



Nitranion as intermediate in the decomposition of azides electrocatalytically synthesized. A CASSCF and CASPT2 study

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ABSTRACT

In this work, we propose that nitranion (nitrene negatively charged) is an intermediate in the decomposition of azides electrocatalytically synthesized. This assertion is based on CASSCF and CASPT2 calculations, which show that (1) the radical anion of (1-azidovinyl)benzene is energetically most stable than its neutral partner [13 kcal/mol]; (2) the azidic radical anion decomposes into nitranion and molecular nitrogen after surmounting a very low barrier [4 kcal/mol].

1. Introduction

The metal-catalyzed electrochemical azidation of alkenes was first published by Fu et al. [1] (Scheme 1a). After this seminal article, many works have been published on the electrocatalytic azidation of different compounds which start with the electrochemical azidation of the initial alkene derivative as reactant, for example, the synthesis of amines [2] or azo compounds [3]. To explain such synthesis, in which the azide moiety ($-N_3$) is decomposed, the proposed reaction mechanisms that we can find in the literature, give a key step, which is a pure chemical decomposition (non-electrochemical) of the organic azide, that is, dissociation of the azide into molecular nitrogen and the corresponding nitrene derivative [2,3] (Scheme 1b) –the details of such mechanisms are given in Fig. S1–. However, this assumption, i.e. nitrene formation, has a drawback which is the high activation energy at room temperature (~ 40 kcal/mol, [4–7]) for dissociation of the azidyl moiety ($-N=N_2 \rightarrow -N: + N_2$). For this reason, as model of organic azide arising from azidation of styrene (M0, Scheme 1c), we have explored the role of the formation of the radical anion of (1-azidovinyl)benzene (M1 Scheme 1c) from the parent azide generated in an electrochemical cell. The results of this work will show that decomposition of the radical anion of the azide yields the anion of the nitrene derivative (nitranion, M4 Scheme 1d), after surmounting a very low energy barrier. The nitranion is a chemical species in which the extra electron is localized on the nitrogen atom [8,9].

2. Computational details

All the calculations have been performed with the MOLCAS 8.6

program [10,11]. The complete active space self-consistent field (CASSCF) [12–17] and multi-state second-order perturbation (MS-CASPT2) methods [18,19] were applied as implemented in such a program. The ANO-RCC basis sets [20,21], which are extended relativistic basis sets of the atomic natural orbital (ANO)-type basis sets, were used in the multiconfigurational calculations of this study by applying the contraction scheme: (C,N)[4s3p2d1f]/(H)[3s2p1d]. To prevent including invader states in the MS-CASPT2 calculations, an imaginary shift set to 0.1 was used. A standard value (0.25) for the IPEA empirical correction was applied. The molecular orbitals and geometries of the chemical species were analyzed using the programs Gabedit [22] and Molden [23], and the analysis of vibrational normal modes, including saddle point (transition vector) and intersystem crossings (energy difference gradient vector), was carried out using the program MacMolplt [24]. The values of the spin-orbit coupling constants (SOC) between S_0 and T_0 were computed using a one-electron spin-orbit Fock-type Hamiltonian [25–27]. The convention followed to label the electronic states is the energetic order within each multiplicity at the geometry of the ground state; that is, the states are labeled as $S_0, S_1 \dots S_n$ for singlet states, $D_0, D_1 \dots D_n$ for doublet states and $T_0, T_1 \dots T_n$ for triplet states.

3. Results and discussions

Prior to starting the discussion of the results, it should be noted that the energetic data in this section are based on CASPT2 calculations performed on top of CASSCF optimized geometries.

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3.1. Dissociation of the neutral azide [(1-azidovinyl)benzene]

As a first step, we assume that (1-azidovinyl)benzene (**M1**, Scheme 1c) is formed from electrochemical azidation of styrene (**M0**, Scheme 1c). The minimum energy geometry of the parent molecule [(1-azidovinyl)benzene] is optimized with an active space that comprises 16 electrons distributed in 15 orbitals, that is, six π orbitals from the benzene ring, two π orbitals from the alkene moiety, and the following orbitals associated to the azidyl group: two σ (NN) orbitals, two π (NNN) orbitals, two π_{σ} (NN) orbitals and one non-bonding n_{π} (NNN) orbital (Fig. S2).

