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Kinetic Studies of the Copper-Catalyzed Cross-Coupling of 1-Phenyltetrazole-5-thiol and Iodobenzene

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Abstract—Kinetics of the copper-catalyzed cross-coupling of 1-phenyltetrazole-5-thiol and iodobenzene under thermal and dielectric heating has been studied; the kinetic parameters of the reaction have been calculated. Microwave irradiation has not influenced significantly the reaction molecular mechanism; the process acceleration can be due to macrokinetic effects.

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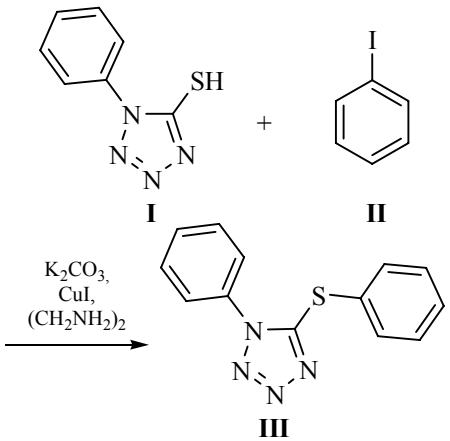
Cross-coupling with formation of carbon–heteroatom bond is one of the most efficient methods for heterocyclic compounds modification [1]. Such reactions are convenient for preparation of biologically active compounds. Kinetics and mechanism of the copper-catalyzed C–N cross-coupling have been studied in a number of works [2–4], however, similar studies of C–S cross-coupling have not been reported.

Recently, we have discovered that 1-substituted tetrazole-5-thiols can participate in the copper-catalyzed cross-coupling with aryl iodides, and have noticed that microwave irradiation influences the reaction duration [5]. Extending the study of this reaction, in this work we investigated its kinetics under convectional and dielectric heating.

The cross-coupling of 1-phenyltetrazole-5-thiol (**I**) with iodobenzene (**II**) was chosen as a model reaction.



We suggested that the reaction proceeded via formation of the soluble copper complex with iodobenzene that further interacted with 1-phenyl-tetrazole-5-thiol in dimethylformamide (DMF) solution upon heating.

Kinetic measurements were performed at 65, 80, and 95°C both with convectional and microwave heating. The initial substances and products concentrations were determined by high-performance liquid chromatography.

Kinetic curves of the product, 1-phenyl-5-sulfanyltetrazole **III**, formation at different temperatures are shown in Figs. 1 and 2 (under convectional heating and microwave activation, respectively).

As seen from the curves, the microwave activation significantly affected the product formation rate.

In the frame of the activated complex theory, the rate constant, the reaction activation energy (E_a), enthalpy ($\Delta H^{\neq}$), and entropy ($\Delta S^{\neq}$) were calculated from the experimental data, in the cases of both convectional and microwave heating. The calculations were performed using differential method and method of stationary concentrations.

Differential method is based on the differential form of the equation linking the product formation rate with the rate constant and reaction orders with respect to the starting compounds.

$$\ln w = \ln k + p_{\mathbf{I}} \ln c_{\mathbf{I}} + p_{\mathbf{II}} \ln c_{\mathbf{II}}. \quad (1)$$

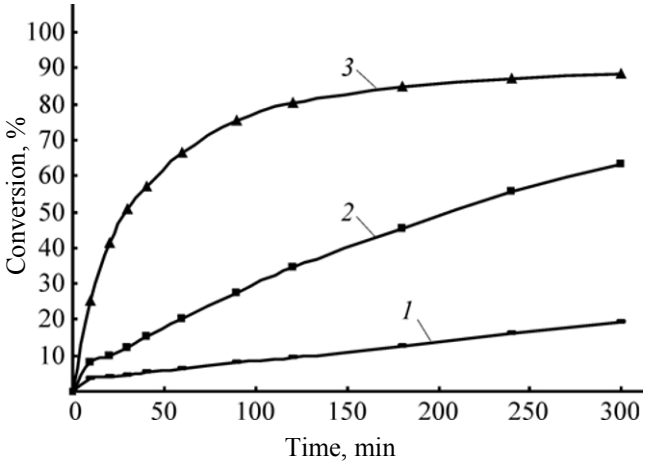


Fig. 1. Kinetic curves of 1-phenyl-5-sulfanyltetrazole accumulation under convection heating at (*1*) 65, (*2*) 80, and (*3*) 95°C.

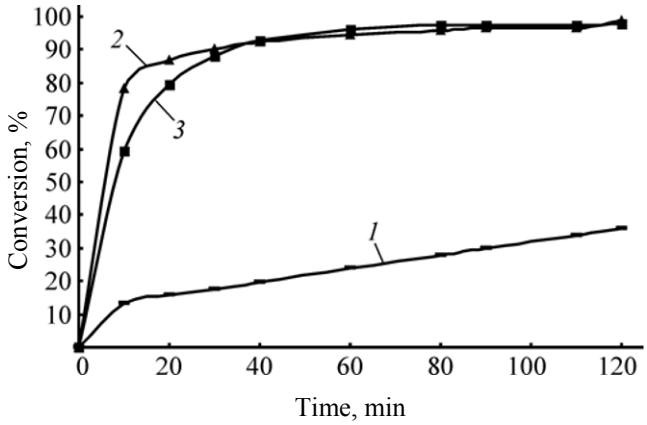


Fig. 2. Kinetic curves of 1-phenyl-5-sulfanyltetrazole accumulation under microwave heating at 65 (*1*) 65, (*2*) 80, and (*3*) 95°C.

