
CHEMICAL KINETICS
AND CATALYSIS

Kinetics and Mechanism of Structural Transformations of 2-(5-Ethoxycarbonylmethyl-4-oxothiazolidin-2-ylidene)- N-(2-phenylethyl)-ethanamide During Heating¹

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Abstract—The kinetics and mechanism of the structural transformation of 2-(5-ethoxycarbonylmethyl-4-oxothiazolidin-2-ylidene)-N-(2-phenylethyl)-ethanamide in non-isothermal conditions were studied by using isoconversion as well as non-isoconversion techniques. It was shown that the crystal, *Z*-form of compound, was stable in the temperature range from room temperature to melting point, when *E*-form of compound was formed. This process involves the breaking of crystal structure and the forming of glass material as a new phase, which by cooling forms crystal of the *E*-form of compound very slowly. The dependences of kinetic parameters on fractional extent conversion were determined indicating a very complex process which involves more than one elementary step, as can be expected for most solid state reactions. The possible mechanism of the process was discussed according to the algorithm concerning the form of these dependences. The evaluation of kinetics parameters and isokinetic relationships were done by combination of model fitting and model-free approach.

Keywords: activation energy, phase transformation, glass materials.

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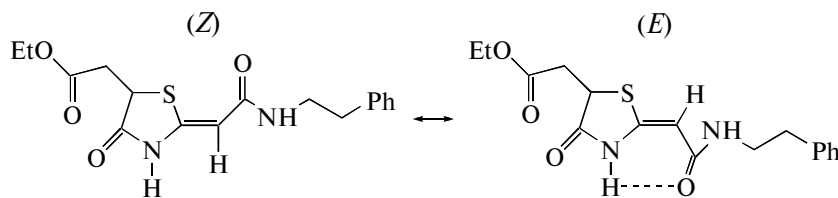
INTRODUCTION

Many new and different reactions, concerning isomerization, dimerization and polymerization, activated thermally and photochemically, which modify the state of the molecules in the crystalline media have been the focus of recent research efforts [1–5] to a point where one can say that solid-state reactions have now entered into the mainstream of organic chemistry. The *push-pull* alkenes represent an excellent model for investigation of the effects of weak non-covalent interactions on relationships between structure and reactivity in solution and in the solid state [6–8].

The series of stereo-defined oxothiazolidines, synthesized according to procedures we reported [9, 10],

attracted our attention because of their potential biological activity and application as precursors for the synthesis of *push-pull* polyenes. We have shown that the equilibrated mixtures of structurally related 4-oxothiazolidines consist of the intra-molecularly H-bonded *E*-isomer and inter-molecularly H-bonded *Z*-isomer in varying proportions depending on the solvent polarity and temperature [11].

As a part of our wider study on the synthesis, characterization and thermal behavior of *push-pull* 5-substituted-4-oxothiazolidines [9–16] we have reported here the study of kinetics of structural transformation of 2-(5-ethoxycarbonylmethyl-4-oxothiazolidin-2-ylidene)-N-(2-phenylethyl)-ethanamide induced by heating according to the scheme:



The kinetics of the configurational isomerization of
stereodefined of *push-pull* 5-substituted-4-oxothiazo-

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lidines in non-isothermal conditions were studied by X-ray powder crystallography, IR spectroscopy, ^1H NMR spectroscopy and differential scanning calorimetry (DSC)[15,16]. It was shown that the crystal *Z*-form of compounds were stable in the temperature range from room temperature to melting point. This process involves the breaking of the crystal structure and the forming a glass material as a new phase that forms very slowly the crystal of the *E*-form of compounds after cooling [15]. The *Z/E* transformation was rationalized in terms of non-covalent interactions, involving intermolecular and intramolecular hydrogen bonding and directional non-bonded 1,5-type $\text{S}\cdots\text{O}$ interactions [16]. The thermodynamic and activation parameters of the process were determined and the kinetics of transformation was studied by using iso-conversion as well as non-isoconversion techniques. The kinetic triplet was established, taking into consideration the overall values of kinetic parameters.

Having in mind the complexity of solid state reaction and the dependence of the kinetics parameters on the fractional conversion of transformation, we have studied in detail the kinetics as well as mechanism of the process by combining the fitting model and free model methods in order to establish the mechanism and the kinetics parameters of thermal isomerization of *push-pull* 5-substituted-4-oxothiazolidines.

