



A dramatic change of kinetic conditions and molecular mechanism of decomposition processes of nitroalkyl carboxylates catalyzed by ethylammonium cations



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ABSTRACT

DFT calculations at different theory levels, indicate consistently, that in the presence of ethylammonium cation, a nitroethyl benzoates decomposition process is expected to take place much faster than under “conventional” (non-catalyzed) conditions. The one-step mechanism being replaced by a two-step mechanism involving a zwitterionic intermediate.

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1. Introduction

Conjugated nitroalkenes (CNA) are valuable building blocks for the synthesis of many interesting compounds, which are difficult to obtain in an alternative, synthetic way. In particular, based on reactions involving CNA three-, four-, five- and six-membered carbo- and heterocycles may be prepared [1–3], via cycloaddition or cyclocondensation processes. The presence of a nitro group in the molecule makes them highly reactive components in reaction with nucleophilic reagents [4,5]. Additionally, the introduction of a nitro group to target compounds provides many opportunities for further functionalization due to the possibilities for the transformation of nitro compounds into carbonyl compounds (Nef reaction) [3,6,7] nitrile N-oxides (Mukaiyama reaction) [8], hydroxylamines [9,10] aminoalcohols (via a Henry reaction/reduction sequence) [3,11–13], esters and nitronic acid salts [3,14] and many others.

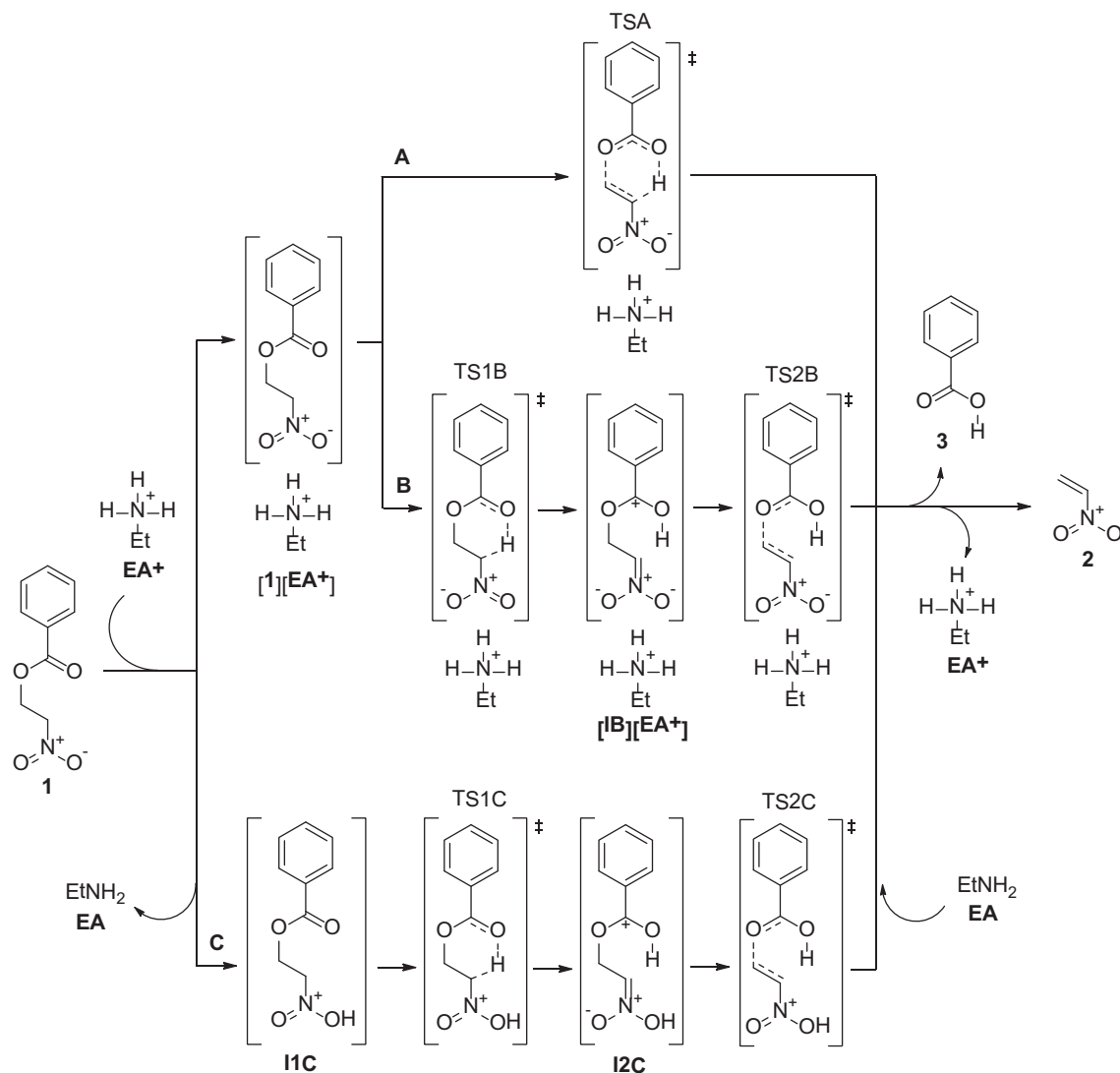
The most universal strategy for the preparation of CNA is decomposition of the appropriate nitroalkyl carboxylates [15]. Unfortunately, many of these processes require relatively dramatic conditions. For example, decompositions of nitroalkyl phthalates proceed at 180–200 °C [16]. Similar elimination of carboxylic acid from nitroalkyl benzoates are carried out at temperatures higher

