

Kinetics, mechanism, and DFT calculations of thermal degradation of a Zn(II) complex with *N*-benzyloxycarbonylglycinato ligands

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Abstract A Zn(II) complex with *N*-benzyloxycarbonylglycinato ligands was studied by non-isothermal methods, in particular Kissinger–Akahira–Sunose's method, and further analysis of these results was performed by Vyazovkin's algorithm and an artificial compensation effect. Density functional theory calculations of thermodynamic quantities were performed, and results obtained by both methods are consistent, thus clarifying the mechanism of this very interesting multi-step degradation.

Keywords Transition metals compounds · Thermochemistry · Density functional theory · Reaction mechanisms

Introduction

Transition metal complexes with *N*-substituted amino acid ligands have attracted considerable attention because of their structural and biological properties, e.g., anticonvulsant, anti-inflammatory, and antineoplastic properties [1–9]. Although there are a significant number of papers dealing with the synthesis and characterization of new complexes and their thermal properties [10–14], a relatively small number of papers deal with detailed kinetic studies of their thermal degradation [15–17]. There are only a few papers dealing with both the mechanism of thermal degradation and density functional theory (DFT) calculations of transition metal complexes [18]. Most of the DFT calculations in those papers were performed either to determine the most stable molecular structure because of the lack of crystal data [19], or to compare DFT calculation results with experimental data obtained by X-ray structure analysis and FT-IR spectroscopy [20–22].

Our interest in *d*-metal complexes (Co(II), Cd(II), and Zn(II)) with *N*-benzyloxycarbonylglycine (*N*-Boc-gly) as ligand arises for several reasons. Firstly these complexes show different thermal stability as a consequence of the different chemical composition concerning the presence of water molecules in the inner or outer sphere of the complex ($[\text{Co}(\text{N-Boc-gly})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cd}(\text{N-Boc-gly})_2(\text{H}_2\text{O})_2]$, $[\text{Zn}(\text{N-Boc-gly})_2]$) and different structure [23, 24]. The Co(II) complex with water molecules in the inner and outer sphere shows octahedral geometry, the Cd(II) complex with water molecules in the inner sphere shows a pentagonal-bipyramidal polymeric structure, and the Zn(II) complex containing no water molecules shows tetrahedral geometry. The presence of water molecules in the inner and/or outer sphere determines the thermal stability of the

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complexes [24], as expected. Degradation of different complexes starts with loss of water molecules from the outer sphere, followed by loss of water molecules from the inner sphere. Further degradation of all complexes goes through the same mechanism involving loss of two $\text{C}_6\text{H}_5\text{CH}_2\text{O}-$ fragments followed by loss of two $-\text{C}(=\text{O})\text{NHCH}_2-$ fragments.

In this work we report the study of a Zn(II) complex with *N*-benzyloxycarbonylglycinato ligands (*N*-Boc-gly) by non-isothermal methods, to obtain detailed thermal and kinetic data. Furthermore, we performed a DFT study to supplement experimental data, and to clarify the microscopic origin of the system under study.

Results and discussion

In order to study the kinetics of thermal decomposition of the Zn(II) complex, TG and DTA curves were recorded under nitrogen atmosphere at different heating rates ($\beta = 5, 10, 15, 20\text{ }^\circ\text{C min}^{-1}$). TG and DTG curves for $\beta = 20\text{ }^\circ\text{C min}^{-1}$ are shown in Fig. 1. On the basis of these data, thermal decomposition of the Zn(II) complex is a multi-step process involving three main steps. The first step, assigned to fragmentation of two $\text{C}_6\text{H}_5\text{CH}_2\text{O}-$ fragments, occurs in the temperature range $175\text{--}297\text{ }^\circ\text{C}$ (all temperature ranges are given for $\beta = 20\text{ }^\circ\text{C min}^{-1}$). The subsequent degradation step in the temperature range $297\text{--}627\text{ }^\circ\text{C}$ corresponds to the loss of two $-\text{C}(=\text{O})\text{NHCH}_2-$ fragments [24]. The third degradation step at temperatures higher than $627\text{ }^\circ\text{C}$ is assigned to the release of two molecules of CO_2 and some Zn [24].

The obtained TG curves with three clearly separated steps were allowed the detailed study of the degradation

kinetics of the Zn(II) complex and well-defined DTG curves (Fig. 1) were used for better recognition of individual steps. Curves of the degree of conversion (α) versus temperature (T) were calculated, constructed, and used for further analysis of the mechanism and kinetics of degradation of the complex. The obtained sigmoid shape for all three degradation steps and for all heating rates is expected for non-isothermal data.

