

DFT study of the decomposition reactions of nitroethyl benzoates catalyzed by the 1,3-dimethylimidazolium cation

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CHRONICLE

Article history:

Received August 21, 2016

Received in revised form

October 24, 2016

Accepted 8 November 2016

Available online

9 November 2016

Keywords:

Thermal elimination

Quantum chemical study

Nitroalkenes

ABSTRACT

DFT calculations indicate that the decomposition reaction of nitroethyl benzoates in the presence of 1,3-dimethylimidazolium cation takes place much faster than in the case of the non-catalyzed process. Additionally, our calculations suggest one-step polar mechanism of title reactions.

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1. Introduction

The synthesis of nitroalkenes is very significant in organic chemistry. Conjugated nitroalkenes (CNA) have been recognized as versatile synthetic intermediates in various organic syntheses because of their easy conversion to a variety of diverse functionalities.¹⁻⁵ They react as dienophiles, heterodienes, 1,3-dipoles and, above all, as Michael acceptors.⁶⁻⁸ Conjugated nitroalkenes are also distinguished by their biological properties.⁹⁻¹¹ Among various biological properties, the anticancer activity of nitroalkenes and their novel MBH adducts with other activated alkenes has highlighted the enormous potential of nitroalkene derivatives as bioactive molecules.¹²⁻¹⁴ Furthermore, nitroalkenes are important precursors of many insecticides,¹⁵ fungicides¹⁶ and pharmaceuticals.¹³

Several methods are available for the preparation of nitroalkenes.^{1,17-20} However, a great demand still exists for a method to prepare nitroolefins in a convenient and effective way. The present work is a continuation of our comprehensive study about the synthesis and fundamental properties of CNA.²¹⁻²⁸ Our previous works^{27,28} present the decomposition of nitroalkyl carboxylates under thermal conditions. DFT calculations confirmed that these processes proceed via the one step mechanism, not “pericyclic”, but quite a strong asynchronous one-step, two-stage mechanism.

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doi: 10.5267/j.ccl.2016.11.001

This work is a continuation of our quantum chemical study of the decomposition reaction of nitroethyl benzoates in the presence of the 1,3-dimethylimidazolium (DMIM) cation. It should be mentioned, that our recent studies show that some nitroalkene cycloaddition reactions catalyzed by the imidazolium cation proceed via a stepwise, zwitterionic mechanism,^{29,30} instead of the one step mechanism, which was noted in the case of non-catalytic conditions. This cation can be introduced for reaction as an ionic liquid. Such ionic liquid was used in organic reactions.³¹⁻³⁴

2. Results and Discussion

2.1 Computational details

All calculations were carried out using the Prometheus computer cluster in the CYFRONET regional computer centre in Cracow. The mechanism of the decomposition of nitroalkyl benzoates catalyzed by the 1,3-dimethylimidazolium cation have been examined as implemented in the GAUSSIAN 09 package.³⁵ The geometric parameters for all the reactants, transition states and products of the reactions studied were fully optimized using the density functional theory (DFT) method. The calculations were performed using the B3LYP³⁶ with 6-31G(d) basic set. Additionally, calculations in more advanced 6-31+G(d) and 6-31G(d,p) basis sets, were carry out.

B3LYP is a combination of Becke's three parameter hybrid exchange functional³⁷ with the Lee, Yang and Parr correlated functional.³⁸ Geometry optimization calculations have been carried out to obtain the global minima for the reactant and products, and to locate the saddle point for the transition state. Stationary points were characterised by frequency calculations. All reactants, and products had positive Hessian matrices. All transition states showed only one negative eigenvalue in their diagonalized Hessian matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration. Transition states were located using the (QST2) algorithm. For the optimization process, the Bery analytical gradient was employed. Intrinsic reaction coordinate (IRC) calculations³⁹ have been made in all events to verify that the localized transition state structures connect with the corresponding minimum stationary points associated with reactants and products. The reaction environment polarity was simulated using PCM.⁴⁰ It was assumed that the reaction environment has dielectric constant, $\epsilon=13$, for the reaction catalyzed by the 1,3-dimethylimidazolium cation (the most typical 1,3-dimethylimidazolium ionic liquids have $\epsilon\sim 11,6-15,1$ ⁴¹).

Charge global electron density transfer (GEDT)⁴² was calculated according to the formula:

$$\text{GEDT} = -\sum q_A, \quad (1)$$

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 with the standard statistical thermodynamics at 25°C and 1 atm.⁴³

2.2 Energetical aspects of the decomposition reaction catalyzed by the DMIM cation

The reaction pathway of the decomposition reaction was studied using the B3LYP/6-31G(d) theoretical level. Recently published reports^{26,44-48}, indicate that a similar approach was used successfully for the exploration of a reaction involving several different nitrocompounds. These calculations proved that the first step of the decomposition of nitroethyl benzoate (**1a**) is the establishment of a pre-reaction complex ([1][DMIM]) between the ester molecule and the 1,3-dimethylimidazolium cation. Consequently, the creation of a pre-reaction complex entails the drop of reaction enthalpy by 3.54 kcal·mol⁻¹ (**Fig. 1** and **Fig. 2**). The DMIM cation is located near to the oxygen atom of the nitro group. We also analyzed many other orientations of the DMIM cation to the ester molecule. For further research we chose the most stable form.

