Does a fluorinated Lewis acid catalyst change the molecular mechanism of the decomposition process of nitroethyl carboxylates?

Agnieszka Kącka¹ · Luis R. Domingo² · Radomir Jasiński¹

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Abstract The molecular mechanism of the decomposition reaction of nitroethyl benzoates catalyzed by Lewis acids based on boron element— BH_3 and BF_3 —was studied using density functional theory methods. These reactions take place much faster than the uncatalyzed process. However, the presence of fluorinated Lewis acids has a unique influence on the molecular mechanism. In the case of BF_3 , a change from a one-step mechanism to a two-step one involving a zwitterionic intermediate is observed.

Keywords Thermal elimination · DFT study · Nitroalkene · Fluorine effect

Introduction

Conjugated nitroalkenes (CNAs) are valuable precursors for a wide variety of building blocks and intermediates in organic synthesis [1–3]. These compounds are found to be important because of their biological activities, such as insecticidal [4, 5], fungicidal [5–8], bactericidal [9, 10], and antitumor effects [11], including pharmacologically valuable substances [6–9]. They have proved to be valuable precursors for a wide variety of target molecules. The versatility of the nitro group enables its transformation into many compounds with diverse functionalities [12–14]. Furthermore, CNAs are strong electrophilic ethylenes participating in polar

✉ Agnieszka Kącka
akacka@chemia.pk.edu.pl

¹ Institute of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland

² Departamento de Química Orgánica, Universidad de Valencia, Dr. Moliner 50, Burjassot, 46100 Valencia, Spain

Diels–Alder reactions, and alternatively these electrophilic species readily undergo addition reactions with various nucleophiles, thus providing an array of valuable products [11].

Thermal decomposition of alkyl esters to produce alkenes and carboxylic acids is a well-established process that has been studied for over a century [15, 16]. Although some of the decomposition reactions for preparation of nitroalkenes are productive, many of them require strict reaction conditions, are expensive, and lead to low yield of nitroalkenes. Examples include elimination of carboxylic acid from nitroalkyl benzoates carried out at temperature of 180–190 °C [17], and decomposition of nitroalkyl phthalates, which proceeds at 170–185 °C [18]. Additionally, highly reactive nitroalkenes rapidly polymerize under these conditions [19]. Research in this field to identify benign conditions for obtaining conjugated nitroalkenes is therefore essential.

This work is a continuation of our extensive study on the synthesis and fundamental properties of CNAs. Previously [20, 21], we analyzed mechanistic aspects of the decomposition of nitroalkyl carboxylates under thermal conditions. We demonstrated that thermal decomposition of nitroethyl carboxylates should not be recognized as a pericyclic but rather as a two-stage one-step process [22]. We also performed quantum-chemical calculations on the decomposition of nitroalkyl carboxylates catalyzed by triethylsulfonium (TES), triethylphosphonium (TEP) [23], and 1,3-dimethylimidazolium (DMIM) [24] cations. We proved that, in presence of TES, TEP, and DMIM cations, the decomposition process of nitroethyl benzoates takes place much faster than in the same process without catalyst.

It is well known that use of Lewis acids can lead to significant changes in the nature of the molecular mechanism in comparison with the uncatalyzed process [25]. The aim of this work is a quantum-chemical study on the molecular mechanism of the decomposition reactions of model nitroethyl benzoates, without or in presence of inorganic Lewis acid (LA) catalysts, viz. borane (BH₃) and boron trifluoride (BF₃) (Scheme 1).

These catalysts have also been applied for other types of fundamental reaction, for instance, polar Diels–Alder [26–28] or [3 + 2]-cycloaddition reactions [29]. The decomposition process of nitroethyl carboxylates is carried out in dichloromethane environment, because it is a good solvent for LAs [26, 27, 30, 31].

