ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 2, 1983

Bożenna Mazurkiewicz

KINETICS AND ANALYTICAL APPLICATION OF THE REACTION BETWEEN THIOUREA AND TRIMETHYLSULPHOXONIUM IODIDE

The course of interaction between thiourea and trimethylsulphoxonium iodide in N,N-dimethylformamide has been investigated at the temperature 80°C. It has been shown that the reaction runs according to the kinetic equation of first-order. It has been found that introduction of potassium iodide to the system results in higher rate of the reaction whereas water strongly inhibits the course of the reaction between thiourea and trimethylsulphoxonium iodide. Based on kinetic investigations thiomercurimetric method of determination of trimethylsulphoxonium iodide has been worked out.

Sulphoxides, compounds containing electrodonor group =SO, under the influence of alkylating agents change into O-alkyl derivatives showing the character of salts [1, 2]. Among the investigated sulphoxides only DMSO under the influence of such alkylating agents as for instance methyl iodide changes into S-alkyl derivative forming trimethylsulphoxonium salt [3, 4].

In the present paper we investigated kinetics of reaction between thiourea and trimethylsulphoxonium iodide in N,N-dimethylformamide. The investigations enabled us to work out thiomercurimetric method of determination of trimethylsulphoxonium iodide.

EXPERIMENTAL

Trimethylsulphoxonium iodide was obtained according to Corey [5]. treating dimethylsulphoxide with methyl iodide. The contents of sulphur in the preparation was 14.50% (teoret. 14,57%). Thiourea was crystallized from water B.p 180 C.

Kinetics of the reaction of thiourea with trimethylsulphoxonium iodide was investigated in the solution of N,N-dimethylformamide at the temperature 80°C.

Concentration of the S-methylisothiourea being formed was determined by thiomercurimetric method [6].

The effect of concentration of potassium iodide and water on the efficiency of the above reaction was studied.

DISCUSSION AND CONCLUSION

It has been shown that the rate of S-alkylation of thiourea reaction increases with concentration of trimethylsulphoxonium iodide. No essential differences in the course of kinetic curves at the increase of thiourea concentration were observed if its concentration was higher than that of trimethylsulphoxonium iodide. When we assume that in such strongly polar solvent as DMF, sulphoxonium salt is completely dissociated and the stage determining the rate of the reaction is that of decomposition salt to sulphoxide and methyl iodide which afterwards rapidly reacts with thiourea,

$$(CH_3)_3\overset{+}{S}O + J^- \xrightarrow{DMF} (CH_3)_2SO + CH_3J$$

$$CH_3J + NH_2CSNH_2 \longrightarrow [NH_2CS(CH_3)NH_2]^+ + J^- \qquad (1)$$

we can describe the rate of the reaction with the following equation:

$$\frac{dx}{dt} = [k\ (CH_3)_3\overset{+}{S}O] \cdot [J^-] \qquad (2)$$

where:

x - concentration of S-methylisothiourea.

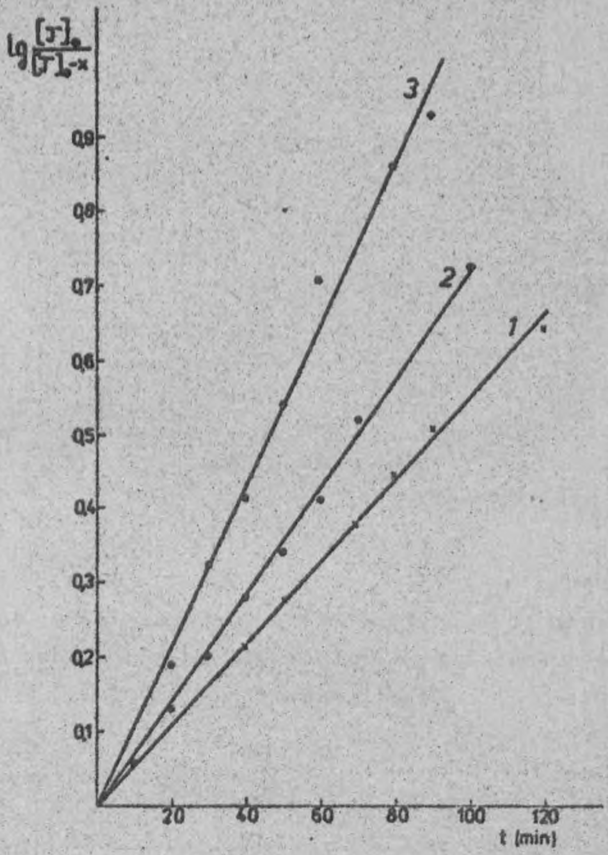

Fig. 1. Course of reaction between thiourea and $S(CH_3)_3OJ$ in DMF medium at temperature 80°C in the system $\lg \frac{[J^-]_o}{[J^-]_o - x}$, t 1 - thiourea 0.0989 mol./dm^3, $S(CH_3)_3OJ$ - 0.0111 mole/dm^3; 2 - thiourea 0.0989 mol./dm^3, $S(CH_3)_3OJ$ - 0.0220 mole/dm^3; 3 - thiourea 0.0989 mol./dm^3, $S(CH_3)_3OJ$ - 0.0387 mole/dm^3

