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KINETIC INVESTIGATION OF THE ALKYLATION OF SALTS OF 2,5-DIMERCAPTO-1,3,4-THIADIAZOLE

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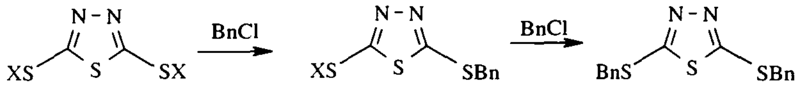
A kinetic investigation has been carried out, using electronic absorption spectra, of the alkylation with benzyl chloride of the dihydrazine, monohydrazine, and the disodium salts of 2,5-dimercapto-1,3,4-thiadiazole, and also of the hydrazine and sodium salts of 5-benzylthio-2-mercapto-1,3,4-thiadiazole. The rates orders and constants were established for the benzylation reaction and it was noted that the reaction rate depends on the cation of these salts and the degree of substitution of the 2,5-dimercapto-1,3,4-thiadiazole.

Keywords: salts of 2,5-dimercapto-1,3,4-thiadiazole, alkylation, kinetics, electronic absorption spectra.

The difference in values of λ_{max} in the electronic absorption spectra of mono- and dibenzyl substituted 2,5-dimercapto-1,3,4-thiadiazole was shown in [1]. We have established [2] that the difference in λ_{max} values of salts of 2,5-dimercapto-1,3,4-thiadiazole from the λ_{max} of mono- and disubstituted 2,5-dimercapto-1,3,4-thiadiazole gave the possibility of studying the kinetics of the alkylation of salts of 2,5-dimercapto-1,3,4-thiadiazole using electronic absorption spectra.

For this purpose the electronic absorption spectra have been taken of test samples taken from reaction mixtures during the alkylation of the dihydrazine (**1a**) and the disodium (**1b**) salts of 2,5-dimercapto-1,3,4-thiadiazole with benzyl chloride at a reactant ratio of 1 : 2.



1a,b **2a,b** **3**

1a, 2a X = NH_3NH_2; **1b, 2b** X = Na

On the basis of the spectral data obtained, and of the spectra of the initial salts **1a,b** and of the alkylation products of the hydrazine (**2a**) and sodium (**2b**) salts of 5-benzylthio-2-mercapto-1,3,4-thiadiazole and of 2,5-di(benzylthio)-1,3,4-thiadiazole (**3**), the changes of concentration with alkylation time were calculated by the procedure of Firordt [3] for three-component systems and kinetic curves were plotted (Figs. 1,2). From the curve of the consumption of the initial reactants it is seen that the alkylation rate of salt **1b** is greater than the alkylation rate of salt **1a**. From the curves of the formation of the final product **3** it follows that the alkylation rate of salt **2b** also exceeds the alkylation rate of salt **2a**.

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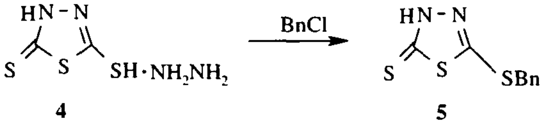
To establish the reaction rate constants for the alkylation of salts **2a** and **2b** with benzyl chloride the reactions were carried out at a reactant ratio of 1 : 1 and electronic absorption spectra were taken for test samples taken while carrying out the reactions. Since the reaction rate for the alkylation of salt **2a** is far less than the reaction rate for the alkylation of salt **2b** it was carried out with a twofold increase in reactant concentration. The concentrations of the compounds participating in the reactions were calculated by the procedure of Firordt [4] for two-component systems and kinetic curves were plotted (Figs. 3,4).

On the basis of the kinetic data (Fig. 3) the reaction half-lives ($t_{1/2}$) were calculated according to the procedure of [4] and a graph of the dependence of half-life on concentration ($1/[C]^2$) was plotted (Fig. 5). The straight line obtained shows that the alkylation reaction of salt **2a** corresponds to the third order. The rate constant for **2a** was determined from the slope of the straight line as $k_3 = 2.84 \cdot 10^{-2}$ $M^{-2}sec^{-1}$ (correlation coefficient $R^2 = 0.9993$). The half-lives ($t_{1/2}$) of the reaction were calculated from the kinetic data for the dialkylation of salt **2b** (Fig. 4) by the same procedure and a graph was plotted for the dependence of half-life on concentration ($1/[C]$) (Fig. 6). The straight line obtained shows that the alkylation of **2b** corresponds to the second order. The rate constant for **2b** was found from the slope of the straight line as $k_2 = 1.93 \cdot 10^{-3}$ $M^{-1}sec^{-1}$ (correlation coefficient $R^2 = 0.9996$).

In order to estimate the alkylation rate of the monohydrazine salts we have carried out the alkylation of the monohydrazine salt of 2,5-dimercapto-1,3,4-thiadiazole (**4**).