Results and discussion

As shown by M06-2X/6-31 + G(d) calculations, the first step of the decomposition reaction of nitroethyl benzoate (**1a**) is formation of a prereaction complex (**1a**[BH₃]) between the ester and the LA- BH₃. Electron-deficient molecules, such as BF₃ and BH₃, contain less than an octet of electrons around one atom, showing a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. As a result, a bond is formed. The bond formed between a Lewis acid (BH₃) and nitroethyl benzoate (**1a**) is a coordinate covalent bond, because both electrons are provided by only one of the atoms. After it is formed, however, a coordinate covalent bond behaves like any other covalent single

Scheme 1 Mechanism of LA-catalyzed decomposition reaction of nitroethyl benzoates **1a–c**

bond. Consequently, the creation of a prereaction complex entails a drop in reaction enthalpy by 15.0 kcal mol^{−1} (Fig. 1, Table 1). The LA catalyst—BH₃—is located near to the oxygen atom of the nitro group. We also analyzed many other orientations of the LA BH₃ catalyst to the ester molecule. For subsequent research, we chose the most stable form.

Further conversion of the reacting system along the reaction coordinate leads to the transition state structure (**TS**). As these data from M06-2X/6-31 + G(d) calculations show, this is related to an enthalpy increase of over 31.9 kcal mol^{−1} for the reaction catalyzed by the LA BH₃. This barrier, however, is much smaller than suggested by the DFT calculations for a similar decomposition reaction without LA catalysis (about 39.5 kcal mol^{−1}) (Fig. 1, Table 2). Afterwards, the **TS** is converted to products **2** and **3a** (Figs. 1, 2).

In the structure of transition states, a C–H single bond between O5 and H6 atoms is formed. Two double bonds are formed between the C1–C2 and O3–C4 atoms, the C4–O5 bond is changed to a single bond, and the H6–C1 bond becomes broken (Fig. 3, Table 3).

On the basis of the calculations performed, we also analyzed the influence of the LA BH₃ catalyst in the structure of **TS**. It turned out that the H6–C1 bond in the reaction catalyzed by the LA BH₃ is broken earlier than in the uncatalyzed process. In **TS**, the rupture of the O5–H6 single bond is in any case very advanced. The global electron density transfer (GEDT) value for the transition state for the

Fig. 1 M06-2X/6-31 + G(d) enthalpy profiles for decomposition of nitroethyl benzoate **1a**, catalyzed by BH_3 and without catalyst

Table 1 M06-2X/6-31 + G(d) kinetic and thermodynamic parameters for decomposition of nitroethyl benzoates catalyzed by BH_3 according to M06-2X calculations ($T = 298 \text{ K}$; ΔH , ΔG in kcal mol^{-1} , ΔS in $\text{cal mol}^{-1} \text{ K}^{-1}$; **1a** R = H, **1b** R = NO_2 , **1c** R = NMe_2)

Ester	Transition	ΔH	ΔG	ΔS
1a	1a + $\text{BH}_3 \rightarrow [\mathbf{1a}][\text{BH}_3]$	−15.0	−4.2	−36.1
	$[\mathbf{1a}][\text{BH}_3] \rightarrow \text{TS}$	31.9	32.2	−1.0
	$[\mathbf{1a}][\text{BH}_3] \rightarrow [\mathbf{2}][\text{BH}_3] + \mathbf{3a}$	17.3	5.2	40.6
1b	1b + $\text{BH}_3 \rightarrow [\mathbf{1b}][\text{BH}_3]$	−14.9	−3.1	−39.5
	$[\mathbf{1b}][\text{BH}_3] \rightarrow \text{TS}$	34.1	33.8	0.4
	$[\mathbf{1b}][\text{BH}_3] \rightarrow [\mathbf{2}][\text{BH}_3] + \mathbf{3b}$	17.3	4.3	43.6
1c	1c + $\text{BH}_3 \rightarrow [\mathbf{1c}][\text{BH}_3]$	−15.3	−4.2	−37.5
	$[\mathbf{1c}][\text{BH}_3] \rightarrow \text{TS}$	29.2	30.3	−3.9
	$[\mathbf{1c}][\text{BH}_3] \rightarrow [\mathbf{2}][\text{BH}_3] + \mathbf{3c}$	17.8	5.6	40.7

decomposition reaction catalyzed by the Lewis acid BH_3 is 0.40[e]. This value is comparable to the GEDT value for the transition state of similar noncatalytic processes. **TS** structures have a polar nature, as proved by the values of GEDT indices and their dipole moments (Table 3).