Mechanism of degradation

In order to discuss the mechanism of individual steps of degradation of the complex the apparent activation energies (E_a) as function of degree of conversion (α) were calculated by the isoconversional Kissinger–Akahira–Sunose (KAS) method [25, 26] (Fig. 2). Since activation energies change with the degree of conversion, the studied processes are multi-step involving more than one elementary step. Similar shapes of E_a versus α curves for the first and third degradation steps and a completely different shape of the curve for the second step of degradation denote similar mechanisms for the first and third steps and different mechanism for the second step.

For the first step of degradation, the apparent activation energy determined by the KAS method (Fig. 2a) increases from 297.8 kJ mol^{-1} at $\alpha = 0.05$, reaches the value of 759.6 kJ mol^{-1} at $\alpha = 0.2$, and then decreases to 98.5 kJ mol^{-1} at $\alpha = 0.9$. For the third step the apparent activation energy increases from 167.7 to 171.9 kJ mol^{-1} , reaches a maximum at $\alpha = 0.2$, and then decreases to 125.5 kJ mol^{-1} at $\alpha = 0.9$ (Fig. 2c).

The observed convex shape of these curves according to Vyazovkin's algorithm [27] indicates a mechanism that involves a series of competitive steps of degradation. As the reactions of the first and third degradation step progress, diffusion of gaseous products (Scheme 1) and CO_2 through the solid product becomes dominant and the E_a value gradually decreases [28].

The continuous decrease of apparent activation energy in degree of conversion range $0.1\text{--}0.9$ ($454.9\text{--}285.0$) indicates a multi-step mechanism for the second step of degradation (Fig. 2b). According to Vyazovkin's algorithm [27] a decreasing dependence corresponds to a kinetic scheme involving an endothermic reversible reaction followed by an irreversible one [29]. The effective activation energy is limited by the sum of the activation energy of the irreversible reaction and the enthalpy of the reversible reaction at low conversions, and by the activation energy of the irreversible reaction at high conversions [30].

In order to confirm multi-step mechanisms for all three degradation steps, determined according to Vyazovkin's

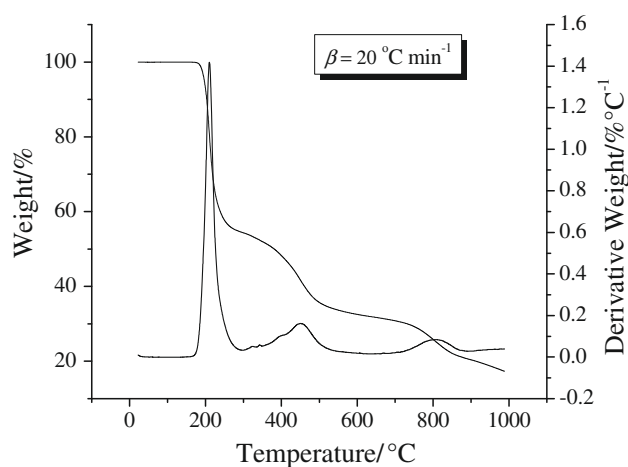


Fig. 1 TG and DTG curves of $[\text{Zn}(\text{N-Boc-gly})_2]$ in nitrogen atmosphere at $\beta = 20\text{ }^\circ\text{C min}^{-1}$

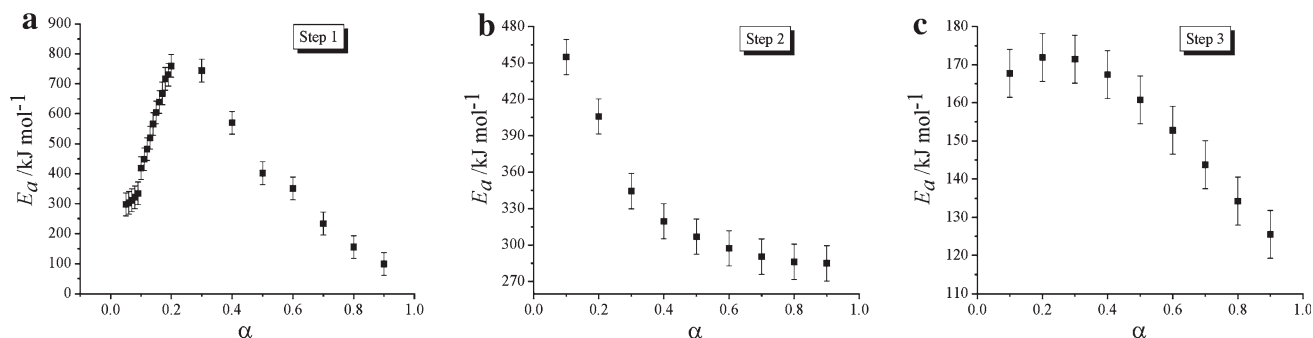


Fig. 2 Apparent activation energy with standard deviation as a function of degree of conversion determined by the KAS method for individual degradation steps

