ROLE OF PYROMUCIC ACID IN THE AUTOOXIDATION OF FURFURAL

I. OXIDATION OF PYROMUCIC ACID IN WATER

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Pyromucic acid (PA) in aqueous solution is oxidized by molecular oxygen with opening of the furan ring and formation of β-formylacrylic, fumaric, and formic acids. The process is accompanied by the interlinked oxidative decarboxylation of PA and the acids formed from it. PA is the major intermediate in the autooxidation of furfural. When PA and furfural are cooxidized,the rate of transformation of each compound increases by a factor of two; this is a sign of the interlinking of two radical processes evolving in one system. A probable scheme for the oxidation of PA in water by molecular oxygen is proposed.

The yield of pyromucic acid (PA) in the autooxidation of furfural does not exceed 10%, based on the amount of absorbed oxygen. In this connection, PA is considered to be a side product [1, 2], and it is assumed that the chief direction of attack by oxygen is the furan ring rather than the aldehyde group of furfural. These concepts are valid only if PA is a final, stable product which only accumulates but is not consumed. It has repeatedly been noted in studies of the autooxidation of furfural that the total acidity increases up to a certain limit, after which one observed a decrease; this is associated with polymerization of the acids [3, 4] or their adsorption by resins [2]. In addition, there are data [5] that PA in aqueous solutions in sunlight is oxidized by oxygen to β-formylacrylic acid, while succinic acid is decomposed to formic acid and CO_2. We have established [6] that pyromucic acid is the first of the acids to appear in the oxidation of furfural with oxygen, and the other acids are formed only after a certain time. The amount of PA decreases during the process and, at the end of the experiment, either vanishes completely or is present in very small quantities. Thus the analytically determined values do not reflect the entire quantity of acids formed but only their equilibrium concentrations at a given period.

In this investigation we examine the behavior of PA in aqueous solutions under the conditions for autooxidation of furfural in order to elucidate its role in the autooxidative transformations of furfural.

The observations were made at room temperature for dilute (10^{-5} M) PA and furfural (F) solutions; this made it possible to create the required excess of dissolved oxygen and also to exclude the possible effect of polymerization of PA or its adsorption by resins during cooxidation with furfural. PA gradually disappears under the influence of molecular oxygen (Fig. 1, I) and is converted to compounds with low molar extinctions which do not have characteristic absorption bands in the near-UV zone. PA (λ_{max} 245 nm) is initially formed from furfural, and the percentage of it reaches a maximum corresponding to the instant of complete decomposition of furfural (Fig. 1, II, and IV, curves b and c). After this, the rate of decomposition of PA becomes the same as for sample I [kinetic curve a is parallel to the descending branch of curve c (Fig. 1, IV)]. A similar picture is observed during examination of the behavior of an equimolecular mixture of F and PA (Fig. 1, III). However, a comparison of kinetic curves b and d indicates that, in the absence of PA, the rate of transformation of furfural is initially lower by a factor of 1.7 than for the mixture of F and PA. PA therefore accelerates its decomposition. The yield of PA under the conditions used is 83-

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TABLE 1. Change in the Composition of an Aqueous PA Solution at 100° (O_2 = 89% and N_2 = 11% above the solution)*

τ, h	PA	PA decomposition products				
		A	H_2O_2	P	FP, h,† cm/liter	
		10^{-3} N			$\varepsilon_{\frac{1}{2}} = -0,48$	$\varepsilon_{\frac{1}{2}} = -0,78$
Start (4 min)	56,2	2,0	2,1	1,5	1,2	1,9
1	55,4	3,1	5,4	2,9	2,8	3,3
2	54,5	6,2	4,3	4,6	3,7	4,7
4	53,5	6,9	4,0	2,9	5,6	8,2
5	52,6	7,8	3,3	2,9	6,4	9,5

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*The following symbols were adopted in the tables and graphs: τ is the heating time, A denotes acids without PA, P are peracids, FP are polarographically reduced furan peroxides, FAA is β-formylacrylic acid, and FA is fumaric acid.

†h denotes the polarograph readings under the standard conditions used to carry out the analysis.

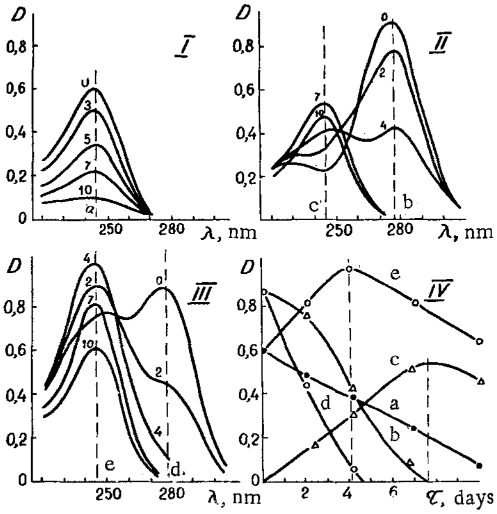


Fig. 1. Transformations of pyromucic acid and furfural in water at 25°, (PA) = $5.35 \cdot 10^{-5}$ M, (F) = $5.35 \cdot 10^{-5}$ M (the numbers on the curves are the times in days); a, b, c, d, and e): portions of spectra I-III from which the corresponding kinetic curves in graph IV are constructed; I) PA; II) F; III) PA:F = 1:1.