4 **5**

It was noted that solutions of salt **4** and of 5-benzylthio-1,3,4-thiadiazole-2(3H)-thione (**5**) do not obey the Bouguer–Lambert–Beer law. Probably on reducing the concentrations of these compounds the associates break up and the extinction coefficients change. However at a constant total concentration of compounds **4** and **5** the extinction coefficients are unchanged. We are convinced of this, having taken the electronic absorption spectra of solutions of mixtures with different concentrations of compounds **4** and **5**, but at constant total concentration. The concentrations of compounds **4** and **5** calculated by the procedure of Firordt corresponded to the actual values. This makes it possible to study the alkylation of salt **4** using electronic absorption spectra.

Concentrations were calculated on the basis of the electronic absorption spectra obtained and kinetic curves were plotted (Fig. 7). From the latter data a straight line dependence of the half-life ($t_{1/2}$) on concentration ($1/[C]$) was obtained (Fig. 8), from which it follows that this reaction is of the second order. From the slope of the straight line the rate constant for **4** was determined as $k_2 = 1.75.10^{-3}$ $M^{-1}sec^{-1}$ (correlation coefficient $R^2 = 0.9986$).

The comparison of the half-lives at identical initial concentrations is suitable for a visual comparison of the alkylation reaction rates of salts of 2,5-dimercapto-1,3,4-thiadiazole. The half-life of the alkylation of salt **2b** at a concentration of 0.025 M was 5.7 h, and of salt **4** 6.2 h. The half-life for the alkylation of salt **2a** was calculated from the formula: $t_{1/2} = 3/2k_3[C]^2 = 23.5$ h.

On comparing the half-lives of the alkylation of salts **2a** and **2b** with their structures it is evident that the reaction rate depends on cation X to a significant degree, but on comparing the half-lives of salts **2a** and **4** it is seen that the alkylation rate also depends on the degree of substitution of 2,5-dimercapto-1,3,4-thiadiazole.

The third order alkylation reaction of salt **2a** indicates that this reaction consists of several stages and that its study requires further investigation.

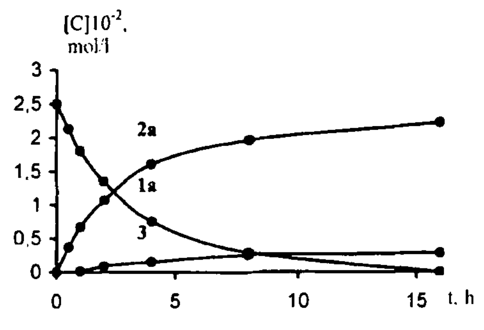


Fig. 1. Changes in the concentrations of compounds **1a**, **2a**, and **3** with time in the alkylation of salt **1a** (the labeling of curves corresponds to the numbering of the compound).

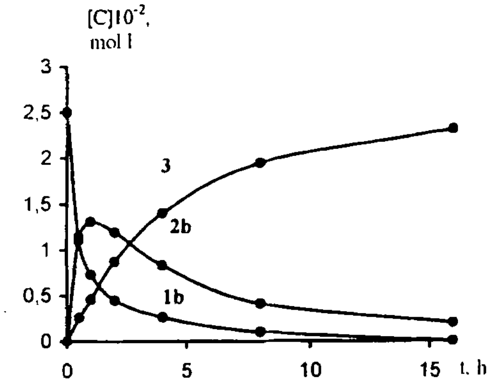


Fig. 2. Changes in the concentrations of compounds **1b**, **2b**, and **3** with time in the alkylation of salt **1b**.

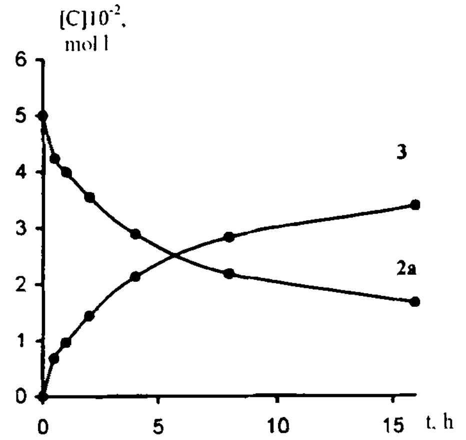


Fig. 3. Changes in the concentrations of compounds **2a** and **3** with time in the alkylation of salt **2a**.

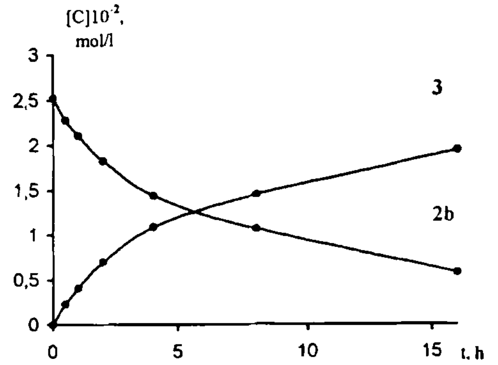


Fig. 4. Changes in the concentrations of compounds **2b** and **3** with time in the alkylation of salt **2b**.