Scheme 1

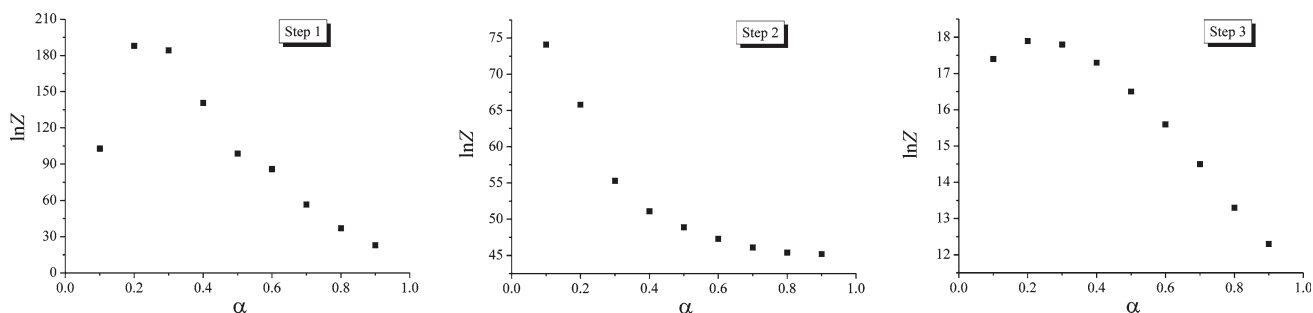
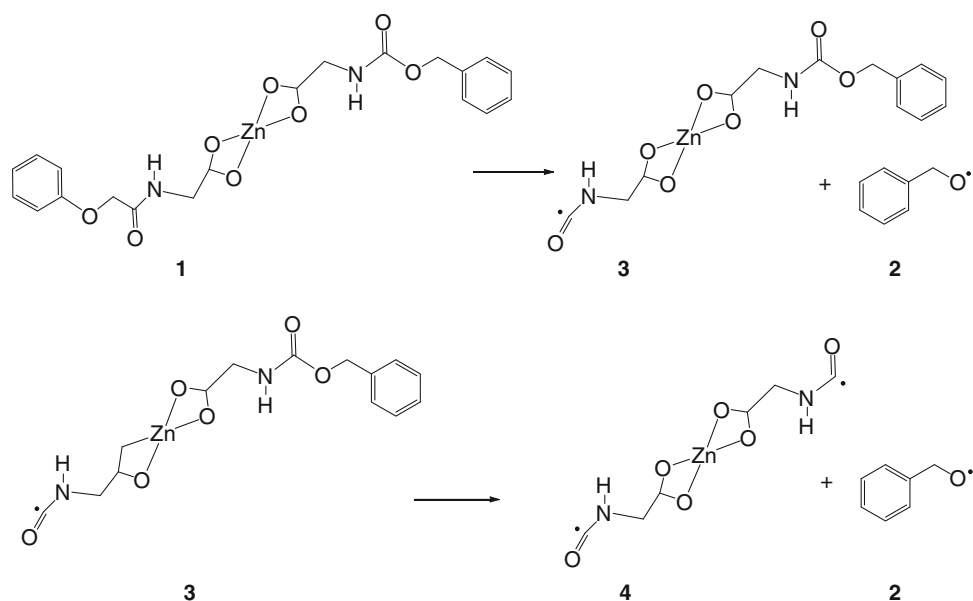


Fig. 3 Dependence of $\ln Z$ versus α for all three steps of Zn(II) complex degradation

algorithm, we plotted the dependence of $\ln Z$ versus α (where Z is the pre-exponential factor) using an artificial compensation effect (Fig. 3).

As it can be seen from Figs. 2 and 3 for all three steps, the curves of apparent activation energy and pre-exponential factor versus the degree of conversion have the same shapes, which indicates the same dependence of these parameters on the degree of conversion.

