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Liquid-Phase Catalytic Oxidation of 5-Methylfurfural

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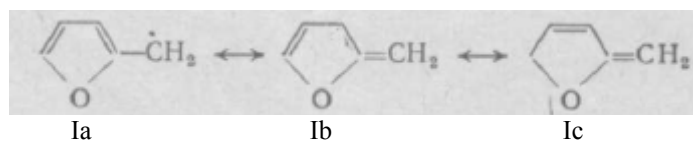
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Liquid-phase catalytic oxidation of 5-methylfurfural has been poorly investigated. Liquid-phase oxidation of 5-methylfurfural with hydrogen peroxide was previously studied [1-3]. The reaction products are β -acetylacrylic acid, levulinic acid and other compounds.

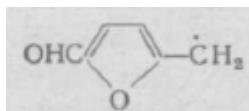
In order to develop a catalytic method for synthesis of 2,5-furandicarboxylic acid, we investigated oxidation of 5-methylfurfural with atmospheric oxygen under pressure in the presence of a cobalt-manganese catalyst and bromine-containing compounds as initiators in acetic acid solution. 2,5-Furandicarboxylic acid, 2,5-furandialdehyde, 5-formyl-2-furancarboxylic acid and also products of destruction of the 5-methylfurfural molecule (oxalic acid and other compounds) were detected in the products of oxidation of 5-methylfurfural.

Under optimal conditions of liquid-phase oxidation of 5-methylfurfural to 2,5-furandicarboxylic acid, the yield of the latter is 36 mol%.

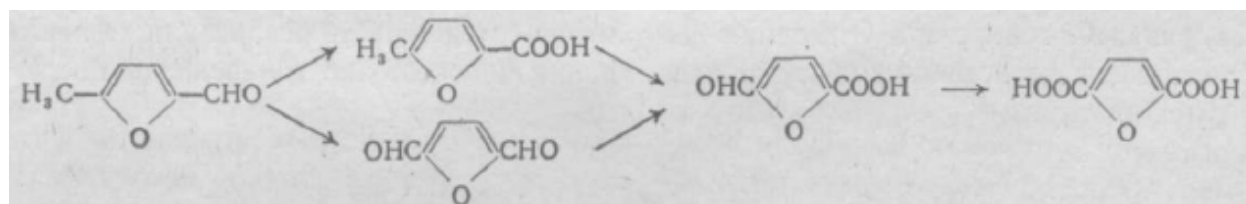
Formation of 2,5-furandialdehyde as intermediate suggests that (together with oxidation of the aldehyde group) the first stage of the reaction is oxidation of the methyl group of 5-methylfurfural. Similar to formation of 2-furanylmethyl radical (Ia), having resonance hybrids (Ib) and (Ic) [4],



we can assume that the 5-formyl-2-furanylmethyl radical is one of the leading radicals of oxidation during liquid phase oxidation of 5-methylfurfural



Apparently liquid-phase oxidation of 5-methylfurfural to 2,5-furandicarboxylic acid occurs according to a parallel-consecutive scheme through formation of 5-methyl-2-furancarboxylic acid and 2,5-furandialdehyde:



The mentioned reactions are accompanied by oxidative cleavage of the furan ring, which is responsible for the comparatively low selectivity of oxidation of 5-methylfurfural to oxygen-containing derivatives of the furan series in comparison with the selectivity of oxidation of alkylbenzenes to corresponding aromatic carboxylic acids. Thus, during liquid-phase oxidation of pseudocumene at 130-150°C, at concentrations of pseudocumene of 0.2-0.3 mol/L, Co^{2+} acetate $0.75 \cdot 10^{-2}$ mol/L, Mn^{2+} acetate $0.89 \cdot 10^{-3}$ mol/L, ammonium bromide $0.85 \cdot 10^{-2}$ mol/L, air pressure 10-15 kg/cm², the yield of trimellitic acid is 83 mol%.

Thus, liquid phase oxidation of 5-methylfurfural with atmospheric oxygen in the presence of a cobalt-manganese catalyst is a one-stage method for synthesis of 2,5-furandicarboxylic acid. Only multistage methods are known for preparation of the latter [5-9].

If during liquid-phase oxidation of 5-methylfurfural with hydrogen peroxide products of oxidative hydrolysis and lactones are obtained, then during catalytic oxidation of 5-methylfurfural with atmospheric oxygen, 2,5-furandicarboxylic acid and other oxygen-containing compounds of the furan series are obtained.

Experimental Part

The studies were conducted at 100 to 135°C, initial concentration of 5-methylfurfural of 0.5-0.9 mol/L, cobalt acetate 0.06-0.09 mol/L, manganese acetate $(0.8-1.5) \cdot 10^{-3}$ mol/L and ammonium bromide $(3.5-5.0) \cdot 10^{-3}$ mol/L, air consumption 1.5 L/min per 1 L of reaction mixture, air pressure 10-30 kg/cm². Liquid-phase oxidation of 5-methylfurfural was investigated using an

apparatus for oxidation of liquefied hydrocarbon gases UOSUG-12M with a teflon coating on the inside surface of the reactor.

The content of unreacted 5-methylfurfural, 2,5-furandialdehyde and 5-formyl-2-furancarboxylic acid was determined by polarographic methods on an electronic self-regulating polarograph PE-312 (characteristics of the capillary 2.47 mg/s, $t = 1.90$ s). 0.1N HCl was used as inert electrolyte. To plot the calibration curves in determining 2,5-furandialdehyde, 5-formyl-2-furancarboxylic acid and 5-methylfurfural we used polarographic waves with $E_{1/2}$ -0.36; -0.71; -0.93 V respectively.

The amount of 2,5-furandicarboxylic acid in the form of dimethyl ester was determined by gas-liquid chromatography, using a mixture of 3% polyethylene glycol adipate and 1% H_3PO_4 applied to chromosorb W as stationary phase. Flame ionization detector. Column temperature 170°C. Diethyl phthalate was used as internal standard.

Catalytic synthesis of 2,5-furandicarboxylic acid was accomplished as follows. 6.6 g (0.06 mol) 5-methylfurfural, 1.868 g ($0.75 \cdot 10^{-2}$ mol) cobalt acetate, 0.024 g ($0.1 \cdot 10^{-3}$ mol) manganese acetate and 0.041 g ($0.4 \cdot 10^{-3}$ mol) ammonium bromide are charged to the reactor, 100 mL acetic acid is added and the reaction run for 4.5 hours at a temperature of 118°C and a pressure of 20 atm, air consumption 2 L/min per 1 L of reaction mixture. The temperature is then raised to 130°C, the pressure to 30 atm, the air consumption to 5 L/min. The process is run to complete termination of oxygen absorption (1.5 h). The product of oxidation is cooled, the precipitate filtered off and dried at 100°C. The amount of unreacted 5-methylfurfural is 0.58 g (8.8%). The obtained 2,5-furandicarboxylic acid is purified by recrystallization from water. Yield of 2,5-furandicarboxylic acid 3.26 g (36 mol%), mp > 320°C. Found, %: C 46.07, 45.79; H 2.56, 2.56. $C_6H_4O_5$. Calculated, %: C 46.16; H 2.58.

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