In this subsection, we study the energetic of the dissociation reaction of **M1** into the nitrene derivative and molecular nitrogen. Thus, Fig. 1 represents the dissociation curves of **M1** into the nitrene intermediates (triplet or singlet) and molecular nitrogen. Such curves were obtained with the linear interpolation method [28,29] by taking as initial point the minimum energy geometry of **M1** (Fig. 2a) and the final point corresponds to triplet nitrene (**M2**, Fig. 2b) and N_2 separated by 4.7 Å. As is shown in Fig. 1, the lowest energy barrier for dissociation corresponds to the spin forbidden channel. The minimal energy crossing point corresponding to such a channel has been optimized (ISC1, Fig. 2c) starting at the *p*ISC1 geometry localized on Fig. 1 and yields an energy 44 kcal/mol above **M1**, the spin-orbit coupling constant of the singlet and triplet states at this geometry is 43.2 cm^{-1} . The allowed channel to yield singlet nitrene has an exit barrier height that is predicted to have an upper limit of 59 kcal/mol, estimated on top the high energy point of the singlet potential energy surface of Fig. 1.

3.2. Formation of the radical anion of (1-azidovinyl)benzene

Because the energy barriers of the dissociation of the neutral azide **1** are relatively high for a catalytic process, since the reaction proceeds in an electrochemical cell, we have considered the possibility of the formation of the radical anion (**M3**, Fig. 2d) of **M1**. It is found that radical anion **M3** is 13 kcal/mol more stable than the neutral molecule **M1**. The reference active space of the radical anion is similar to that of the neutral species and is represented in Fig. S3. In addition, the molecular orbital occupied by the extra electron is depicted in Fig. 3 along with the

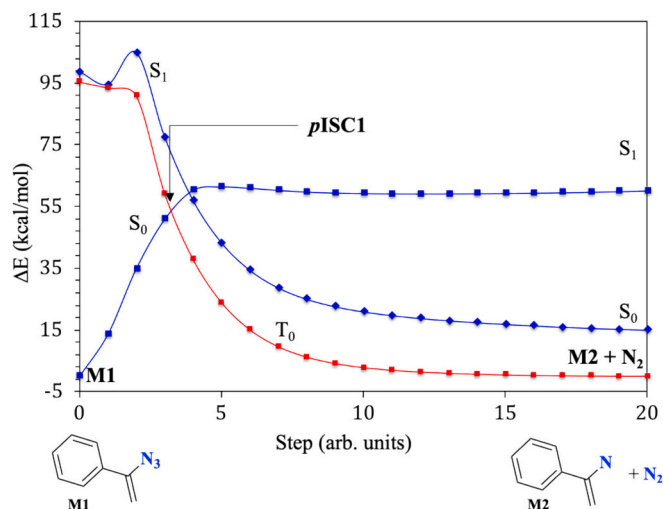
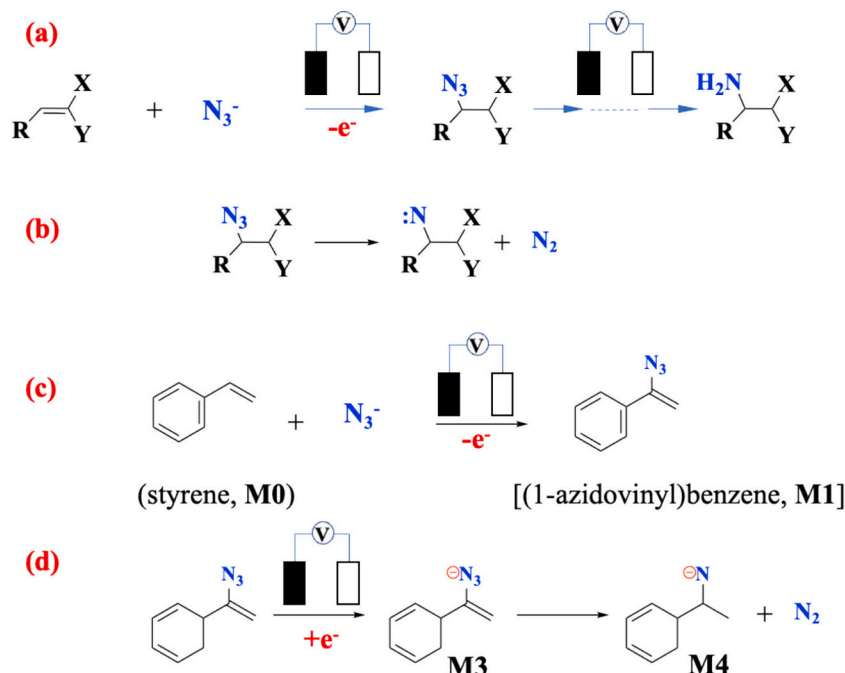


Fig. 1. CASPT2 potential energy curves for the dissociation of **M1** into nitrene **M2** and molecular nitrogen.

diagrammatic representation of the energy levels of the neutral an anionic azidyl species.

