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Multibond-Breaking Reactions

A One-Step Four-Bond-Breaking Reaction Catalyzed by an Electron**

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Low-energy electron (LEE)-induced molecular bond breaking has been the subject of intense research in regards to its significance in high-energy radiation damage of DNA.[1,2] It has always been thought that the type of DNA damage cells find hard to repair is caused by high-energy primary electrons generated by the radiation. However, recent research has shown that low-energy (secondary) electrons can cause long-lasting damage to DNA by inducing multibond breaking.[1,2] Energy- and site-selective molecular manipulation is another fascinating aspect of the LEE-induced reactions.[3–9] As the motivation also continues towards further miniaturization of molecular electronic materials and nanodevices, recent years have witnessed a great stride forward for molecular manipulations using electron-controlled bond-breaking reactions.[3,4,6–11] Low-energy electron beams and tunneling electrons have been developed as comparative method for energy- and site-selective bond breaking in individual molecules.[5,8–12]

Many reactions of LEE with molecules are a composite of several sequential bond-breaking reaction steps. The overall sequence to the final products involves either radical or ionic processes with the formation of intermediates that may or may not be isolable. Molecular bond breaking induced by LEE occurs through resonant capture of the electron by the target molecule. The electron–molecule compound state formed in this way causes the molecule to make a transition from the ground-state internuclear potential energy surface of the neutral molecule to the potential surface of the negative ion. On a femtosecond timescale, the compound state can relax either by autodetaching the extra electron or by disposing excess energy to its molecular framework, a path which may ultimately rupture chemical bonds of the target molecules.[1,2,13–15]

Typically, the reaction initiated by the resonant capture of LEE leads to the breaking of a single bond, but the breaking of several bonds has also been detected,[16] which, however, is due to a sequential (multistep) reaction. It has been understood for a long time that the first elementary step of the overall process is always a single bond-breaking reaction, known as dissociative electron attachment (DEA).[17] In the DEA process, the electron–molecule compound state $(AB)^{-*}$, in which A and B are chemically bonded through a σ bond, fragments to form radical products A and B^-:

$$e^- + AB \rightarrow (AB)^{-*} \rightarrow A + B^- \quad \text{(DEA)} \tag{1}$$

A wide variety of chemical transformations initiated by resonant capture can be attributed to DEA. Indeed, extensive studies have contributed considerable progress in understanding many of these important reactions. However, in sharp contrast to the widely studied DEA, a recent study by our group has demonstrated a new elementary process, namely "bond breaking by a catalytic electron" (BBCE), in which more than one bond can be broken in the first elementary step associated with the breaking of the electron–molecule compound state.[18] The BBCE for a general molecule, CD, can be represented as:

$$e^- + CD \rightarrow (CD)^{-*} \rightarrow C + D + e^- \quad \text{(BBCE)} \tag{2}$$

where C and D are chemically bonded through more than one σ bond that can dissociate to form closed-shell neutral molecules C and D.

The main difference between DEA and BBCE is that in the case of DEA, only one bond is broken in the first elementary step associated with the dissociation of the electron–molecule compound state and hence a neutral radical and an anion are formed. In the BBCE case, the first elementary step of dissociation is associated with more than one bond breaking, and only closed-shell products are formed. More importantly, unlike in the DEA process, the induced electron is freed in the course of the reaction, and thus we refer this process as a catalytic electron process. The catalytic nature of the BBCE comes from the fact that at dissociation limit, none of the closed-shell neutral fragments supports a stationary anionic state.

Both DEA and BBCE reactions can be understood to a large degree from the bonding character of the electron–molecule compound state. Like in the case of the DEA process, the incoming electron selects the orbital according to its kinetic energy. Whenever, the kinetic energy of the electron matches with the energy of the Dyson orbital[19] corresponding to the anionic state that leads to BBCE or DEA, the electron can be captured and the process can take place. A DEA process is determined by an anionic state formed by the capturing of the electron into a two-center antibonding virtual orbital of the target molecule, which, at the dissociation limit, can be mathematically represented as a linear combination of two *partially filled* fragment orbitals centered on the fragments. In contrast, the participating orbital in a BBCE process is a multicenter virtual orbital of the target molecule which at the dissociation limit can be represented as an antibonding combination of two *filled* multicenter molecular orbitals of C and D.

