Pericyclic Reactions of Radical Cations

Nicolas J. Saettel,[a] Jonas Oxgaard,[a] and Olaf Wiest*[a]

Dedicated to the memory of Eberhard Steckhan

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Electron transfer catalysis is an efficient method for the catalysis of symmetry-forbidden or slow pericyclic reactions. Accurate quantum mechanical calculations are an important tool for gaining insights into the mechanistic details of these fast reactions involving radical cations. The current "state of the art" of computational studies of pericyclic reactions of radical cations is reviewed. In particular, four parent reaction types are discussed: (i) the ring-opening of the cyclobutane radical cation; (ii) the [2+2] cycloreversion of the cyclobutane radical cation; (iii) the radical cation Diels–Alder reaction of 1,3-butadiene and ethylene; and (iv) the [1,3] methylene shift in the vinylcyclopropane radical cation. The transfer of these findings to chemically more relevant substituted systems is also briefly discussed. The potential energy hypersurfaces obtained are very flat and have activation barriers that are significantly lower than the ones for the corresponding neutral reactions, which is in agreement with the large rate acceleration observed experimentally. Many of the located radical cation structures closely resemble their biradical counterparts in the neutral, stepwise pathways. The reactions generally follow a lower symmetry pathway, due to Jahn–Teller distortions induced by the unpaired electron. Finally, the results from computationally efficient B3LYP/6-31G* calculations are found to be in good agreement with those from highly correlated MO calculations.

Introduction

The search for new reactions with new properties and selectivities to expand the tools available in organic chemistry is an important area of research. Progress in the synthetic applicability of these reactions is often triggered by a better understanding of the reactive species involved. Examples of this include the elegant applications of radical reactions that were preceded by fundamental studies of the relative rates and reactivities of these species, and also the widespread application of pericyclic reactions in organic synthesis that followed the Woodward−Hoffmann rules.

Radical cations are a class of reactive intermediates that have significant potential for the development of new reactions. They can be formed from neutral species by oxidative single electron transfer (SET). After undergoing the desired reaction, reductive SET or other reactions such as nucleo-

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[a] Department of Chemistry and Biochemistry, University of Notre Dame,
Notre Dame, Indiana 46556-5670, USA
E-mail: Olaf.G.Wiest.1@nd.edu

Nicolas Saettel (right) was born in Lyon, France, in 1974. After three years of "Classes Préparatoires aux Grandes Ecoles" in Besançon, he entered CPE Lyon (Chemistry-Physics-Electronics), where he studied Chemistry and Chemical Engineering for two years. He completed his French Master's diploma through an agreement with the University of Notre Dame, where he began Ph.D. studies in physical organic chemistry under Olaf Wiest. His current areas of interest include strained radical cations, pericyclic reactions, and the synthesis of an artificial DNA photolyase based on macrocyclic recognition and electron transfer-induced repair of thymine dimers.

Jonas Oxgaard (left) was born in Gothenburg, Sweden, in 1974. He studied chemical engineering at Chalmers University of Technology and graduated with an M.S. under Gunnar Westman in 1997. During his studies he realized he was not that fond of distillation towers after all, and started his Ph.D. studies in chemistry at the University of Notre Dame with Olaf Wiest. His current research is focused on experimental and computational studies of the structure and reactivity of hydrocarbon radical cations.

Olaf Wiest (middle) was born in Germany and received his Ph.D. under the guidance of E. Steckhan at the University of Bonn in 1993. After spending two years as a Feodor-Lynen Fellow with K. N. Houk at the University of California, Los Angeles, he moved to the University of Notre Dame, where he is currently Assistant Professor in the Department of Chemistry and Biochemistry. His research interests center around electron transfer induced processes and their application in organic and bio-organic chemistry, as well as in molecular computing. In his free time, he enjoys the Chicago Symphony Orchestra and good food.

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philic trapping or deprotonation[1] can then produce a neutral product. Since the reactivities and selectivities of the radical ions differ significantly from those of the corresponding neutral compounds, a large number of new reactions can be envisioned. The application of electron transfer catalysis (ETC) − i.e. the formation of the final product by back electron transfer from the product radical ion − to pericyclic reactions was first proposed by Woodward in 1942,[2] but was not achieved until almost three decades later.[3] Subsequent work by Steckhan,[4] Bauld,[5] and others[6] provided many examples of formal pericyclic reactions of radical cations. While much progress has been made in the experimental study and application of these reactions,[7] the fundamental principles underlying these reactions are less well understood. Therefore, a scientifically and practically unsatisfying trial-and-error approach to the development of new reactions is often necessary.