3.3. Dissociation of the radical anion of (1-azidovinyl)benzene to yield the nitranion and N_2

The dissociation of anion **M3** into nitranion (**M4**, Fig. 2e) and molecular nitrogen is represented in Fig. 4. The reaction occurs via a transition state (**TS1**, Fig. 2f) that was optimized at the CASSCF level, and whose CASPT2 energy is only 4 kcal/mol above the radical anion of the azide **M3**. Fig. 4, in fact, represents two interpolations: the first goes from the minimum of radical anion **M3** to transition state **TS1**, the second goes from transition state **TS1** to the separated fragments (nitranion **M4** and N_2), so that, the vertical line of the Fig. indicates that the two interpolations are not strictly along a straight line.



Scheme 1. Electrocatalytic synthesis of amines (a); formation of nitrene intermediate from neutral azide (b); electrochemical azidation of styrene (1c).

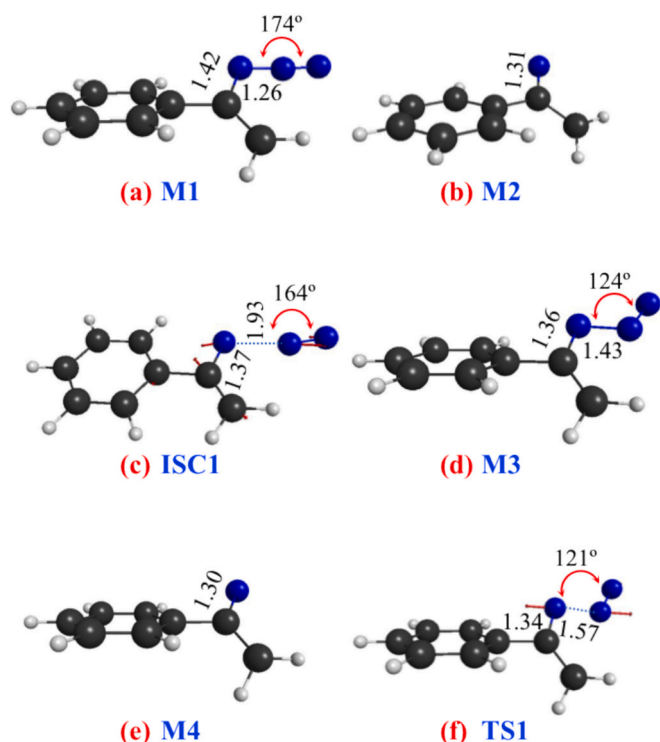


Fig. 2. CASSCF geometries of the critical structures of this work. (a) S_0 minimum of (1-azidovinyl)benzene; (b) T_0 minimum of nitrene (neutral); (c) S_0/T_0 minimum energy intersystem crossing; (d) D_0 minimum of the radical anion of M1. (e) D_0 minimum of nitranion; (f) D_0 transition state for dissociation of M3 into M4 and molecular nitrogen. Distances in Å; angles in degrees.

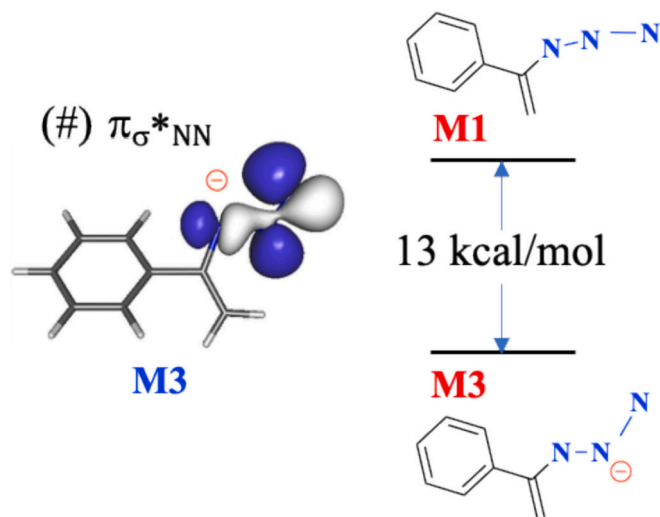


Fig. 3. Left, CASSCF molecular orbital occupied by the extra electron of the radical anion M3. Right, schematic energy-level diagram of the electronic energy difference between M3 and M1. (#) π_{σ}^* denotes antibonding π interaction of the p -type atomic orbitals of the $-N_3$ moiety on the plane defined by such a moiety.

