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Catalytic Electrons

# Electron Impact Catalytic Dissociation: Two-Bond Breaking by a Low-Energy Catalytic Electron**

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In low-energy electron impact on neutral molecules, the free electron and the molecule often form an intermediate metastable electron–molecule compound.[1–3] This compound may either release the excess electron by autodetachment (AD)[1] or fragment by a reaction called dissociative electron attachment [DEA, Eq. (1)]:[1–3]

$$e^- + AB \rightarrow (AB)^{-*} \rightarrow \begin{cases} AB + e^- & (AD) \\ A^\bullet + B^{\bullet -} & (DEA) \end{cases} \quad (1)$$

A wide variety of chemical transformations initiated by electron impact can be attributed to DEA.[1–3] In particular, it is well known that in organic molecules DEA efficiently leads to bond dissociation, producing radical and radical-anion molecular fragments. In general, in all examples studied and understood theoretically, DEA leads to an anionic fragment and a neutral fragment.[1–3] Recently, mass spectroscopic measurements monitoring DEA of fructose have shown that several neutral fragments may appear in addition to the anionic fragment.[4] The underlying mechanisms have not been clarified yet, but it may be suspected from the detected products that the two fragments initially formed by DEA as in Equation (1) have further fragmented by several stepwise reactions. In any case, electron–molecule reactions are seen to be chemically rich and are of chemical interest.

Herein we report on a new elementary reaction (i.e., single-step reaction) mechanism of an electron and a molecule in a metastable compound which we call (two or more) bond breaking by a catalytic electron (BBCE). Unlike in DEA, the formed compound anion dissociates into non-radical neutral molecular subunits and a free electron, which plays the role of a catalyst [Eq. (2)]:

$$e^- + AB \rightarrow (AB)^{-*} \rightarrow A + B + e^- \quad (BBCE) \quad (2)$$

where we stress that at least two bonds (not a double bond) break in the elementary reaction path. Notice that the electron is freed in the course of the elementary reaction, that is, the electron is not attached to any of the chemical products of the elementary reaction and, thus, we refer to this mechanism as an electron-catalyzed mechanism. This elementary reaction involves both bond breaking and detachment of the electron. The key differences between BBCE and DEA are as follows:

1. More than one σ bond (two-center bond) is broken in the elementary BBCE reaction.
2. The products formed in the BBCE are neutral.
3. The electron is released in the course of the elementary BBCE reaction.

Below, we illustrate this mechanism more precisely by investigating electron impact on the quadricyclanone (QDCO) molecule. As will become clearer, the low-energy electron impact on QDCO can be viewed as proceeding via a compound negative ion metastable state. We have acquired considerable experience in the ab initio computation of energy and lifetime of metastable anions using non-Hermitian quantum chemical methods.[5–7] Recently, the introduction of a so-called continuum remover complex absorbing potential[8] and its implementation in Green's function methods[9] have made non-Hermitian quantum chemical methods applicable to larger systems. The efficient identification of the metastable states and the correct scaling of the electronic energy with respect to the number of electrons are the most indispensable ingredients of the non-Hermitian Green's function method when applied to electron–molecule collision problems.

Before discussing QDCO, it is convenient to turn to a possible neutral nonradical cycloelimination product, norbornadienone (NBDO). These two molecules can be interconverted by cycloaddition–cycloelimination mechanisms. In the cycloaddition, two new bonds are formed between the two ethylene subunits of NBDO. Concerted reactions of this type are photoinduced.[10] In the cycloelimination, these bonds break (Scheme 1). To understand the electron impact on QDCO, we begin by ignoring its substituents, the bridge, and its carbonyl group, and considering only those parts of the π-conjugate system that are directly involved in the cycloaddition–cycloelimination reactions. We shall return to the crucial role of the substituents later in the discussion. Thus the QDCO–NBDO transformation is simplified to that of the cyclobutane–ethylene transformation (see Scheme 1), and a brief illustration of the π molecular orbitals of the ethylene–cyclobutane cycloaddition–cycloelimination mechanism[11] might be useful to understand the corresponding mechanism in the QDCO–NBDO system.

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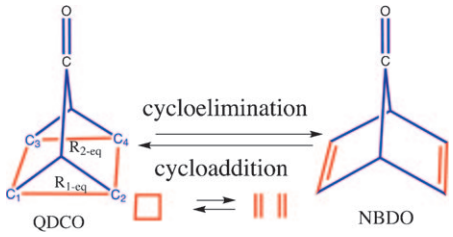


***Scheme 1.*** The cycloaddition–cycloelimination reactions in the QDCO–NBDO system. The fragments shown in red identify the simplest model, the cycloaddition–cycloelimination in the cyclobutane–ethylene system.