87%, i.e., it is the major product of the oxidative transformations of furfural in water but is an unstable compound.

The oxidation of PA in 10^{-2} M solutions is markedly accelerated on heating to 100-150° with an excess oxygen pressure of 10-15 atm (Table 1 and Fig. 2). Hydrogen peroxide, peracids, and furan peroxides (with half-wave potentials of -0.48 ± 0.02 V and -0.78 ± 0.04 V), the concentrations of which increase rapidly to a certain maximum and then drop, appear immediately after preparation of the solution. This indicates that peroxides are intermediates and themselves participate in secondary oxidative reactions. β-Formylacrylic, fumaric, and formic acids were detected among the acids formed. The gas phase contains carbon dioxide, the yield of which at 150° is 45 to 46 mole % of the converted PA.

When the partial pressure of oxygen above the solution is decreased by a factor of seven to eight, the rate of transformation of PA and the rate of formation from it of peroxides and acids are decreased by a factor of ~2.5 (Fig. 2). The qualitative composition of the oxidation products remains the same, but the quantitative ratios change: the peroxides only accumulate, i.e., the stage where their rate of formation is greater than their rate of consumption has not yet occurred. The major component in the mixture of acids formed becomes β-formylacrylic acid, and only traces of fumaric acid are detected. Just the opposite is true when excess oxygen is present. This is a consequence of a decrease in the oxidation potential of the system. In addition, carbon dioxide is not detected in the gas phase despite the fact that up to 30% of the PA has decomposed at the end of the experiment. Carbon dioxide is clearly manifested even at 100° (when only 7% of the PA has decomposed) when there is excess oxygen above the solution. Depending on the conditions, the ratio of the sum of the acids formed to the amount of transformed PA varies (Table 2). At 100° and high oxygen partial pressures, ΔA/ΔPA is considerably greater than unity, which attests to the formation of several carboxyl groups during the decomposition of one PA molecule. At 150° (O_2 = 89%) decarboxylation acquires greater significance and the acidity decreases. When the oxygen pressure is decreased, β-FAA forms and accumulates in the solution.

TABLE 2. Dependence of the Composition of the Acids in the Oxidate on the Conditions Used to Oxidize PA in Water (based on converted PA)

τ, h	$\Delta PA \cdot 10^3$ N	$\Delta A \cdot 10^3$ N	$\Delta A/\Delta PA$	β-FAA/ FA	CO_2, mole %
100°; above the solution O_2 = 89 %					
1	0,8	1,1	1,25	<1	2—3
2	1,7	4,2	2,48		
3	2,7	4,9	1,83		
5	3,6	5,8	1,65		
150°; above the solution O_2 = 89 %					
1	5,0	4,9	0,98	≪1	45—46
2	9,6	9,1	0,95		
3	14,9	13,6	0,91		
4	20,2	20,6	1,02		
5	20,2	17,2	0,86		
150°; above the solution O_2 = 12 %					
1	1,7	1,6	0,94	≫1	Traces
2	3,2	3,1	0,97		
3	4,6	4,5	0,98		
4	5,8	5,7	0,98		

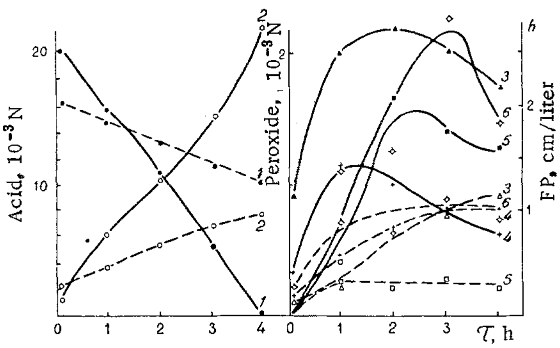
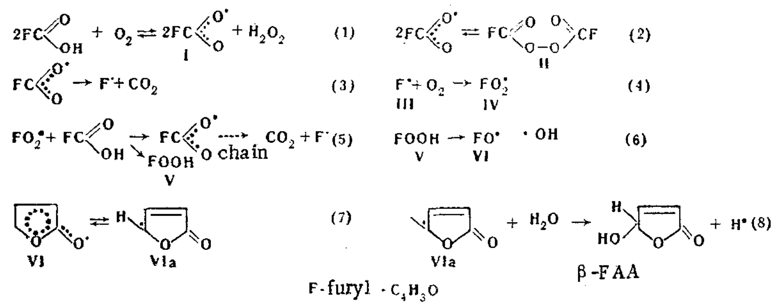