DFT calculations of bond dissociation enthalpies

To allow a more systematic and detailed study of the decomposition of this complex we compared predicted mechanisms of thermal degradation, based on isoconversional methods, with results of conventional DFT calculations.

For different isotopomers of coordination number 4 we performed geometry optimization calculations, and obtained



Fig. 4 DFT optimized geometry of $[\text{Zn}(\text{N-Boc-gly})_2]$ complex

a distorted tetrahedron as the most stable conformation. The optimized minimum energy structure of the complex $[\text{Zn}(\text{N-Boc-gly})_2]$ is given in Fig. 4, and the optimized fragments upon decomposition are depicted in Fig. 5.

The heterolytic and homolytic bond dissociation enthalpies (BDE) for the first degradation step (see Fig. 2), in the temperature range 175–297 °C with a step of 10 °C, were obtained from the difference between the enthalpy of the investigated complex and the enthalpies of the separated fragments at a given temperature. The computed change of enthalpy for heterolytic bond cleavage ($\Delta H_{175} = 1,835.9 \text{ kJ mol}^{-1}$, $\Delta H_{297} = 1,923.7 \text{ kJ mol}^{-1}$) is much higher than the enthalpy for homolytic dissociation ($\Delta H_{175} = 713.8 \text{ kJ mol}^{-1}$, $\Delta H_{297} = 708.5 \text{ kJ mol}^{-1}$), supporting the radical mechanism of dissociation, which in a given temperature range does not depend on the temperature.

Scheme 1 represents the first step of degradation (see Fig. 2a), where $[\text{Zn}(\text{N-Boc-gly})_2]$ complex loses $(\text{C}_6\text{H}_5\text{CH}_2\text{O}\cdot)$ fragments. All calculated thermodynamic

data for this decomposition at the two different temperatures are given in Table 1. Calculated ΔH (Table 1) showed that the first step is endothermic followed by small exothermic changes, which is in excellent agreement with previously described mechanisms determined according to Vyazovkin's algorithm, thus confirming a very complex mechanism of fragmentation (Scheme 1).

The double phase degradation of $[\text{Zn}(\text{OOCCH}_2\text{NHC}\cdot\text{O})_2]$ (Scheme 2) in the second step indicates that loss of the $\text{H}_2\text{C}\cdot\text{NHC}\cdot\text{O}$ triplet fragment is endothermic, consistent with Vyazovkin's algorithm. However, further decomposition of the triplet $\text{H}_2\text{C}\cdot\text{NHC}\cdot\text{O}$ fragment leads first to a singlet state which exothermically decomposes to CO and CH_2NH particles ($\Delta H_{297} = 284.1 \text{ kJ mol}^{-1}$, $\Delta H_{627} = 401.7 \text{ kJ mol}^{-1}$). All calculated thermodynamic results at different temperatures are summarized in Table 2.

Conclusion

This work showed that results obtained by non-isothermal kinetic methods and DFT calculations are consistent, thus confirming the complicated thermal degradation of the $[\text{Zn}(\text{N-Boc-gly})_2]$ complex. The decomposition occurs in three multi-steps involving more than one elementary step. DFT calculations can provide useful information concerning the electronic structure, the energetics, and the mechanism of the fragmentation of complex molecules and are thus helpful in experimental interpretation and clarification of proposed mechanisms.

Fig. 5 DFT optimized intermediate species in the process of fragmentation of $[\text{Zn}(\text{N-Boc-gly})_2]$

