## STUDY OF THE MECHANISM OF RECYCLIZATION OF FURANS INTO THIOPHENES AND SELENOPHENES IN CONDITIONS OF ACID CATALYSIS. 4.\* STUDY OF THE EFFECT OF THE SOLVENT AND DIRECTION OF REACTIONS OF HYDROLYSIS AND RECYCLIZATION OF 2,5-DIMETHYLFURAN

## T. I. Gubina, V. I. Labunskaya, G. K. Kornienko, L. A. Borodina, and V. G. Kharchenko

The kinetics of hydrolysis of 2,5-dimethylfuran and its recyclization into the corresponding thiophene were investigated in water—alcohol medium in 95, 80, and 50% ethyl alcohol in the presence of HCl. It was found that the rates of these reactions are a function of both the initial concentration of the acid component and the concentration of water in the alcohol. The rate of hydrolysis is a function of the dilution of the alcohol to a greater degree than the rate of recyclization.

We continued the investigation of recyclization of furans into thiophenes and selenophenes under the effect of nucleophiles in conditions of acid catalysis in the present study. It was previously found that the rate of recyclization of furans in absolute alcohol is a linear function of the concentration of acid [2]. When the process was conducted in 95% alcohol in the presence of hydrochloric acid (2.4 M), hydrolysis took place at the same time as recyclization [3]. The study of the behavior of mono-, di-, tri-, and tetraalkylfurans in recyclization and hydrolysis reactions showed that the rate of these reactions is a different function of the position of the substituents in the furan [1].

The results of kinetic studies of recyclization and hydrolysis of 2,5-dimethylfuran (I) in water—alcohol media with different concentrations of ethyl alcohol (95, 80, and 50%) and the acid component (1.5-3.5 M) are reported here. The reactions were conducted in identical conditions: at a constant temperature of  $35^{\circ}$ C with energetic stirring of the reaction mixture. The evolution of the reactions was monitored with GLC. The reaction rate was estimated both by the change in the concentration of starting compound I and by accumulation of the target products, 2,5-dimethylthiophene (II) and 2,5-hexanedione (III). In the calculations of the quantitative composition of the samples, *o*-xylene was used as the internal standard.

The analysis of the kinetic curves of consumption of furan in water—alcohol media showed that the recyclization reaction is first-order in 2,5-dimethylfuran and can be numerically expressed with the effective rate constant of a first-order reaction ( $\kappa_{ef}$ ). It also follows from Table 1 that for low concentrations of the acid component (1.5-2.0 M), the rate of consumption of furan increases in going from 95 to 50% ethanol, and the rate of formation of thiophene changes analogously. For 2.5-3.5 M concentrations of the acid component, the rate of consumption of furan and formation of thiophene is a function of the concentrations of the acid to a greater degree and of dilution of the alcohol to a smaller degree. In this range of concentrations of HC1, recyclization takes place with the highest rate in absolute alcohol [2]. In going to water—alcohol solutions, the highest recyclization rate is in 80% ethanol (see Table 1). The shapes of the kinetic curves for compounds I, II, and III in 80 and 50% ethanol (Figs. 1-4) indicate that hydrolysis and recyclization take place parallelly, but the last reaction is the only one in 80% ethanol for  $C_{HC1} = 3.5$  M.

<sup>\*</sup>See [1] for Communication 3.

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Concentration of ethanol, wt. %	c <sub>HCI</sub> , M	$\kappa_{\rm ef} \cdot 10^{-4} \cdot {\rm sec}^{-1}$	∗2. mole/liter min
05	1.5	0.40	0.35
95	1,5	0,40	0,25
	2,0	1,21	0,55
	2,5	1,62	0,81
	3,0	1,89	1,10
	3,5	2,03	1,42
80	1,5	0,85	0,35
	2,0	1,62	0,60
	2,5	2,03	1,00
	3,0	2,07	1,51
	3,5	2,31	2,13
50	1,5	1,10	0,50
	2,0	1,75	0,91
	2,5	3,06	1,25
	3,0	3,10	1,30
	3,5	3,15	1,37
	⊂ Mole/liter		
	90 70 30 20 50 900	W(V) K0 200 / 200 / min	

TABLE 1. Rates of Consumption of 2,5-Dimethylfuran ( $\kappa_{ef}$ ) and Formation of 2,5-Dimethylthiophene ( $\kappa_2$ ) as a Function of the Concentration of Alcohol and Acid Component





Fig. 2. Kinetic curves of recyclization of 2,5-dimethylfuran I in 2,5-dimethylthiophene II in 50% ethanol for  $C_{\rm HCl} =$  3.5 M.

The use of water—alcohol media thus increases the rate of recyclization to some degree, probably due to the better solubility of hydrogen sulfide in them, and the effect of the elevated protonation power of hydrogen chloride in this medium is also possible.