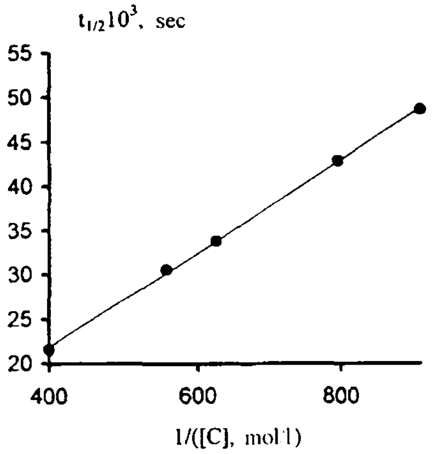


Fig. 5. Dependence of the half-life on concentration for the alkylation of salt **2a**.

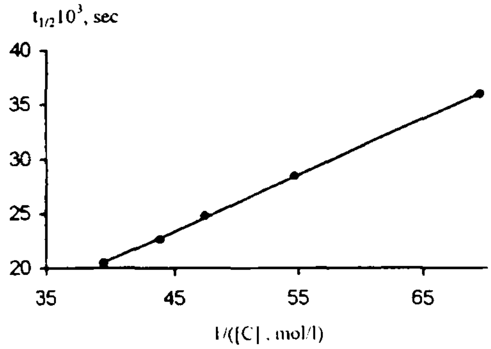


Fig. 6. Dependence of the half-life on concentration for the alkylation of salt **2b**.

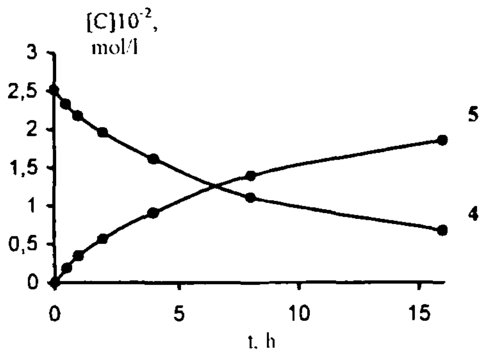


Fig. 7. Changes of concentration of compounds **4** and **5** during the alkylation of salt **4**.

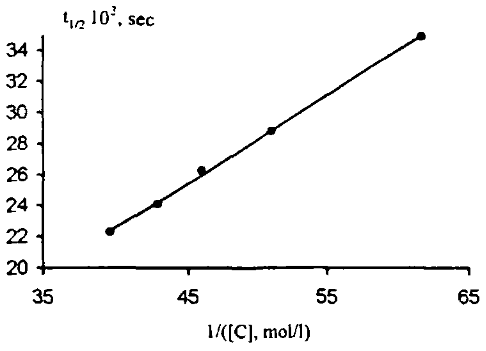


Fig. 8. Dependence of the half-life on concentration in the alkylation of salt **4**.

EXPERIMENTAL

A flask thermostatted at 20°C was used for studying the kinetics. The synthesis of compounds **1a**, **2a**, and **3-5** has been described in [2]. Solutions of salts **1b** and **2b** were obtained by dissolving 2,5-dimercapto-1,3,4-thiadiazole (0.5 mmol) or compound **5** (0.5 mmol) in ethanol (20 ml) and adding sodium hydroxide (1 or 0.5 mmol). In the alkylation reaction benzyl chloride (1 mmole for **1a,b** and 0.5 mmol for **2a,b** and **4**) was introduced into a solution of salts **1a,b**, **2b**, or **4** (0.5 mmol) in ethanol (20 ml) or of **2a** (0.5 mmol) in ethanol (10 ml). After selected time intervals (0, 0.5, 1, 2, 4, 8, and 16 h from the start of the reaction) aliquotes (0.04 ml for **2a**, 0.08 ml for the remainder) were removed by pipette from the flask. These were diluted with ethanol to 25 ml in a measuring flask and electronic absorption spectra were taken on a Perkin–Elmer Lambda 20 UV-vis spectrometer. The analytical wavelengths for calculating the concentrations of the components of mixtures were determined by the procedure of [3,4] and were: for salt **1a** 294, 323, and 345 nm, for salt **1b** 294, 321, and 345 nm, for salt **2a** 294 and 323 nm, for salt **2b** 294 and 321 nm, and for salt **4** 323 and 345 nm.

REFERENCES

1. N. Petri and O. Glemser, *Chem. Ber.*, **94**, 566 (1961).
2. Z. Kuodis, A. Rutavichyus, and S. Valiulene, *Khim. Geterotsikl. Soedin.*, in press.
3. I. Ya. Bershtein and Yu. L. Kaminskii, *Spectrophotometric Analysis in Organic Chemistry* [in Russian], Khimiya, Leningrad (1975), pp. 65, 85.
4. P. Atkins, *Physical Chemistry* [Russian translation], Vol. 2, Mir, Moscow (1980), p. 414.