The molecular orbitals of cyclobutane and ethylene involved in the cycloaddition–cycloelimination reaction, as derived from simple Hückel molecular orbital theory, are shown schematically in Figure 1. The subscripts L (left) and R (right) are used to differentiate the two isolated ethylene fragments of the cyclobutane molecule. The orbitals of the two interacting ethylene molecules are derived from $\pi$ and $\pi^*$ orbitals of the isolated ethylene fragments. There are four possible combinations: two bonding orbitals ($\pi_L+\pi_R$) and ($\pi_L^*+\pi_R^*$) and two antibonding orbitals ($\pi_L-\pi_R$) and ($\pi_L^*-\pi_R^*$). Likewise, the bonding and antibonding orbitals of cyclobutane can be formed. To illustrate the idea behind the process of catalytic cycloelimination, we name the relevant orbitals of cyclobutane by those of the interacting ethylene molecules, although the true orbitals lie in the molecular plane and are thus usually termed σ orbitals, which are subject to overlap and hybridization.

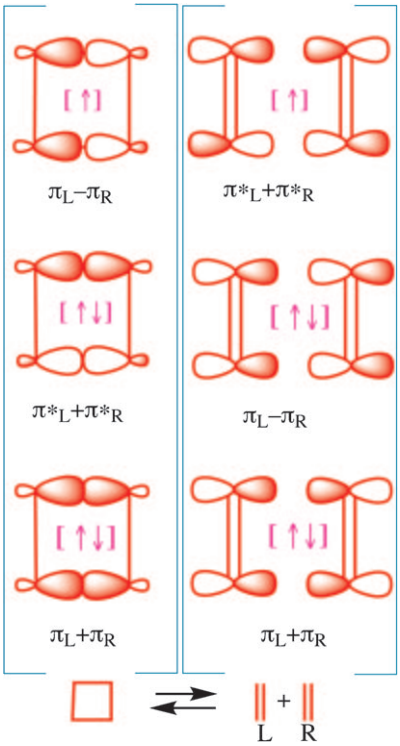


***Figure 1.*** A schematic picture of the two highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbital (LUMO) of neutral planar cyclobutane and the $\pi$ orbitals of two non-interacting ethylene molecules. The orbitals of cyclobutane are named using those of ethylene. The orbital picture of cyclobutane is over-simplified and ignores the contribution of orbital hybridization, but it is useful to illuminate the process of electron-impact catalytic cycloelimination discussed in the text. The excess electron is captured in the LUMO.

The four-center LUMO ($\pi_L-\pi_R$) of cyclobutane is antibonding along the inter-ethylene separation axis. Consequently, according to orbital theory, a molecular cycloelimination (in which the two bonds that connect the two molecular subunits are broken) is possible if the LUMO is occupied with an electron. In particular, occupying the antibonding virtual orbital of cyclobutane ($\pi_L-\pi_R$) with a projectile electron initiates cycloelimination. However, as the molecule fragments, this singly occupied antibonding orbital interchanges its energetic position with the doubly occupied bonding orbital ($\pi_L^*+\pi_R^*$, see Figure 1). The net effect is an efficient transfer of electron density from the bonding orbital to the antibonding orbital, which will accelerate the cycloelimination process. We may thus expect that the minimum-energy path (MEP) of the electronic energy of the anionic compound favors the cycloelimination process.

What will happen to the excess electron in the course of fragmentation into two ethylene units? Orbital theory tells us that the electron will localize in a $\pi^*$ orbital of one of the ethylene molecules, either L or R, which can be formed by mixing the degenerate orbitals ($\pi_L^*+\pi_R^*$) and ($\pi_L^*-\pi_R^*$) of the fully separated ethylene molecules. On the other hand, it is well known that an excess electron in a $\pi^*$ orbital of ethylene is a shape-resonance state and will autodetach from the system.[12] This situation explains the mechanism of catalytic activity, in which the electron leaves the system in the course of cycloelimination.

In general terms, for a cycloelimination reaction to be experimentally feasible, the compound state between the incoming electron and the target molecule must have a sufficiently long lifetime to allow for the required bond stretching. The non-Hermitian quantum chemical methods addressed above provide appropriate tools to accurately predict lifetimes of anions.