MATERIALS AND METHODS

The kinetic information on processes occurring in a solid phase can be obtained from dynamic experiments by using different methods. Here we investigated the process of structural transformation of (*Z*)-2-(5-ethoxycarbonylmethyl-4-oxothiazolidin-2-ylidene)-*N*-(2-phenylethyl)-ethanamide non-isothermally with differential scanning calorimetry (DSC), using a DuPont Thermal Analyzer (model 1090). In this case, samples weighing several milligrams were heated in the DSC cell from room temperature to 340 K, at heating rates in the range 5–20 K min^{-1} , in a stream of nitrogen at normal pressure. The sample masses were in the range 3–7 mg. The temperature peaks (T_p) were determined from DSC curve using the program INTERACTIVE DSC VI.1. DSC system has been calibrated using In as the standard for the each heating rate. The compound was prepared by the previously published method [9].

The methods of thermal analysis such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are very popular for kinetic analysis of the structural transformation in solid phase, such as crystallization and phase transformations, which don't involve any loss of mass. The structural transformations during heating, occurring in a solid phase, can be performed in several ways. In calorimetric measurements, two basic methods are in use: isothermal and non-isothermal. To establish the kinetic parameters from DSC data, the following assumptions should

be accepted: a reaction extent is connected with the fractional conversion of transformation, α ; the conversion rate, $d\alpha/dt$, is proportional to the measured heat flow, dQ/dt ; the temperature dependence of the rate constant $k(T)$, is described by the Arrhenius equation [13].

According to the kinetic studies, the isothermal conversion rate is a linear function of the temperature-dependent rate constant, $k(T)$ and a temperature-independent function of the reaction model (or conversion function), $f(\alpha)$, representing the reaction model [14]:

$$d\alpha/dt = k(T)f(\alpha), \quad (1)$$

where α is the extent of reaction.

According to the Arrhenius equation, the temperature-dependent rate constant, $k(T)$ is defined as:

$$k(T) = Z\exp(-E_a/RT), \quad (2)$$

Z is the pre-exponential factor independent of a temperature, E_a is the activation energy and R is the gas constant.

From these equations, the general equation describing the solid state reaction is as follows:

$$d\alpha/dt = Z\exp(-E_a/RT)f(\alpha). \quad (3)$$

The kinetic description of the data of solid state reaction is usually defined in terms of a kinetic triplet, such as an activation energy, E_a , a pre-exponential factor, Z , and an algebraic expression of the reaction model function, $f(\alpha)$. It is obvious that the constant value of the activation energy can be expected only for a single-step reaction, but E_a in Eq. (3) can be an apparent quantity based on quasi single reaction step.

For non-isothermal measurements at the constant heating rate $\beta = dT/dt$, Eq. (3) is transformed to:

$$\beta \frac{d\alpha}{dT} = Z\exp\left(-\frac{E_a}{RT}\right)f(\alpha). \quad (4)$$

The integral form of the reaction model, function $g(\alpha)$, can be obtained by applying the integration on Eq. (4) and separating variables:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{ZE_a}{R\beta}p(x), \quad (5)$$

$p(x)$ is the temperature integral:

$$p(x) = \int_0^x \frac{\exp(-x)}{x^2} dx, \quad x = \frac{E_a}{RT}. \quad (6)$$

The Eq. (5) can be applied once the form of the function, $p(x)$ is known. The temperature integral $p(x)$ can't be solved analytically. This problem can be overcome by using a different approximation and numerical methods.

Table 1. Algebraic expressions of conversion functions usually applied on thermal decomposition of solids

Kinetic model	$f(\alpha)$	$g(\alpha)$
Power law P4	$4\alpha^{3/4}$	$\alpha^{1/4}$
Power law P3	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law P3/2	$3/2\alpha^{1/3}$	$\alpha^{2/3}$
Avrami–Erofeev A3/2	$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
Avrami–Erofeev A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avrami–Erofeev A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avrami–Erofeev A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Prout–Tompkins B1	$\alpha(1-\alpha)$	$\ln[\alpha(1-\alpha)^{-1}]$
One dimensional phase boundary R1	1	α
Contracting cylinder R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Contracting sphere R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
D1 One-dimensional diffusion	$1/2\alpha$	α^2
D2 Two-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha) + \alpha$
D3 Three-dimensional diffusion	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
D4 Ginstling–Brounshtein	$3/2[(1-\alpha)^{-1/3} - 1]^{-1}$	$(1-2\alpha/3) - (1-\alpha)^{2/3}$
F1 First-order	$1-\alpha$	$-\ln(1-\alpha)$
F2 Second-order	$(1-\alpha)^2$	$(1-\alpha)^{-1}$
F3 Third-order	$1/2(1-\alpha)^3$	$(1-\alpha)^{-2}$

