

## 2-FORMYLOXYFURAN AS AN INTERMEDIATE IN THE HYDROGEN PEROXIDE OXIDATION OF FURFURALDEHYDE

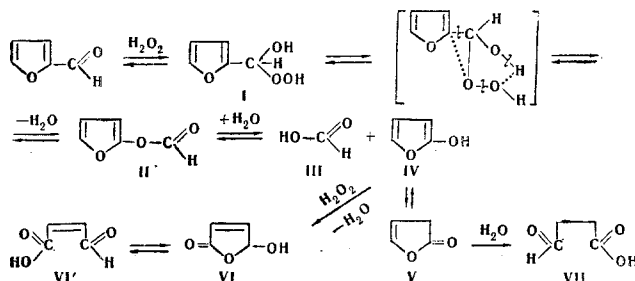
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The main intermediate in the hydrogen peroxide oxidation of furfuraldehyde is the unstable 2-formyloxyfuran.

The oxidation of furfural with hydrogen peroxide gives rise to valuable products such as  $\beta$ -formylacrylic acid, maleic acid, succinic acid, and malic acid [1-5].

We have previously suggested, and in part proved, that the reaction mechanism of the oxidation proceeds via the hydroxyhydroperoxide (I), 2-formyloxyfuran (II), and hydrolysis of the latter to formic acid (III), and 2-hydroxyfuran (IV). The last compound is capable of reacting in either the enol (IV) or the lactone (V) form, leading to  $\beta$ -formylacrylic acid (VI and VI') or the monoaldehyde of succinic acid (VII), respectively [6].



Organic peroxides accumulate in the reaction products, and formic acid is produced quantitatively [5, 6]. The isolation or detection of the proposed intermediates is difficult due to the instability of such esters [7], hydroxyfuran [8], and the lactone [9, 10].

Using the spectrophotometric calculation method [11], the presence in the reaction mixture of substances with  $\lambda_{max}$  at 215, 250, and 270-273 nm was observed. These were absent in the starting mixture, but accumulated and underwent conversion during the reaction. The principal intermediate was a compound with a sharp maximum at 215 nm ( $\epsilon$  1125) and a weak maximum at 273 nm ( $\epsilon$  94) (Fig. 1). The IR spectrum contained bands characteristic for monosubstituted furans (736, 846, 904, 948, 991, 1006, 1377, and  $1459\text{ cm}^{-1}$ ) [12]. Vibration of the C-O-C-O-C group gave rise to a series of bands due to symmetrical and asymmetrical valence vibrations ( $1027, 1063, 1114, 1202, \text{ and } 1238\text{ cm}^{-1}$ ), resulting from the interaction of the =C-O-C= of the furan ring and the =C-O-C of the side chain [13, 14]. The IR spectra show that the isolated compound is 2-formyloxyfuran (II), which must subsequently be hydrolyzed to formic acid III and succinic acid aldehyde (VII). The formation of succinic acid aldehyde from esters of a similar type has been observed previously [7].

The structure of the isolated product was determined by alkaline and acid hydrolysis. The UV spectrum shows that hydrolysis of the ester II ( $\lambda_{max}$  215 nm) gives a compound with a maximum at 273 nm

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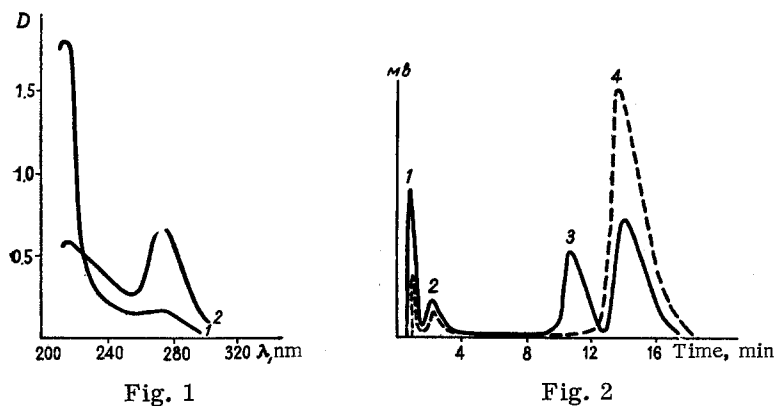


Fig. 1. UV Spectrum of 2-formyloxyfuran, in water at a concentration of  $22 \cdot 10^{-4}$  M: 1) before hydrolysis, 2) after hydrolysis.