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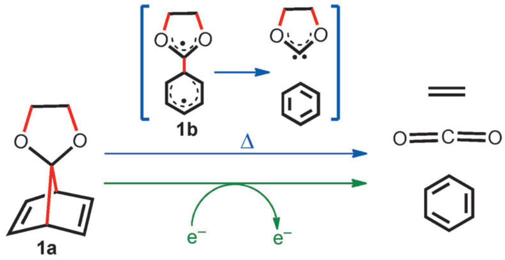
The take-home message from the theoretical revelation of the BBCE process is clear: capturing an electron in a multicenter antibonding molecular orbital can, in principle, offer a route to fragment the molecule in a one-step reaction through multiple bond breaks. In our earlier work, we demonstrated the process for the simplest model: the cycloelimination (two-bond breaking) in a four-membered ring.[18] Two questions arise: Is it possible to break more than two bonds in a one-step process, and can the process even be barrierless? Herein, we present an quantum-chemical identification of a barrierless synchronous four-bond breaking of norbornadienone ketal (**1a** in Scheme 1) upon impact of a LEE:

$$e^- + C_9H_{10}O_2 \rightarrow (C_9H_{10}O_2)^{-*} \rightarrow C_6H_6 + CO_2 + C_2H_4 + e^- \tag{3}$$

The consequences are far-reaching: LEE can very efficiently break up large molecules into several if not many stable, neutral, non-reactive, products and be available again for further reactions.



Scheme 1. Representation of thermal and LEE catalyzed decompositions of a bicyclic norbornadienone ketal into closed-shell products. The bonds that are broken in these processes are shown in red. The thermal decomposition of the neutral molecule is a multistep reaction (indicated by blue arrows) and the LEE catalyzed reaction is a one-step barrierless reaction (indicated by a green arrow).

Although not directly related to the present study of electron-induced four-bond breaking, a brief mention of thermal and photochemical multibond-breaking reactions might be useful. Multibond-breaking reactions have intrigued chemists for decades and were pursued with enormous experimental efforts especially in laser chemistry.[20–22] Most of the widely studied photochemical and thermal multibond-breaking reactions belong to multistep processes, and only a few are best described as one-step processes.[21–28] The observation that the products formed in the multibond-breaking step are closed-shell neutral molecules is also scarce.[21–28] To the best of our knowledge, breaking of four chemical bonds in a one-step process had not been observed (or computed) in any thermal or photochemical reactions before.

Multistep thermal decompositions of appropriately bridged bicyclic norbornadienone ketals similar to those in Scheme 1 into carbon dioxide, benzene, and olefins have long been known,[29] and a series of similar thermal reactions has also been observed for analogous strained molecules.[30] For clarity of presentation and feasibility of accurate ab initio calculations, we have selected an unsubstituted bicyclic norbornadienone ketal, 7,7-ethylenedioxy-bicyclo[2,2,1]-hepta-2,5-diene (**1a** in Scheme 1) for our electron-induced bond-breaking studies. Our numerical calculations also support the experimental evidence[29] for a multistep thermal decomposition process of the neutral molecule as depicted in the Scheme 1, in which the highest barrier (ca. 35 kcal mol^{-1}) is associated with the formation of **1b**. The thermal one-step four-bond-breaking path is very unlikely, because the barrier (ca. 64 kcal mol^{-1}) is very high in energy. In this work, we concentrate on the electron-induced bond-breaking reaction.

How can a bicyclic norbornadienone ketal break four bonds in one step to yield three closed-shell products in an electron-induced reaction? The minimum energy path (MEP) for a synchronous one-step four-bond decomposition reaction of the electron–**1a** compound state is investigated using high-level ab initio quantum chemical computations. The molecular quantum mechanical method we use herein has been described in much detail previously,[31–36] and therefore, we give here only a short outline. The electron–molecule compound state is characterized by its electron detachment rate Γ (inverse lifetime), and the electron binding energy (EBE), which is the electronic energy relative to the neutral molecule. The values of Γ and EBE along the MEP are calculated by employing the state-of-the-art ab initio non-Hermitian Green's function method at the CAP/$\Sigma^{(2)}$ level.[31–33] We used the continuum remover complex absorbing potential (CAP) to identify and to compute the electron–molecule compound states.[34] Because electron binding energies are, by nature, small quantities, EBE and Γ must be computed with high absolute accuracy to achieve reliable results. The latter fact requires that the atomic orbital basis set be flexible enough to describe accurately the spatial distributions of the electrons as well as their so-called dynamical correlation. To achieve this, we have used doubly augmented correlation-consistent basis set (d-aug-cc-pVDZ), which is further augmented with a large set of even-tempered Gaussian centered at the coordinate center of the molecule (see the Supporting Information, Table S1 for the additional even-tempered Gaussian basis set).

The nuclear geometries corresponding to the MEP are computed using the increased nuclear charge stabilization technique (Z-stabilization method)[35,36] at the restricted open-shell Møller–Plesset second order perturbation (ROMP2) level with the correlation consistent double zeta basis set (see the Supporting Information, Tables S2–S12, for nuclear Cartesian coordinates along the MEP). The MEP of the BBCE mechanism is obtained by synchronously varying the four intramolecular bond lengths that are being broken in the process (Scheme 1). The multistep thermal decomposition of the neutral molecule is also calculated using the second-order Møller–Plesset perturbation (MP2) method employing correlation-consistent double-zeta basis set.