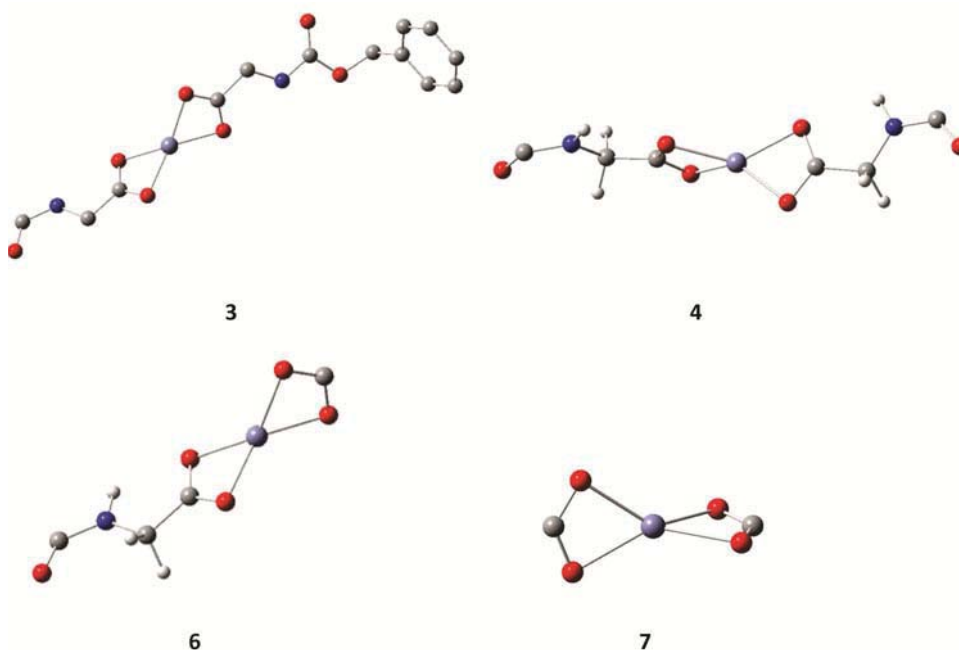


Table 1 Calculated thermodynamic data at 175 and 297 °C for the first step of fragmentation of [Zn(*N*-Boc-gly)₂]

Structure ^a	Fragments ^a	$\Delta H_{175}/\text{kJ mol}^{-1}$	$\Delta S_{175}/\text{kJ mol}^{-1} \text{ K}^{-1}$	$\Delta G_{175}/\text{kJ mol}^{-1}$	$\Delta H_{297}/\text{kJ mol}^{-1}$	$\Delta S_{297}/\text{kJ mol}^{-1} \text{ K}^{-1}$	$\Delta G_{297}/\text{kJ mol}^{-1}$
1	2 + 3	797.5	0.2339	692.7	790.7	0.2359	656.0
3	2 + 4	-83.7	0.2649	-202.4	-82.2	0.2667	-234.5

^a Numbers of structures and fragments are given in Scheme 1 and Fig. 5

Scheme 2

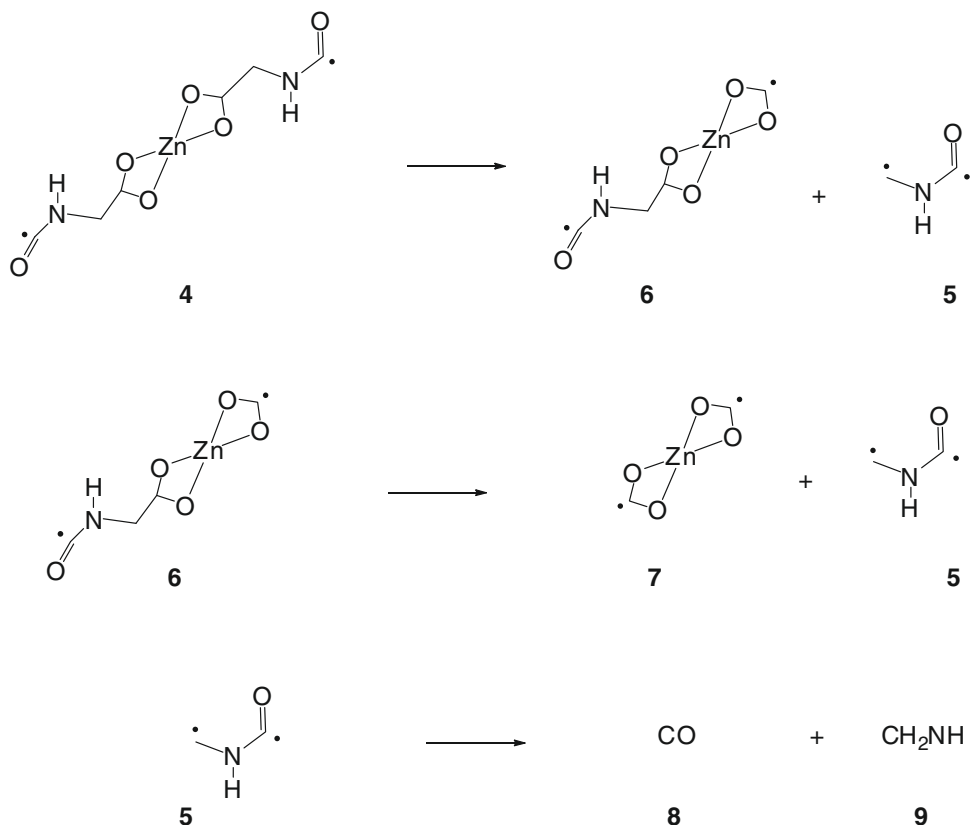


Table 2 Calculated thermodynamic data at 297 and 627 °C for the second step of fragmentation of [Zn(*N*-Boc-gly)₂]