The nature of the substituent on the benzene ring also has an impact on the **TS**, in the case of catalytic reactions and those carried out without presence of catalyst. In the case of the reactions $[\mathbf{1b}][\text{BH}_3] \rightarrow [\mathbf{2}][\text{BH}_3] + \mathbf{3b}$, the H6–C1 and C2–O3 bonds are broken more slowly than the same bonds in the reaction $[\mathbf{1a}][\text{BH}_3] \rightarrow [\mathbf{2}][\text{BH}_3] + \mathbf{3a}$. In turn, the H6–C1 and C2–O3 bonds in the case

Table 2 M06-2X/6-31 + G(d) kinetic and thermodynamic parameters for decomposition of nitroethyl benzoates according to M06-2X calculations ($T = 298\text{ K}$; ΔH , ΔG in kcal mol^{-1} , ΔS in $\text{cal mol}^{-1}\text{ K}^{-1}$; **1a** R = H, **1b** R = NO_2 , **1c** R = NMe_2)

Ester	Transition	ΔH	ΔG	ΔS
1a	1a $\rightarrow$ TS	39.5	40.2	-2.2
	1a $\rightarrow$ 2 + 3a	18.2	6.4	39.8
1b	1b $\rightarrow$ TS	41.4	42.6	-4.2
	1b $\rightarrow$ 2 + 3b	18.3	6.6	39.3
1c	1c $\rightarrow$ TS	37.4	38.3	-2.9
	1c $\rightarrow$ 2 + 3c	18.4	6.6	39.5

Fig. 2 M06-2X/6-31 + G(d) Gibbs free energy profiles for decomposition of nitroethyl benzoate **1a**, catalyzed by BH_3 and without catalyst

of the reaction $[\mathbf{1c}][\text{BH}_3] \rightarrow [\mathbf{2}][\text{BH}_3] + \mathbf{3c}$ are broken faster than in the case of the reaction $[\mathbf{1a}][\text{BH}_3] \rightarrow [\mathbf{2}][\text{BH}_3] + \mathbf{3a}$ (Table 3).

It should also be mentioned that DFT study using the same M06-2X functional but with larger 6-31 + G(d,p) and 6-311 + G(d) basis sets gives a similar representation of these reactions. These calculations show that the mechanism of the decomposition reaction of nitroalkyl carboxylates catalyzed by the LA BH_3 and without catalyst are also suggestive of a one-step mechanism. In the case of calculations based on M06-2X/6-31 + G(d,p) theory level, we observed a decrease in the activation enthalpy (Figs. 1, 2).

Fig. 3 M06-2X/6-31 + G(d) geometry of **TSs** of decomposition of nitroethyl benzoate **1a**, catalyzed by BH_3 and without catalyst

The situation is quite different in the case of the decomposition reaction of nitroethyl carboxylate catalyzed by the LA BF_3 . The results of M06-2X/6-31 + G(d) calculations showed that the first step of the decomposition of nitroethyl benzoate (**1a**) is also formation of a prereaction complex (**1a**[BF_3]). Consequently, the creation of a prereaction complex entails a drop of reaction enthalpy by $10.5 \text{ kcal mol}^{-1}$ (Fig. 4). Nonetheless, the Gibbs free energy for this transition is equal to $1.0 \text{ kcal mol}^{-1}$ (Fig. 4). This is a consequence of large negative entropy changes, linked to an increase in the ordering of the reaction system. The BF_3 molecule is also located near to the oxygen atom of the nitro group, but is bonded to an oxygen atom other than the BH_3 molecule. We analyzed many other orientations of the BF_3 catalyst to the ester molecule, but for further research we chose the most stable form.

Thereafter, the prereaction complex is recast to **TS₁**. This transition requires an activation enthalpy which is more than 22 kcal mol^{-1} (Fig. 4, Table 4). However, it is significantly less than in the case of the decomposition process of **1a** without presence of the LA BF_3 (about $39.5 \text{ kcal mol}^{-1}$).