Thereafter, the pre-reaction complex is recast to **TS**, which is associated with an increase in the enthalpy of activation over $33.31 \text{ kcal}\cdot\text{mol}^{-1}$ (**Fig. 2**). The decomposition reaction of nitroethyl benzoate **1a** catalyzed by the DMIM cation proceeded faster than the same reaction without the catalyst. The enthalpy of the activation of the uncatalyzed process is equal to $38.73 \text{ kcal}\cdot\text{mol}^{-1}$.²⁸ Subsequently, the **TS** is converted to products **2** and **3** (**Scheme 1**).

Similar studies have been performed for the decomposition reactions of other nitroethyl benzoates which are substituted by NMe_2 (**1b**) and NO_2 (**1c**) functional groups. The decomposition process of substituted ester with the electrodonating group (NMe_2) will lower the activation barrier. In particular, for the decomposition of compound **1b**, the activation barrier is $30.61 \text{ kcal}\cdot\text{mol}^{-1}$. The decomposition process of the **1c** compound with an NO_2 group has an activation barrier of $35.13 \text{ kcal}\cdot\text{mol}^{-1}$. Therefore, as could be expected, the presence of an electroaccepting group will make the process more difficult (**Table 1**). For comparison, the uncatalyzed process give similar results ($\text{NMe}_2 - 37.52 \text{ kcal}\cdot\text{mol}^{-1}$, $\text{NO}_2 - 39.65 \text{ kcal}\cdot\text{mol}^{-1}$).²⁸ It turned out that, regardless of the nature of the substituent in the benzene ring, the decomposition process always followed the same mechanism (**Scheme 1**).

We have also performed similar a DFT study using more advanced B3LYP/6-31+G(d) and B3LYP/6-31G(d,p) theory levels. These calculations show that the mechanism of the decomposition reaction of nitroalkyl carboxylates also indicate one-step mechanism and makes that process proceed more mildly. The value of the enthalpy of activation for compound **1a** are $30.07 \text{ kcal}\cdot\text{mol}^{-1}$ and $30.47 \text{ kcal}\cdot\text{mol}^{-1}$, respectively (**Table 1**).

Table 1. Kinetic and thermodynamic parameters for the decomposition of nitroethyl benzoates catalyzed by 1,3-dimethylimidazolium cation ($T=298 \text{ K}$; ΔH , ΔG in $\text{kcal}\cdot\text{mol}^{-1}$, ΔS in $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; **1a** - $R=\text{H}$, **1b** - $R=\text{NMe}_2$, **1c** - $R=\text{NO}_2$)

Ester	Theoretical level	Transition	ΔH	ΔG	ΔS
1a	6-31G(d)	1a +DMIM→[1a][DMIM]	-3.54	3.99	-25.24
		[1a][DMIM]→TS	33.31	34.31	-2.86
		[1a][DMIM]→[2][DMIM]+ 3a	3.54	-3.99	26.00
	6-31+G(d)	1a +DMIM→[1a][DMIM]	-0.47	6.43	-23.14
		[1a][DMIM]→TS	30.07	32.20	-3.02
		[1a][DMIM]→[2][DMIM]+ 3a	-20.54	-28.29	26.00
	6-31G(d,p)	1a +DMIM→[1a][DMIM]	-4.22	4.88	-30.51
		[1a][DMIM]→TS	30.47	31.98	-5.09
		[1a][DMIM]→[2][DMIM]+ 3a	4.22	-4.88	30.51
1b	6-31G(d)	1b +DMIM→[1b][DMIM]	-3.74	3.54	-24.44
		[1b][DMIM]→TS	30.61	31.23	-2.06
		[1b][DMIM]→[2][DMIM]+ 3b	14.94	1.05	46.59
	6-31+G(d)	1b +DMIM→[1b][DMIM]	-0.66	6.09	-22.64
		[1b][DMIM]→TS	29.38	30.98	-5.36
		[1b][DMIM]→[2][DMIM]+ 3b	11.14	-1.97	43.97
	6-31G(d,p)	1b +DMIM→[1b][DMIM]	-3.86	3.28	-23.95
		[1b][DMIM]→TS	27.78	28.60	-2.76
		[1b][DMIM]→[2][DMIM]+ 3b	11.61	-1.33	45.51
1c	6-31G(d)	1c +DMIM→[1c][DMIM]	-3.24	3.66	-23.15
		[1c][DMIM]→TS	35.13	36.56	-4.80
		[1c][DMIM]→[2][DMIM]+ 3c	14.09	1.11	43.56
	6-31+G(d)	1c +DMIM→[1c][DMIM]	12.30	7.29	-25.28
		[1c][DMIM]→TS	31.80	35.61	-4.24
		[1c][DMIM]→[2][DMIM]+ 3c	-1.80	-2.60	43.65
	6-31G(d,p)	1c +DMIM→[1c][DMIM]	-3.32	3.4	-22.52
		[1c][DMIM]→TS	34.28	34.28	-6.67
		[1c][DMIM]→[2][DMIM]+ 3c	-1.23	-1.23	42.11

