

Isoenthalpy Catalytic Effects of Pyridines in Reactions of Phenylloxirane with *N*-Aroylbenzenesulfonamides

I. V. Shpanko^{a,*} and I. V. Sadovaya^b

^a V. Stus Donetsk National University, Vinnitsa, 21021 Ukraine

^b Donetsk National University, Donetsk, Ukraine

*e-mail: shpanko16@ukr.net

Received June 4, 2019; revised June 4, 2019; accepted June 11, 2019

Abstract—Additive nature of the combined effect of the structure (X, Y substituents) and temperature on the rate and free activation energy has been established for the reactions of phenylloxirane with Y-substituted *N*-aroylbenzenesulfonamides catalyzed by X-substituted pyridines. The cross reaction series is isoenthalpic with respect to the structural effects. The mechanism of the catalytic process has been discussed.

Keywords: phenylloxirane, *N*-aroylbenzenesulfonamides, pyridines, activation parameters, cross-correlation analysis

DOI: 10.1134/S1070363219120053

Unique synthetic potential of oxiranes, their practical value, catalytic aspects, and the reaction mechanisms have attracted the researchers attention during many decades, and the interest to their chemistry has remained unabated (see, e.g., [1–4]). However, in spite of intense studies of the oxiranes by experimental and theoretical methods, quantitative relationships taking into account the effects of the structure, medium, temperature, and other internal and external factors on the rate, regioselectivity, and the mechanisms of oxirane reactions with various reagents in both catalytic and noncatalytic conditions have remained poorly understood. Knowledge of these relationships will aid in the development of quantitative theory of the reaction of oxiranes. In this regard, the reactions of 2-aryl- and 2,3-diaryloxiranes with arenesulfonic and arenecarboxylic acids are interesting, in which the effects of cross-varied factors (structure of the substrate, reagent, and catalyst, temperature) are nonadditive [5–9]. These reactions are described by the principle of multilinearity including cross terms [10], whose presence leads a phenomenon of isoparametricity manifested as the zero coefficient of sensitivity to the effect of one of the factors in one-parameter correlations at a value of another factor equal to a value called isoparametric point.

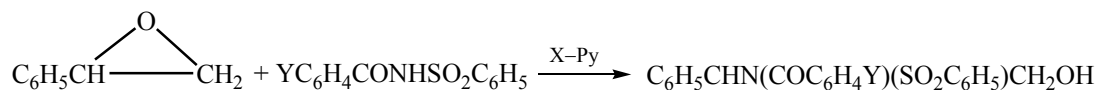
Pronounced nonadditivity of the structure and temperature effects in a series of isoparametric (isokinetic) cross reaction series [6, 8, 9] has provided experimental evidence of such an intriguing aspect of isoparametricity

as enthalpy-entropy compensation effect widely discussed in the literature [11–16]. The isoparametric points in temperature T^P (T_{iso}) have been reached for the considered reaction series; moreover, transitions through these points with inversion of the effects of structural factors on the rate and free activation energy of the oxirane ring opening reactions (isoparametricity paradox) have been demonstrated.

In contrast, no compensation effect has been observed in the reactions of phenylloxirane with such NH-acids as diarenesulfonimides $(YC_6H_4SO_2)_2NH$ [17] and *N*-aroylarenesulfonamides $YC_6H_4CONHSO_2C_6H_4Z$ [18], due to additive influence of the structural effects and the temperature. The two cross reaction series have been isoenthalpic with respect to variation of substituents Y and Z [$\Delta H_{Y(Z)}^\ddagger = \text{const}$, $\delta_{Y(Z)}\Delta H^\ddagger = 0$]. The influence of substituents Y and Z in these series has been exclusively due to variation of the activation entropy [$\delta_{Y(Z)}\Delta G^\ddagger = -T\delta_{Y(Z)}\Delta S^\ddagger$]. It was therefore interesting to elucidate the character of combined effects of the structure and temperature in these reaction series under catalytic conditions.

The present study aimed to investigate the combined influence of substituents X, Y and temperature on the rate and activation parameters of the reactions of phenylloxirane **2** with Y-substituted *N*-aroylbenzenesulfonamides $YC_6H_4CONHSO_2C_6H_5$ **3a–3c** [Y = 4-CH₃ (**3a**), H (**3b**), 4-NO₂ (**3c**)] catalyzed by X-substituted pyridines X-Py **1a–1d** [X = 4-Et (**1a**), H (**1b**), 3-COOEt (**1c**), 3-CN (**1d**)]

Scheme 1.



in acetonitrile, to perform the cross correlation analysis of the multifactor kinetic experiment data, and to use them for interpretation of the mechanism of the catalytic process (Scheme 1).