Mechanistic studies of radical cations, which would lay the foundations for a more rational approach to their use as reactive intermediates, are difficult because of a number of problems. Many of the classical methods for the study of reaction mechanisms are not easily applicable here because of the complex ECE (electron transfer − chemical step − electron transfer) mechanism. Solvent or substituent effects will be active during all three steps, thus convoluting the effect on the mechanism of interest. Direct observation of the radical cations is experimentally difficult, due to the short lifetime of these very reactive intermediates. Finally, theoretical analysis in the FMO context, which has been so successful for the understanding of neutral pericyclic reactions, is ambiguous because in open-shell species there are three potentially relevant orbital interactions present: HOMO−LUMO, HOMO−SOMO, and SOMO−LUMO.

Therefore, the most promising approach to an understanding of the mechanism of these interesting reactive intermediates is the use of quantitative quantum mechanical calculations. During the last decade, with the development of new theoretical methods, especially density functional theory, and more powerful computer hardware, such calculations have now resulted in a reasonable understanding of reactions of radical cations, which are formally, but not necessarily mechanistically, pericyclic. Over the last few years, studies from our laboratory and others have examined the most important parent reactions of the different classes of known pericyclic reactions. In this article we will review the current state of research into three types of pericyclic reactions: (i) electrocyclic ring-openings, (ii) [4+2] and [2+2] cycloadditions, and (iii) sigmatropic shifts. The parent systems will be discussed in some detail and the application of the findings to chemically more relevant, substituted systems will be explored. The recent computational results from studies of these reactions will be summarized in order to point out some generalities in the pericyclic reaction of radical cations.

Computational Methodology

Because of the close energy spacing of the orbitals, an adequate treatment of electron correlation is crucial for accurate calculation of radical cations. The best way to treat electron correlation for these systems, however, is a matter of intense current discussion.[8] A CASSCF treatment, which has been very successful in the treatment of other open-shell species such as diradicals, is difficult to apply to radical cations because the choice of the active space is ambiguous, or leads to prohibitively large calculations. Coupled cluster and the related quadratic configuration interaction calculations appear to recover the dynamic and nondynamic correlation quite efficiently. However, the unfavorable scaling of these methods and the relatively large basis sets desirable for accurate energy calculations with these methods limit their use to small model systems. They have therefore been used predominantly for the parent reactions and as benchmark methods to test other methods.

It is now widely accepted that low-order perturbative treatments of electron correlation such as the UMP2 method are not adequate for the calculation of radical cations.[8,9] The relative energies calculated for different species on the potential energy hypersurface (PES) depend strongly on the spin contamination of the underlying Hartree−Fock wave function, thus making direct comparison of different species impossible. Furthermore, these methods are known to overestimate the stability of localized structures, resulting in a large number of local minima on the PES that are not present on the PES obtained by higher level calculations.

Computationally efficient DFT methods − in particular, hybrid DFT methods such as the B3LYP functional − have become very popular in the last decade. DFT methods suffer to various extents from the opposite problem, i.e. a bias towards delocalized structures, which in some cases completely prevents the localization of spin and charge.[10] This behavior has in principle been known for almost two decades,[11] but its importance in the context of modern DFT calculations has only been realized recently.[12]

For the parent reaction discussed in this review, the application of several methods to the same systems has been described in the literature. We will therefore briefly discuss the advantages and disadvantages on a case-by-case basis for the individual species, where appropriate.

Electrocyclic Reactions: The Ring-Opening of Cyclobutene Radical Cation

The analysis of the ring-opening of cyclobutene was one of the early success stories of the Woodward−Hoffmann rules.[13] Similar orbital correlation studies have been performed to develop a set of rules for pericyclic reactions on open-shell species,[14] amongst them cyclobutene radical cation ring-opening. However, simple FMO analysis have generally not been successful for the reasons discussed above.

The large rate acceleration induced by electron transfer has been demonstrated on numerous substituted cyclobutenes,[15] and its use in synthesis demonstrated.[16] However, experimental studies did not produce conclusive evidence about the mechanism of the reaction.[15f,15g] In the matrix, the parent cyclobutene radical cation was observed to yield *trans*-butadiene,[17] and a product study of the substituted *cis*-3,4-diphenylcyclobutene radical cation led the authors to conclude a *conrotatory* pathway.[15e] Measurement of activation energies gave contradictory results. Mass spectroscopic studies estimated it to be less than 7 kcal/mol, increasing to 14 kcal/mol with phenyl or methyl substitution at the 1-position, or decreasing to 4 kcal/mol at the 3-position.[18] Other studies indicated significantly higher activation energies,[14d,17,19] but the most reliable estimate of the activation energy is 16.5 kcal/mol for the ring-opening of 1,2-diphenyl-3,3′,4,4′-tetramethylcyclobutene.[19b,19c] In any case, this shows the potential of electron transfer catalysis when this activation energy is compared to the neutral activation energy of 32.8 kcal/mol for the parent reaction.[20]

The radical cation reaction − with a calculated reaction energy of −21.6 kcal/mol or −17.9 kcal/mol at the QCISD(T)//QCISD level of theory for the formation of *trans*-butadiene $\mathbf{2}^{\bullet +}$ or *cis*-butadiene $\mathbf{4}^{\bullet +}$, respectively − is approximately 10 kcal/mol more exothermic than the corresponding neutral reaction.[21] This is due to better stabilization by conjugation of the radical cation in $\mathbf{2}^{\bullet +}$ or $\mathbf{4}^{\bullet +}$, as observed by the ionization potentials of **2** and **4**, which are lower than those of **1**.