In **TS₁**, one single bond breaks (Fig. 5, Table 5). It is the bond between the C1 and H6 atoms. Subsequently, a new single bond between atoms H6 and O5 is formed. It should be mentioned that, in contrast to the LA- BH_3 -catalyzed decomposition reaction of **1a** and to the uncatalyzed process, the second single bond C2–O3 is not broken at this reaction stage. **TS₁** has an evidently polar, “zwitterionic-like” nature. This is substantiated by the value of the global electron density transfer (GEDT), which is equal to $0.43[\text{e}]$.

Further advance of the reaction leads to intermediate **I**. **I** has a polar, zwitterionic nature, as confirmed by the GEDT value ($0.46[\text{e}]$) and dipole moment ($15.67[\text{D}]$). Decomposition of this intermediate proceeds via **TS₂**. This step requires energy of

Table 3 Key parameters for structures in decomposition of nitroethyl benzoates **1a–c**, catalyzed by BH₃ and without catalyst, according to M06-2X/6-31 + G(d) data (**1a** R = H, **1b** R = NO₂, **1c** R = NMe₂)

Reaction	Structure	Interatomic distances (Å)					GEDT [e]	$\bar{v}$	Dipole moment, μ (D)
		H6–C1	C1–C2	C2–O3	O3–C4	C4–O5			
1a → 2 + 3a	1a	1.088	1.516	1.429	1.349	1.212			
	TS	1.840	1.418	1.709	1.258	1.300	0.39	–374.01	11.33
	2 + 3a		1.325		1.213	1.343			
1b → 2 + 3b	1b	1.088	1.517	1.431	1.344	1.210			
	TS	1.784	1.421	1.705	1.255	1.293	0.36	–396.25	7.70
	2 + 3b		1.325		1.210	1.339			
1c → 2 + 3c	1c	1.088	1.518	1.425	1.357	1.216			
	TS	1.920	1.412	1.731	1.262	1.312	0.40	–355.19	15.83
	2 + 3c		1.325		1.218	1.350			
[1a][BH₃] → [2][BH₃] + 3a	[1a][BH₃]	1.088	1.519	1.425	1.353	1.212			
	TS	2.090	1.405	1.780	1.249	1.309	0.40	–319.72	16.40
	[2][BH₃] + 3a		1.327		1.213	1.343			
[1b][BH₃] → [2][BH₃] + 3b	[1b][BH₃]	1.088	1.531	1.425	1.348	1.209			
	TS	2.059	1.411	1.748	1.248	1.302	0.39	–317.02	13.61
	[2][BH₃] + 3b		1.327		1.210	1.339			
[1c][BH₃] → [2][BH₃] + 3c	[1c][BH₃]	1.088	1.527	1.420	1.362	1.216			
	TS	2.479	1.402	1.786	1.265	1.322	0.43	–376.68	15.45
	[2][BH₃] + 3c		1.327		1.218	1.350

Fig. 4 M06-2X/6-31 + G(d) enthalpy and Gibbs free energy profiles for decomposition of nitroethyl benzoate **1a** catalyzed by BF_3

Table 4 M06-2X/6-31 + G(d) kinetic and thermodynamic parameters for LA BF_3 -catalyzed decomposition of nitroethyl benzoates according to M06-2X calculations ($T = 298 \text{ K}$; ΔH , ΔG in kcal mol^{-1} , ΔS in $\text{cal mol}^{-1} \text{ K}^{-1}$; **1a** $R = \text{H}$, **1b** $R = \text{NO}_2$, **1c** $R = \text{NMe}_2$)