As the concentration of iodides in the reaction system is constant $[J^-] = [J^-]_o$ and $[(CH_3)_3\overset{+}{S}O] = [J^-]_o - x$ equation (2) can be expressed:

$$\frac{dx}{dt} = k_1([J^-]_o - x) \qquad (3)$$

where:

$[J^-]_o$ - concentration of iodides for $t = 0$

$$k_1 = k[J^-]_o$$

and we can present the equation (3) as:

$$k_1 = \frac{2,303}{t} \lg \frac{[J^-]_o}{[J^-]_o - x}$$

Figure 1 presents the dependence

$$\lg \frac{[J^-]_o}{[J^-]_o - x} = f(t).$$

Graphically determined values of constant k_1 and calculated values of constant k are given in tab. 1.

Table 1

Values of constants $k[\mathrm{mol.}^{-1}\mathrm{s}^{-1}\mathrm{dm}^3]$ and $k_1[\mathrm{s}^{-1}]$ of thiourea alkylation with trimethylsulphoxonium iodide in DMF at the temperature 80°C

Concentration of $S(CH_3)_3OJ$ [mol./dm^3]	0,0111	0,0220	0,0387	0,0219	0,0220
Concentration of thiourea [mol./dm^3]	0.0989	0.0989	0.0989	0.0791	0.0494
$k_1 \cdot 10^4$	2.16	2.74	4.18	2.61	2.77
$k \cdot 10^2$	1.94	1.24	1.08	1.19	1.26

The observed derease of constant k value with the increase in the concentration of sulphoxonium salt is due to the increase in ionic strength of the solution. According to the equation (1) the increase in ionic strength should inhibit the reaction. Figure 2 presents the effect of potassium iodide within the concentration range 0.04-0.12 mol./dm^3 and water on the course of reaction of trimethylsulphoxonium iodide with thiourea.

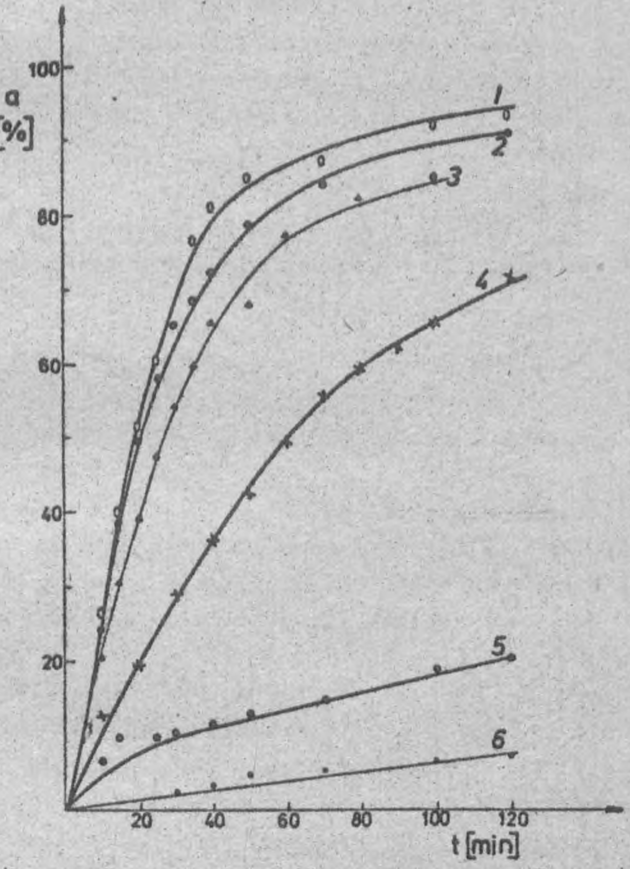

Fig. 2. Degree of conversion of $S(CH_3)_3OJ$ into isothiuronium salts as a function of time and conditions at temperature 80^{o}C. Intial concentration $S(CH_3)_3OJ$ - 0.0101 mol./dm^3, thiourea 0.0494 mol./dm^3. Curves: 1 - 0.120 mol./dm^3 KJ, 100% DMF; 2 - 0.080 mol./dm^3 KJ, 100% DMF; 3 - 0.040 mol./dm^3 KJ, 100% DMF; 4 - 100% DMF; 5 - 90% DMF; 6 - 80% DMF

Introduction of potassium iodide to the system has a positive effect on the rate of the reaction. However, this effect is reduced with the increase in concentration of iodides (fig. 2, curves 1-3). According to equation (2) the increase in concentration of iodides in the system should result in a greater rate of the reaction. However, simultaneously ionic strength increases which is a factor inhibiting the reaction grows. Therefore the effect of iodides on the rate of the reaction will be a resultant effect of the concentration of iodides and ionic strength of the solution. As it follows from fig. 2 (curves 4--6) the presence of water strongly inhibits the course of the reaction. In solutions containing 50% vol. of water and 50% vol. of DMF S-methylisothiourea was not formed.

