COMPARISON OF THE REACTIVITIES OF KETONES AND ALDEHYDES OF THE FURAN SERIES DURING OXIDATION WITH HYDROGEN PEROXIDE

L. V. Tsygankova and V. G. Kul'nevich

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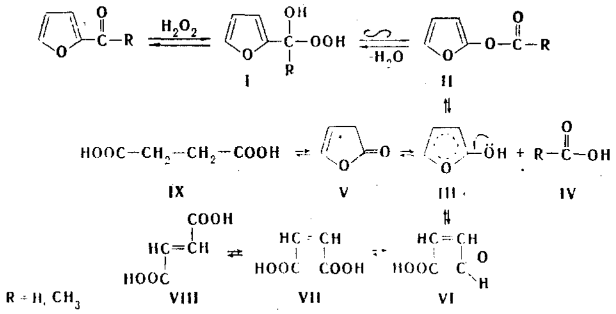
The rates of oxidation of 2-acetylfuran, 5-methyl-2-acetylfuran, furfural, and 5-methylfurfural with hydrogen peroxide were compared. The intermediate and final oxidation products were determined. The possibility of identical reaction mechanisms for furan aldehydes and ketones is demonstrated.

A mechanism for the oxidation of aldehydes of the furan series with hydrogen peroxide, according to which the reaction is considered to be a series of successive ion-molecular processes including a Baeyer–Villiger rearrangement, was proposed and partially experimentally confirmed in [1-3]. It can be assumed that the mechanism of the peroxide oxidation of furan ketones should correspond to the scheme proposed for the aldehydes.



The kinetic investigations of the oxidation of furfural [1] and the isolation and characteristics of the intermediate products (I and II) [3] are evidence in favor of a heterolytic mechanism for the reaction. The primary migration of a furyl group in comparison with hydrogen during the sextet rearrangement of I to II can be explained by the considerable electron-donor properties of the furyl group [4]. The latter explains the absence (sometimes traces) of pyromucic acid in the products of the reaction and the primary direction of the process to favor the formation of β-formylacrylic (VI), maleic (VII), fumaric (VIII), and succinic (IX) acids. β-Acetylacrylic [5] and levulinic acids are formed in the oxidation of 5-methylfurfural.

There is no information in the literature relative to the behavior of furan ketones in peroxide oxidation. It seemed of interest to compare the reactivities of the ketones and aldehydes of the furan series during oxidation with hydrogen peroxide, to uncover some kinetic principles of the process, and to determine the intermediate and final products in order to solve the problem of the reaction mechanism.

The oxidation of 2-acetylfuran (AF), 5-methyl-2-acetylfuran (MAF), furfural (F),* and 5-methylfurfural (MF) was carried out under strictly identical conditions. This series of substances provided a possi-

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*The data on the oxidation of furfural were obtained in collaboration with G. F. Muzychenko and L. A. Badovskaya.

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bility for evaluating the mutual effect of the groups of atoms in the molecules on the reaction rate. The results of the investigations are presented in Figs. 1 and 2 and in Table 1.

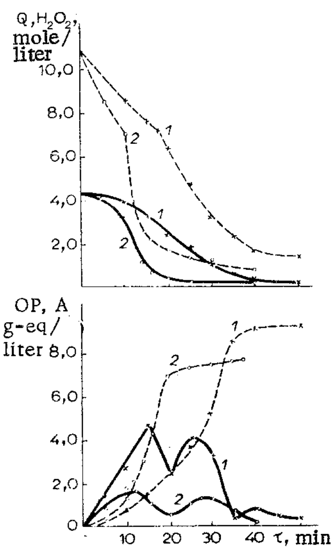

Fig. 1. Oxidation of furan aldehydes with 50% hydrogen peroxide at 60°C for [Q] : $[H_2O_2]$ = 1 : 2.5: 1) F; 2) MF (the continuous lines pertain to Q and OP, while the dash lines pertain to H_2O_2 and A).

The character of the curves of the change in the percentages of carbonyl compounds (Q), hydrogen peroxide, organic peroxide compounds (OP), and acids (A) for the investigated substances is identical (Figs. 1 and 2), but the reaction rates differ markedly. In all cases, the process occurs with a considerable induction period, for which a low rate of change in the percentages of the starting substances and buildup of acids is characteristic, and τ_{ind} is close to $\tau_{1/4}$, which corresponds to a 25% degree of conversion of the carbonyl compound. The induction period terminates as soon as a definite concentration of hydrogen ions is achieved due to the acids that appear during the process; i.e., the reaction has autocatalytic character. This sort of phenomenon can be explained if one takes into account the effect on the reaction rate of prior protonation of the carbonyl group before attack by a H_2O_2 molecule. The effect of protonation is confirmed by experimental data on acid catalysis. Thus for AF the introduction of 0.051 g-eq. of sulfuric acid per mole of ketone in the reaction mixture completely liquidates the induction period and increases the rate constant by a factor of four.

The reaction is apparently first order in carbonyl-containing compounds for all of the investigated substances. The rate constants were determined from the slope of the semilogarithmic anamorphoses and are presented in Table 1. The periods of 25% ($\tau_{1/4}$), 50% ($\tau_{1/2}$), and 75% ($\tau_{3/4}$) conversion of the carbonyl compound are also shown in Table 1, since some data on the rate constants are insufficient for the characteristics of the investigated process (in view of the different durations of the induction period).