The values of rate constants k_{XYT} of reaction (Scheme 1) at temperatures $T = 293, 308, \text{ and } 323 \text{ K}$ are given in Table 1. For quantitative evaluation of the effects of cross-varied factors, the results of multifactor kinetic experiment were subject to correlation analysis.

To take into account electronic effects of substituents X(Y), the substituents Y(X) and temperature being fixed, the Hammett equation was used in the form of relationships (1) and (2).

$$\log k_{\text{XYT}} = \log k_{\text{HYT}} + \rho_{\text{X}}^{\text{YT}} \sigma_{\text{X}}, \quad (1)$$

$$\log k_{\text{XYT}} = \log k_{\text{XHT}} + \rho_{\text{Y}}^{\text{XT}} \sigma_{\text{Y}}. \quad (2)$$

The results of the kinetic data processing using Eq. (1) showed that the coefficient of sensitivity $\rho_{\text{X}}^{\text{YT}}$ to the influence of substituent X at fixed substituent Y = H in imide **3b** was practically independent of temperature: $\rho_{\text{X}}^{\text{YT}}(T, \text{K}) = -0.85 \pm 0.02$ (293), -0.77 ± 0.05 (308), -0.816 ± 0.005 (323). The coefficient of sensitivity $\rho_{\text{Y}}^{\text{XT}}$ to the influence of substituent Y at fixed substituent X = H in pyridine **1b** remained constant with varying the temperature as well: $\rho_{\text{Y}}^{\text{XT}}(T, \text{K}) = 1.21 \pm 0.04$ (293), 1.21 ± 0.02 (308), 1.21 ± 0.04 (323). Such behavior of $\rho_{\text{X}}^{\text{YT}}$ and $\rho_{\text{Y}}^{\text{XT}}$ was indicative of the absence of interaction between the effects of substituents X and temperature, on the one hand, and substituents Y and temperature on the other hand.

To take into account the effect of temperature on the rate of reaction (Scheme 1), the Eyring equation (3) was used:

$$\log(k_{\text{XYT}}/T) = A_{T=\infty}^{\text{XY}} + B_{\text{T}}^{\text{XY}} 1000/T, \quad (3)$$

with $A_{T=\infty}^{\text{XY}} = \log(k_{\text{B}}/h) + \Delta S_{\text{XY}}^{\ddagger}/2.3R$, $B_{\text{T}}^{\text{XY}} = -\Delta H_{\text{XY}}^{\ddagger}/2.3R$ (k_{B} —Boltzmann constant, h —Planck constant, R —gas constant).

Table 2 shows the coefficients of Eq. (3) for specific reaction series in which substituent X in pyridines **1a–1d** was varied, the substituent in imide **3b** being fixed, Y = H. The activation parameters calculated using those coefficients are given in Table 2 as well. No influence of substituent X on the coefficient of sensitivity to temperature B_{T}^{XY} confirmed the conclusion about the absence of interaction of the effects of substituents X and temperature. Consequently, the enthalpy-entropy compensation effect in the investigated catalytic process was absent. Constant activation enthalpy with varying substituents X suggested the isoenthalpic character of the process.

Analysis of the data of Table 3, where the coefficients of Eq. (3) and activation parameters are given for specific reaction series in which substituent Y in mixed imides **3a–3c** was varied at fixed substituent X = H in pyridine **1b**, suggested the isoenthalpic character of the effect of substituent Y in the reaction presented in Scheme 1.