The results of our ab initio CAP/$\Sigma^{(2)}$ calculation are summarized in Figure 1 (see the Supporting Information, Table S13, for the corresponding numerical data for EBE). These results indicate several important points. The initially unbound compound anionic state (see Figure 1b for the corresponding Γ values) becomes a bound state (where $\Gamma =$

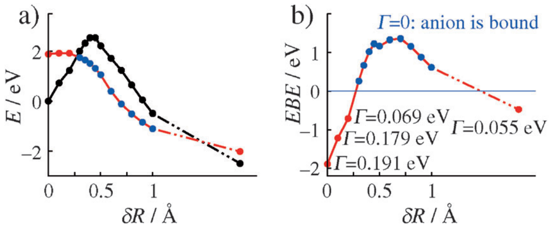


Figure 1. Computed minimum-energy path (MEP), excess electron binding energy (EBE), and electron detachment decay rate (*Γ*). a) The total energies *E* of the electron–molecule compound state along the MEP (red line) and of the neutral molecule at the same geometries (black line) are plotted as a function of the bond stretching parameter δ*R* for a concerted synchronous stretching of the four bonds; that is, each of the four bonds constituting the reaction coordinate is stretched uniformly from its equilibrium distance R_{eq} to $R_{eq}+\delta R$. The first point in these curves corresponds to the equilibrium geometry of the neutral molecule (C_{2v} symmetry) and the last point to that of the neutral products. C_{2v} symmetry is preserved throughout the calculation. All the values are given relative to the ground-state energy of the neutral molecule at its equilibrium geometry. b) The electron binding energies (EBE) and the decay rates *Γ* (inverse lifetime) at the geometries along the MEP.

0 eV) along the MEP. The lifetime we find for the ion at the equilibrium geometry of the neutral is comparable to that found in many cases where DEA is observed and this certainly implies that the BBCE process should be favorably observed.[1,2,13–15] Actually, the lifetime we find is about an order of magnitude longer than that found in some examples of DEA, for instance about 0.1 fs for the σ* resonance of HCOOH[37,38] and 0.59 fs for the π* resonance of C_2H_2.[39,40] The calculated barrier (ca. 0.046 eV) for the synchronous four-bond breaking is very small and within the accuracy of our method; the reaction can be viewed as being barrierless. In any case, a barrier of about 0.046 eV can be easily overcome by temperature, which is well below room temperature. As one may notice, the captured electron in our case does not carry enough kinetic energy for the system to cross its concerted synchronous thermal barrier. In BBCE, the electron binding energy plays a key role in lowering the energy barrier. The binding energy increases along the minimum energy path and lowers the barrier (Supporting Information, Table S13; see also Table S15 in the Supporting Information of Ref. [18]). Aromatization combined with relief of strain in the bicyclic system is probably the reason for such electron correlation effects that lead to high electron binding energies. An electron reorganization mechanism that explains the barrierless behavior of the process will be discussed below. For geometries at which $\text{EBE} > 0$ (above the horizontal blue line), the electron–molecule compound is bound (infinite lifetime; $\Gamma = 0$). It can be seen that after attachment of an electron (at an energy ca. 1.89 eV above the ground state of the neutral molecule at its equilibrium geometry), the anion relaxes its geometry and becomes bound over a large range of geometries until all the four bonds break. Towards the end of the reaction, the lifetime of the anion becomes short and the excess electron is freed as soon as all the four bonds are stretched and the energy of the anion is above that of the neutral; that is, finally, in the course of the bond-breaking reaction as soon as the energy of the anion is above that of the neutral, the compound state becomes short lived and the rate of autodetachament for the electron increases. This explains the mechanism of catalytic activity, where the electron leaves the system in the course of the multibond-breaking reaction (see the Supporting Information, Section 3, for the discussion of EBE and catalytic nature of the electron). These results clearly imply that a catalytic synchronous four-bond breaking is taking place in a barrierless reaction. We have also performed a few calculations along asynchronous paths, but these calculations support a synchronous mechanism (see the Supporting Information, Section 5, for a discussion about the asymmetric reaction path). A discussion about the observability of BBCE process is included in the Supporting Information, Section 6.