Ester	Transition	ΔH	ΔG	ΔS
1a	1a + $\text{BF}_3 \rightarrow [\mathbf{1a}][\text{BF}_3]$	−10.5	1.0	−38.6
	$[\mathbf{1a}][\text{BF}_3] \rightarrow \text{TS}_1$	22.8	24.3	−5.1
	$[\mathbf{1a}][\text{BF}_3] \rightarrow \text{I}$	20.9	22.9	−6.7
	$[\mathbf{1a}][\text{BF}_3] \rightarrow \text{TS}_2$	25.3	26.1	−2.5
	$[\mathbf{1a}][\text{BF}_3] \rightarrow [\mathbf{2}][\text{BF}_3] + \mathbf{3a}$	17.5	5.4	40.7
1b	1b + $\text{BF}_3 \rightarrow [\mathbf{1b}][\text{BF}_3]$	−10.1	1.8	−39.9
	$[\mathbf{1b}][\text{BF}_3] \rightarrow \text{TS}_1$	24.9	26.0	−3.5
	$[\mathbf{1b}][\text{BF}_3] \rightarrow \text{I}$	23.5	24.0	−1.8
	$[\mathbf{1b}][\text{BF}_3] \rightarrow \text{TS}_2$	26.8	27.6	−3.0
	$[\mathbf{1b}][\text{BF}_3] \rightarrow [\mathbf{2}][\text{BF}_3] + \mathbf{3b}$	17.2	4.8	41.7
1c	1c + $\text{BF}_3 \rightarrow [\mathbf{1c}][\text{BF}_3]$	−11.1	−0.3	−35.6
	$[\mathbf{1c}][\text{BF}_3] \rightarrow \text{TS}_1$	20.1	22.4	−7.8
	$[\mathbf{1c}][\text{BF}_3] \rightarrow \text{I}$	16.2	19.0	−9.4
	$[\mathbf{1c}][\text{BF}_3] \rightarrow \text{TS}_2$	23.1	25.6	−8.2
	$[\mathbf{1c}][\text{BF}_3] \rightarrow [\mathbf{2}][\text{BF}_3] + \mathbf{3c}$	18.1	7.2	36.5

$25.3 \text{ kcal mol}^{-1}$ (Fig. 4, Table 4). In the structure of TS_2 , the C2–O3 single bond breaks (Fig. 5, Table 5).

We also performed quantum-chemical study on the decomposition of the other nitroethyl benzoates **1b** and **1c**. In the reaction $[\mathbf{1b}][\text{BF}_3] \rightarrow [\mathbf{2}][\text{BF}_3] + \mathbf{3b}$, it was found that the H6–C1 and C2–O3 single bonds are broken more slowly ($2.798 \text{ \AA}$ and $1.845 \text{ \AA}$) than in the reaction $[\mathbf{1a}][\text{BF}_3] \rightarrow [\mathbf{2}][\text{BF}_3] + \mathbf{3a}$. In turn, the H6–C1

Fig. 5 M06-2X/6-31 + G(d) geometries of the **TSs** and intermediate associated with LA- BF_3 -catalyzed decomposition of nitroethyl benzoate **1a**

and C2–O3 single bonds are broken faster (2.952 Å and 1.938 Å) in the reaction $[\mathbf{1c}][\text{BF}_3] \rightarrow [\mathbf{2}][\text{BF}_3] + \mathbf{3c}$ than in the case of the reaction $[\mathbf{1a}][\text{BF}_3] \rightarrow [\mathbf{2}][\text{BF}_3] + \mathbf{3a}$.

The decompositions of the nitroethyl benzoates **1a–c** proceed according to a similar mechanistic scheme at the higher theory levels of M06-2X/6-31 + G(d,p) and M06-2X/6-311 + G(d). Calculations at M06-2X/6-31 + G(d,p) level gave slightly lower activation enthalpy (Fig. 4).

On the grounds of the quantum-chemical calculations, we propose the mechanisms of the decomposition reactions of nitroethyl benzoates **1a–c** catalyzed by the LAs BH_3 and BF_3 shown in Scheme 2. It turned out that the LA BH_3 -catalyzed decomposition reactions of nitroethyl carboxylates proceed via a polar one-step mechanism. In turn, the decomposition of nitroethyl carboxylates catalyzed by the fluorinated LA BF_3 proceeds via a two-step mechanism involving a zwitterionic intermediate.