Therefore, the influence of structural effects on the free activation energy $\Delta G_{\text{XY}}^{\ddagger}$ of the reaction in Scheme 1 and, hence, on their rates, was exclusively due to variation of the entropy term $[\delta_{\text{X(Y)}} \Delta G^{\ddagger} = -T \delta_{\text{X(Y)}} \Delta S^{\ddagger}]$, as confirmed, for example, by linear relationships (4)–(7).

$$\Delta S_{\text{XY=H}}^{\ddagger} = (-99.4 \pm 0.4) + (-12 \pm 1) \sigma_{\text{X}}, \quad (4)$$

$$S = 0.862, r = 0.992, n = 4;$$

$$\Delta S_{\text{X=HY}}^{\ddagger} = (-100.1 \pm 0.1) + (22.0 \pm 0.2) \sigma_{\text{Y}}, \quad (5)$$

$$S = 0.185, r = 0.999, n = 3;$$

Table 1. Rate constants $k_{\text{XYT}} \times 10^5$ ($\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$) for **1a–1d**-catalyzed reactions of oxirane **2** with imides **3a–3c** in acetonitrile at different temperatures

Imide (σ_{Y})	Pyridine (σ_{X})	293 K	308 K	323 K
3a (–0.17)	1b (0)	0.42±0.01	1.7±0.1	6.81±0.03
3b (0)	1a (–0.15)	0.79±0.01	3.35±0.07	12.9±0.3
	1b	0.617±0.005	2.3±0.2	9.7±0.3
	1c (0.37)	0.292±0.007	1.26±0.01	4.92±0.04
	1d (0.56)	0.20±0.01	0.93±0.02	3.41±0.03
3c (0.78)	1b	5.80±0.02	23±1	92.2±0.1

Table 2. Coefficients in Eq. (3) and activation parameters $\Delta H_{\text{X}}^{\ddagger}$, kJ/mol, $\Delta S_{\text{X}}^{\ddagger}$, J mol⁻¹ K⁻¹, $\Delta G_{\text{XT}}^{\ddagger}$, kJ/mol for the pyridine **1a–1d**-catalyzed reaction of oxirane **2** with imide **3b** in acetonitrile at 298, 308, and 323 K

Parameter	Pyridine			
	1a	1b	1c	1d
$A_{T=\infty}^{\text{XY}}$	5.30±0.07	5.1±0.6	4.98±0.01	4.8±0.4
B_1^{XY}	-3.77±0.02	-3.7±0.2	-3.81±0.01	-3.8±0.1
r	0.999	0.999	0.999	0.999
S	0.005	0.040	0.001	0.025
$\Delta H_{\text{X}}^{\ddagger}$, kJ/mol	72	71	73	73
$\Delta S_{\text{X}}^{\ddagger}$, J mol ⁻¹ K ⁻¹	-97	-100	-104	-106
$\Delta G_{\text{XT}=293}^{\ddagger}$, kJ/mol	100	101	103	104
$\Delta G_{\text{XT}=308}^{\ddagger}$, kJ/mol	101	102	105	106
$\Delta G_{\text{XT}=323}^{\ddagger}$, kJ/mol	102	103	106	107

$$\Delta G_{\text{XY=HT}=293}^{\ddagger} = (56 \pm 3) \times 10^3 + (-451 \pm 27) \Delta S_{\text{X}}^{\ddagger}, \quad (6)$$

$$S = 268, r = 0.996, n = 4;$$

$$\Delta G_{\text{X=HYT}=293}^{\ddagger} = (67 \pm 1) \times 10^3 + (-339 \pm 16) \Delta S_{\text{Y}}^{\ddagger}, \quad (7)$$

$$S = 256, r = 0.999, n = 3.$$

In view of the absence of mutual influence of structural effects and temperature in the reaction in Scheme 1, the effect of the cross-varied factors on its rate should be described by the additive Eq. (8):

$$\log k_{\text{XYT}} = \log k^{\text{st}} + \rho_{\text{X}}^{\text{st}} \sigma_{\text{X}} + \rho_{\text{Y}}^{\text{st}} \sigma_{\text{Y}} + B_1^{\text{st}} 1000/T, \quad (8)$$

with k^{st} being the rate constant under standard conditions ($\sigma_{\text{X}} = \sigma_{\text{Y}} = 0, T = \infty \text{K}$), $\rho_{\text{X}}^{\text{st}}, \rho_{\text{Y}}^{\text{st}}, B_1^{\text{st}}$ being the parameters of sensitivity of the standard reactions, respectively, at $\sigma_{\text{Y}} = 0$ and $T = \infty \text{K}$, $\sigma_{\text{X}} = 0$ and $T = \infty \text{K}$, $\sigma_{\text{X}} = \sigma_{\text{Y}} = 0$. Processing of the multifactor kinetic experiment results (Table 1) using Eq. (8) gave the multilinear regression with satisfactory statistic parameters (R —coefficient of multiple correlation, F —Fischer criterion).