On the basis of electronic state correlations between the reactant and the product, it is possible to predict the symmetry conserving reaction path taken by a symmetric molecule for electrocyclic ring-opening.[17] Starting from the C_{2v}-symmetric cyclobutene radical cation, only a *conrotatory* pathway connects the ground states of cyclobutene $\mathbf{1}^{\bullet +}$ and *trans*-butadiene $\mathbf{2}^{\bullet +}$. Any other symmetry-conserving pathway would result in an excited state. Alternatively, an asymmetric, concerted, or a stepwise process would be possible. A C_2-symmetric stationary point was first located by our group at the UHF, MP2, QCISD(T)/QCISD, B3LYP, and BLYP levels of theory.[22] At the best level of theory used, this stationary point was 23.4 kcal/mol higher in energy than $\mathbf{1}^{\bullet +}$. However, a frequency analysis revealed a second negative frequency. The symmetry-breaking mode perpendicular to the reaction coordinate was rationalized in terms of pseudo Jahn−Teller effects, or vibronic interaction, with the close-lying excited state of opposite symmetry.[10a] Therefore, the stationary point located is not a true transition state, but rather a second-order saddle point. Following the symmetry-breaking mode in this second-order saddle point resulted in an asymmetric transition state $\mathbf{3}^{\bullet +}$, which was 5 kcal/mol lower in energy than the second-order saddle point and connected $\mathbf{1}^{\bullet +}$ to the *cis*-butadiene radical cation $\mathbf{4}^{\bullet +}$. An activation energy of 18.6 kcal/mol was found at the QCISD(T)//QCISD level of theory. The value of 18.1 kcal/mol obtained by the moderately demanding Becke3-LYP method is quite comparable. This transition state was also located by Bally et al.[10a] starting from the ^{2}B/^{2}A conical intersection for the symmetry-forbidden cyclobutene $\mathbf{1}^{\bullet +} \rightarrow$ *cis*-butadiene $\mathbf{4}^{\bullet +}$ conrotatory path.

Although no C_2-symmetric transition state could be found for the ring-opening to *trans*-butadiene $\mathbf{2}^{\bullet +}$ (following the perpendicular mode *in the other direction* led to a transition state for the interconversion of *cis*-butadiene radical cation with bicyclo[1.1.0]butane radical cation), a C_1-symmetric structure $\mathbf{5}^{\bullet +}$ was located by Bally and co-workers.[10a] The activation energy associated with this reaction pathway was calculated to be 16.9 kcal/mol at the RCCSD(T)/cc-pvTZ//QCISD/6-31G* level of theory (with B3LYP/6-31G* zero-point correction), virtually identical to the QCISD(T)//QCISD result for the cyclobutene $\mathbf{1}^{\bullet +} \rightarrow$ *cis*-butadiene $\mathbf{4}^{\bullet +}$ reaction via $\mathbf{3}^{\bullet +}$. At the B3LYP/6-31G* level of theory used in both studies, $\mathbf{3}^{\bullet +}$ is 2.8 kcal/mol more favorable than $\mathbf{5}^{\bullet +}$. The preference for this pathway over the other was reversed and the gap greater upon inclusion of a solvent polarizable continuum model.[23] The transition structure resembled a previously postulated intermediate cyclopropyl carbinyl radical cation $\mathbf{6}^{\bullet +}$, calculated at the MINDO/3 and SCF MO level of theory by Bauld and co-workers.[24] However, this intermediate on the cyclobutene $\mathbf{1}^{\bullet +} \rightarrow$ *cis*-butadiene $\mathbf{4}^{\bullet +}$ pathway could only be located by UHF[24] and UMP2[22] calculations as a shallow minimum, 16.8 kcal/mol higher than $\mathbf{1}^{\bullet +}$ at the UMP2 level on a very flat potential energy hypersurface, the so-called "Bauld Plateau".[10] Given the bias of these two methods, this result has to be interpreted with caution, since $\mathbf{6}^{\bullet +}$ could not be located either by the B3LYP or by the QCISD method. However, it was possible to locate several cyclopropyl carbinyl radical cations in the case of 3-substituted cyclobutenes.[25] Figure 1 summarizes three possible pathways obtained for the ring-opening of cyclobutene radical cation:

- a conrotatory, concerted C_1-symmetric pathway for cyclobutene $\mathbf{1}^{\bullet +} \rightarrow$ *cis*-butadiene $\mathbf{4}^{\bullet +}$
- a stepwise, charge- and spin-localized pathway via the elusive cyclopropyl carbinyl radical cation $\mathbf{6}^{\bullet +}$ for cyclobutene $\mathbf{1}^{\bullet +} \rightarrow$ *cis*-butadiene $\mathbf{4}^{\bullet +}$
- a concerted, conrotatory, "cyclopropyl carbinyl"-like C_1-symmetric pathway for cyclobutene $\mathbf{1}^{\bullet +} \rightarrow$ *trans*-butadiene $\mathbf{2}^{\bullet +}$

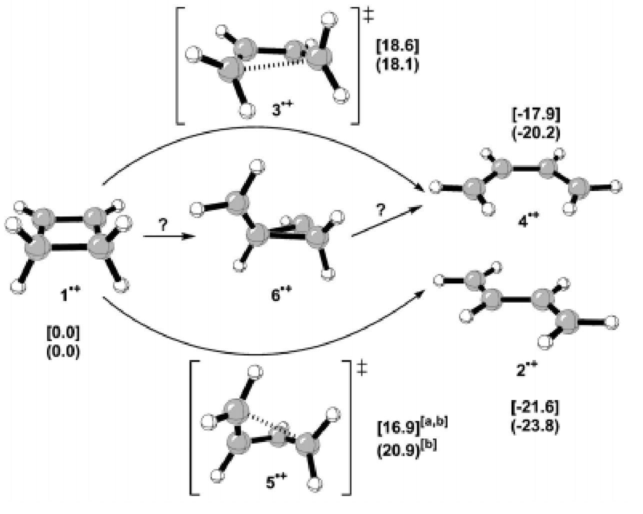

Figure 1. Reaction pathways for the ring-opening of the cyclobutene radical cation $\mathbf{1}^{\bullet +}$ through the asymmetric transition structure $\mathbf{3}^{\bullet +}$, the elusive cyclopropyl carbinyl intermediate $\mathbf{6}^{\bullet +}$ (UMP2 optimized) or the asymmetric transition structure $\mathbf{5}^{\bullet +}$; QCISD(T)//QCISD energies (corrected for zero-point energies with the B3LYP values) are given in brackets, B3LYP energies (corrected for zero-point energies) are given in parenthesis and are relative to $\mathbf{1}^{\bullet +}$; the basis set 6-31G* was used: [a] RCCSD(T)/cc-pVTZ//QCISD/6-31G* corrected with B3LYP/6-31G* zero-point energies; [b] values from ref.[10a]

We performed the first systematic study of substituent effects in a radical cationic pericyclic reaction.[25] Substitution at the 3-position of the cyclobutene moiety by methyl, methoxy, cyano, and aldehyde groups breaks the symmetry of the molecule and allows a study of electronic and steric effects on the ring-opening. Electron-donating substituents increase the exothermicity of the reaction and stabilize the cyclopropyl carbinyl radical cation $\mathbf{6}^{\bullet+}$ in the stepwise pathway. This structure resembles a nonclassical cyclopropyl carbinyl cation and becomes a local minimum on the hypersurface. The extent of the stabilization is found to be qualitatively correlated with the Brown−Okamoto σ^+ parameter. With no stabilization or destabilization of the cyclopropyl carbinyl radical cation, no intermediates for the stepwise pathway could be located. However, substituent effects also act on the concerted pathways, which is found to be the lowest energy pathway in all cases. The relative stability of the different diastereoisomers of the transition structure and the (*E*)/(*Z*) outcome of the ring-opening reaction can be rationalized in terms of steric interactions.

The Structure and [2+2] Cycloreversion of the Cyclobutane Radical Cation

The structure of cyclobutane radical cation has been the subject of debate over the years. Depending on the method used, a long bond intermediate[26] (also rationalized in terms of resonance forms of a tetramethylene radical cation),[27] together with rhomboid,[28−30] rectangular,[31] and trapezium[32,33] structures have all been located. Each species has been claimed to account for the ESR hyperfine coupling constants observed experimentally, either for geometrical reasons[29,31] or thanks to available tunneling pathways.[33] The cyclobutane radical cation hypersurface is highly symmetric and thus prone to Jahn−Teller distortions. This type of "topomerization of a σ-conjugated system"[34] with reaction channels of reduced symmetry has been studied by Simkin et al.[35] Dewar's,[33] Radom's,[32] and Bally's[36] groups. The possible distortions that lead from a hypothetical square cyclobutane radical cation of D_{4h} symmetry to various species of lower symmetry, are shown in Figure 2.

