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MECHANISM OF RECYCLIZATION OF FURANS TO THIOPHENES AND SELENOPHENES UNDER ACID CATALYSIS.

1. KINETIC STUDIES OF THE REACTION OF 2,5-DIALKYLFURANS WITH HYDROGEN SULFIDE IN THE PRESENCE OF HYDROCHLORIC ACID

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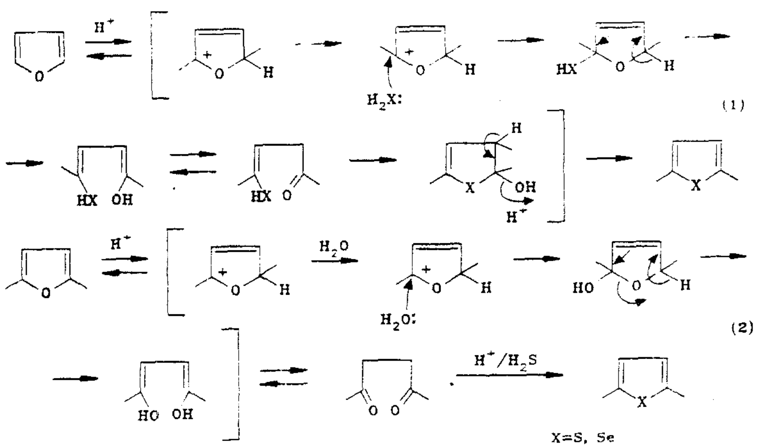
The transformation of 2,5-dialkylfurans to thiophenes by reaction with hydrogen sulfide in the presence of hydrochloric acid was studied. The reaction was found to be first order with respect to the furan; the rate of consumption of the furan did not change with increasing length of one of the alkyl substituents. Recyclization in the presence of acid proceeds in two independent directions: through the formation of an intermediate dicarbonyl compound, and by direct conversion of the furan to a thiophene. Kinetic data showed that the reaction occurs mainly by the second route.

Earlier we reported the acid-catalyzed recyclization of furans to thiophenes and selenophenes [1-4]. The aim of the present round of work is to study the mechanism of this chemical change.

Based on existing experimental and literature data [2, 3] the following reaction mechanism was proposed:



The important step in scheme (1) is the protonation of the α-carbon atom of the furan ring, and this is followed by nucleophilic attack by a hydrogen sulfide or a hydrogen selenide molecule, leading in the end to the formation of thiophene or selenophene.

When the process was carried out in the presence of concentrated acid (HCl, $HClO_4$), i.e., with a competing nucleophile (a water molecule) present, in addition to the desired reaction product, the 1,4-dicarbonyl compound was also formed [3]. Based on this, we proposed that

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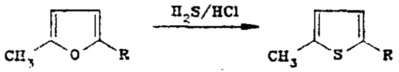
the formation of the thiophene or selenophene can also proceed by path (2), including the stage in which the 1,4-dicarbonyl intermediate is formed.

To explain the mechanism of the reaction of furans with hydrogen sulfide and hydrogen selenide in ethanol solution in the presence of concentrated acids, we studied the kinetics of the reaction. Identical results were obtained for the reaction of the furans with hydrogen sulfide and with hydrogen selenide, and kinetic studies were therefore carried out on a sample reaction between 2,5-dialkylfurans and hydrogen sulfide in the presence of concentrated hydrochloric acid:

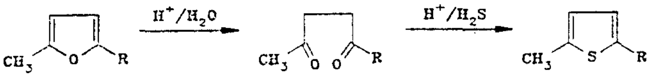


a $R=CH_3$; b $R=C_2H_5$; c $R=C_3H_7$; d $R=C_4H_9$

Kinetic studies were carried out in a closed system; the concentration of hydrogen sulfide was maintained at a constant value during the course of the reaction. The reaction was followed chromatographically; kinetic curves were constructed describing the change of concentration of each component of the reaction mixture.

Figure 1 shows the kinetics of the recyclization of 2,5-dimethylfuran (Ia) to 2,5-dimethylthiophene (IIa) and 2-methyl-5-butylfuran (Id) to 2-methyl-5-butylthiophene (IId). Analysis of these curves, which describe the changes in concentration of the furan Ia-d, indicate that the reaction is first order with respect to the furan: the experimental plot of log c versus τ gives a satisfactorily straight line; c is the concentration of the starting furan compound, and τ is the reaction time. The rate at which the furans Ia-d are consumed in the reaction changes very little on increasing the length of the alkyl substituents from one to four carbon atoms. Rate constants were determined from the time taken for half the conversion to occur, and were approximately the same: $k \approx (1.5 \pm 0.1) \cdot 10^{-4}$ sec^{-1} .