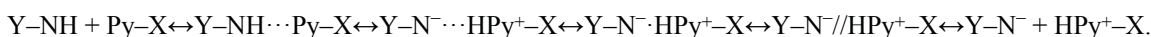
$$\log k_{\text{XYT}} = (7.8 \pm 0.2) + (-0.84 \pm 0.02) \sigma_{\text{X}} + (1.22 \pm 0.02) \sigma_{\text{Y}} + (-3.82 \pm 0.05) 1000/T, \quad (9)$$

$$S = 0.026, r = 0.999, F = 4075, n = 18.$$

Joint effect of substituents X, Y and temperature on the free activation energy $\Delta G_{\text{XYT}}^{\ddagger}$ of reactions in Scheme 1 was estimated by Eq. (10).

$$\Delta G_{\text{XYT}}^{\ddagger} = \Delta G^{\ddagger \text{st}} + Q_{\text{X}}^{\text{st}} \sigma_{\text{X}} + Q_{\text{Y}}^{\text{st}} \sigma_{\text{Y}} + Q_1^{\text{st}} T. \quad (10)$$

Scheme 2.



where $\Delta G^{\ddagger \text{st}}$ is free activation energy under standard conditions ($\sigma_{\text{X}} = \sigma_{\text{Y}} = 0, T = 0 \text{K}$), $Q_{\text{X}}^{\text{st}}, Q_{\text{Y}}^{\text{st}}, Q_1^{\text{st}}$ are parameters of sensitivity of standard reactions respectively at $\sigma_{\text{Y}} = 0$ and $T = 0 \text{K}$, $\sigma_{\text{X}} = 0$ and $T = 0 \text{K}$, $\sigma_{\text{X}} = \sigma_{\text{Y}} = 0$. Calculation of coefficients of Eq. (10) using the values of $\Delta G_{\text{XYT}}^{\ddagger}$ from Tables 2 and 3 gives the following result:

$$\Delta G_{\text{XYT}}^{\ddagger} = (79 \pm 3) + (6.6 \pm 0.6) \sigma_{\text{X}} + (-7.8 \pm 0.5) \sigma_{\text{Y}} + (0.08 \pm 0.01) T, \quad (11)$$

$$S = 0.586, r = 0.976, F = 188, n = 18.$$

In the reaction system (Scheme 1), the catalytic role of pyridines consists in the enhancement of nucleophilic properties of the acidic reagent Y-NH (Y—substituted imides) due to the acid-base interactions (Scheme 2).

Free ions: imide anion $\text{Y-N}^- = (\text{YC}_6\text{H}_4\text{CO})(\text{SO}_2\text{C}_6\text{H}_5)\text{N}^-$ and pyridinium cation HPy^+-X should possess the strongest catalytic effect among the possible H-complexes and ionic intermediates in the equilibrium system in acetonitrile medium. The mechanism of catalytic action of pyridines shown in Scheme 3 can be regarded as basic with electrophilic assistance.

That mechanism corresponds to the overall third reaction rate order of the catalytic reaction (the first rate order with respect each of the reagents and the catalyst). As follows from Scheme 3, the catalytic constant k_{XYT} was a compound value ($k_{\text{XYT}} = Kk$), therefore, the parameter of sensitivity $\rho_{\text{X}}^{\text{YT}}$ to effects of substituents X in pyridines

Table 3. Coefficients in Eq. (3) and activation parameters $\Delta H_{\ddagger}^{\ddagger}$, kJ/mol, $\Delta S_{\ddagger}^{\ddagger}$, J mol⁻¹ K⁻¹), $\Delta G_{\ddagger}^{\ddagger}$, kJ/mol for the pyridine **1b**-catalyzed reaction of oxirane **2** with imides **3a–3c** in acetonitrile at 298, 308, and 323 K

Parameter	Imide		
	3a	3b	3c
$A_{T=\infty}^{XY}$	4.9±0.2	5.1±0.6	6.0±0.3
B_T^{XY}	-3.74±0.07	-3.7±0.2	-3.7±0.1
r	0.999	0.999	0.999
S	0.015	0.040	0.023
$\Delta H_{\ddagger}^{\ddagger}$, kJ/mol	71	71	71
$\Delta S_{\ddagger}^{\ddagger}$, J mol ⁻¹ K ⁻¹	-104	-100	-83
$\Delta G_{\ddagger}^{\ddagger}$, kJ/mol	102	101	95
$\Delta G_{\ddagger}^{\ddagger}$, kJ/mol	103.5	102	96
$\Delta G_{\ddagger}^{\ddagger}$, kJ/mol	105	103	97