Because of the degeneracy of the only partially occupied ^1e_u orbitals, first-order Jahn−Teller distortions lead to *rectangle* and *rhombus* structures along b_{2g} and b_{1g} vibrational modes, respectively. These two distortions and the equivalent orbitals are shown in the top part of Figure 2.[37] Possible mixing of low-lying excited configurations with the ground state (second-order Jahn−Teller effects) can lead to further distortion of the rhombus to a *trapezium* and of the rectangle to a *kite* structure, respectively, by deformation along b_{2u} modes. In addition, the authors mentioned, but did not discuss further, a *parallelogram* structure with C_{2h} symmetry, formed by the interaction of a $b_{3u}\rightarrow b_{2u}$ excited state with the ground state of the rhombus structure along a b_{1g} vibration.[36]

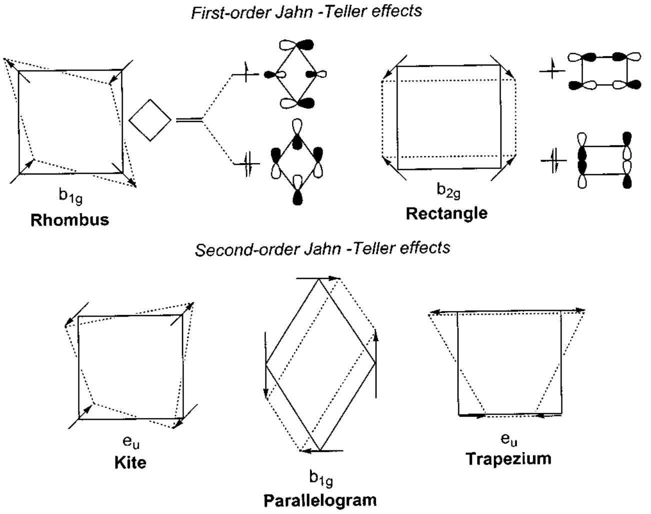

Figure 2. Schematic representation of the first- and second-order Jahn−Teller distortions of the D_{4h}-symmetric cyclobutane radical cation

Neutral cyclobutane is a D_{2d}-symmetric, puckered square with a small barrier of inversion.[38] It was pointed out by Dewar et al.[33] that the barrier in the radical cation should be even less. Therefore, in our reinvestigation of the cyclobutane radical cation at the UHF, UMP2, QCISD(T)/QCISD, BLYP, and B3LYP levels of theory, we initially focused on its planar forms.[39] Our QCISD(T)/QCISD results, the best level of theory used in this study, as well as the results of the computationally efficient B3LYP method, indicated the parallelogram $\mathbf{7}^{\bullet+}$ as the minimum on the potential energy hypersurface. A frequency analysis revealed that, although there were a large number of low-frequency modes expected for a flat hypersurface, no negative modes corresponding to a puckering motion were obtained. The rhombus was found to be a transition state connecting two parallelograms. The rectangle was characterized as a second-order saddle point connecting the parallelogram and the rhombus. It is interesting to note that, despite the fact that ESR spectra were interpreted as indicative of a puckered, rhomboid geometry,[29] no negative frequencies corresponding to a puckering mode were calculated either at the QCISD or at the B3LYP level of theory. Although − not surprisingly for a highly fluctional structure such as the cyclobutane radical cation − no quantitative agreement between computed and experimental hyperfine coupling constants could be obtained, we were able to demonstrate that the different hybridizations in the parallelogram are sufficient to induce quite different hyperfine coupling constants. Therefore, the different observed coupling constants do not necessarily imply a puckered structure.

A number of experiments were performed in order to analyze the [2+2] cycloreversion of the cyclobutane radical cation fragmentation[40] to form the [ethene•ethene]$^{\bullet+}$ ion-molecule complex $\mathbf{8}^{\bullet+}$.[41] The cycloaddition of ethylenes to form cyclobutanes was the first class of pericyclic reactions recognized as catalyzed by electron transfer,[3,42] opening new possibilities in synthetic chemistry. The [2+2] cycloreversion attracted interest because of potential applications of the rearrangement of quadricyclane to norbornadiene[43] for photochemical energy storage,[44] while the electron-catalyzed cycloreversion of the cyclobutane pyrimidine dimers, which is part of the skin cancer protection mechanism of many organisms, demonstrated the biological importance of this reaction.[45,46]

The mechanism of the radical cation [2+2] cycloreversion has been studied extensively on a number of model systems,[7d,7h,13b,13c,14e,47] and the reaction was postulated to proceed through an intermediate 1,4-butanediyl, or tetramethylene, radical cation **10**$^{•+}$.[40f,41a] Computational explorations[27,35,48] of the $C_4H_8^{•+}$ hypersurface concentrated on a trapezoidal or rectangular complex and long bond product complex without conclusive evidence for or against an acyclic intermediate and a barrierless process, until it was recognized that another geometry,[49] close to the MCSCF/STO-3G transition structure for the stepwise dimerization of neutral ethylene,[50] was more favorable. Bally's group studied this hypersurface extensively at a high level of theory,[51] but could not locate an intermediate corresponding to a tetramethylene radical cation **10**$^{•+}$.

