

Bożenna Mazurkiewicz

KINETICS OF THE REACTION OF THIOUREA WITH METHYL IODIDE

Kinetics of the reaction of thiourea with methyl iodide in aqueous solutions at the temperatures 25°, 35° and 40°C has been investigated.

The reaction was found to be dimolecular. The rate of the reaction is not affected by pH of solution within the range 4.00-9.06. Activation energy of the reactions is 74.07 KJ/mole K.

Thiuronium salts, basic compounds for obtaining thiols are most frequently synthesized by S-alkylation of thioureas with alkyl halides which are easily accessible compounds and secure good efficiency of S-alkylation reaction.

Kinetics of the reaction of thiourea with selected alkyl halides in alcohol environment was examined by Pearson, Sobel, Songstad [1] and Bhatti and Ralhan [2]. Pearson, Sobel and Songstad [1] determined a constant rate of the reaction of thiourea with methyl iodide in methanol at the temperature 25°C under conditions of pseudo-first-order reaction at high excess of methyl iodide in the solution.

Investigations over the kinetics of the reaction of thiourea with ethyl bromide and alkyl chloride in ethanol led Bhatti and Ralhan [2] to a conclusion that the reactions are dimolecular. The authors explain the mechanism of this reaction by a simple electrophilic attack on sulphur. This paper presents the results of investigations over the kinetics of the reaction of thiourea with methyl iodide in aqueous environment which allowed us to work out a thiomercurimetric method of quantitative determination of halidealkanes [3]. Water was chosen

as a solvent in order to avoid side reactions which may occur in alcohol environment when acids are present in it.

Experimental

Reagents and solutions: thiourea crystallized from water t.t. 180°C, methyl iodide were distilled and fraction was collected at the temperature 41.5-42°C. Initial concentration of aqueous solutions of thiourea was tested by desulphurizing [4]. Concentration of aqueous solution of methyl iodide was determined by thiomercurimetric method [5]. Progress of the interaction between thiourea and methyl iodide was investigated by determination of the increase in concentration of S-methylisothiurea.

Concentration of S-methylisothiurea was determined as follows: a sample of the solution was introduced to a separatory funnel and then extracted with the same volume of carbon tetrachloride in order to remove unreacted methyl iodide. A part of the solution containing no methyl iodide was titrated with $5 \cdot 10^{-3}$ mole/dm³ solution of o-hydroxymercuribenzoic acid (HMB) at the presence of dithiofluorescein after S-methylisothiurea had been decomposed to thiol and ammonium salts has been added. The course of the reaction was observed at the temperature 25°, 35° and 40°C.

Initial molar concentrations of the substrates ranged from 0.01-0.003 mole/dm³. The effect of pH of solutions was investigated within the range 4.00-9.06 using Britton's and Robinson's buffers and the effect of hydrochloric acid on the course of reaction was examined within the concentration range 0.1-1.0 mole/dm³.

Discussion and conclusions

The reaction runs according to the kinetic equation of second-order reaction:

$$\frac{dx}{dt} = k [\text{TM}] \cdot [\text{CH}_3\text{J}]$$

where:

x - concentration of S-methylisothiurea.

Such course of the reaction is indicated by a linear dependence

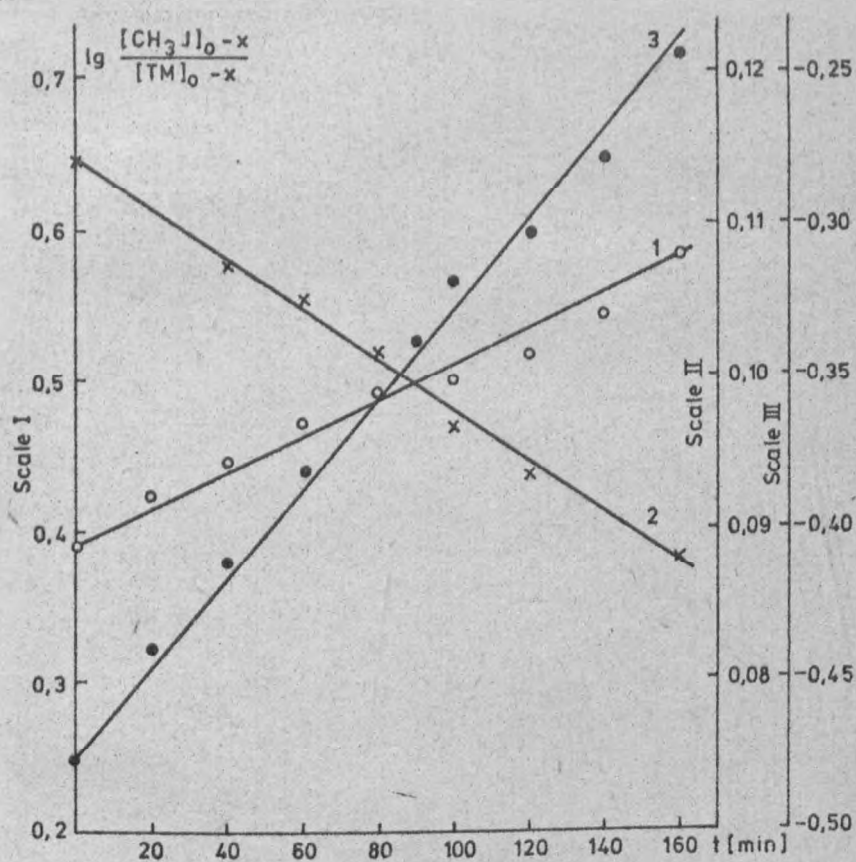


Fig. 1. Course of reaction between thiourea and methyl iodide in the system $\lg \frac{[\text{CH}_3\text{J}]_0 - x}{[\text{TM}]_0 - x} = f(t)$ at temperature 25°C