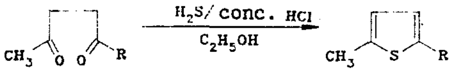
The exponential decrease in the concentration of the starting furan, and the presence of a maximum in the curve, describing the change in concentration of 1,4-dicarbonyl intermediate, is typical for the following reaction:



Ia-d IIIa-d IIa-d

I—III a $R=CH_3$; b $R=C_2H_5$; c $R=C_3H_7$; d $R=C_4H_9$

It was demonstrated that the maximal concentration of 1,4-diketone increased with increasing length of the alkyl substituent; 13% for compound Ia, 21% for Ib, 27% for Ic, and 36% for Id. For successive reactions, the increase in the maximal concentration of the intermediate was related to the decreasing rates of the second steps (the rates of the first steps being equal). In order to determine the relevance of that finding to the reaction studied, we compared the cyclization rates of diketones IIIa-d to the corresponding thiophenes:



III a-d II a-d

It was demonstrated that diketone IIIa completely cyclized to thiophene IIa in 30 min, while diketone IIIb went to thiophene IIb in only 50% yield in 4 h 30 min.

In summary, this is all consistent with the recyclization of furans to thiophenes occurring as is presented in scheme (2). However, it's already been shown in preliminary experiments that in a reaction mixture of furans Ia-d with hydrogen sulfide, the correspond-

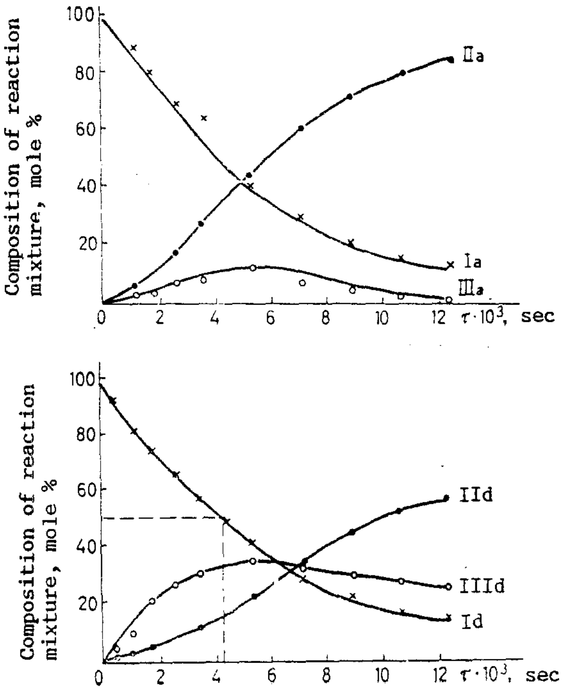


Fig. 1. Kinetics of the recyclization of 2,5-dimethylfuran (Ia) to 2,5-dimethylthiophene (IIa) and 2-methyl-5-butylfuran (Id) to 2-methyl-5-butylthiophene (IId) in the presence of hydrochloric acid.

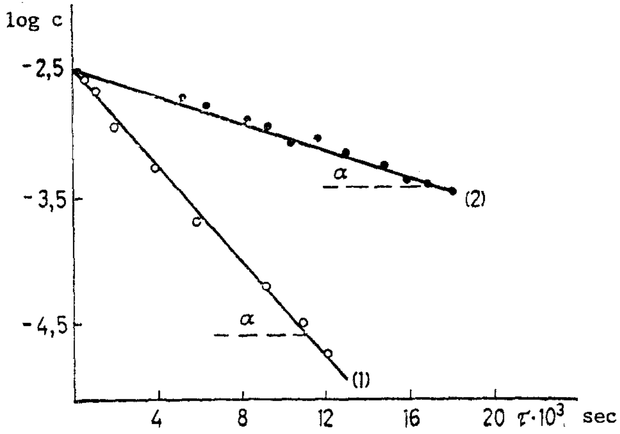
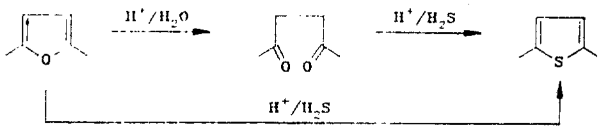


Fig. 2. Anamorphic kinetic plot for the consumption of 2,5-dimethylfuran in (1) the recyclization to 2,5-dimethylthiophene and (2) hydrolysis.