In our study of the cycloreversion,[39] summarized in Figure 3, we were able to locate an asynchronous transition structure **9**$^{•+}$, with C_s symmetry. The reaction enthalpy, determined from experimental data, of 34.7 kcal/mol was reproduced well by the QCISD(T)/QCISD and B3LYP calculations, and the activation energy was lowered by almost 50 kcal/mol relative to the neutral reaction was achieved as a result of electron transfer. An intrinsic reaction coordinate (IRC) calculation at the B3LYP level of theory clearly showed a concerted pathway, with no involvement of an intermediate such as **10**$^{•+}$. In the computed pathway, the two ethylene moieties shift parallel to each other in a $[2_s+2_s]$ fashion. Furthermore, while the neutral $[2_s+2_s]$ transition state is antiaromatic according to the Woodward−Hoffmann rules, NICS calculations[52] showed no significant aromaticity or antiaromaticity in the transition state **9**$^{•+}$ of the radical cation reaction.

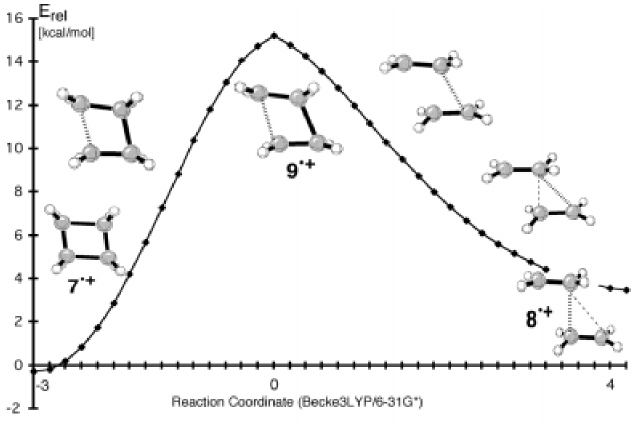

Figure 3. B3LYP/6-31G* intrinsic reaction coordinate for the [2+2] cycloreversion of the cyclobutane radical cation **7**$^{•+}$

The Radical Cation Diels−Alder Reaction

The Diels−Alder reaction is one of the most frequently used reactions in organic chemistry. Consequently, it is also one of the most studied reactions, both experimentally and theoretically. Computational chemists have studied the mechanism of the reaction of 1,3-butadiene and ethylene at virtually all feasible levels and have debated whether this prototype Diels−Alder reaction has a concerted pericyclic mechanism or is a stepwise process involving a diradical intermediate.[53,54] A consensus has been reached that the parent reaction proceeds through a concerted mechanism with an aromatic transition state. Even though the radical cation Diels−Alder reaction has been extensively employed in organic synthesis,[4−7] the mechanism of the radical cation reaction is much less well understood. Experimental investigations have failed to reach a definite conclusion.[55] Early theoretical works using MINDO/3 and UHF calculations[56] suggested a stepwise pathway, while refinements of these calculations at the MP3 level indicated a concerted, nonsynchronous cycloaddition pathway.[57] However, the use of these methods for the study of reactions involving radical ions is at least questionable, for the reason discussed earlier.[8,9]

Recently, the potential energy hypersurface of the reaction between the butadiene radical cation (**11**$^{•+}$) and ethene (**12**) was independently investigated at the QCISD(T)/6-31G*//QCISD/6-31G*[58] and UCCSD(T)/DZP//UMP2(fc)/DZP[59] levels of theory. Both studies agree that this reaction proceeds through a stepwise mechanism, producing cyclohexene radical cation **13**$^{•+}$, as shown in Figure 4. The transition state, **14**$^{•+}$, of the C_s-symmetric concerted mechanism appears to be reasonable when the geometry is examined, but a frequency analysis reveals that it is a second-order saddle point, presumably due to a second-order Jahn−Teller distortion.

In the stepwise mechanism, **11**$^{•+}$ and **12** first form an ion-molecule complex, **15**$^{•+}$, by a barrierless process. The intermediate is 7.6 kcal/mol lower in energy than the separated substrates. The butadiene and ethene moieties in **15**$^{•+}$ are separated by ca. 2.52 Å, and lack significant pyramidalization, indicating no significant covalent interactions. Intermediate **15**$^{•+}$ then transforms into the intermediate **16**$^{•+}$, with an activation energy of only 0.4 kcal/mol at the QCISD(T)//QCISD level. The transition state of the **15**$^{+•}$ → **16**$^{•+}$ pathway is a true transition state, with one negative vibrational mode leading to **16**$^{•+}$. This result is in contrast with earlier investigations, which found no connection between the ion-molecule complex and any viable intermediate.[58,59] The intermediate **16**$^{•+}$ has an *anti* conformation, with the cation delocalized over the allyl moiety, while the radical is largely localized at C^6. The structure of **16**$^{•+}$ has a striking similarity to that of the calculated biradical intermediate in the neutral Diels−Alder reaction,[60] the only significant difference being an elongated C^4-C^5 bond in **16**$^{•+}$, due to reduced electron density in the radical cation.