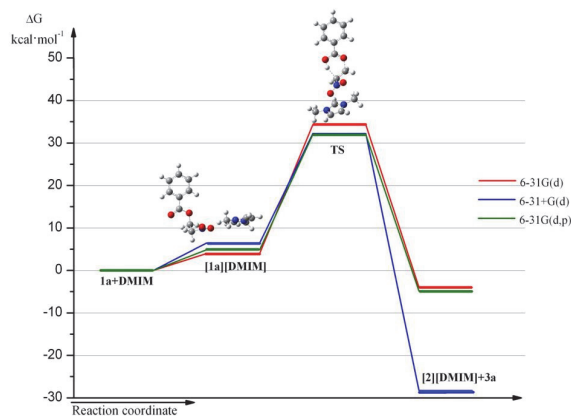


Fig. 1. Gibbs free energy profiles for the decomposition of nitroethyl benzoate **1a** catalyzed by the 1,3-dimethylimidazolium cation

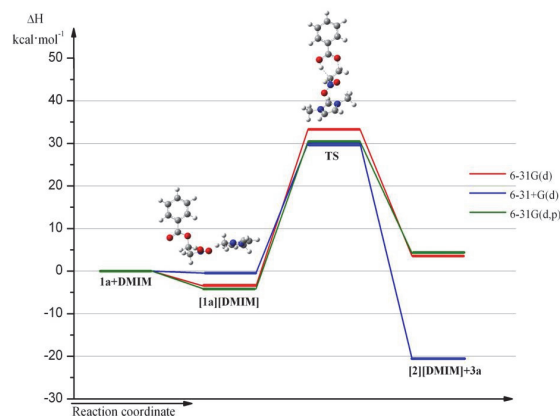
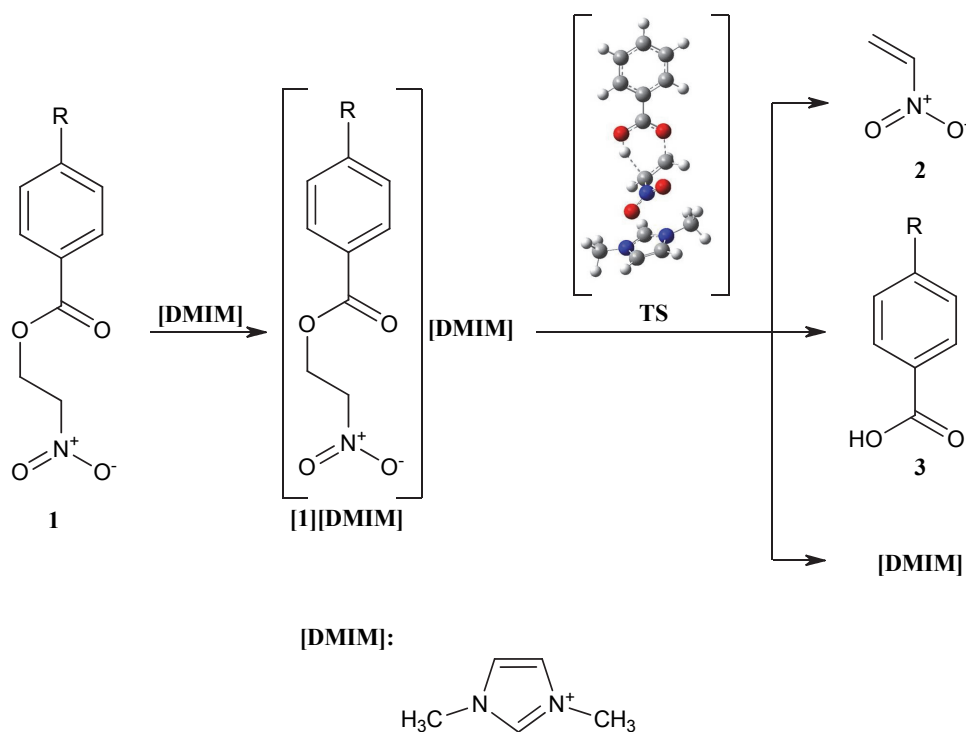