The decrease of the reaction rate in aqueous solutions is due to a different way of decomposition of trimethylsulphoxonium iodide

$$(CH_3)_3SOJ + H_2O \longrightarrow (CH_3)_2SO + CH_3OH + HJ$$

The products formed in the process of hydrolysis are not, in the experimental conditions, compounds S-alkylating thiourea. Summing up we can say that reaction of thiourea with trimethylsulphoxonium iodide in the solution of DMF satisfies kinetic equation of first-order reaction. The rate of this reaction is strongly influenced by iodide concentration and the presence of water in the system.

Thiomercurimetric determination of trimethylsulphoxonium iodide. The conclusions from the investigations of kinetic reactions of thiourea with trimethylsulphoxonium iodide (and especially the temperature, time and system of reactions, the effect of iodides) were applied for purposes the determination of trimethylsulphoxonium iodide.

The procedure of determination: To test-tubes 10 cm long and having 1 cm in diameter equipped with air reflux condersers one meter long we introduced 0.1-1.0 cm^3 of the solution of trimethylsulphoxonium iodide in DMF and 2 cm^3 of dimethylformamide solution 0,1 mol./dm^3 in relation to KJ and 1 mol./dm^3 in relation to thiourea. The solutions were heated on a boiling water bath for 3 hours. Afret coding they were diluted in measurement flasks to 50 cm^3 with water and proper amount of the solution was titrated with $5 \cdot 10^{-3}$ mol./cm^3 solution of o-hydroxymercuribenzoic acid (HMB) after having been decomposed to thiol and after ammonium salts had been added [6]. The results of the thiomercurimetric determination of trimethylsulphoxonium iodide are given in tab. 2.

Table 2

Thiomercurimetric determination of trimethylsulphoxonium iodide

Amount µmole		Average recovery [%]
taken	found	
11.2	11.2	100.00
31.9	31.0	97.18
130.3	131.2	100.69
154.3	150.2	97.34
363.2	362.6	99.84
458.8	464.7	101.29
576.0	591.5	102.70
		99,86

The above method can be applied for determination of trimethylsulphoxonium iodide in solid preparations and in non-aqueous solutions.

REFERENCES

[1] Ahmed M. G., Adler R. W., James G. H., Sinoff M. L., Whiting M. C., Chem. Commun., 1533 (1968).

[2] Tsumori K., Minato H., Kobayashi M., Bull. Chem. Soc. Japan, 46, 3503 (1973).

[3] Smith S. G., Winstein S., "Tetrahedron", 3, 317 (1958).

[4] Kuhn R., Trischmann H., Libigs Ann. Chem., 611, 117 (1958).

[5] Corey F. J., J. Am. Chem. Soc., 87, 1353 (1965).

[6] Wroński M., Mazurkiewicz B., Chem. Anal., 20, 621 (1975).

Institute of Chemistry
University of Łódź

Bożenna Mazurkiewicz

KINETYKA REAKCJI TIOMOCZNIKA Z JODKIEM TRÓJMETYLOSULFOKSONIOWYM. TIOMERKURYMETRYCZNE OZNACZANIE JODKU TRÓJMETYLOSULFOKSONIOWEGO

Zbadano przebieg reakcji między tiomocznikiem i jodkiem trójmetylosulfoksoniowym w N,N-dwumetyloformamidzie w temperaturze 80°C. Wykazano, że reakcja przebiega według równania kinetycznego pierwszego rzędu.

Wprowadzenie jodku potasowego do układu powoduje wzrost szybkości reakcji. Woda natomiast silnie hamuje przebieg reakcji między tiomocznikiem i jodkiem trójmetylosulfoksoniowym.

Na podstawie przeprowadzonych badań kinetycznych opracowano tiomerkurymetryczną metodę oznaczania jodku trójmetylosulfoksoniowego.

Боженна Мазуркиевич

КИНЕТИКА РЕАКЦИИ ТИОМОЧЕВИНЫ С ИОДИСТЫМ ТРИМЕТИЛСУЛЬФОКСОНИОМ ТИОМЕРКУРЫМЕТРИЧЕСКИЕ ОПЕРЕДЕЛЯНИЕ ИОДИСТОГО ТРИМЕТИЛСУЛЬФОКСОНИЯ

Иследовано реакцию тиомочевины с иодистым триметилсульфоксонием в температуре 80°C при исспользовании N,N-диметилформамида в качестве расстворителя.

Порядок реакции оказался первым. Установлено чмо добавка иодистого каля до реакционной среды повысшает скорость реакции в отличие от воды которая резко снижает скорость реакции.

На основании кинетических исследовании разработано тиомеркурыметрический метод опеределяния иодистого триметилсульфоксония.