Structure ^a	Fragments ^a	$\Delta H_{297}/\text{kJ mol}^{-1}$	$\Delta S_{297}/\text{kJ mol}^{-1} \text{ K}^{-1}$	$\Delta G_{297}/\text{kJ mol}^{-1}$	$\Delta H_{627}/\text{kJ mol}^{-1}$	$\Delta S_{627}/\text{kJ mol}^{-1} \text{ K}^{-1}$	$\Delta G_{627}/\text{kJ mol}^{-1}$
4	5 + 6	373.2	0.2006	258.6	334.3	0.2005	153.8
6	5 + 7	339.3	0.1751	239.3	336.4	0.1711	182.4
5	8 + 9	-214.2	0.1419	-295.2	-134.5	0.1359	-256.8

^a Numbers of structures and fragments are given in Scheme 2 and Fig. 5

Materials and methods

The [Zn(*N*-Boc-gly)₂] complex was prepared in a simple reaction between ZnCl₂ and *N*-Boc-glyH (molar ratio 1:2, ethanol–water mixture, pH 5–6), as previously described [23].

Non-isothermal thermal degradation was studied by using an SDT Q600 (TA Instruments) apparatus for simultaneous TG–DTA analysis. TG experiments and simultaneously

recorded DTA signals were performed from room temperature to 900 °C at different heating rates (5–20 °C min⁻¹) with sample masses about 6 mg in a dry nitrogen atmosphere (flow rate 100 cm³ min⁻¹) using Pt crucibles. The Pt crucible with a small amount of Al₂O₃ was used as a reference.

For degradation kinetics studies the degree of conversion of the reaction (α) at any temperature was determined for all heating rates as $\alpha = (m_i - m)/(m_i - m_f)$, where m is

the mass of a sample at a certain time, m_i and m_f are the initial and final masses, respectively. The mechanism of each step can be evaluated from the activation energy dependence of α . This can be done using isoconversional methods also known as “model-free methods”. These methods require the determination of the temperature T_α at which an equivalent stage of the reaction occurs for various heating rates [30]. A widely accepted procedure is the KAS method [25, 26] in the form:

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

In this sense [25, 26], the linear isoconversional relationship of $\ln(\beta/T_\alpha^2)$ versus $1/T_\alpha$ can be used to determine the following kinetic parameters: apparent activation energies $E_{a,\alpha}$ and intercepts $\ln[(ZRf(\alpha))/E_{a,\alpha}]$ for selected degrees of conversion, even without the knowledge of the true conversion function. If E_a does not depend on α , the investigated process can be treated as single-step process and should be described by a unique kinetic triplet. If E_a changes with α the process is complex [31–34]. In this case, on the basis of the interrelationship $E_a = f(\alpha)$, Vyazovkin and co-workers [27] proposed a very simple algorithm for discussing the mechanism of complex processes.

The dependence of $\ln Z$ on α was found using an artificial compensation effect [35]. It is manifested as a linear correlation of Arrhenius parameters: $\ln Z = a + bE_a$, where a and b are compensation parameters. Calculating the compensation parameters a and b by using the super-relation $a = \ln Z - bE_a$ and values of E_a previously determined by the KAS method allowed us to determine $\ln Z$ for different degrees of conversion.

The DFT calculations were carried out using the Amsterdam Density Functional program package ADF2009.01 [36–38]. An all-electron triple-zeta Slater-type orbital (STO) plus one polarization function (TZP) basis set was used for all atoms. The local density approximation (LDA) characterized by the Slater exchange and PW92 correlation [39] with included gradient corrections (GGA) for exchange (OPTX [40]) and correlation (PBEc [41]), i.e., OPBE functional [42], was used. Open shell species were treated with unrestricted formalism, and no spin contamination was observed. Analytical harmonic frequencies [43, 44] were calculated to determine the statistical thermodynamic corrections needed to compute BDE. All equilibrium structures and presumed intermediates for the fragmentation processes are characterized by the absence of vibrational modes with negative force constants, and were ascertained to be minima on the potential energy surface.

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