In Eq. (1), w is the product formation rate, k is the rate constant. The reaction rate was calculated using the second order polynomial interpolation (2):

$$c = a\tau^2 + b\tau + d, \quad (2)$$

where τ being time; a, b, d being the coefficients deduced from three products concentrations c_{i-1}, c_i, c_{i+1} at times τ_{i-1}, τ_i, τ_{i+1}, respectively. The reaction rate at time τ_i was determined according to Eq. (3).

$$w_i = 2a\tau_i + b. \quad (3)$$

The rate constant and the reaction orders were obtained via solution of the equations set emerged from the partial least square method. The advantage of that approach was possibility of independent determination of the reaction orders and the rate constant. Kinetic experiment with the excess of one of the reagents was not required. The results are collected in Table 1.

Upon microwave irradiation, the calculated rate constant at 80°C was higher than that at 95°C, the indirect measurements accuracy being the worst of all the measurements; thus, the data obtained at 80°C were neglected in subsequent calculations of the activation energy.

The activation energy was calculated from the rate constants determined at different temperatures; the

Table 1. Reaction order and rate constants of 1-phenyltetrazole-5-thiol arylation with iodobenzene under microwave and convectional heating

Temperature, °C	k, s^{-1}		Partial reaction order with respect to the reagents			
	microwave heating	convectional heating	microwave heating		convectional heating	
			I	**II**	**I**	**II**
65	$(5.1\pm2.7)\times10^{-5}$	$(1.0\pm0.4)\times10^{-5}$	1.0	1.0	1.0	0.8
80	$(7.7\pm4.2)\times10^{-3}$	$(6.0\pm1.8)\times10^{-5}$	1.2	1.2	1.9	1.2
95	$(2.3\pm0.5)\times10^{-3}$	$(1.7\pm1.4)\times10^{-3}$	1.0	1.2	1.9	1.6

Table 2. Kinetic parameters of 1-phenyltetrazole-5-thiol arylation with iodobenzene under microwave and convectional heating

Method	E_a, kJ mol^{-1}		$\Delta S^{\neq}$, J mol^{-1} K^{-1}	
	microwave activation	convectional heating	microwave activation	convectional heating
Differential	131	175	10.3	14.2
Stationary concentrations	126	135	9.5	10.0

calculations were performed according to the Arrhenius equation in its differential form, taking advantage of the partial least square method. In the frame of the activated complex theory, E_a being equal to the activated complex enthalpy $H^{\neq}$, the corresponding enthalpy $\Delta S^{\neq}$ was calculated.

$$k(T) = Ae^{\Delta H^{\neq}/RT}, \quad (4)$$

$$A = \chi \frac{kT}{h} \cdot e^{\Delta S^{\neq}/R}. \quad (5)$$

In Eq. (5), χ is the transmission coefficient, $\chi \approx 1$; h is Planck's constant. The activation entropy was calculated as in Eq. (6).

$$\Delta S^{\neq} = R\ln A \frac{h}{kT}. \quad (6)$$

The values of E_a, and $\Delta S^{\neq}$ were calculated according to the stationary concentrations method as well. The results were in good agreement with those from the differential method (Table 2).

From Table 2, the activation energy and entropy from different methods were similar for the cases of convectional and microwave heating. The close values of E_a under different heating conditions showed the absence of any specific microwave effect. The acceleration of the copper-catalyzed 1-phenyltetrazole-5-thiol arylation with iodobenzene under conditions of microwave irradiation could be due to intensification of the macrokinetic processes.

EXPERIMENTAL

1-Phenyl-5-sulfanyltetrazole was prepared according to [5]. Starting 1-phenyltetrazole-5-thiol was recrystallized from propanol-2; iodobenzene was distilled under reduced pressure.

Kinetic studies were performed with Shimadzu Prominence LC-20 HPLC instrument [eluent: MeCN–H_2O (3:2), column temperature of 30°C, column: SUPEL-CO Supelcosil LC-18-DB 150×4.6 mm, flow rate of 1 ml min^{-1}].

General procedure [5]. A mixture of 0.5 g (2.79 mmol) of 1-phenyltetrazole-5-thiol, 0.56 g (2.79 mmol) of iodobenzene, 0.96 g (7 mmol) of K_2CO_3, 0.106 g (0.56 mmol) of CuI, and 0.033 g (0.56 mmol) of ethylenediamine in 10 ml of DMF was heated at a chosen temperature upon stirring.

REFERENCES

1. Niu, L.-F., Cai, Y., Liang, C., Hui, X.-P., and Xu, P.-F., *Tetrahedron*, 2011, vol. 67, p. 2878.
2. Larsson, P.-F., Bolm, C., and Norrby, P.-O., *Chem. Eur. J.*, 2010, vol. 16, p. 13613.
3. Larsson, P.-F., Bolm, C., and Norrby, P.-O., *Beilstein J. Org. Chem*., 2012, vol. 8, p. 1909.
4. Sperotto, E., van Klink, G.P.M., van Koten, G., and de Vries, J.G., *Dalton Trans*., 2010, vol. 39, p. 10338.
5. Dmitrieva, U.N., Ramsh, S.M., Zevatskii, Yu.E., Artamonova, T.V., and Myznikov, L.V., *Chem. Heterocyclic Comp.*, 2012, vol. 48, no. 2, pp. 355–357.