDITIONS ON THE NATURE OF THE HYDROGEN PEROXIDE OXIDATION PRODUCTS OF FURFURAL

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UV irradiation causes no acceleration of the oxidation of furfural by hydrogen peroxide but maintains its occurrence at a uniform rate. Both with UV irradiation and without it, the oxidation of furfural by hydrogen peroxide takes place via the formation of intermediate peroxide compounds, with their subsequent conversion mainly into a mixture of β-formylacrylic, maleic, and succinic acids. The ratio between the acids depends on the reaction conditions. The possibility has been shown of a directed oxidation to β-formylacrylic acid.

In spite of the fact that a large number of investigations have been carried out on the oxidation of furfural, many aspects of this process have not been studied [1]. Even the autoxidation of furfural and its oxidation by molecular oxygen, about which an extremely large number of papers have been published, are treated differently by different authors [1–3]. There is little information, and that contradictory, on the use of hydrogen peroxide as an oxidizing agent for furfural, but what there is indicates the formation of a mixture of maleic and succinic acids with a small amount of β-formylacrylic acid [4–9]. The investigation of methods of preparing β-formylacrylic acid is of particular interest in view of the high reactivity of this compound [10–12].

To study the possibility of initiating or directing the reaction and to obtain information as to whether the mechanism is heterogeneous or homogeneous, we have studied the influence of UV irradiation on the direction and intensity of the oxidation of furfural by hodrogen peroxide. It is known that UV light accelerates the decomposition of H_2O_2 into hydroxyl radicals [13–15]. If the oxidation processes studied are radical processes in the course of which the hydroxyl radical $OH^\bullet$ takes part, UV irradiation should accelerate them.

During the reaction, the furfural was determined spectrophotometrically on an SF-4 instrument at λ_{max} 278 nm [16]. The amounts of hydrogen peroxide and of organic peroxide compounds were found by a method developed previously [17]. The acids were identified and determined quantitatively by descending chromatography on paper and in a column of silica gel [18]. The total acidity of the reaction mixture was determined by titrating samples with 0.01 N ethanolic NaOH.

It can be seen from Fig. 1 (curve I) that in the case of the uninitiated process, if the heat liberated intensively in the course of the reaction is not removed, 8 hr after the mixing of the reagents the reaction becomes vigorous and the temperature of the medium rapidly rises to 108° C. The rates of the decomposition of the furfural and of the accumulation of acids and peroxide compounds rise sharply. In order to elucidate the action of UV radiation on the course of the oxidation, the reaction mixture was irradiated with a mercury lamp for 8 hr. No acceleration of the process was observed (curve II, Fig. 1). To complete the reaction, the irradiated mixture was left under different conditions: in a Dewar vessel (curve II, section a), at room temperatures (section b) and in the refrigerator at 5° C (c). It can be seen from the curves of Fig. 1 and from the UV spectra of the oxidation products (Fig. 2) that previous photochemical initiation of the reaction mixture ensures a uniform completion of the reaction at room temperature. In the case of thermal isolation in a Dewar vessel, the reaction goes to completion 2 hr 30 min after irradiation, passing through a vigorous stage. Removal of heat in the refrigerator slows down the process. Thus, UV irradiation, by initiating the oxidation of furfural gradually, changes its nature and permits the reaction to be carried out at the temperature of the surrounding medium so that it changes from a self-accelerating process to a stationary process. The absence of an acceleration under the action of UV light indicates that the process takes place predominantly by an ionic and not a radical mechanism. The uniformity of the reaction so achieved may apparently be explained by the excitation of the electronic system and an increase in the lability of the intermediate peroxides.

The simultaneous action of radiation and heating at an average temperature of 40° C (curve III) increases the rate of reaction almost twofold (half-decomposition time of furfural $\tau^{40}_{1/2} = 5$ hr, while $\tau^{26}_{1/2} = 9$ hr).

The analysis of the acids showed that in the experiments with initiation and in those without it the main products were formylacrylic, maleic, succinic, and formic acids with small amounts of malic, fumaric, tartaric, and pyromucic acids. The fumaric acid was detected in UV radiation at all stages of the reaction. Without irradiation it was found only at temperatures above 70° C. During the reaction, the ratio of maleic and formylacrylic acids changed in the direction of a decrease in the amount of formylacrylic acid and the accumulation of maleic acid. The ratio between the maleic and succinic acids also changed (see table).