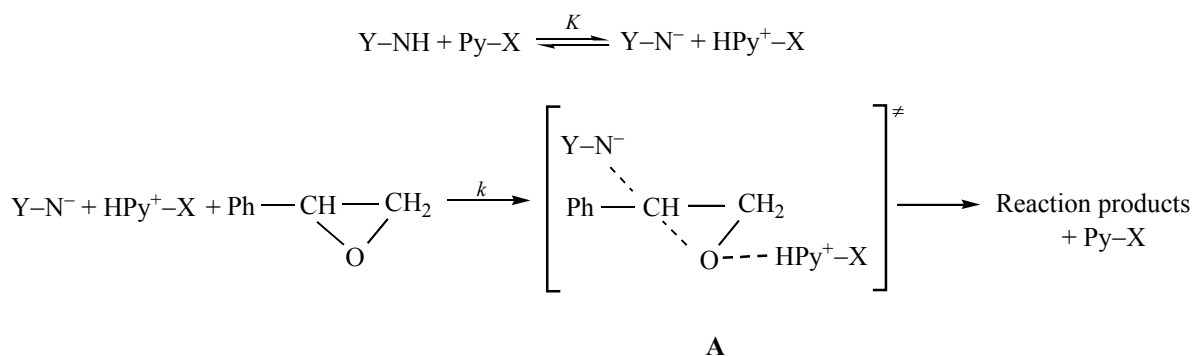
consisted of two terms: $\rho_X^{YT} = \rho_X^I + \rho_X^{II}$, where $\rho_X^I < 0$ at the first stage of protonation of pyridines and formation of $Y-N^-$ and $\rho_X^{II} > 0$ at the second rate-limiting stage of electrophilic assistance to the oxirane ring opening by pyridinium cation HPy^+-X .

The negative value of ρ_X^{YT} over the particular reaction series was indicative of weak $O \cdots H$ hydrogen bonding in the transition state **A** of the rate-limiting step ($\rho_X^{II} < |\rho_X^I|$), i.e. negligible electrophilic assistance to the oxirane ring opening. That was also confirmed by the absence of temperature effect on the ρ_X^{YT} value. If the H-bond in the transition state **A** played important role, its strengthening (weakening) would be favored by a decrease (increase) in the temperature, which would lead to the increase (decrease) in ρ_X^I , and, hence, to the decrease (increase) in $|\rho_X^{YT}|$. In that case, a compensation effect in variation of the enthalpy and entropy components of the

free activation energy should have been observed because of the interplay between the effects of substituents X and temperature.

That was the situation we have observed for the reactions of phenyloxirane with Y-substituted benzoic acids in acetonitrile catalyzed by X-substituted pyridine [6]. In these reactions, we have observed strong interplay between the effects of substituent X effects and temperature due to strong assistance to the oxirane ring opening by H-bonding, and the value of ρ_X^{YT} has changed drastically with variation of the temperature, the sign inversion being observed on passing through the isokinetic point T^{IP} (where $\rho_X^{YT} = 0$). The observed phenomenon has been a consequence of the enthalpy-entropy compensation effect, namely, full compensation of the enthalpy and entropy contributions to the free activation energy under the action of substituents X in the catalyst at $T^{IP}(\delta_X \Delta H^\ddagger = T^{IP} \delta_X \Delta S^\ddagger)$,

Scheme 3.



due to which the $\delta_X \Delta G^{\neq IP} = \delta_X \Delta H^{\neq} - T^{\neq} \delta_X \Delta S^{\neq} = 0$, $\Delta G_X^{\neq IP} = \text{const}$ condition has been met, and the reactions of the series have exhibited the same rate.