Intermediate **16**$^{•+}$ undergoes further rearrangement to **13**$^{•+}$, with an activation energy of 1.2 kcal/mol. The transition state has one imaginary frequency, corresponding to rotation around the C^4-C^5 bond. IRC calculations at the B3LYP level confirm that no further intermediates are involved in the formation of **13**$^{•+}$. The overall heat of reaction is calculated as 44.7 kcal/mol, close to the experimentally deduced value of 42.5 ± 0.8 kcal/mol.[61]

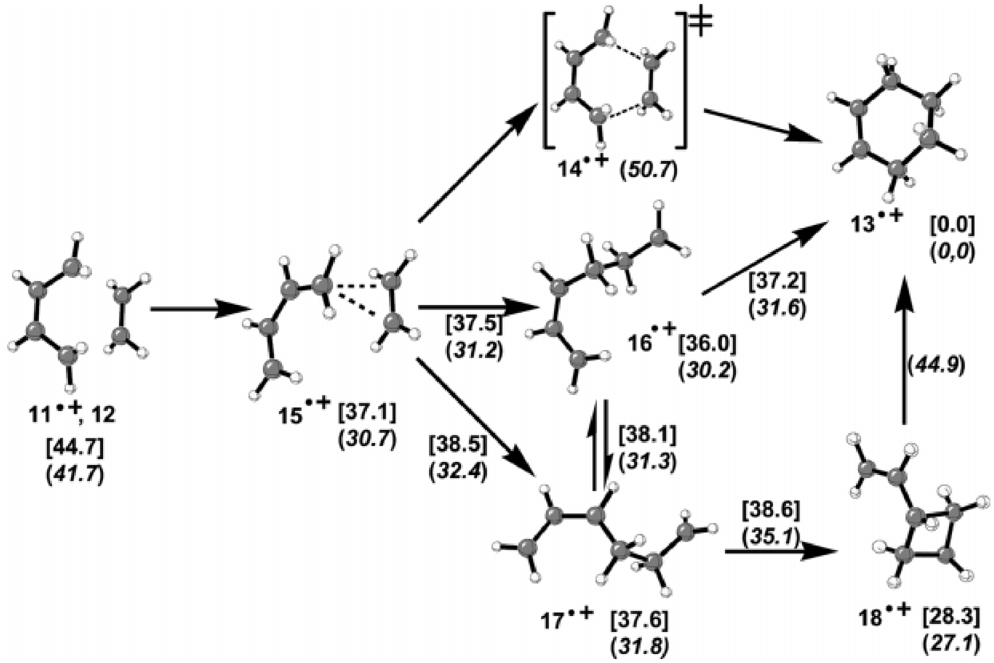

Figure 4. Reaction pathways for the parent radical cation Diels−Alder reaction; QCISD(T)//QCISD energies are given in brackets, B3LYP energies are given in parenthesis and are relative to $\mathbf{13}^{\bullet+}$

There is also a possibility of a stepwise pathway via an "out-gauche" intermediate $\mathbf{17}^{\bullet+}$, 1.6 kcal/mol higher in energy than $\mathbf{16}^{\bullet+}$. Intermediate $\mathbf{17}^{\bullet+}$ can either form directly from $\mathbf{15}^{\bullet+}$, with an activation energy of 1.4 kcal/mol, or through isomerization by rotation around the C^4-C^5 bond of $\mathbf{16}^{\bullet+}$, with an activation energy of 2.1 kcal/mol. Ring closure of $\mathbf{17}^{\bullet+}$ gives the vinylcyclobutane $\mathbf{18}^{\bullet+}$, with an activation energy of 1.0 kcal/mol. Intermediate $\mathbf{18}^{\bullet+}$ can rearrange to $\mathbf{13}^{\bullet+}$, with an activation energy of 17.8 kcal/mol at the B3LYP level. This pathway is generally not competitive with the stepwise pathway through intermediate $\mathbf{16}^{\bullet+}$, although it should be pointed out that vinylcyclobutane radical cation can be the exclusive product of a reaction with a geometrically constrained *trans*-1,3-butadiene radical cation.[48,62]

Proceeding in parallel to our work was an independent study of the same system at the UCCSD(T)/DZP//UMP2(fc)/DZP level, undertaken by Hofmann and Schaefer.[59,63] While Hoffmann and Schaefer found stationary points corresponding to our structures in Figure 4, they also located numerous additional stationary points on the hypersurface, in contrast to our findings. Several other pathways leading to quite different products such as methylcyclopentene and fulvene were also located. This, to the best of our knowledge, has never been observed experimentally. The reason for these additional stationary points can most probably be found in the low-order perturbation methods employed, which, as discussed earlier, are unsuitable for calculations of radical cations.[8,9] Analysis of the stationary point wave functions reveals severe spin contamination, and so the validity of these studies is, at best, doubtful.