The algebraic expressions of the functions $g(\alpha)$ for different types of solid state reaction are given in Table 1 [14]. A plot of $g(\alpha)$ versus $1/T$ (fitting method) must be a straight line for the possible mechanism and non-linear for the wrong one. The criterion of validity of chosen algebraic expression is the value of the correlation coefficient, which must be very close to 1.

The fraction conversion of a reaction (or the extent of conversion, α) can be deduced from DSC measurements at any temperature T . In this case $\alpha = S_T/S$ where S is the total area of the peak between the tem-

perature T_i where the reaction is just beginning and the temperature T_f where the reaction is just completed; S_T is an area between the initial temperature and an arbitrary temperature T , between T_i and T_f . It is always possible to obtain α and $d\alpha/dt$ from DSC curves, by drawing the straight line between the beginning and the end of the peak as the baseline. The overall apparent activation energy of the investigated process under linear heating was determined using Kissinger's as well as by the Ozawa's peak methods, relating the dependence of peak temperature T_p on heating rate β [15].

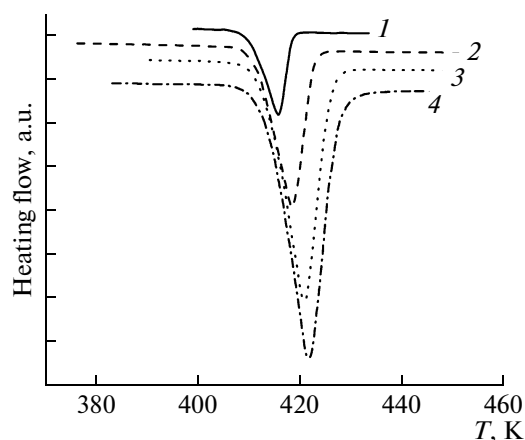


Fig. 1. DSC curves for different heating rates; $\beta = 5$ (1), 10 (2), 15 (3), and 20 K min^{-1} (4).

RESULTS AND DISCUSSION

The investigation of the thermal behavior between 293–450 K shows that the crystal *Z*-2-(5-ethoxycarbonyl-methyl-4-oxothiazolidin-2-ylidene)-*N*-(2-phenylethyl)-ethanamide is stable up to approximately 410 K, when the processes of breaking the crystal structure and melting occurs ($T_p = 417$ K, for $\beta = 5$ K min^{-1} Fig. 1). Cooling of the melt gives a glass. Analysis of the X-ray diffraction data and the IR spectra shows that the obtained glass forms crystal *E*-2-(5-ethoxycarbonylmethyl-4-oxothiazolidin-2-ylidene)-*N*-(2-phenylethyl)-ethanamide very slowly [15]. The formed *E*-isomer melts at a significantly lower temperature ($T_p = 404$ K). All these phenomena are quite common for large organic molecules and have been well studied in pharmaceutical research [17, 18]. The increase of the peak temperature with the increase of the heating

Table 2. Apparent activation parameters, according to the Coats–Redfern equation for all used conversion functions at different heating rates