The QDCO molecule (Scheme 1) is the simplest substituted cyclobutane bridge molecule suitable to check the new mechanism. A criterion for this choice is that an electron-attracting group should help to localize the projectile electron at the cyclobutane reaction center without undergoing DEA. Additionally, it is known that carbonyl-substituted bridge compounds show $\pi_{ethylene}-\pi_{CO}^*$ orbital mixing.[13] This attribute is helpful in capturing the electron in the carbonyl group and transferring it efficiently to the reaction center, the cyclobutane part of the molecule.

We first outline the computational procedure that we used for calculating the lifetime and the MEP for the catalytic cycloelimination process in the electron–QDCO compound system. The lifetime and energy along the MEP are calculated employing the state-of-the-art ab initio non-Hermitian Green's function calculation at the CAP/$\Sigma^{(2)}$ level[5,6,9] using the d-aug-cc-pVDZ basis set. We used the continuum remover CAP to identify the physical resonance states.[8]

  

The nuclear geometries corresponding to the MEP are computed using the increased nuclear charge stabilization technique (Z-stabilization method)[14,15] at the ROMP2 level with the correlation-consistent double zeta basis set (see Tables S.1–S.14 in Supporting Information for nuclear Cartesian coordinates along the MEP). The reaction coordinate of the BBCE mechanism is obtained by varying the two intramolecular bond lengths that are being broken in the cycloelimination process, that is, the C1–C3 and C2–C4 bonds (Scheme 1). To determine the MEP of the BBCE mechanism, a two-dimensional potential-energy surface of the electron–QDCO system is first calculated in which the C1–C3 and C2–C4 bonds are varied in small steps and all the other bonds are relaxed. The MEP is then defined as the minimum-energy path that connects the reactant (electron–QDCO, where the QDCO is in its neutral geometry) to the product (electron–NBDO) in this computed two-dimensional potential-energy surface.

The results of our ab initio non-Hermitian calculation on the electron–QDCO system are summarized in Figure 2 (see Section 2 in Supporting Information for the corresponding numerical data). The central findings of this calculation are: 1) the MEP is two-bond-breaking with a small barrier of only 0.2 eV; 2) the lifetime of the compound state along the MEP is very long, and the metastable anionic state even becomes a bound state along the path, and 3) in the course of the bond-breaking reaction, as soon as the energy of the anion is above that of the neutral system, the compound state becomes short-lived. These results clearly imply that a catalytic cycloelimination is indeed taking place. The bond breaking occurs in a concerted, but asynchronous, manner.

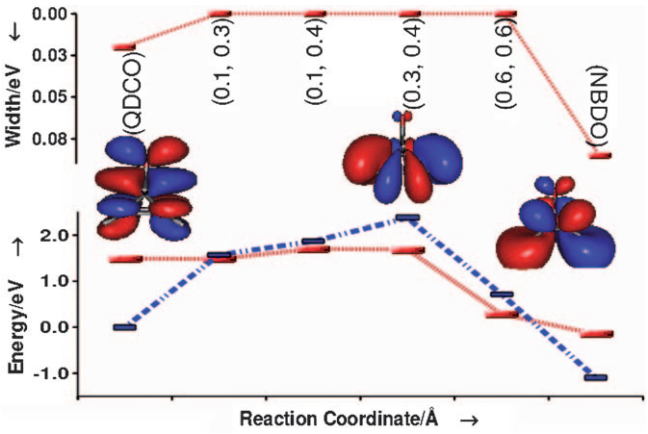


***Figure 2.*** The lower panel shows the computed MEP of cycloelimination of the electron–QDCO anionic compound (red curve). The total energy of the ground state of neutral QDCO is also plotted along this MEP (blue curve). The first and last points in this curve correspond to the equilibrium geometry of neutral QDCO and neutral NBDO, respectively. All the values are given relative to the ground-state energy of neutral QDCO in its equilibrium geometry. The upper panel shows the decay width (inverse lifetime) corresponding to the geometries along the MEP. This panel also shows in parenthesis the deviations of the C1–C2 and C3–C4 bond lengths (see Scheme 1) from their equilibrium positions along the dissociation path. Between the two panels, the real part of the singly occupied Dyson orbital is also shown for three points along the MEP. Dyson orbitals are characteristic of the anionic state in question.[16] It can be seen that after attachment of an electron to the LUMO (at an energy ca. 1.5 eV above the ground state of QDCO in its equilibrium geometry), the anion distorts and becomes bound (the decay width becomes zero) over a large range of geometries until both bonds break. In the course of the reaction, the lifetime of the anion becomes short and the excess electron is freed as soon as both the bonds are stretched, and the energy of the anion is above that of the neutral species.