TABLE 1. Relationship between the Composition of the Reaction Mixture and the Time for the Recyclization Reaction

Time, sec	Composition of reaction mixture, mole %					
	Ib	IIIb	IIb	Ic	IIIc	IIc
600	95	3	2	94	3	3
1200	90	7	3	88	8	4
1800	84	13	3	83	12	5
2700	69	21	10	78	15	7
3600	58	25	17	67	21	12
5400	34	25	41	48	27	25
7200	22	20	58	36	24	40
9000	7	10	83	26	23	51
10800	4	7	89	19	21	60
12600	2	6	92	14	17	69

ing thiophenes are present. Therefore, we proposed the presence of a parallel process, the direct conversion of 2,5-dialkylfurans to the corresponding 2,5-dialkylthiophenes, without a step for the formation of the intermediate diketones:



The possibility of the occurrence of such a process is confirmed by the data for the conversion of furans to thiophenes and selenophenes in scheme (1) under anhydrous conditions (i.e., as required), ruling out the formation of intermediate 1,4-dicarbonyl compounds [1-4].

In order to confirm this hypothesis, we compared the rates of recyclization of furan Ia (1) to thiophene IIa and the hydrolysis of furan Ia to diketone IIIa under identical conditions. If the reaction occurs only by way of the 1,4-diketone the rate of the reaction should be equal to the rate of hydrolysis.

It's known that the hydrolysis reaction of furans, in the presence of excess water, proceeds with pseudo-first-order kinetics [5-7]. In the recyclization reaction of furans to thiophenes and selenophenes, the acid concentration does not vary with time, which has been shown experimentally, while that of hydrogen sulfide is kept constant by vigorously bubbling it through the reaction mixture at all times. Therefore, the rate equation can be represented as $V = k[Ia][H+][H_2S]$.

We have shown that the reaction studied is first order for the furan compound, i.e., also apparently pseudo-first-order. As a result, its rate, as in the case of hydrolysis, may be expressed numerically as a first order rate constant.

In Fig. 2 we present a kinetic curve, showing semilogarithmic anamorphosis, depicting the change in the concentration of furan Ia in the reaction to thiophene IIa and in the hydrolysis reaction to diketone IIIa. The relative rate constants of the reactions are calculated from the values of the slopes of the tangents to the corresponding anamorphic plots.

From test data, values of $(0.58 \pm 0.02)\cdot 10^{-4}$ and $(1.68 \pm 0.10)\cdot 10^{-4}$, respectively were obtained for the rate constants of hydrolysis and recyclization. Comparison of the values obtained for the rate constant showed that the hydrolysis of the furan Ia proceeds approximately 2.5 times slower than recyclization to the thiophene IIa. This confirms that the main process in the acid-catalyzed reaction of the 2,5-dialkylfurans with hydrogen sulfide, even in aqueous media, is the direct conversion to thiophene shown in scheme (1).

EXPERIMENTAL

A Tsvet-101 chromatograph with flame-ionization detector, column 2 m in length and 3 mm in diameter containing 15% apiezon L on chromatone N—AW—DMCS, was used to follow the conversion of the furans Ia-d to the thiophenes IIa-d and the diketones IIIa-d to the thiophenes IIa-d, and to characterize the starting and final compounds; argon was used as carrier gas and the column temperature was 160°C.

The starting furans Ia-d were synthesized by the method described in [3]. The diketones IIIa-d were obtained by the acid hydrolysis of the furans Ia-d. Properties and spectral characteristics of the thiophenes IIa-d are described in the literature.

The Kinetics of Recyclization of the Furans Ia-d to the Thiophenes IIa-d. A solution of the furan Ia-d (0.016 moles in ethanol (30 ml) was mixed in a thermostatically controlled vessel at 35 ± 0.1°C, furnished with a gas intake tube, dropping funnel, reflux condenser, and magnetic stirrer. The reaction mixture was saturated with hydrogen sulfide for 1 hour and 30 min. Without stopping the saturation with hydrogen sulfide, concentrated HCl (0.096 mole) was added to the reaction mixture. The reaction time was measured from the moment of addition of the acid. At intervals, 0.5 ml samples were taken from the reaction mixture, neutralized with saturated sodium carbonate (2 ml) and extracted with ether (0.5 ml). The mixture was analyzed by gas-liquid chromatography. The method of internal normalization was used for calculations. The change in concentration of the components of the reaction mixture with time was plotted for furans Ia and d (Fig. 1) and, furans Ib and d (Table 1).

The rate of the reaction of the diketones III a and d with hydrogen sulfide was determined by the method described above, starting from 0.0038 mole of the diketones IIIa and d and 0.096 mole of concentrated HCl. The course of the reaction was followed by GLC.

Determination of the Rate of Recyclization of the Furan Ia to the Thiophene IIa and Hydrolysis of the Furan Ia to the Diketone IIIa. The reaction was carried out by the method described above, starting from 0.003 mole of furan Ia and 0.096 mole of concentrated HCl. Hydrolysis of the furan Ia was carried out using the same conditions, but without the hydrogen sulfide. The course of the reaction was followed by GLC. Calculations were done using the internal standard method; 2,5-dimethylselenophene was used as internal standard. Results of kinetic studies are given in Fig. 2.

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