- 1 - $[\text{CH}_3\text{J}]_0 = 0.0392$ mole/dm³, $[\text{TM}]_0 = 0.0159$ mole/dm³ (scale I)
 2 - $[\text{CH}_3\text{J}]_0 = 0.0169$ mole/dm³, $[\text{TM}]_0 = 0.0319$ mole/dm³ (scale III)
 3 - $[\text{CH}_3\text{J}]_0 = 0.0379$ mole/dm³, $[\text{TM}]_0 = 0.0319$ mole/dm³ (scale II)

$$\lg \frac{[\text{CH}_3\text{J}]_0 - x}{[\text{TM}]_0 - x}$$

as a function of time presented in Fig. 1 and 2. $[\text{CH}_3\text{J}]_0$ and $[\text{TM}]_0$ denote initial molar concentration of methyl iodide and thiourea respectively.

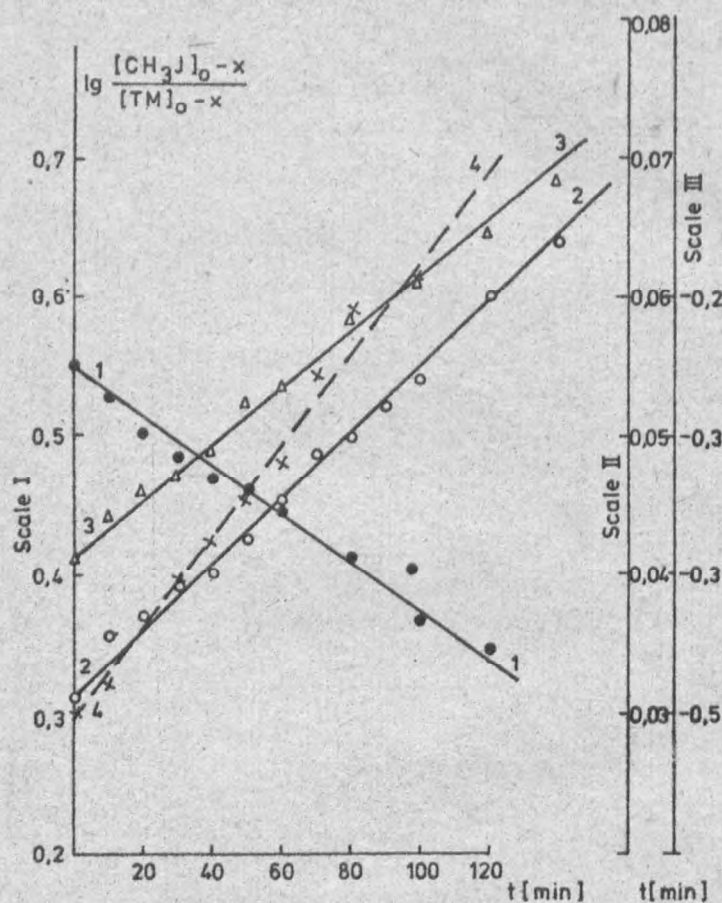


Fig. 2. Course of reaction between thiourea and methyl iodide in the system $\lg \frac{[\text{CH}_3\text{J}]_0 - x}{[\text{TM}]_0 - x} = f(t)$

1 - $[\text{CH}_3\text{J}]_0 = 0.0181$ mole/dm³, $[\text{TM}]_0 = 0.0319$ mole/dm³ temp. 35°C (scale III), 2 - $[\text{CH}_3\text{J}]_0 = 0.0324$ mole/dm³, $[\text{TM}]_0 = 0.0159$ mole/dm³ temp. 35°C (scale I), 3 - $[\text{CH}_3\text{J}]_0 = 0.0157$ mole/dm³, $[\text{TM}]_0 = 0.159$ mole/dm³ temp. 35°C (scale II), 4 - $[\text{CH}_3\text{J}]_0 = 0.0318$ mole/dm³, $[\text{TM}]_0 = 0.0159$ mole/dm³ temp. 40°C (scale I)

Constant rates of reactions for given measurements series were determined by graphic method. For temperatures 25°, 35° and 40° they were $1.89 \cdot 10^{-3}$, $5.17 \cdot 10^{-3}$ and $7.53 \cdot 10^{-3}$ (mole⁻¹sec⁻¹ dm³) respectively. Activation energy calculated from Arrhenius formula is 74.07 KJ/mole K.

It was also found that variation of pH within the range 4.00 to 9.06 does not affect the change of the course of kinetic curves. Thus the investigated process is not a reaction of acid-base catalysis type. The presence of hydrochloric acid within the concentration range 0.1-1 mole/dm³ does not influence the course of the above reaction.

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Department of Technology Chemistry
Institute of Chemistry
University of Łódź

Bożenna Mazurkiewicz

KINETYKA REAKCJI TIOMOCNIKA Z JODKIEM METYLU

Badano kinetykę reakcji tiomocznika z jodkiem metylu w roztworach wodnych w temperaturze 25, 35, 40°C. Stwierdzono, że jest to reakcja dwucząsteczkowa. Na szybkość reakcji nie wpływa pH roztworu w zakresie 4.00-9.06. Energia aktywacji reakcji wynosi 74.07 kJ/mol K.

Боженна Мазуркевич

КИНЕТИКА РЕАКЦИИ ТИОМОЧЕВИНЫ С ИОДИСТЫМ МЕТИЛОМ

Исследовано кинетику реакции тиомочевинны с иодистым метилом в температурах 25, 35, 40°C. Реакция оказалась бимолекулярной pH реакционной среды в пределах 4.00-9.06 не имеет влияния на скорость реакций. Энергия активации изучаеной реакции равна 74.07 кJ/моль К.