Fig. 2. Decomposition of pyromucic acid in water at 150°; the solid line represents data for O_2 = 89% and N_2 = 11% (PA = $20.2 \cdot 10^{-3}$ M), while the dash line represents data for O_2 = 12% and N_2 = 88% (PA = $16.1 \cdot 10^{-3}$ M): 1) PA; 2) A (○); 3) H_2O_2 (△); 4) P (+); 5) FP (□) ($\varepsilon_{1/2} = -0.48$ V); 6) FP (–|–) ($\varepsilon_{1/2} = -0.78$ V).

The dependence of the rate of formation of CO_2 on the O_2 pressure indicates that oxidation of PA evolves as a process of interlinked oxidative decarboxylation [7] and is not a consequence of thermal decomposition of pyromucic and other acids present in the system.

Furfural accelerates the oxidation of PA, and PA in turn substantially increases the rate of decomposition of furfural. At 150°, for separate oxidation, the half-decomposition times for PA and F are 2.1 h and 2.3 h, respectively. When PA:F = 1:6, $\tau_{1/2}$ is 1.1 and 1.2 h, respectively, i.e., the rate of oxidation of each component in the mixture increases by a factor of 2. The composition of the oxidate remains the same as in the separate oxidation of PA and F, but maleic acid is found instead of the acids listed above. A total of 2.4 moles of CO_2, i.e., 41.5% of the amount which would be obtained from complete combustion of both compounds to CO_2 and H_2O, is formed from 1 mole of F and 0.16 mole of PA. This demonstrates convincingly that the monobasic acids as well as the dibasic acids undergo oxidative decarboxylation.

The experimental data obtained make it possible to propose a mechanism for one of the probable paths for the transformations of PA in water under the influence of molecular oxygen.



Chain propagation can be accomplished only via reaction (1) since the polar O – H bond in the carboxyl group reacts more readily than a nonpolar bond, although somewhat less readily than the strong C – H bond [8]. The furoyloxy radical (I) formed is stabilized by conjugation, which lowers the energy for its formation and is the reason for the low reactivity. Conjugation is aggravated by solvation of the radical by polar water molecules. As a result, I is not in a state to carry on the chain, and it therefore is either decarboxylated or recombines to difuroyl peroxide (II). Furyl radical III in the presence of oxygen is immediately converted to furyl peroxide radical IV, which reacts with new PA molecules [reactions (3), (4), and (5)]. This evolving of a chain process is unusual since the chief radical (III) propagating the kinetic oxidation chain arises not as a result of cleavage of a hydrogen from the PA molecule but as a consequence of its interlinked oxidative decarboxylation (5). As hydroperoxide V accumulates,the initial reaction may be somewhat accelerated due to $\mathrm{F\dot{O}}$ and $\mathrm{\mathring{O}H}$ radicals [degenerate branching (6)], but homolysis of the hydroperoxide is insignificant in a polar medium. The major portion of the H_2O_2 and organic peroxides is consumed by a nonchain route. It is extremely likely that radical VI rearranges (7) to VIa with subsequent formation of β-formylacrylic acid, which is then oxidized to maleic and fumaric acids. The predominant evolution of reactions (2) or (3) depends on the conditions (primarily the temperature). When the temperature is raised, the hydrogen bonds are weakened, the stability of the $\mathrm{FC\mathring{O}_2 \ldots mH_2O}$ complex radical decreases, and the rate of decarboxylation increases, which is in agreement with the experimental results.

The cooxidation of PA and F is an example of crossover reactions of two chain processes evolving in a single system [8, 9]. In the process, additional chain propagation and chain termination reactions appear, and the prerequisites for acceleration or retardation of the rates of transformations of the components of the mixture are created.

EXPERIMENTAL

Recrystallized PA with mp 128° and freshly vacuum-distilled furfural, which did not contain peroxides and acids, were used for the investigations. The experiments were carried out with an apparatus [10] that made it possible to accomplish the kinetic investigations during heating at high pressures of an oxygen–nitrogen mixture under isothermal conditions (± 1°). The dilute (10^{-5} M) solutions were stored at room temperature in glass flasks with free access to the air. PA and F were determined by a computational spectrophotometric method [11], hydrogen peroxide was determined by cerimetry [12], the peracids were determined by iodometry [12], and the organic acids were determined by titration with 0.05 N KOH. The composition of the acids was determined by paper chromatography and by polarography on a background of 0.3 M LiCl, carbon dioxide was determined with a UKh-1 gas chromatograph and a GPKh-3M gas analyzer, and the furan peroxides were determined with a P-60 polarograph on a background of 0.3 M LiCl.

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