Chemical Physics Letters 683 (2017) 598–605

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

A computational study of the Diels-Alder reactions between 2,3-dibromo-1,3-butadiene and maleic anhydride ☆

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ARTICLE INFO

Article history:
Received 5 January 2017
In final form 21 March 2017
Available online 23 March 2017

Keywords:
Diels-Alder reaction
Maleic anhydride
2,3-Dibromo-1,3-butadiene
DFT
RRKM

ABSTRACT

The neutral and cationic Diels-Alder-type reactions between 2,3-dibromo-1,3-butadiene and maleic anhydride have been computationally explored as the first step of a combined experimental and theoretical study. Density functional theory calculations show that the neutral reaction is concerted while the cationic reaction can be either concerted or stepwise. Further isomerizations of the Diels-Alder products have been studied in order to predict possible fragmentation pathways in gas-phase experiments. Rice-Ramsperger-Kassel-Marcus (RRKM) calculations suggest that under single-collision experimental conditions the neutral product may reform the reactants and the cationic product will most likely eliminate CO_2.

1. Introduction

The Diels-Alder reaction is one of the most important reactions for the synthesis of cyclic compounds in organic chemistry because of its high regio- and stereo-selectivity [1,2]. In this reaction, a diene reacts with a dienophile to form a cyclic product. Two σ bonds and one π bond are formed from three π bonds as depicted in Scheme 1.

This reaction has been the subject of many experimental and computational studies aiming to decide if it takes place in a concerted fashion and if so, whether or not it is a synchronous process and how the mechanism depends on the geometric and electronic properties of the reactants [3–14].

The concertedness of a mechanism is determined by the topology of the potential energy surface (PES) [15]. A concerted mechanism occurs when the PES exhibits only one transition state (TS) between reactants and products so that the process takes place in a single step. A mechanism will be stepwise (taking place in two or more elementary steps) when the system has to overcome at least two TSs separated by an intermediate species (a local minimum on the PES) to evolve from reactants to products.

Synchronicity refers to the time elapsed between the formation of the first and the second bond [15]. It is usually defined by the TS geometry [4]. Symmetric TSs give rise to synchronous processes in which both bonds are formed at the same time. Asymmetric TSs lead to asynchronous processes in which first one bond is formed and then the second follows. This definition of synchronicity has recently been questioned by some authors who argue that synchronicity should not be defined from a geometric but from a dynamic point of view because the connection between spatial quantities and temporal concepts may not always be valid [5]. A synchronous process is always concerted while an asynchronous one can be concerted or stepwise depending on the absence of a (stable) intermediate.

There has been a long-standing discussion about synchronicity and concertedness of Diels-Alder reactions which is not yet resolved [3,6]. The picture that organic chemistry textbooks usually give is that it is a concerted, synchronous reaction governed by the Woodward-Hoffmann rules that involves an aromatic TS [2,16]. However, experiments and calculations show that this is not that simple in many cases. In principle, one can think of three possible mechanisms (see Scheme 1): (a) synchronous concerted, (b) stepwise with a short lived intermediate whose lifetime is not long enough for the system to rotate around a C–C bond, and (c) stepwise with a long lived intermediate. Note that when the system cannot rotate around a C–C bond, as is the case in (a) and (b), the reaction is stereo-selective and only the s-cis conformer of the diene will yield the cyclic Diels-Alder product. On the contrary, mechanism (c) is not stereo-selective and the s-trans conformer of the diene could also in principle yield a Diels-Alder product.

Zewail and his group have performed different experiments involving retro Diels-Alder reactions in which they detected intermediates [7,8]. This suggests that the reaction must happen, at least partially, in a non-concerted fashion in these cases.

☆ Dedicated to the memory of Prof. Ahmed Zewail.

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http://dx.doi.org/10.1016/j.cplett.2017.03.063
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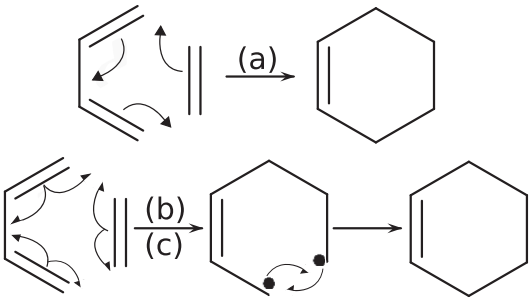

Scheme 1.

However, since the experiment is started with the excitation of the Diels-Alder product, excited states play a role in the dynamics [17]. There also exist several studies involving kinetic isotope effects that compare experimental and calculated results in order to determine if the reaction is concerted or stepwise. The picture emerged that neutral Diels-Alder reactions tend to take place in a concerted way while ionic Diels-Alder reactions usually happen in a stepwise manner [9–11].