4. Conclusions

In this work, we have shown as the radical anion of an azide (M3) is energetically more favorable (13 kcal/mol) than its neutral counterpart (M1) and we have found that the extra electron is localized in the orbitals of the azide moiety of the radical anion. However, such an anion easily decomposes into nitranion (M4) and N_2 after surmounting a small

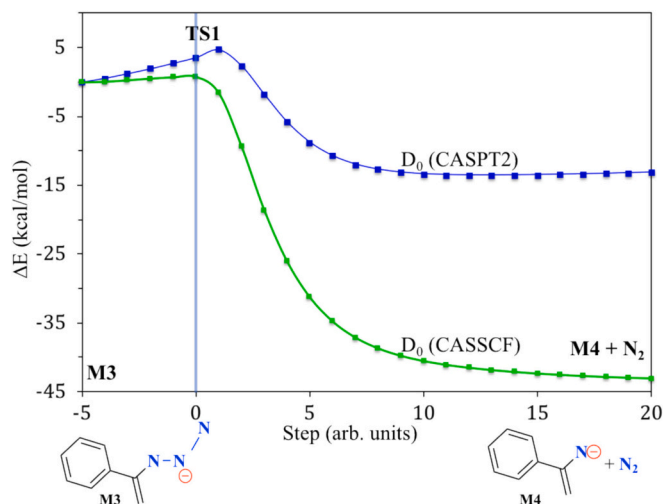
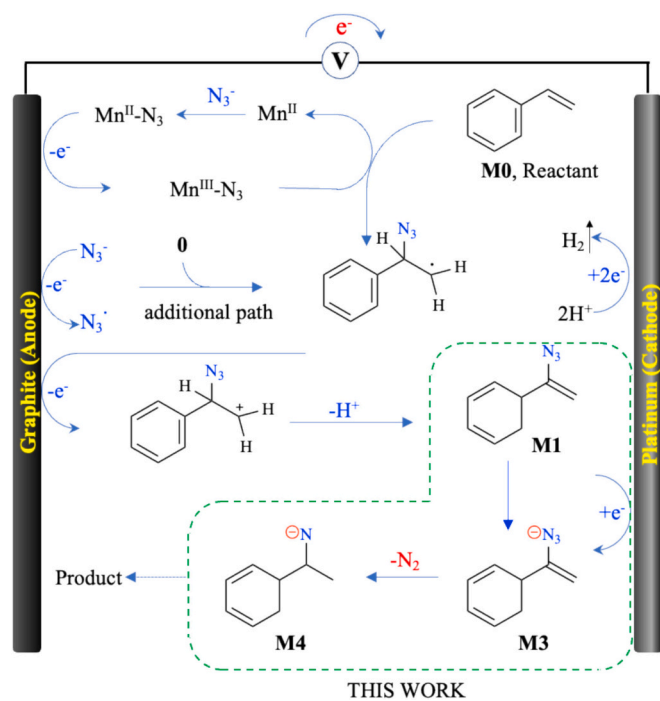


Fig. 4. CASPT2 and CASSCF potential energy curves for the dissociation of M3 into nitrene M4 and molecular nitrogen.

energy barrier (4 kcal/mol). Once formed the nitranion intermediate in an electrochemical cell, it can suffer subsequent reactions. Thus, the electrochemical mechanism proposed for the formation of such nitranion is depicted in Scheme 2. This mechanism represents only a subtle but important modification of the mechanism proposed by the authors of the excellent articles published in references [2,3].

CRediT authorship contribution statement

Juan Soto: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.



Scheme 2. Proposed reaction mechanism for the electrochemical formation of the nitranion derivative after dissociation of the radical anion of (1-azidovinyl)benzene, M3.

Declaration of competing interest

The author declares that he has no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2025.142281>.

Data availability

No data was used for the research described in the article.

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