An analysis of the peroxide compounds showed the formation of organic peroxides, the structures of which has not yet been determined. In the first stages, the accumulation of peroxides prevails over their decomposition. Then the decomposition of the peroxides accelerates, the extent of decomposition being particularly appreciable with a rise in the temperature (Fig. 1, C). There were no organic peroxides in the final oxidation product. However, the fact that they were

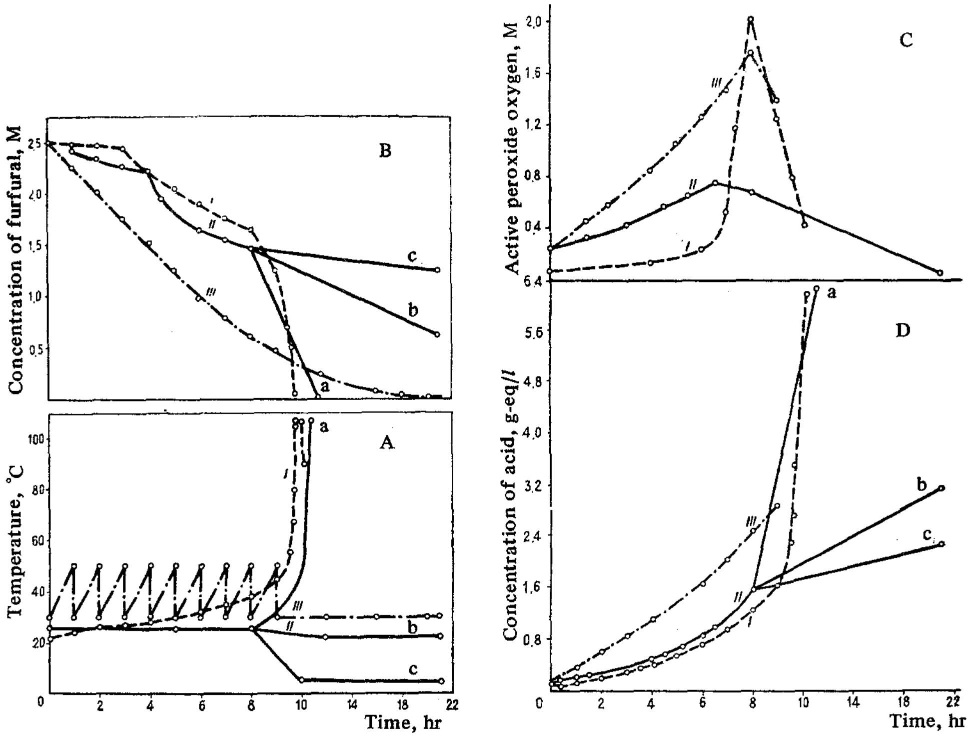

Fig. 1. Changes in the temperature (A) and in the concentrations of furfural (B), organic peroxide compounds (C), and acids (D) in the oxidation of furfural by hydrogen peroxide: I) without irradiation at 26° C ; II) with UV irradiation at 26° C followed by maintenance of the irradiated mixture: a) in a Dewar vessel, b) at 22° C, c) at 5° C; III) with UV irradiation at 30–50° C.

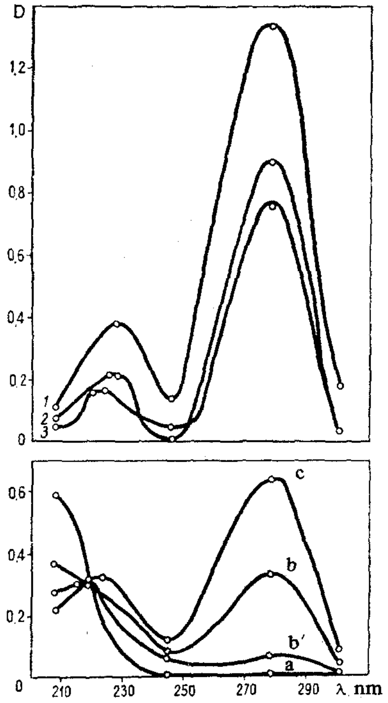

Fig. 2. Change in the UV spectra of the products of the oxidation of furfural by perhydrol on irradiation with a mercury lamp: 1) initial mixture; 2) after 5 hr; 3) after 8 hr; with the irradiated mixture kept: a) in a Dewar vessel for 2 hr 45 min; b) at 22° C for 13 hr; b') at 22° C for 21 hr; c) at 5° C for 13 hr.

Ratio Between the Acids at Different Stages of the Oxidation of Furfural by Hydrogen Peroxide

Conditions		Yield in % of the total crystalline acids			
		β-formylacrylic	maleic	succinic	other*
Without irradiation	Before the vigorous reaction (50° C)	37.6	29.3	25.5	7.6
	At the moment of the vigorous reaction (108° C)	41.5	31.5	22.0	5.0
	After the vigorous reaction (90° C)	26.0	32.8	37.5	3.7
With irradiation by a mercury lamp	After irradiation for 8 hr at 26° C	66.8	15.0	10.0	8.2
	After irradiation for 8 hr at 40° C	36.0	27.9	28.0	8.1

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*Fumaric, malic, tartaric, oxalic, and pyromucic acids were detected.

formed in the intermediate stages of the reaction leads to a treatment of the mechanism of furfural oxidation by hydrogen peroxide different from the existing hypothetical variants [4–8].