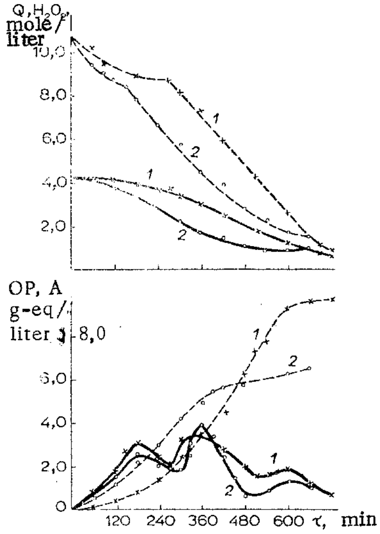

Fig. 2. Oxidation of furan ketones with 50% hydrogen peroxide at 60°C for [Q] : $[H_2O_2]$ = 1 : 2.5: 1) AF; 2) MAF (the continuous curves pertain to Q and OP, while the dash lines pertain to H_2O_2 and A).

A comparison of the UV and IR spectra of AF and F and data on their polarographic reduction [6] demonstrated that the shift in electron density in the furan ketone as compared with the shift in the aldehyde as a consequence of the electron-donor effect of the CH_3 group occurs primarily on the carbonyl group and has virtually no effect on the redistribution of the electron density between the carbonyl group and the heteroring. Hence one should expect identical reactivities for the heteroring in the ketone and aldehyde for the process under consideration. As for the carbonyl group, the reactivity of the carbonyl oxygen with respect to protonation, like the behavior of carbonyl-containing compounds of other classes [7, 8], increases in the furan ketones, and the tendency of the carbonyl carbon to be susceptible to nucleophilic attack decreases. Thus the sharply reduced rate of oxidation of furan compounds by hydrogen peroxide as compared with the rate of oxidation of the aldehydes confirms that the carbonyl group rather than the heteroring is responsible for the process.

A donor methyl group in the 5 position of the furan ring facilitates the reaction, and the acceleration factor is higher for aldehydes than for ketones, which can be explained by the effect of steric hindrance created by the CH_3 group attached to the reaction center.

TABLE 1. Characteristics of the Rate of Oxidation of Furan Ketones and Aldehydes with 50% Hydrogen Peroxide*

Compound	$\tau_{1/4}$, min	$\tau_{1/2}$, min	$\tau_{3/4}$, min	$k \cdot 10^3$, min^{-1}
Furfural	16	23	32	65,8
5-Methylfurfural	10	12	14	253,0
2-Acetylfuran	325	465	615	3,4
5-Methyl-2-acetylfuran	210	310	480	4,3

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*For $[Q] : [H_2O_2] = 1 : 2.5$ at 60°C.

A qualitative analysis of the acids and peroxides in different stages of the reaction demonstrated that the substances formed from the ketone and aldehyde are identical. The major products of the oxidation of both AF and F are β-formylacrylic, maleic, and fumaric acids, while tartaric and succinic acids are present in small amounts. Pyromucic acid is not detected under the given conditions. β-Acetylacrylic and levulic acid are obtained in the oxidation of both MAF and MF. The aldehyde and ketone groups are converted to formic and acetic acids, respectively. In all cases, the reaction is accompanied by buildup and conversion to intermediate stages of considerable amounts of organic peroxide compounds. One of the peroxides was identified in the oxidation of AF as a hydroxyhydroperoxide of furfural (I) – 1-(α-furyl)-1-hydroxy-1-hydroperoxyethane.

The experimental data obtained make it possible to assume that the oxidation of furan ketones and aldehydes with hydrogen peroxide under the examined conditions proceeds via the same mechanism. The dependence of the intensity of the process on the polarity and basicity of the solvent is also evidence for this. A similar dependence was previously demonstrated for F [2].

EXPERIMENTAL

2-Acetylfuran and 5-methyl-2-acetylfuran were synthesized via the method in [9]. Furfural and 5-methylfurfural were purified by vacuum distillation. The oxidation was carried out in a two-necked flask equipped with a stirrer and a reflux condenser. The flask was charged with 0.219 mole of the ketone (or aldehyde) and 0.548 mole of 50% H_2O_2. The reaction temperature was 60 ± 0.1° (with thermostatting).

The percentages of carbonyl compound [10], peroxide compounds, and hydrogen peroxide [11], and the titrable acidity were monitored during the reaction. Qualitative analysis was accomplished by paper chromatography of the acids and thin-layer chromatography of the 2,4-dinitrophenylhydrazones [12] and peroxides. An n-butyl alcohol–formic acid–water (9 : 1 : 4) mixture was used as the solvent for separation of the acids by paper chromatography. The developers were bromphenol blue for the carboxyl group, 2,4-dinitrophenylhydrazine for the carbonyl group, and potassium permanganate for the double bond and hydroxyl group. The peroxides were separated on a fixed layer of aluminum oxide with acetone–carbon tetrachloride–petroleum ether (2 : 1 : 0.5). The developers were a saturated solution of potassium iodide in acetic acid and 2,4-dinitrophenylhydrazine. Acetic and formic acids were determined by gas-liquid chromatography with a PAKhV-03 chromatograph with a 2-m-long column. The liquid phase was polyethylene glycol-1500, the solid support was Cellite, the column temperature was 120°, and the gas (hydrogen)-carrier flow rate was 120 ml/min.

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