Fig. 2. Enthalpy profiles for the decomposition of nitroethyl benzoate **1a** catalyzed by the 1,3-dimethylimidazolium cation



Scheme 1. Mechanism of the decomposition reaction of nitroethyl benzoates catalyzed by the 1,3-dimethylimidazolium cation

2.3 Transition structure of the decomposition reaction

The **TS**, also in the decomposition reaction catalyzed by the 1,3-dimethylimidazolium cation, has a six-membered structure (**Fig. 3**). Simultaneously, new bonds are formed: between atoms O5-H6 and between atoms C1-C2 and O3-C4 double bonds. The C4-O5 bond is change to a single bond, and H6-C1 and C2-O3 bonds become broken (**Table 2**).

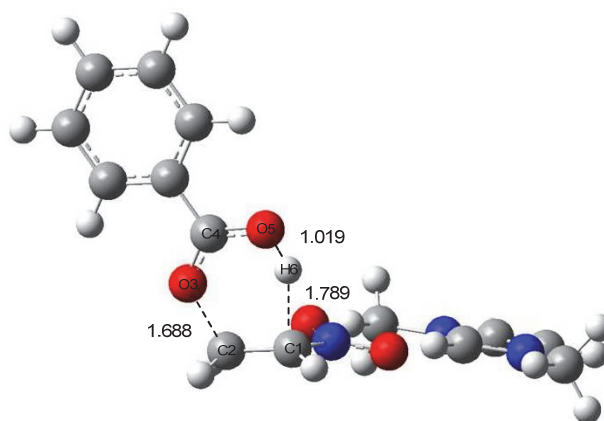


Fig. 3. Transition state TS structure for the decomposition of nitroethyl benzoates **1a** catalyzed by the DMIM cation

Table 2. Key parameters for structures of the decomposition of nitroethyl benzoates catalyzed by the DMIM cation according to B3LYP/6-31G(d) data (**1a** - R=H, **1b** - R=NMe₂, **1c** - R=NO₂)

Reaction	Structure	Interatomic distances [Å]						GEDT [e]
		H6-C1	C1-C2	C2-O3	O3-C4	C4-O5	O5-H6	
[1a][DMIM]→[2][DMIM]+3a	[1a][DMIM]	1.088	1.517	1.437	1.360	1.218	2.727	0.30
	TS	1.789	1.432	1.688	1.270	1.304	1.019	
	[2][DMIM]+3a		1.329		1.219	1.353	0.976	
[1b][DMIM]→[2][DMIM]+3b	[1b][DMIM]	1.088	1.517	1.434	1.368	1.223	2.752	0.35
	TS	1.885	1.422	1.721	1.276	1.318	1.000	
	[2][DMIM]+3b		1.329		1.224	1.361	0.976	
[1c][DMIM]→[2][DMIM]+3c	[1c][DMIM]	1.088	1.516	1.440	1.353	1.216	2.744	0.28
	TS	1.730	1.436	1.682	1.268	1.296	1.036	
	[2][DMIM]+3c		1.329		1.216	1.348	0.976	

Finally, we analysed the influence of the DMIM cation of structure TS. It was found that the H6-C1 bond in the reaction catalyzed by the DMIM cation is broken faster than in the uncatalyzed process. In turn, the C2-O3 bond of the TS of reaction with the ionic liquid cation is broken more slowly than in the case of the uncatalyzed reaction.²⁸ The nature of the substituent in benzene ring also has an impact on the transition structure. In the case of reaction [1b][DMIM]→[2][DMIM]+3b, the H6-C1 and C2-O3 bonds are broken faster than the same bonds in reaction [1a][DMIM]→[2][DMIM]+3a. By contrast, the H6-C1 and C2-O3 bonds in the case of reaction [1c][DMIM]→[2][DMIM]+3c are broken more slowly than in the case of reaction [1a][DMIM]→[2][DMIM]+3a (Table 2).

The GEDT value for the transition state for the decomposition reaction catalyzed by the 1,3-dimethylimidazolium cation is 0.30. This value is bigger than the same GEDT value for the transition states of similar non-catalytic processes.

3. Conclusions

Our quantum chemical study proved that the decomposition reaction of nitroethyl benzoates catalyzed by the 1,3-dimethylimidazolium cation proceeded via a polar one-step mechanism. Compared to the uncatalyzed process, the decomposition reaction in the presence of the 1,3-dimethylimidazolium cation proceed faster. All other research for the localization of different reaction channels lead via the ionic intermediate failed.

Acknowledgements

This research was supported in part by PL-Grid Infrastructure and financial support from the Polish State Committee (Grant no. C-2/88/2016/DS) are gratefully acknowledged.

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