Conversion function j	$\beta = 5 \text{ K min}^{-1}$			$\beta = 10 \text{ K min}^{-1}$			$\beta = 15 \text{ K min}^{-1}$			$\beta = 20 \text{ K min}^{-1}$		
	$\ln Z_\beta$ [min ⁻¹]	E_β , kJ mol ⁻¹	r	$\ln Z_\beta$ [min ⁻¹]	E_β , kJ mol ⁻¹	r	$\ln Z_\beta$ [min ⁻¹]	E_β , kJ mol ⁻¹	r	$\ln Z_\beta$ [min ⁻¹]	E_β , kJ mol ⁻¹	r
P4	37.32	132.0	0.988	28.8	102.0	0.974	24.3	86.0	0.980	22.0	77.6	0.974
P3	51.0	178.4	0.988	39.5	138.3	0.975	33.4	117.0	0.981	30.3	105.8	0.975
P2	78.1	271.0	0.988	60.7	210.9	0.976	51.4	179.0	0.981	46.7	162.3	0.976
P3/2	105.1	363.6	0.988	160.2	555.8	0.982	69.4	241.0	0.982	63.0	218.7	0.976
A3/2	147.1	506.1	0.999	115.6	399.0	0.997	97.8	338.3	0.999	89.3	308.4	0.998
A2	109.7	377.9	0.999	86.2	297.5	0.997	72.9	252.0	0.999	66.5	229.6	0.998
A3	72.1	249.6	0.999	56.6	196.0	0.997	47.8	165.6	0.999	43.6	150.7	0.998
A4	53.3	185.5	0.999	41.7	145.3	0.997	35.2	122.5	0.999	32.1	111.3	0.998
B1	413.4	1424.6	0.981	276.0	957.8	0.982	232.7	809.6	0.983	202.3	704.2	0.974
R1	159.0	548.9	0.989	123.7	428.7	0.978	105.0	365.0	0.982	95.4	331.5	0.977
R2	186.7	645.3	0.997	145.8	506.7	0.990	123.2	430.7	0.993	112.4	392.1	0.990
R3	197.0	682.0	0.998	154.1	536.4	0.993	130.4	455.8	0.996	118.7	415.2	0.993
D1	320.1	1104.6	0.989	249.0	864.3	0.977	211.4	737.0	0.982	192.0	670.1	0.977
D2	353.7	1221.8	0.994	275.9	958.8	0.985	233.8	816.7	0.989	212.6	743.4	0.985
D3	395.9	1371.0	0.998	309.6	1079.8	0.993	261.9	918.5	0.996	238.4	837.5	0.993
D4	366.6	1270.8	0.996	285.9	998.6	0.988	242.1	850.1	0.992	220.0	774.3	0.989
F1	221.8	762.6	0.999	174.3	601.9	0.997	147.5	510.9	0.999	134.6	466.2	0.998

rate indicates that a well defined endothermic peak on DSC curves involves some thermal activated steps participating in this phase transformation, besides the melting of the compound.

Model Fitting Approach

In order to apply model fitting method, the dependences of α versus T at different heating rates were constructed. The sigmoid-shaped curves (not presented in the paper) are shifted to higher temperatures with an increase of heating rate, verifying the presence of thermal activation steps in the transformation of *Z*-isomer. This suggests that the investigated process should not be characterized by a definite critical temperature independent of the heating rate.

In order to obtain the kinetic parameters of the process, α versus T data were modeled by conversion functions given in Table 1. The Arrhenius parameters for every conversion function and for each heating rate were evaluated by applying Coats–Redfern method [19] (Table 2). As can be seen from data in Table 2, although all correlation coefficients, r , are very close to 1, the Arrhenius parameters for applied heating rates are highly variable, exhibiting a strong dependence on the selected conversion function. This means that, under non-isothermal conditions, $\alpha = f(T)$ curves and Coats–Redfern’s method do not permit us to determine the true kinetic parameters as well

as the true conversion function. This is due to the fact that kinetic curves contain information about the temperature and conversion components in non-separate form.

Having determined the values of apparent activation energies, in order to determine the kinetic model, the conversion function of experimental data and theoretically proposed conversion functions from Table 1, were reconstructed numerically by applying the “master plot” method [20]. According to this method, for a single-step process, the following equation is easily derived from Eq. (1) by using a reference point at $\alpha = 0.5$

$$\frac{d\alpha/dt}{(d\alpha/dt)_{\alpha=0.5}} \frac{\exp(E_a/RT)}{\exp(E_a/RT_{0.5})} = \frac{f(\alpha)}{f(0.5)}, \quad (7)$$

where $f(0.5)$ is a constant for given conversion function. Equation (7) means that, for selected α , the experimentally determined value of the reduced-generalized reaction rate in the form $\frac{d\alpha/dt}{(d\alpha/dt)_{\alpha=0.5}} \frac{\exp(E_a/RT)}{\exp(E_a/RT_{0.5})}$ and theoretically calculated value of $f(\alpha)/f(0.5)$ are equal when an appropriate conversion function, $f(\alpha)$, is applied.

