MALEIC ANHYDRIDE IN THE PRODUCTS OF OXIDATION OF FURFURAL BY MOLECULAR OXYGEN

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The volatile products of oxidation of furfural with molecular oxygen were separated by preparative gas-liquid chromatography (GLC). Maleic anhydride was isolated from the reaction mixture for the first time and identified.

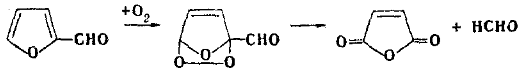
A study of the qualitative and quantitative composition of the oxidates is of great importance in solving the fundamentally important problem of the role of the furan ring and of α-substituents in the oxidative transformations of furan compounds with molecular oxygen.

The available data [1-3] attest to the fact that the furan rings of both the starting furan and its derivatives participate directly in the oxidative transformations. At the same time, it is assumed in several communications [4] that the furan ring does not have sufficient reactivity in the oxidation of furfural, and the oxidation proceeds exclusively at the aldehyde group of this compound.

In the present paper, the products of oxidation of furfural with molecular oxygen were studied by gas-liquid chromatography (GLC).

A compound, the physicochemical constants, chromatographic characteristics, and IR spectrum of which corresponded to maleic anhydride, was detected during the identification of the reaction products.

The determination of maleic anhydride in the furfural oxidate is evidence for participation of the furan ring of this compound in the oxidative transformation. The most probable mechanism for the formation of maleic anhydride is elimination of the aldehyde group as formaldehyde, which was identified in the oxidate, and cleavage of the endo peroxide bond of the intermediate ozonidelike compound that is formed during the oxidation of furfural:



The relatively low yield of maleic anhydride (0.5% of the amount of changed furfural) is evidence that the oxidation of the furan ring is not the primary reaction in the reaction of furfural with molecular oxygen.

EXPERIMENTAL

A sample of pure furfural (2500 ml) was oxidized with molecular oxygen at 100° for 72 h at an O_2 flow rate of 200 ml/min. The oxidate was extracted with benzene after removal of the volatile reaction products by distillation. A fraction with bp 80-100° (6 mm) was isolated from the benzene extract and separated with a UKh-1 chromatograph with a preparative column (500× 0.8 cm) containing 25% PEGA (polyethylene glycol adipate) on Chezasorb (0.36-0.58 mm) at 165° and a helium flow rate of 40 ml/min. The retention time of maleic anhydride was 9.0 min.

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