Fig. 2. Chromatogram of 2-formyloxyfuran on a PAKhV-0.3 chromatograph before (—) and after (---) hydrolysis: 1) unknown compound, 2) water, 3) 2-formyloxyfuran, 4) formic acid. Column with 10% polyethylene glycol (mol wt 15,000) on celite, length 3 m, temperature  $104^{\circ}$  C, velocity of carrier gas (hydrogen) 102 ml/min.

(Fig. 1), corresponding to succinic acid aldehyde VII [15]. As a result of partial hydrolysis of the ester II by traces of water, the aldehyde VII is present in small amounts in the starting ester II, as indicated by the absorption maximum at 273 nm. The formation of succinic acid aldehyde was confirmed by thin layer chromatography [16, 17].

The presence of formic acid in the hydrolysis products was confirmed by chromatography (Fig. 2) and by polarography, which gave  $E_{1/2} = -1.62$  V, characteristic of formic acid.

Thus we have shown that the principal unstable intermediate in the oxidation of furfural with hydrogen peroxide is 2-formyloxyfuran, which has been isolated for the first time.

## EXPERIMENTAL

**Experimental Conditions.** a) A mixture of 41.3 ml (0.5 mole) of furfuraldehyde and 140.3 ml (1.25 mole) of 27.5% hydrogen peroxide was stirred in a thermostat at  $65^{\circ}$  C. The temperature rose to  $108^{\circ}$  C, and volatile material distilled over and was collected in a Dean and Stark apparatus. The distillate was extracted successively with benzene, heptane, chloroform, ether, and butanol. The butanol fraction was dried over  $\text{Na}_2\text{SO}_4$  and redistilled, bp  $103.5\text{--}105^{\circ}$  C.

b) The process was carried out at a constant temperature of  $65^{\circ}$  C, until all the furfuraldehyde had been consumed. The volatile products were distilled from the oxidate at  $25^{\circ}$  C (10 mm), and were condensed in four traps cooled in a dry-ice-acetone mixture. The product which collected in the traps was dried over  $\text{Na}_2\text{SO}_4$  and then distilled to give a fraction bp  $103.5\text{--}105^{\circ}$  C, identified as 2-formyloxyfuran (II). It amounted to 2-3% of the reacted furfuraldehyde. Compound II was soluble in butanol, ether, and water and insoluble in benzene and heptane.

UV Spectra were taken on an SF-4 spectrophotometer, in water at a concentration of  $22 \cdot 10^{-4}$  mole/liter, the layer thickness being 1 cm. IR Spectra were taken on an IKS-14 spectrophotometer with NaCl prisms.

Thin layer chromatography was carried out on  $\text{Al}_2\text{O}_3$ , without a binder, in a formic acid-butanol mixture (1:9); paper chromatography was carried out using butanol-formic acid-water (9:1:4).

The polarogram was recorded on an LP-60 polarograph, using 0.3 M aqueous LiCl as base. The mercury dropping velocity was 5.57 sec.

Gas chromatographic analysis was carried out on a PAKhV-0.3 chromatograph. The column packing was 10% polyethylene glycol (mol. wt. 15,000) on celite, length 3 m, temperature 104° C, velocity of carrier gas (hydrogen), 102 ml/min.

2-Formyloxyfuran was hydrolyzed with water, 5% H<sub>2</sub>SO<sub>4</sub>, or 10% KOH. The hydrolysis time in each case was 3 hr.

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