

**STUDY OF THE MECHANISM OF
RECYCLIZATION OF FURANS TO
THIOPHENES AND SELENOPHENES
UNDER THE CONDITIONS OF ACID
CATALYSIS. 7.* THE EFFECT OF THE
NATURE OF THE NUCLEOPHILE.
THE COMPETITION CONSTANT**

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Kinetic investigations into the reactions of 2,5-dimethylfuran with mixtures of hydrogen sulfide and selenide in various quantitative ratios were undertaken, and the competition constant was determined. This made it possible to correlate numerically the nucleophilicity of hydrogen sulfide and selenide in the reaction.

According to the results of investigations into the recyclization of furans to thiophenes and selenophenes in acidic media in dry ethanol it was established that the reaction takes place by a mechanism of specific acid catalysis and has first order in the furan, zero order in the nucleophile, and second order in the acid component [2]. The zero order in the nucleophile was established on the basis of the similar values obtained for the rate constants of the recyclization of 2,5-dimethylfuran to 2,5-dimethylthiophene and 2,5-dimethylselenophene with identical concentration of hydrogen chloride or with identical reaction temperature and was predetermined by the experimental conditions (an excess of hydrogen sulfide and selenide maintained throughout the reaction).

The data from experiments with labeled compounds and the results of quantum-chemical calculations, obtained during study of the recyclization and hydrolysis, showed that the difference in these two processes is due primarily to the different degrees of nucleophilicity of the employed reagents: $\text{H}_2\text{O} < \text{H}_2^{18}\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se}$ [1].

In order to determine the effect of the nature of the nucleophile on the recyclization reaction in the present work we studied the kinetics of recyclization of 2,5-dimethylfuran (I) to 2,5-dimethylthiophene (II) and 2,5-dimethyl-selenophene (III) and determined the dependence of the yield of the products II and III on the concentration of the employed nucleophiles. Mixtures of solutions of hydrogen sulfide and hydrogen selenide with specific $\text{C}_{\text{H}_2\text{S}}/\text{C}_{\text{H}_2\text{Se}}$ ratios in absolute ethanol that had previously been saturated with dry hydrogen chloride (1.56 N) were used in the reaction. The concentration of the hydrogen sulfide and selenide was determined by iodometric back titration. The content of compounds II and III in the reaction mixture was determined by GLC with an internal standard.

The data from GLC for samples taken 1 and 2 h after the beginning of the reaction were used to plot the relation between the concentration ratios of the products on the concentration ratios of the nucleophiles in the mixture (Fig. 1). Graphical interpolation gave the ratio of the concentrations of the final products $\text{C}_{\text{II}}/\text{C}_{\text{III}}$ for

* For Communication 6, see [1].

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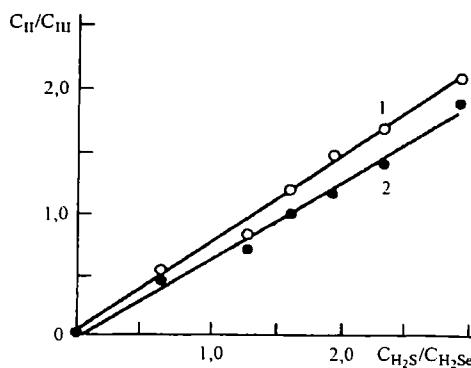


Fig. 1. The dependence of the concentration ratios of 2,5-dimethylthiophene (II) and 2,5-dimethylselenophene (III) in the reaction mixture on the concentration ratios of the nucleophilic reagents H_2S and H_2Se : 1) sample after 1 h; 2) sample after 2 h.

$\text{C}_{\text{H}_2\text{S}}/\text{C}_{\text{H}_2\text{Se}} = 1$, which enabled us to correlate the nucleophilicity of the hydrogen sulfide and selenide in numerical form. The competition constant was calculated from the slopes of the lines of the lines (Fig. 1):

$$\text{tg}\alpha_1 = 0,734 \pm 0,02 \text{ (sample 1); } \text{tg}\alpha_2 = 0,646 \pm 0,02 \text{ (sample 2).}$$

Thus, it was established that the reaction rate in the recyclization of furans to thiophenes and selenophenes with mixtures of nucleophiles in acidic media depends on the nature of the nucleophile; the nucleophilicity of hydrogen selenide is 1.4 times higher than that of hydrogen sulfide. This agrees with the data from quantum-chemical calculations obtained during discussion of the mechanisms of recyclization and hydrolysis [1].

EXPERIMENTAL

The reactions were monitored and the products were identified on a Tsvet-101 chromatograph with a flame-ionization detector. The stationary phase was 15% Apiezon L on Chromaton N-AW-DMCS; column 3 m \times 3 mm; thermostat temperature 180°C; carrier gas, helium, flow rate 2 liter/h; internal standard toluene.

2,5-Dimethylfuran (I) was obtained by a known method [3].

General Procedure for the Reaction of Compound I with H_2S and H_2Se . In a 50-ml hydrogenation flask fitted with a shaker was placed a solution of dry hydrogen chloride (1.56 M) in absolute ethanol saturated with hydrogen sulfide and selenide at specific concentrations. The reactor was purged with argon, and a weighed amount of the mixture of compound I and toluene was added. 1-ml samples were taken after 1 h and 2 h, neutralized with 2 ml of a saturated solution of alkali, and extracted with 1 ml of ether. The composition of the sample was monitored by GLC.

REFERENCES

1. T. I. Gubina, A. N. Pankratov, V. I. Labunskaya, S. P. Voronin, and V. G. Kharchenko, *Khim. Geterotsikl. Soedin.*, No. 8, 1035 (1997).
2. S. P. Voronin, T. I. Gubina, S. A. Trushin, I. A. Markushina, and V. G. Kharchenko, *Khim. Geterotsikl. Soedin.*, No. 11, 1458 (1989).
3. V. G. Kharchenko, T. I. Gubina, and I. A. Markushina, *Zh. Org. Khim.*, **18**, 394 (1982).