To facilitate the BBCE mechanism in QDCO at the orbital level, it is helpful to recognize the orbital contribution to the ground-state electron configuration of the compound anionic system along the MEP. The orbital nomenclature discussed above for cyclobutane is applicable here as well. The appropriate molecular orbitals for the QDCO anion are shown qualitatively in Figure 3. To understand the capture of the electron and its efficient transfer to the antibonding orbital of the reaction center, Figure 3 should be compared with Figure 1. Interestingly, the lowest antibonding orbital ($\pi_L-\pi_R$) mixes with the charge-separated $\pi^*_{CO}$ orbital of the carbonyl (CO) bridge group. It is the nature of the inter-ethylene antibonding orbitals which is at the focus of the present work. There are three major electronic relaxations that interchange the orbital energy positions during the electron impact cycloelimination. Figure 3 clearly shows that

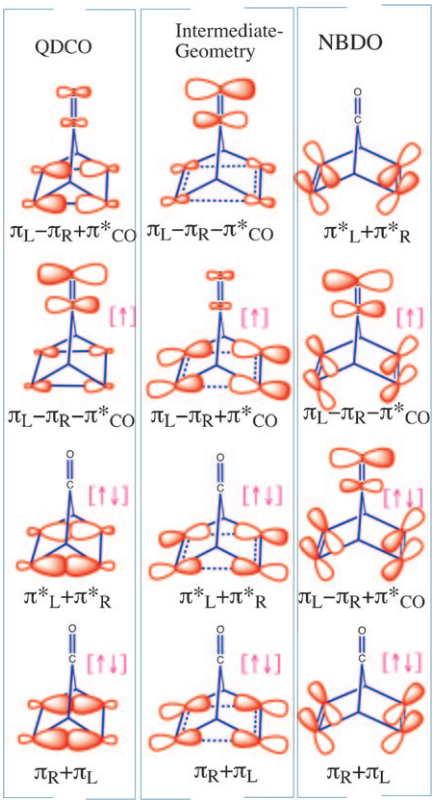


***Figure 3.*** A schematic picture of the interacting orbitals along the MEP of the electron–QDCO system. Initially, the electron is captured in the LUMO of QDCO, which is predominately localized on the CO group. Then, the electron moves to the antibonding orbital, which is the LUMO at intermediate geometry. Finally, there is another interchange of orbitals, where both the HOMO and LUMO are antibonding and the two bonds are broken.

the cycloelimination proceeds by a transfer of electron population from the carbonyl group to the reaction center. In the second electronic relaxation, as we have explained in the case of cyclobutane, the interchange of orbital positions increases the occupation of electrons in the antibonding orbital and decreases the occupation in the bonding orbitals, and this interchange accelerates the cycloelimination process. Note that in the case of the cyclobutane molecule, the excess electron, as the system starts to fragment, will be temporarily captured in the bonding LUMO ($\pi_L^* + \pi_R^*$) of cyclobutane (upper right corner in Figure 1). However, in QDCO this orbital is energetically pushed upwards (upper right corner of Figure 3) as NBDO is formed, because the mixing of $\pi_{CO}^*$ and ($\pi_L - \pi_R$) leads to the LUMO. As a result, the excess electron always remains in an antibonding orbital. Hence, the accelerated process is energetically more favorable in QDCO than in unsubstituted cyclobutane. The catalytic cycloelimination products of the cyclobutane ring of QDCO are the same as those of unsubstituted cyclobutane, except that this time the dissociation products are still connected through the bridge carbon atoms. However, this fact does not affect our predictions and conclusions. We add here that according to our calculations BBCE is the only reaction that can be expected from electron impact on QDCO at low electron energy. No other low-lying metastable states were found.

Finally, the clear pattern which follows from our accurate numerical findings on QDCO and their numerical analysis makes clear that the catalytic process predicted and discussed here is by no means limited to QDCO. The simplest way to pick up another example is to start from a photochemical cycloaddition product or a cyclic molecule which has a low-energy vacant antibonding (with respect to the interfragment separation axis) orbital. When combined with orbital symmetry reasoning, the BBCE mechanism becomes a powerful and predictive tool for catalytic several-bond breaking, yielding only nonradical neutral products. Herein we have demonstrated beyond doubt that the BBCE mechanism is operative for an isolated electron–molecule system. In principle, it may be expected that the mechanism could also be operative if the molecule is embedded in an environment and the electron is provided, for example, by a photoactivated donor. An important process in DNA repair is cycloelimination of cyclobutane pyrimidine dimer.[17] Whether or not the mechanism discussed herein can shed light on this process is currently a speculative question which, however, deserves further attention. We have to mention, though, that the mechanism proposed in reference [17] is a stepwise ring opening of the damaged site and not a concerted reaction as found here.

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