Figure 2 shows the theoretical master plots of $f(\alpha)/f(0.5)$ versus α , assuming various $f(\alpha)$ functions listed in Table 1, together with experimental plots

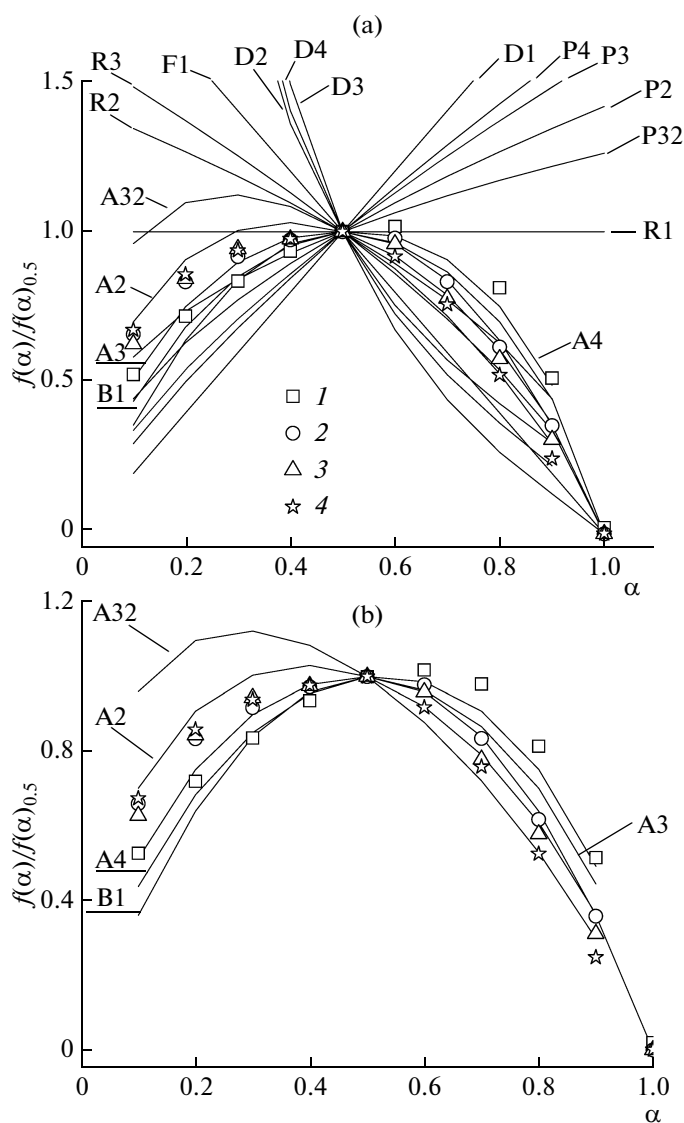


Fig. 2. Theoretical (lines) and calculated on basis of experimental data (symbols) master curves representing $f(\alpha)/f(0.5)$ as a function of α : (a) for all conversion functions describing solid state reactions according to Table 1; (b) for chosen conversion functions showing best fits; 1–4 see Fig. 1.

$\frac{d\alpha/dt}{(d\alpha/dt)_{\alpha=0.5}} \frac{\exp(E_a/RT)}{\exp(E_a/RT_{0.5})}$. As can be seen from

Fig. 2, the experimental data do not fit well into any of the models from Table 1. This indicates that the analyzed process is not a single-step reaction that could be described well by any conversion function from Table 1.

Model-Free Approach

According to the literature [21–24] all reliable methods of activation energy analysis require the determination of the temperature $T_\alpha(\beta)$ at which is an

equivalent stage of the reaction for various heating rates occurs what is known as “isoconversion methods.” The effective activation energy specific for a given extent of conversion can be determined by application of the isoconversional methods, also known as “model-free methods,” such as Kissinger–Akahira–Sunose’s (KAS method) [22, 23] on the data of several thermal analysis experiments performed at different heating rates. This way, it is possible to determine the values of $E_{a,\alpha}$ over a wide range of conversions α even without knowing the conversion function. These methods are based on the Coats–Redfern approximation [21]:

$$p(x) \cong \exp(-x)/x^2 \quad \text{for } 20 < x < 50. \quad (8)$$

Combining Eqs. (5) and (8) we get the KAS method in form the expression:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{ZR}{E_{a,\alpha}g(\alpha)}\right) - \frac{E_{a,\alpha}}{RT_\alpha}. \quad (9)$$