From a computational point of view, studying Diels-Alder reactions is challenging since the relevant systems are comparatively large and the choice of method and basis set will bias the final result [18–20]. The reaction between butadiene and ethene (the simplest Diels-Alder reaction), see Scheme 1, has been studied at various levels of theory [3,12,21–23]. For this symmetric reaction, ab initio and density functional theory (DFT) calculations favor a concerted, synchronous mechanism (as suggested by the symmetry of the system), but multireference methods are needed to accurately calculate the activation energy and the enthalpy of reaction as compared to the experimental values [18,21,22]. DFT methods can also provide good results, but due to the wide range of resulting energies the choice of functional is not trivial [22,23].

The complexity is higher when studying asymmetric reactions due to the fact that a continuous range of possibilities exists between synchronous, concerted processes and asynchronous, stepwise mechanisms [13]. Moreover, there seems to be a correlation between the asymmetry of the TS structure and the rate constant of the process, where asymmetry refers to the difference in the lengths of the newly formed σ bonds in the TS. The more asymmetric the TS geometry, the faster the reaction [4,13]. Diels-Alder reactions are usually activated by electron-withdrawing groups in the dienophile and electron-rich groups in the diene although the contrary situation, in which the electron-rich groups are in the dienophile and the electron-withdrowing ones in the diene, is also possible [2].

In general and compared to experimental values and high level theoretical calculations, Møller-Plesset second order perturbation theory (MP2) was found to underestimate the activation energies because of an overestimation of electron correlation [22]. Complete active space self consistent field (CASSCF) calculations give values close to Hartree-Fock (HF) due to its lack of dynamic correlation, which causes an overestimation of the height of the reaction barrier [21,22]. It is thus necessary to use complete active space second order perturbation theory (CASPT2) to obtain accurate energies [22]. On the other side, DFT methods predict a wide range of activation energies and reaction enthalpies and the widely used B3LYP/6-31G* approach usually overestimates the activation energies while underestimating the reaction enthalpies [20,23,24]. Moreover, it seems that increasing the basis set size does not improve the quality of the results and it can even make them worse. A medium-size basis set, such as 6-31G*, has thus been recommended for the study of Diels-Alder reactions [19,24,25].

Cationic Diels-Alder reactions (polar cycloadditions) are often faster but still show a high degree of stereoselectivity [26–28]. There have been some studies on the conservation of orbital symmetry to try to construct rules analogous to the Woodward-Hoffmann rules widely used for the neutral reactions [28–30]. Wiest and Donoghe proposed a model in which the electronic state symmetry must be conserved throughout the reaction [14]. Gas-phase experiments on the cationic Diels-Alder reaction between butadiene and ethene have been unable to isolate the Diels-Alder product. As no efficient deactivation was possible in the gas phase, the product fragmented under the experimental conditions [31]. Subsequent computational studies explored the possible fragmentation pathways of the Diels-Alder product in order to interpret the experimental findings [32,33].

In summary, these results corroborate the picture that neutral reactions usually occur in a concerted fashion while in cationic systems a non-concerted mechanism is favored [3,14]. However, the border between asynchronous, concerted and stepwise mechanisms is not yet clear [9,10,13]. It has also been argued that both concerted and stepwise mechanisms can be present at the temperatures at which these reactions are usually performed (around 500 K and above) due to the energetic proximity of both pathways in many systems [5,7,8]. When a stepwise process takes place, the competition between the closure of the ring and the isomerization of the intermediate state needs to be studied in order to determine whether or not the reaction will be stereo-selective.

From an experimental perspective, the most precise data on reaction mechanisms and dynamics can be gained from gas-phase studies performed under single-collision conditions. As the progress in molecular-beam experiments allows the probing of ever-larger systems under precisely defined conditions [34], the open questions pertaining to the mechanistic details of Diels-Alder reactions become an attractive target of study. However, a crucial difference to the solution phase, for which the vast majority of experimental data is available, is that the energy released into the products over the course of the reaction cannot be quenched by the environment under single-collision conditions on the time-scales of experiments and is therefore available to drive consecutive fragmentations or isomerizations. This effect is particularly important for Diels-Alder processes in which the total energy release of the reaction remains locked in a single product. As only scarce information is available on these important mechanistic aspects [35], we present here a comprehensive computational characterization of the mechanisms, decay pathways and kinetics of the products of the neutral and ionic Diels-Alder reaction between 2,3-dibromo-1,3-butadiene (DBB) and maleic anhydride (MA) which highlights these effects and may serve as a guide to future experiments.

We have chosen DBB as the diene because it is a generic, activated diene which fulfills the experimental requirements for conformational separation of its isomers by electrostatic deflection of a molecular beam [34] thus enabling the characterization of conformational aspects and specificities of the reaction. MA is a widely used, activated dienophile which due to its symmetry simplifies the possible outcomes of the reaction. The reaction of DBB and MA thus serves as a prototypical system well suited to explore general mechanistic aspects of Diels-Alder processes under gas-phase conditions.

In this paper, we present computational results on this system using DFT and multi-reference (CASPT2) approaches (Section 3.1). We also study the evolution of the Diels-Alder products by exploring different isomerization and fragmentation pathways (Section 3.2) based on RRKM theory [36] in order to obtain qualitative trends for the time evolution of the system under collisionless conditions (Section 3.3).