The parameter of sensitivity ρ_Y^{XT} to the influence of substituent Y in acids **3a–3c** was also a compound value: $\rho_Y^{\text{XT}} = \rho_Y^{\text{I}} + \rho_Y^{\text{II}}$, with $\rho_Y^{\text{I}} > 0$ at the first step of the catalytic process and $\rho_Y^{\text{II}} < 0$ at the second step. The positive value of ρ_Y^{XT} for the particular reaction series suggested higher sensitivity to the effects of substituents Y for proton transfer from the NH-acid to the catalyst than for nucleophilic attack of the imide anion $Y-N^-$ at the oxirane ring carbon atom ($\rho_Y^{\text{I}} > |\rho_Y^{\text{II}}|$), which was possible for the reagent-like transition state **A** with low degree of the N–C bond formation and the C–O bond rupture. The formation of such transition state required small energy (enthalpy) of activation. In view of that fact and small impact of the enthalpy factor on the acid-base interactions [19], one could conclude that, first, the catalytic effect of pyridines in the reactions (Scheme 1) should have been due to the decrease in the activation enthalpy with respect to the noncatalytic process, and, second, the effect of structural factors (substituents X and Y) on the changes of activation enthalpy should have been weak. No effect of the structure on the value of the activation enthalpy observed in the reactions (Scheme 1) (Tables 2 and 3) was indicative of their isoenthalpic nature.

The comparison of activation parameters (Tables 2 and 3) of the catalytic (Scheme 1) and the corresponding noncatalytic reactions [18] showed that the catalytic effect of pyridines was mainly due to much larger decrease in the enthalpy term of the free activation energy than to the increase in its entropy term. For example, the comparison of activation parameters of the reaction of oxirane **2** with acid **3b** in acetonitrile in the presence of catalyst **1b** ($\Delta H_{\text{XY}}^{\neq} = 71$ kJ/mol, $\Delta S_{\text{XY}}^{\neq} = -100$ J mol⁻¹ K⁻¹, $\Delta G_{\text{XYT}=323}^{\neq} = 103$ kJ/mol) and in its absence [18] ($\Delta H_{\text{XY}}^{\neq} = 88$ kJ/mol, $\Delta S_{\text{XY}}^{\neq} = -87$ J mol⁻¹ K⁻¹, $\Delta G_{\text{XYT}=323}^{\neq} = 116$ kJ/mol) revealed that the decrease in the free activation energy in the catalytic process by 13 kJ/mol at $T = 323$ K (and, thus, the process acceleration) occurred due to the decrease in the activation enthalpy by 17 kJ/mol as compared to the noncatalytic process, which far exceeded the increase in $\Delta G_{\text{XYT}=323}^{\neq}$ (by 4 kJ/mol) due to the entropy term $T\Delta S_{\text{XY}}^{\neq}$, leading to the rate decrease.

EXPERIMENTAL

Acetonitrile (“analytical pure” grade) was dried and distilled sequentially over P₂O₅ and over CaH₂. Phenyl-

loxirane (98% purity) purchased from Merck and pyridines (“chemical pure” grade) were distilled in vacuum. Imides **3a–3c** were synthesized and purified as described elsewhere [20]. The products of the reactions in Scheme 1 were primary alcohols: 2-(*N*-aroyl-*N*-benzenesulfonyl) amino-2-phenylethanol [18].

The reaction rates were measured as described in Ref. [21]. The kinetics of the reactions (Scheme 1) was studied at more than 10-fold excess of the oxirane substrate (S) with respect to initial concentrations of the acidic reagent (NH): $[S]_0 \gg [NH]_0 = 0.477\text{--}1.91$ mol/L; in turn, the concentration of pyridines ranged within $m = 0.0116\text{--}0.0860$ mol/L. Under those conditions, the reaction was of the first reaction rate order with respect to the reagents and the catalyst, so that the kinetics of the process was described by equation at the constant concentration of the catalyst m (12).

$$-d[NH]/dt = k_1[NH] = k_3[S]_0[NH]m. \quad (12)$$

The observed pseudo-first order rate constants k_1 (s⁻¹) were constant up to 70–80% conversion of the acidic reagent (the error in measuring k_1 was $\leq 5\%$). The second-order rate constants k_2 (L mol⁻¹ s⁻¹) were obtained as $k_2 = k_1/[S]_0$. Numerical values of the effective catalytic third-order rate constants k_{XYT} (L² mol⁻² s⁻¹) were calculated from three kinetic runs at different concentrations m using the $k_2 = k_{\text{XYT}}m$ linear equation (correlation coefficient $r \geq 0.998$), extrapolation to the origin suggesting the absence of the noncatalytic term. The error of the kinetic and correlation parameters was estimated as mean-square deviation S determined by statistical method from the number of experimental points n .