For resolution of this problem Flynn and Wall [24] and Ozawa [25] independently use Doyle’s approximation of $p(x)$ [26] in the form:

$$p(x) \cong -2.315 - 0.4567x \quad \text{for } 20 < x < 60. \quad (10)$$

Using Eqs. (5) and (10) we obtain FWO method in form the expression:

$$\ln\beta = \ln\left(\frac{ZE_{a,\alpha}}{Rg(\alpha)}\right) - 1.0518 \frac{E_{a,\alpha}}{RT_\alpha}. \quad (11)$$

The left parts of the Eqs. (9) and (11) are linear with respect to the inverse temperature $1/T_\alpha$, and the apparent activation energy can be evaluated using a linear regression method for every value of α . The constant value of $E_{a,\alpha}$ indicates a single step process, while the change of the $E_{a,\alpha}$ with the change of α indicates a complex process involving more than one elementary step possessing different activation energies.

Using the linear dependences of $\ln(\beta/T^2)$ on $1/T$ and $\ln\beta$ on $1/T$, which describe the non-isothermal DSC data well, we determined the kinetic parameters according to the Eqs. (9) and (11), respectively (Fig. 3).

The values of kinetic parameters determined by both methods are in agreement, within the limits of experimental error. A very similar shape of the dependences of activation energy and intercepts (did not show in Fig. 3) on fractional conversion indicates that both kinetic parameters depend on same way on the fractional conversion.

The determined values of the apparent activation energies as well as the intercepts show a decrease for the whole interval of the fractional extent, α . The changes of the activation energies and intercepts with conversion degree indicate complex processes involving more than one elementary step. The decreasing transformation-degree dependence of the activation energy is characteristic of a process involving parallel

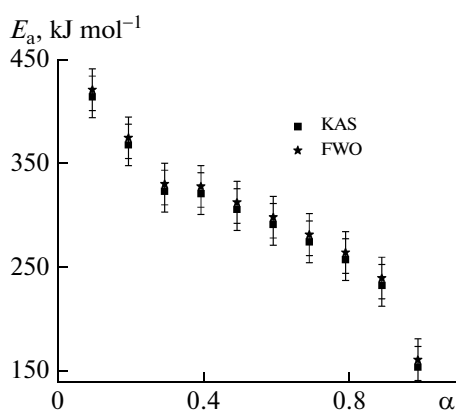


Fig. 3. Apparent activation energies as a function of fractional conversion α for Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) methods.

steps. The concave Arrhenius dependences at the beginning (decreasing transformation-degree dependences of activation energy) are typical of complex processes involving some intermediate reverse step. In this case the intermediate reverse step can be connected with the intermediate step of thermal Z/E isomerization of the compound through non-covalent interactions, involving intermolecular and intramolecular hydrogen bonding and directional non-bonded 1,5-type $S\cdots O$ interactions [16]. The observed decrease is very fast at the beginning, as well as at the end of the reaction, and very moderate in between, showing the transition from concave to convex shape of dependences. This transition from concave to convex shape of Arrhenius dependences indicates the change in the limiting step and specifically indicates the transition to the diffusion regime. In the case of complex processes involving the parallel steps, as we have here, the isoconversional methods give the activation energy that

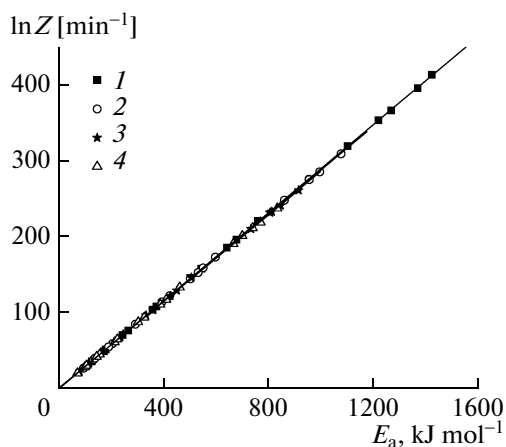


Fig. 4. The dependence of $\ln Z$ on E_a at different heating rates β (see Fig. 1), $r = 0.9999$.

reflect kinetics of entire process [26, 27]. At the beginning ($\alpha = 0.1$), where the first step is predominant, the obtained value of the activation energy corresponds to the first step. At the end of the process ($\alpha = 0.9$) where the second step prevails, the obtained activation energy corresponds, accordingly, to the second step.