Computational details

All calculations reported in this paper were performed on the “Prometheus” computer cluster in the CYFRONET regional computer center in Cracow. The mechanism of decomposition of nitroalkyl benzoates catalyzed by LAs was examined as implemented in the GAUSSIAN 09 package [32]. The geometric parameters for all the reactants, **TSs**, and products of the reactions studied were fully optimized using the density functional theory (DFT) method. The calculations were performed at M06-2X level with the 6-31 + G(d) basis set. The B3LYP functional was replaced by M06-2X because of its increased accuracy. Additionally,

Table 5 Key parameters for structures in decomposition of nitroethyl benzoates catalyzed by BF_3 according to M06-2X/6-31 + G(d) data (**1a** R = H, **1b** R = NO_2 , **1c** R = NMe_2)

Reaction	Structure	Interatomic distances (Å)					GEDT [e]	$\bar{v}$	Dipole moment, μ (D)
		H6-C1	C1-C2	C2-O3	O3-C4	C4-O5			
[1a][BF₃] → [2][BF₃] + 3a	[1a][BF₃]	1.088	1.524	1.423	1.355	1.211			
	TS₁	1.452	1.504	1.464	1.298	1.265	0.43	−1159.63	15.43
	I	2.122	1.484	1.478	1.279	1.291	0.46		15.67
	TS₂	2.811	1.396	1.876	1.249	1.307	0.34	−339.19	14.77
	[2][BF₃] + 3a		1.328		1.213	1.343			0.974
[1b][BF₃] → [2][BF₃] + 3b	[1b][BF₃]	1.089	1.525	1.426	1.349	1.208			
	TS₁	1.487	1.500	1.472	1.290	1.264	0.43	−1024.06	14.47
	I	2.124	1.482	1.486	1.273	1.287	0.40		15.26
	TS₂	2.798	1.400	1.845	1.246	1.300	0.34	−323.39	9.95
	[2][BF₃] + 3b		1.328		1.210	1.339			0.974
[1c][BF₃] → [2][BF₃] + 3c	[1c][BF₃]	1.088	1.526	1.420	1.363	1.216			
	TS₁	1.400	1.508	1.453	1.314	1.269	0.39	−1243.81	18.29
	I	2.105	1.489	1.464	1.295	1.305	0.50		19.71
	TS₂	2.952	1.387	1.938	1.258	1.319	0.31	−370.46	20.52
	[2][BF₃] + 3c		1.328		1.218	1.350			0.973

Scheme 2 Mechanisms of decomposition reaction of nitroethyl benzoates **1a–c** catalyzed by LAs BH_3 and BF_3

calculations using the more advanced 6-31 + G(d,p) and 6-311 + G(d) basis sets were carried out.

Published reports show that a similar approach was used successfully to explore a reaction involving several different nitro and other compounds [33–35]. M06-2X is a hybrid meta exchange–correlation functional developed recently [36], parameterized to include short-range dispersion energy. Geometry optimization calculations were carried out to obtain the global minima for the reactants and products, and to locate the saddle point for the **TS**. Stationary points were characterized by frequency calculations. All reactants and products had positive Hessian matrices. All **TSs** had only one negative eigenvalue in their diagonalized Hessian matrices, and their associated eigenvectors were confirmed to correspond to motion along the reaction coordinate under consideration. **TSs** were located using the (QST2) algorithm. Intrinsic reaction coordinate (IRC) calculations [37] were carried out for all events to verify that the localized **TSs** connected with the corresponding minimum stationary points associated with reactants, products, and intermediates.

The reaction environment polarity was simulated using a relatively simple self-consistent reaction field (SCRF) [38–40] based on the polarizable continuum model (PCM) of Tomasi's group [41–43]. Since the solvent used is usually dichloromethane, we used a dielectric constant at 298.0 K of $\epsilon = 8.93$.

Charge global electron density transfer (GEDT) [44] was calculated according to the formula

$$\text{GEDT} = -\sum q_A,$$

where q_A is the net charge and the sum is taken over all the atoms of the substructure.

The values of enthalpies, entropies, and free energies in all calculations were calculated using standard statistical thermodynamics at 25 °C and 1 atm [45].

Conclusions

This quantum-chemical DFT study demonstrates that the LA BH_3 -catalyzed decomposition reactions of nitroethyl benzoates proceed via a polar one-step mechanism. By contrast, the decomposition reaction of nitroethyl benzoates catalyzed by the fluorinated LA BF_3 proceeds via a two-step mechanism involving formation of a zwitterionic intermediate. These decomposition reactions, catalyzed by the LAs BH_3 and BF_3 , take place much faster than the same reactions without catalyst.

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