Because of the smooth fragmentation of **1a** into three neutral products (benzene, carbon dioxide, and ethylene) it is tempting to postulate a totally concerted pathway for the reaction. There is some uncertainty in the literature as to the correct way to define concertedness in a reaction. In the present context, concertedness implies that the simultaneous bond-breaking path entails a continuous electronic rearrangement that leads to a simultaneous rupture of four σ bonds and creation of the same number of π bonds. It is convenient to describe this electronic reorganization in a condensed form. Along the MEP the process of electron reorganization in a chemical reaction is best represented by molecular orbitals. Figure 2 shows the correlation between those participating orbitals that play an important role in the four-bond-breaking BBCE mechanism. These orbitals are calculated using the nuclear charge stabilization method at the restricted open-

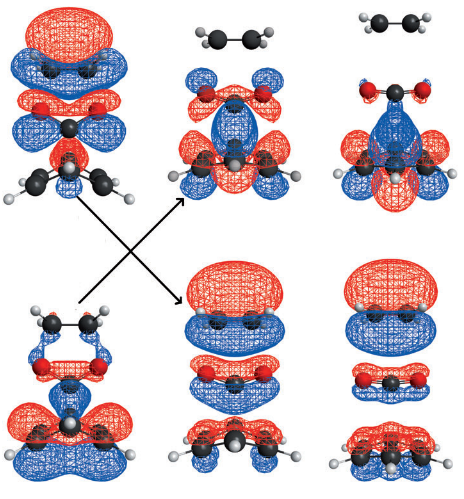


Figure 2. Orbital correlation of the electron–molecule compound state along the dissociation path. The participating singly occupied orbital (1st row) and the doubly occupied orbital (2nd row) are shown for three inter-fragment distances along the bond-breaking path ($\delta R = 0.3$, 0.8, and 1.5 Å from left to right). The excess electron initially occupies the antibonding orbital (orbital in the upper left corner); this antibonding orbital then interchanges its energetic position with the doubly occupied multicenter bonding orbital. The energetic stabilization of the multicenter antibonding orbital and the corresponding destabilization of the bonding orbitals leads to an interchange of orbitals, as indicated by the up and down arrows.

shell Hartree–Fock method using the d-aug-cc-pVDZ basis set. To confirm that the orbital scheme shown in Figure 2 and discussed below is valid, we also computed the Dyson orbitals using the CAP/$\Sigma^{(2)}$ method for the first two geometries shown in Figure 2. Dyson orbitals are unique characteristic of an anionic state and include the effect of electron correlation.[19] The Dyson orbitals corresponding to the anionic states at the two first interfragment distances shown in Figure 2 are depicted in Figure 3.

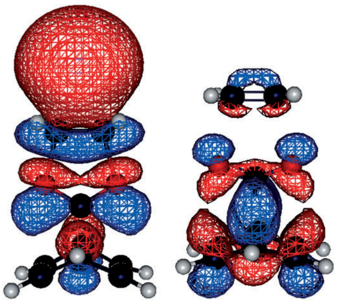


Figure 3. The Dyson orbitals of the electron–molecule compound state for the two first interfragment distances shown in Figure 2. Note the similarity to the Hartree–Fock orbitals shown in Figure 2.

According to the above finding, the concerted barrierless four-bond-breaking mechanism can be illustrated as follows: Initially the electron is captured into a multicenter virtual orbital, which is antibonding in nature with respect to the three fragments. The electronic occupation in the antibonding orbital weakens the corresponding chemical bonds, and consequently, the strength of the interfragment bonds decreases. The anionic molecule can stretch without increasing the total energy, as seen from the flat behavior of the electronic energy at the initial stretching points along the MEP (see Figure 1 a). However a concerted barrierless four-bond-breaking reaction cannot be expected merely by the occupation of an antibonding orbital with an electron. The barrierless bond-breaking reaction is energetically feasible because an efficient transfer of electron density from the bonding orbital to the antibonding orbital occurs in the course of the reaction, and correspondingly, the antibonding orbital becomes energetically more stable and interchanges with the bonding orbital. The net effect is an efficient transfer of electron density from the bonding orbital to the antibonding orbital, which accelerates the fragmentation process. This is all provided by the excess electron. The low-energy catalytic electron not only helps in minimizing the energy barrier for a one-step process, but also in creating a concerted synchronous bond-breaking pathway, which is not possible otherwise.

In conclusion, apart from the revelation of an unprecedented concerted four-bond-breaking pathway for a neutral molecule by a low-energy electron, yielding only closed-shell neutral products, the one-step four-bond-breaking reaction itself stands out as unique. To the best of our knowledge, this is the first report of breaking four chemical bonds in a one-step reaction. Owing to the fact that multistep multibond-breaking reactions are less selective and triggered by radical steps, one-step multibond-breaking reactions are ideally suited for the kind of energy- and site-selective multibond-breaking reactions that chemists are pursuing. It seems that the realm of possibility of efficient bond breaking by low-energy electrons is much larger than anticipated.

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