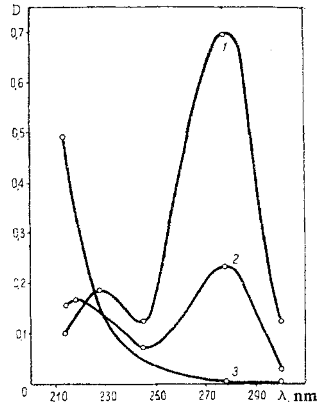
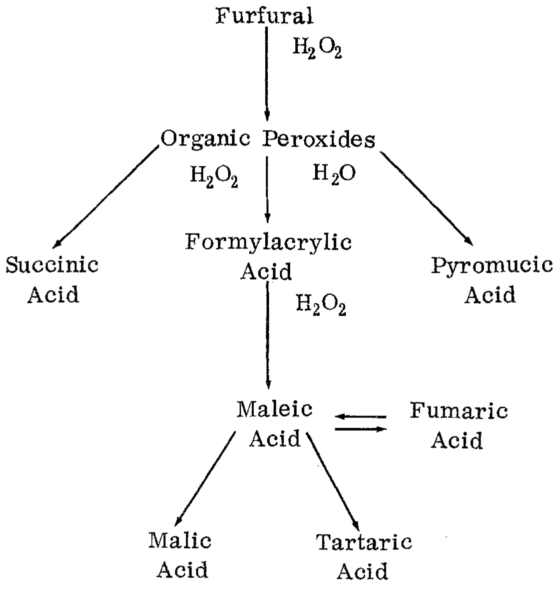


Fig. 3. Change in the UV spectra of the products of the oxidation of furfural with perhydrol without initiation: 1) initial mixture; 2) after 9 hr 40 min, before the vigorous reaction (100° C); 3) after the vigorous reaction.

At various stages, the oxidate was subjected to UV spectroscopic analysis (Figs. 2 and 3). As can be seen, the initial mixtures have λ_{max} 228 and 278 nm, which corresponds to furfural [19]. During the reaction there are quantitative changes at λ_{max} 278 nm, which shows the decomposition of the furfural, and qualitative changes in the 208–228-nm region. The furfural maximum at 228 nm gradually disappears, and the maximum of the spectrum shifts to the 220-nm region. This region of absorption is characteristic for β-formylacrylic acid [20]. When the temperature rises because of self-heating, the absorption maximum begins to shift into the 200-nm region and outside the limits of measurement of the instrument (Fig. 2, curve a; Fig. 3, curve 3). We know from pure samples that absorption in this region is characteristic for formic, fumaric, succinic, and other acids. Obviously, their accumulation as the reaction develops leads to the masking of the spectrum of the β-formylacrylic acid formed initially.

The parallel formation of a number of acids shows the presence of several reactions competing with one another, the dominating ones being the formation of β-formylacrylic, succinic, and maleic acids. The latter arises from the β-formylacrylic acid. Fumaric acid is formed by the isomerization of maleic acid, which is quite possible under conditions of irradiation and high temperatures [21–23]. The formation of malic acid is the result of a transformation of the maleic acid. The possibility of such transformations under the conditions of irradiation and a vigorous reaction without irradiation is confirmed in experiments that we have carried out with the individual acids. The pyromucic acid, in all probability, is the product of a side reaction in the oxidation of furfural. Thus, the formation and conversion of these substances during the oxidation of furfural by hydrogen peroxide can be represented in the form of the following scheme:



A detailed study of the conversion of the acids formed during the reaction has shown methods for the directed synthesis of maleic, formylacrylic, or succinic acid. β-Formylacrylic acid has been obtained with a yield of up to 60% [24].

EXPERIMENTAL

The experiments were carried out with furfural freshly distilled in vacuum (n_D^{25} 1.5234, d^{25} 1.1563) and 27% hydrogen peroxide.

A flask was charged with 41.4 ml (0.5 mole) of furfural and 150.5 ml (1.3 mole) of hydrogen peroxide. The mixture was stirred vigorously. In the case of the experiments with irradiation, quartz flasks were used and the reaction mixture was irradiated with a PRK-4 lamp.

Reaction Conditions

1. Without irradiation: after 9 hr 45 min, the temperature of the mixture reached 108° C, whereupon a vigorous reaction began which lasted 25 min, and then the temperature fell and the reaction ceased. All the furfural reacted.

2. The reaction mixture was irradiated at 26° C for 8 hr, after which part of it was placed in the refrigerator, part in a Dewar vessel, and part was kept at room temperature. In the Dewar vessel, a vigorous reaction took place 2 hr 30 min after the end of irradiation, but no such reaction developed in the refrigerator or at room temperature during a day.

3. The reaction mixture was irradiated at 40 ± 10° C for 9 hr (after each 30 min, the temperature had risen to 50° C, and it was then brought artificially to 30° C). After irradiation, part of the reaction mixture was kept in the refrigerator and part at room temperature. No vigorous reaction was observed during the experiment. At room temperature, all the furfural had reacted in 20 hr.

To elucidate the possible conversions of the β-formylacrylic, maleic, succinic, and malic acids under the reaction conditions, two experiments were carried out with each of these acids. A mixture of 0.5 g (0.05–0.037 mole) of the acid concerned and 25 ml (0.22 mole) of 27% hydrogen peroxide was irradiated with a mercury lamp with stirring for 2 hr, which corresponded to the experiments with photoinitiation. In another case, a mixture of the acid and H_2O_2 was kept at 108° C for 25 min, which corresponded to the vigorous reaction in the experiments without irradiation. The reaction products were separated by descending paper chromatography.

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