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

- Bespalko, Y.N. and Shved, E.N., *React. Kinet. Mech. Cat.*, 2019, vol. 126, no. 2, p. 903. <https://doi.org/10.1007/s11144-018-01524-2>
- Deshpande, N., Parulkar, A., Joshi, R., Diep, B., Kulkarni, A., and Brunelli, N.A., *J. Catal.*, 2019, vol. 370, p. 46. <https://doi.org/10.1016/j.jcat.2018.11.038>
- Ly, U.Q., Pham M.-P., Marks, M.J., and Truong, T.N., *J. Comput. Chem.*, 2017, vol. 38, no. 14, p. 1093. <https://doi.org/10.1002/jcc.24779>

4. Meninno, S. and Lattanzi, S., *Chem. Eur. J.*, 2016, vol. 22, no. 11, p. 3632.
<https://doi.org/10.1002/chem.201504226>.
5. Shpan'ko, I.V., Sadovaya, I.V., and Kulikova, N.V., *Russ. J. Org. Chem.*, 2011, vol. 47, no. 5, p. 687.
<https://doi.org/10.1134/S107042801105006X>
6. Shpan'ko, I.V. and Sadovaya, I.V., *Kinet. Catal.*, 2014, vol. 55, no. 1, p. 56.
<https://doi.org/10.1134/S002315841401011X>
7. Shpan'ko, I.V. and Sadovaya, I.V., *Russ. J. Gen. Chem.*, 2016, vol. 86, no. 11, p. 2418.
<https://doi.org/10.1134/S1070363216110037>
8. Shpan'ko, I.V. and Sadovaya, I.V., *Theor. Exp. Chem.*, 2010, vol. 46, no. 3, p. 176.
<https://doi.org/10.1007/s11237-010-9136-z>
9. Shpan'ko, I.V. and Sadovaya, I.V., *Russ. J. Gen. Chem.*, 2017, vol. 87, no. 11, p. 2552.
<https://doi.org/10.1134/S107036321711007X>
10. Palm, V.A., *Fundamentals of the Quantitative Theory of Organic Reactions*, Leningrad: Khimiya, 1977.
11. Liu, L. and Guo, Q.-X., *Chem. Rev.*, 2001, vol. 101, no. 3, p. 673.
<https://doi.org/10.1021/cr990416z>
12. Sharp, K., *Protein Sci.*, 2001, vol. 10, no. 3, p. 661.
<https://doi.org/10.1110/ps.37801>
13. Cornish-Bowden, A., *J. Biosci.*, 2002, vol. 27, no. 2, p. 121.
<https://doi.org/10.1007/BF02703768>
14. Starikov, E.B. and Norden, B., *J. Phys. Chem. (B)*, 2007, vol. 111, no. 51, p. 14431.
<https://doi.org/10.1021/jp075784i>
15. Parmon, V.N., *React. Kinet. Mech. Cat.*, 2016, vol. 118, no. 1, p. 165.
<https://doi.org/10.1007/s11144-016-1005-x>
16. Zuniga-Hansen, N., Silbert, L.E., and Calbi, M.M., *Phys. Rev. (E)*, 2018, vol. 98, no. 3, p. 032128.
<https://doi.org/10.1103/PhysRevE.98.032128>
17. Shpan'ko, I.V. and Sadovaya, I.V., *Ukr. Khim. Zh.*, 2004, vol. 70, no. 4, p. 104.
18. Shpan'ko, I.V. and Sadovaya, I.V., *Ukr. Khim. Zh.*, 2015, vol. 81, no. 10, p. 124.
19. Dneprovskii, A.S. and Temnikova, T.I., *Teoreticheskie osnovy organicheskoi khimii* (Theoretical Foundations of Organic Chemistry), Leningrad: Khimiya, 1991.
20. Derkach, G.I., Dregval', G.F., and Kirsanov, A.V., *Zh. Obshch. Khim.*, 1960, vol. 30, no. 10, p. 3402.
21. Shpan'ko, I.V., Sadovaya, I.V., and Kitaigorodskii, A.M., *Ukr. Khim. Zh.*, 2003, vol. 69, no. 6, p. 111.