Evaluation of Kinetics Parameters and Isokinetic Relationships

Although isoconversional or model-free methods offer an opportunity to establish the dependency of the activation energy on the conversion degree as well as the mechanism of the reaction, they do not provide any information about the other two members, Z and $f(\alpha)$, of the kinetic triplet. Therefore, based on the conclusion that all three steps of degradation are complex, the results of isoconversional methods (KAS and FWO) are further combined with a model-independent estimation of the pre-exponential factor using an artificial (false) isokinetic relationship (IKR) [28].

Generally speaking, IKR is based on a common point of intersection of Arrhenius lines [29]:

$$\ln Z = \ln k_{\text{iso}} + \frac{E}{R(T_{\text{iso}}^{-1} - T^{-1})},$$

where k_{iso} is the isokinetic rate constant and T_{iso} is the isokinetic temperature, and on a linear correlation:

$$\ln Z_{\xi} = a + bE_{\xi}, \quad (12)$$

where $a = \ln k_{\text{iso}}$ and $b = 1/RT_{\text{iso}}$, also known as “compensation parameters”, are coordinates of the intersection point of Arrhenius lines. The subscript ξ refers to a factor that produces a change in Arrhenius parameters (α , β , j). The Arrhenius lines resulting from the model-fitting method, Table 2, intersect at one point indicating that Arrhenius parameters related to differ-

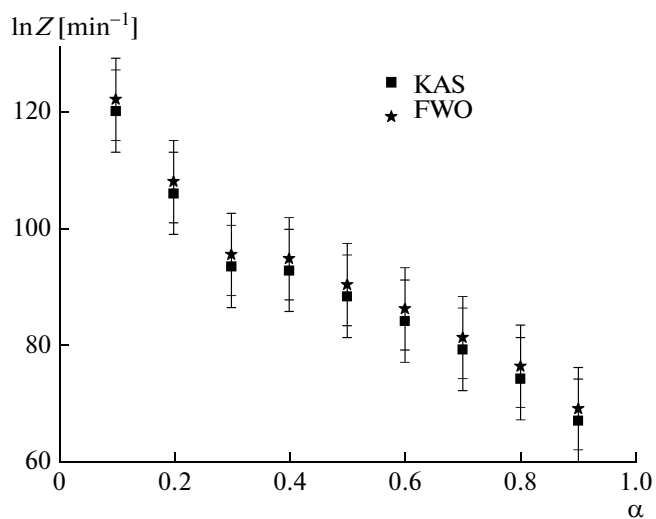


Fig. 5. The dependence of $\ln Z$ versus α .

ent reaction models will show a linear correlation known as “false compensation effect”:

$$\ln Z_j = c + dE_j, \quad (13)$$

where a subscript j denotes a reaction model from Table 1.

In Fig. 4 we present Arrhenius parameters, $\ln Z_j$, determined according to the Eq. (13) for different conversion functions j from Table 2 at different heating rates. The obtained linear dependences indicate the existence of the false compensation effect as defined by equation (13). From these linear dependences we determined the compensation parameters c and d ($d = 2.88 \times 10^{-4}$, $c = -0.18854$, $r = 0.9999$). By substituting the E_a values for E_j in Eq. (13), we estimated the $\ln Z_\alpha$ values presented in Fig. 5. A similarity with curves shown in Fig. 3 is evident confirming the validity of the applied methods.

