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 thiomercuroimetric 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 at 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 thiomercuroimetric method [5]. Progress of the interaction between thiourea and methyl iodide was investigated by determination of the increase in concentration of S-methylisothioura.

Concentration of S-methylisothioura was determined as follows: a sample of the solution was introduced to a separation 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 • 10⁻³ mole/dm³ solution of o-hydroxymercuribenzoic acid (HMB) at the presence of dithiofluorescein after S-methylisothioura 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 mol/dm³.

**Discussion and conclusions**

The reaction runs according to the kinetic equation of second-order reaction.
Kinetics of the reaction of thiourea with methyl iodide

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

where:

\( x \) - concentration of S-methylisothiourea.

Such course of the reaction is indicated by a linear dependence

\[
\lg \frac{[\text{CH}_3\text{J}]_0 - x}{[\text{TM}]_0 - x} = f(t)
\]

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

1 - \([\text{CH}_3\text{J}]_0 = 0.0392 \text{ mole/dm}^3; [\text{TM}]_0 = 0.0159 \text{ mole/dm}^3\) (scale I)
2 - \([\text{CH}_3\text{J}]_0 = 0.0169 \text{ mole/dm}^3; [\text{TM}]_0 = 0.0319 \text{ mole/dm}^3\) (scale III)
3 - \([\text{CH}_3\text{J}]_0 = 0.0379 \text{ mole/dm}^3; [\text{TM}]_0 = 0.0319 \text{ mole/dm}^3\) (scale II)
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 - $[\text{CH}_3\text{J}]_0 = 0.0181 \text{ mole/dm}^3$, $[\text{TM}]_0 = 0.0319 \text{ mole/dm}^3$ temp. $35^\circ\text{C}$ (scale III),
2 - $[\text{CH}_3\text{J}]_0 = 0.0324 \text{ mole/dm}^3$, $[\text{TM}]_0 = 0.0159 \text{ mole/dm}^3$ temp. $35^\circ\text{C}$ (scale I),
3 - $[\text{CH}_3\text{J}]_0 = 0.0157 \text{ mole/dm}^3$, $[\text{TM}]_0 = 0.159 \text{ mole/dm}^3$ temp. $35^\circ\text{C}$ (scale II),
4 - $[\text{CH}_3\text{J}]_0 = 0.0318 \text{ mole/dm}^3$, $[\text{TM}]_0 = 0.0159 \text{ mole/dm}^3$ temp. $40^\circ\text{C}$ (scale I)
Constant rates of reactions for given measurements series were determined by graphic method. For temperatures 25°, 35° and 40° they were $1.89 \times 10^{-3}$, $5.17 \times 10^{-3}$ and $7.53 \times 10^{-3}$ (mole $^{-1} \text{sec}^{-1} \text{dm}^3$) 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/dm$^3$ does not influence the course of the above reaction.

REFERENCES


Department of Technology Chemistry
Institute of Chemistry
University of Łódź

Bożenna Mazurkiewicz

KINETYKA REAKCJI TIOMOCZNIKA Z JODKIEM METYLU

Badano kinetykę reakcji tiomocznika z jodkiem metylu w roztorach 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.
Божена Мазуркевич

КИНЕТИКА РЕАКЦИИ ТИМОЧЕВИНЫ С ЙОДИСТЫМ МЕТИЛОМ

Исследовано кинетику реакции тимочевины с йодистым метилем в температурах 25, 35, 40°С. Реакция оказалась бимолекулярной при реакционной среде в пределах 4,00-9,06 не имеет влияния на скорость реакций. Энергия активации изученной реакции равна 74,07 кДж/моль К.