than 185 °C [17]. Alternatively, some CNA may be obtained via base-catalyzed E1cb elimination in boiling benzene [18]. Unfortunately, simple, high reactive nitroalkenes such as nitroethene, nitropropenes, halonitroethenes and many others, rapidly polymerize under these conditions [15,19]. Therefore, research aimed at searching for relatively mild conditions for a universal methodology for preparation of CNA from nitroalkyl carboxylates is justified.

This work is a continuation of our comprehensive study about the synthesis and fundamental properties of CNA [5,20–26]. Previously [26], we analyzed in detail mechanistic aspects of the decomposition of nitroalkyl carboxylates under thermal (non-catalyzed) conditions. Our DFT calculations suggest, that these processes proceed via a one-step reaction. However, this is not a “pericyclic” mechanism, but rather strong a asynchronous one-step, two-stage mechanism. In presented work, we decided to shed light on a theoretically possible decomposition of model nitroalkyl carboxylates catalyzed by ethylammonium cation (EA⁺). In practice, the source of ethylammonium cation under reaction conditions may be, for example ionic liquid, which has been tested in practice as a reaction medium for several organic reactions [27,28]. It is possible that in the presence of this catalyst, one-step mechanism decomposition of starting molecules may be competed with a two-step, ionic mechanism (Scheme 1). It should be noted at this point, that our recent studies show that some nitroalkene-cycloaddition reactions catalyzed by ammonium cations proceed via a multi-step, zwitterionic mechanism [20,29], instead of the one-step

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Scheme 1. Theoretically possible mechanisms for nitroethene formation process in the presence of the ethylammonium cation.

mechanism, which was observed under non-catalytic conditions [30–32].

2. Computational details

All calculations reported in this thesis were performed on SGI-Altix 3700 computer in the CYFRONET regional computational centre in Cracow. Hybrid functional B3LYP with the 6-31+G(d, p) basis set included in the GAUSSIAN 09 package [33] was used. Recently published reports show that the same functional was used e.g. for the analysis of chemical properties of nitro-functionalized compounds [20–22,26,34] including thermal decomposition process [23,35–37]. In addition, similar simulations using more advanced B3LYP/6-31++G(d, p) as well as B3LYP/6-311+G(d, p) theoretical levels were performed. Optimizations of the stable structures were performed with the Berny algorithm, whereas the transition states were calculated using the QST2 procedure followed by the TS method. 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. For all reactions, intrinsic reaction coordinate (IRC) calculations were performed to connect previously computed transition structures (TS) with suitable minima. The reaction environment polarity were simulated using PCM [38]. It was assumed that the reaction environment has dielectric constant, $\epsilon = 28$, because most typical ethylammonium ionic liquids have $\epsilon \approx 26\text{--}30$ [39]. Similar approach has been successfully used by the Domingo group for the analysis of Diels-Alder reaction between *N*-tosylpyrroles and isoprene in the presence of dialkylimidazolium ionic liquids [40]. Charge global electron density transfer (GEDT) [41] 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 substructure.

3. Results and discussion

In particular, we performed a quantum chemical study about the elimination of benzoic acids from nitroethyl benzoates in the presence of EtNH_3^+ cation. These studies will be the first stage of a comprehensive research project under new, highly effective strategies for the preparation of CNA. Additionally, our studies will

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