CONCLUSIONS

Considering all the presented results, we can conclude that the phase transformation of *Z*-2-(5-ethoxycarbonylmethyl-4-oxothiazolidin-2-ylidene)-*N*-(2-phenylethyl)-ethanamide involving the breaking of the crystal structure, melting and formation of the *E*-2-(5-ethoxycarbonylmethyl-4-oxothiazolidin-2-ylidene)-*N*-(2-phenylethyl)-ethanamide through breaking of inter-molecular and formation of intramolecular hydrogen bonds cannot be described by a unique kinetic triplet. The strong dependence of the kinetic parameter values on the type of model employed for the process (model-fitting method) and the dependences of kinetic parameters, E_a and Z , on extent of reaction (model-free method) indicated a very complex process involving more than one elementary step occurring at the same time. The decreasing concave transformation-degree dependence of the activation energy is characteristic of a process occurring in parallel steps, involving an intermediate reverse step. In this case, the intermediate reverse step can be connected with thermal *Z/E* isomerization of the compound occurring through breaking of the existing and forming of new hydrogen bonds. The obtained transition from concave to convex shape of Arrhenius dependences indicates a change in the limiting step, more specifically, the transition to the diffusion regime.

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REFERENCES

1. G. Kaupp, J. Schmeyers, M. Kato, et al., *J. Phys. Org. Chem.* **15**, 148 (2002).
2. G. M. Schmidt, *Pure Appl. Chem.* **27**, 647 (1971).
3. N. B. Singh, R. J. Singh, and N. P. Singh, *Tetrahedron* **50**, 6441 (1994).
4. W. J. Kusto, M. Bertault, and J. Even, *J. Phys. Chem. B* **103**, 10549 (1999).
5. M. Oda and N. Sato, *J. Phys. Chem. B* **102**, 3283 (1999).
6. E. Forlani, C. Mezzina, and Forconi, *Eur. J. Org. Chem.*, 2779 (2001).
7. P. Gilli, V. Bertolasi, V. Ferreti, and G. Gill, *J. Am. Chem. Soc.* **122**, 10405 (2000).
8. C. J. Zhuo, *Magn. Respon. Chem.* **35**, 311 (1997).
9. R. Marković, Z. Džambaski, and M. Baranac, *Tetrahedron* **57**, 5833 (2001).
10. R. Marković and M. Baranac, *Heterocycles* **48**, 893 (1998).
11. R. Marković and M. Baranac, *J. Serb. Chem. Soc.* **63**, 165 (1998).
12. E. Kleinpeter, A. Koch, M. Heydenreich, et al., *J. Mol. Struct.* **356**, 25 (1995).
13. M. R. P. Kurp, E. Lukose, and K. Muraleedharan, *J. Therm. Anal. Cal.* **59**, 815 (2000).
14. M. E. Brown, D. Dolimore, and A. K. Galwaz, *Reaction in the Solid State, Comprehensive Chemical Kinetics* (Elsevier, Amsterdam, 1980), vol. 22.
15. D. M. Minić, Z. Nedić, and R. Marković, *J. Therm. Anal. Cal.* **95**, 167 (2009).
16. Z. Džambaski, M. Stojanović, M. Baranac-Stojanović, D. M. Minić, and R. Marković, *J. Serb. Chem. Soc.* **76**, 317 (2011).
17. N. Kaneniwa, M. Otsuka, and T. Hayashi, *Chem. Pharm. Bull.* **33**, 3447 (1985).
18. M. Otsuka and N. Kaneniwa, *Chem. Pharm. Bull.* **36**, 4026 (1988).
19. A. W. Coats and J. P. Redfern, *Nature* **201**, 68 (1964).
20. F. J. Gotor, J. M. Criado, J. Malek, and N. Koga, *J. Phys. Chem. A* **104**, 10777 (2000).
21. A. W. Coats and J. P. Redfern, *J. Polym. Sci. B: Polym. Lett.* **3**, 917 (1965).
22. H. E. Kissinger, *Anal. Chem.* **29**, 1702 (1957).
23. T. Akahira and T. Sunose, *Technol. Sci. Technol.* **16**, 22 (1971).
24. J. H. Flynn and A. L. Wall, *J. Res. Natl. Bur. Stand. A* **70**, 487 (1966).
25. T. A. Ozawa, *Bull. Chem. Soc. Jpn.* **38**, 1881 (1965).
26. C. D. Doyle, *Anal. Chem.* **33**, 77 (1961).
27. S. Vyazovkin and W. Linert, *Thermochim. Acta* **269–270**, 61 (1995).
28. N. Z. Lyakhov, M. Maciejewski, and A. Reller, *J. Solid State Chem.* **58**, 398 (1985).
29. S. Vyazovkin and C. A. Wight, *Ann. Rev. Phys. Chem.* **48**, 125 (1997).