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CATALYTIC OXIDATION OF FURAN AND HYDROFURAN COMPOUNDS.
8.* CONVERSIONS OF 2(5H)-FURANONE BY HYDROGEN PEROXIDE IN MEDIA OF VARIOUS pH

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The reaction of 2(5H)-furanone with aqueous hydrogen peroxide in media of pH within the range 1-8 have been studied in the absence of catalysts for the first time. It was discovered that at pH 3 to 8 2(5H)-furanone was almost quantitatively converted into succinic acid and reduction of the acidity of the medium facilitates the reaction. A possible scheme is considered for the conversions of 2(5H)-furanone under the reaction conditions.

Keywords: hydrogen peroxide, 2(5H)-furanone, succinic acid, buffer solutions.

In the previous paper we described the synthesis of 2(5H)-furanone (**1**) from furfural and some of its reactions, including oxidation by the action of H_2O_2 in the presence of compounds of Mo(VI) and Cr(VI) at pH 1-2 , which proceeded with extreme difficulty [1].

Results are given in the present communication on an investigation of the interaction of furanone **1** with aqueous hydrogen peroxide in media of pH 1-8 in the absence of compounds of variable valency metals. This reaction, not studied systematically hitherto, is of independent interest for the chemistry of hydrofuranones, particularly for raising the possibility of the selective synthesis of individual products.

The reaction of furanone **1** with H_2O_2 at various pH values was investigated in buffer solutions with initial concentrations of reactants from 1.0 and 1.5 M respectively, and initial ionic strength of 3 M the same in all experiments. The consumption of starting materials, the accumulation of products, and the final composition of the reaction mixtures was followed by titrimetry, and also spectral methods, paper chromatography (PC), and TLC. On carrying out the reaction in each of the pH intervals studied an appropriate temperature was maintained sufficient for the complete conversion of furanone **1** after 5 h (see Table 1).

Reaction was not carried out at pH >8 due to the active decomposition of H_2O_2 under these conditions.

As is seen from Table 1 reduction in the acidity of the medium contributed to a more intensive proceeding of the reaction. It was carried out at pH 7-8 with the most significant evolution of heat and most readily. It is noteworthy that at pH ~1 and temperature of 100°C furanone **1** underwent no conversion.

The oxidation of furanone **1** in experiments 1-5 was completed almost quantitatively with the formation of succinic acid. Organic peroxide was detected chromatographically in the intermediate stages of the reaction. Succinic acid was isolated in ~60% yield of theoretical from the reaction systems. The losses of this product are

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* For Part 7 see [1].

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TABLE 1. Conditions for the Complete Conversion of 2(5H)-Furanone (**1**) after 5 h at Molar Ratio of **1** to H_2O_2 of 1.0:1.5

Experiment	pH	Temperature, °C
1*	3-4	95-100
2	4-5	70-75
3	5-6	60-65
4	6-7	40-45
5	7-8	20-25

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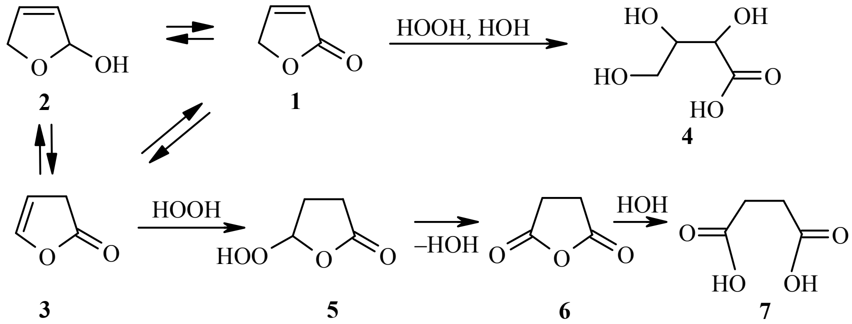
* Conversion was 50%.

related to the difficulty of separating it from the components of the buffer. Trace amounts of malic and an unidentified hydroxy acid were also formed. It should be mentioned that maleic and fumaric acids invariably accompanying furanone **1** on peroxide oxidation of furfural were not detected on oxidizing furanone **1** itself.