Hydrolysis of furans has been sufficiently studied. However, the data from kinetic studies of the mechanism of hydrolysis are contradictory. A mechanism of overall acid catalysis is proposed for hydrolysis of furans in [4], while a mechanism of specific acid catalysis is suggested elsewhere [5-7]. In the cited sources, kinetic studies of hydrolysis of furans were conducted in aqueous solutions of perchloric acid and the only product of the reaction was the corresponding 1,4-dicarbonyl compound. It is also known that treatment of furan and sylvan with an alcohol solution of hydrogen chloride causes the formation of succinaldehyde and levulinaldehyde acetals, respectively [8].



Fig. 3. Kinetic curves of recyclization of 2,5-dimethylfuran I into 2,5-dimethylthiophene II in 80% ethanol for  $C_{\rm HCl} = 1.5$  M.



Fig. 4. Kinetic curves of recyclization of 2,5-dimethylfuran I into 2,5-dimethylthiophene II in 80% ethanol for  $C_{\rm HCl} = 3.5$  M.

We investigated the kinetics of hydrolysis of 2,5-dimethylfuran in 80 and 50% ethyl alcohol. A comparison of the rate constants of hydrolysis and recyclization in 80% ethanol (see Table 2) showed that the recyclization rate is a function of the concentration of the acid component to a greater degree, and for the same acidity of the medium, it is higher than the rate of hydrolysis. It was not possible to determine the rate constant of this reaction for the indicated concentration of alcohol, since compound I was not present in the first samples of the reaction mixture, but two products were observed. One was 2,5-hexanedione III. It was not possible to establish the structure of the second compound, since it easily turned into diketone III when we attempted to separate it. By analogy with the data in [8], formation of ketal (IV) or its semiketal (V) probably takes place:



The study of the kinetics of hydrolysis of 2,5-dimethylfuran in 50% ethanol showed that for low concentrations of HCl, the ratio of products III and IV (V) varied over 24 h with some periodicity. Equilibrium of compounds III and IV (V) was rapidly established for high concentrations of the acid component (Fig. 5). The formation of products III and IV (V) was also observed in conducting recyclization of compound I in 50% ethanol, but in this case, equilibrium of compounds III and IV (V) was also established (see Figs. 1 and 2). More precise definition of these compounds requires additional study and will be the subject of our future research.

TABLE 2. Rates of Hydrolysis and Recyclization of 2,5-Dimethylfuran as a Function of the Concentration of Acid Component in 80% Ethanol

	$\kappa_{\rm ef} \cdot 10^{-4}$ , sec <sup>-1</sup>		
Снсі, М	hydrolysis	recyclization	
1,5		0,85	
2,0	0,73	1,62	
2,5	0,83	2,03	
3,0	1,24	2,07	
3.5	1.60	2.31	



Fig. 5. Kinetic curves of hydrolysis of 2,5-dimethylfuran I into compounds III and IV (V) in 50% ethanol for  $C_{\rm HCl} = 2.0$  and 3.5 M.

## EXPERIMENTAL

The evolution of recyclization and hydrolysis of 2,5-dimethylfuran was monitored on a Tsvet-101 chromatograph with a flame-ionization detector,  $(1.53 \text{ m} \times 3 \text{ mm})$  column with 15% Apiezon L on Chromaton N-AW-DMCS, helium or nitrogen carrier gas, and temperature of 160°C.

2,5-Dimethylfuran, 2,5-dimethylthiophene, and 2,5-hexanedione were prepared by the methods in [2, 3].

Kinetic Studies of Recyclization of 2,5-Dimethylfuran (I) in 95, 80, and 50% Ethyl Alcohol. A three-neck, 50-ml reactor thermostated at  $35\pm1^{\circ}$ C and equipped with a magnetic stirrer, reflux condenser, and bubbler was filled with 30 ml of hydrogen chloride solution in ethanol containing water (see Table 1 for the concentrations of HCl and EtOH) and saturated with hydrogen sulfide for 1.5 h. Then 0.72 g (0.0075 mole) of compound I and 0.21 g (0.0019 mole) of *o*-xylene (internal standard for subsequent analyses) were added, and counting of the reaction time began. At certain intervals, 1-ml samples were taken from the reaction mixture, neutralized with 2 ml of basic solution of the appropriate concentration (see concentration of solutions of HCl), and extracted with 1 ml of ether. The composition of the extracts obtained was determined by GLC. The rate constants were calculated with the tangent of the slope of the corresponding anamorphoses.

Kinetic Studies of Hydrolysis of 2,5-Dimethylfuran (I) in 95, 80, and 50% Ethyl Alcohol. Hydrolysis of compound I was conducted with the described method except for saturation of the reaction mixture with hydrogen sulfide. The evolution of the reaction was monitored with GLC as described above.

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