To explain the formation of succinic acid from furanone **1** we proceeded from the known data on its isomerization to the less stable 2-hydroxyfuran **2** and 2(3H)-furanone **3** [2].



The irreversible conversion of isomer **1**, **2**, or **3** must lead to a shift in the equilibrium in that direction. In the reaction being studied this is possible by the action of aqueous H_2O_2. It is known that an increase in pH leads to growth of the nucleophilicity of H_2O_2 [3]. Among the isomers **1-3** the greatest reactivity in reaction with nucleophilic reagents would be expected for lactones **1** and **3**, since hydroxyfuran **2** has an increased ring electron density. A possible product of the interaction of compound **1** with H_2O_2 is 2,3,4-trihydroxybutanoic acid **4**, which if formed by the reaction, then as mentioned above would be in insignificant amount together with malic acid. We consider it most probable that succinic acid is formed by irreversible oxidation–hydrolytic conversions of isomer **3**, including the formation of hydroperoxide **5**, which is converted into succinic anhydride **6**, itself hydrolyzed in the reaction media to succinic acid **7**.

EXPERIMENTAL

The TLC was carried out on Sorbfil plates, eluent was $CHCl_3$, visualizing agent was acidic $KMnO_4$ solution (for furanone **1** and the oxidized compounds), or KI solution (for peroxy compounds). Paper chromatography (PC) was carried out on No. 2 paper, eluent was BuOH saturated with water and HCOOH, visualizing agent was an alkaline solution of bromophenol blue (for acids) or acidic $KMnO_4$ solution (for hydroxy acids and unsaturated acids). The IR spectra were obtained on an UR 20 spectrometer in nujol. The total acidity was determined by alkalimetric titration with thymolphthalein.

Oxidation of 2(5H)-Furanone (1). Aqueous solution (10 ml) of furanone **1** (5.0 g, 60 mmol) was stirred with 30% aqueous solution of H_2O_2 (50 ml, 10.2 g, 90 mmol), KOH (6.7 g, 120 mmol), and H_3PO_4 (86 wt, %; 6.8 g, 60 mmol). The reaction was carried out at pH 7-8 until complete consumption of compound **1** (TLC). To maintain the pH in the prescribed range the acid formed was neutralized periodically by adding aqueous KOH (12 M). Test samples for the analysis of total acidity, TLC, and PC were taken directly after mixing the reactants, then after 15, 30, 75, 150, and 300 min.

When oxidizing furanone **1** in the pH ranges 6-7, 5-6, 4-5, and 3-4 the amount of KOH was reduced to 5.9 g (105 mmol), 5.0 g (90 mmol), 4.2 g (75 mmol), and 3.4 g (60 mmol) respectively, but for establishing the same initial ionic strength 1.1 g (15 mmol), 2.2 g (30 mmol), 3.4 g (45 mmol), and 4.5 g (60 mmol) of KCl respectively were introduced into the solutions. When oxidizing **1** at pH ~1 KOH was not added to the buffer.

Isolation of Reaction Products. For experiments 2-5 H_3PO_4 was added to the oxidized mixtures to pH 1 and water was distilled off under vacuum. The residue was treated with hot EtOH (100 ml) and insoluble KH_2PO_4 was filtered off. The filtrate was evaporated under vacuum, and the residue recrystallized from water (20 ml). Succinic acid **7** (4.1-4.3 g, 58-61% of theory) was obtained; mp 182-185°C (lit. [4] mp 185°C), R_f 0.80 (PC), which agrees with the R_f of a known sample. The IR spectrum was identical to that given previously in [5]. In the reduced oxidates traces of malic acid (R_f 0.43) and an unknown hydroxy acid (R_f 0.57), possibly 2,3,4-trihydroxybutanoic acid **4,** were detected in addition to acid **7** and H_3PO_4 by PC.

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