In addition to the investigation of the parent reaction, a combined experimental and computational study of the electron transfer-catalyzed Diels−Alder reactions between indole and exocyclic dienes was undertaken.[64] The study shows that the computationally efficient B3LYP method performs very well in predicting both regio- and diastereoselectivity, which can also be correlated qualitatively with the results from semiempirical calculations.[4e,4m,64] The experimental and computational results for substituted analogs also agree very well with the proposed stepwise reaction mechanism outlined above.[4g,65]

The Vinylcyclopropane−Cyclopentene Rearrangement

The thermal rearrangement of vinylcyclopropane to cyclopentene is synthetically useful and has been applied to a number of natural product syntheses.[66] However, the high activation energies of these reactions, often more than 50 kcal/mol, usually make pyrolytic reaction conditions necessary.[67] The unique mechanism of this reaction has been a matter of intense debate for a long time,[68] and was recently settled using computational methods.[69,70]

In 1988, Dinnocenzo and co-workers demonstrated that the vinylcyclopropane rearrangement could be performed within minutes at low temperatures under electron transfer conditions.[72] So far, only a few theoretical investigations of the vinylcyclopropane radical cation have been performed. In early studies, the structures of different conformers of the parent vinylcyclopropane radical cation $\mathbf{19}^{\bullet+}$ and several substituted derivatives were calculated at INDO and UHF/STO-3G levels of theory.[72] More recently, a thorough analysis of the electronic structure of *syn*-$\mathbf{19}^{\bullet+}$ and *anti*-$\mathbf{19}^{\bullet+}$ and its relationship to neutral **19** at the UMP4(SDQ)/6-31G* level was published by Herbertz et al.[73]

The first high level treatment of the parent radical cation vinylcyclopropane rearrangement was published by our

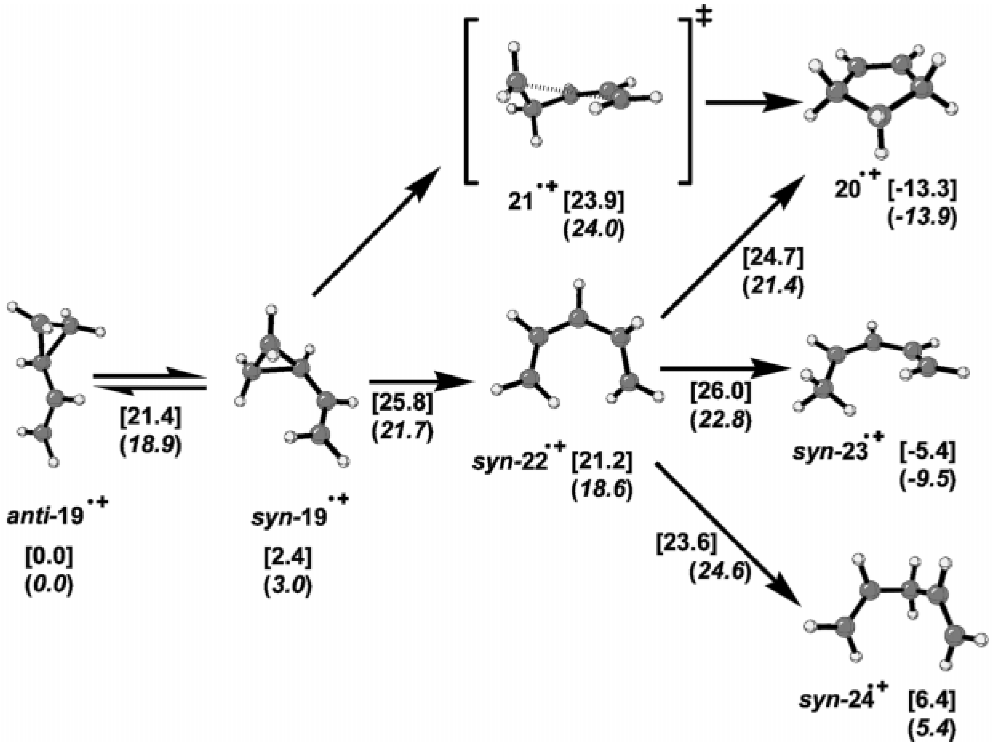

Figure 5. Reaction pathways for the radical cation vinylcyclopropane−cyclopentene rearrangement; QCISD(T)//QCISD energies are given in brackets, B3LYP energies are given in parenthesis and are relative to *anti*-**19**$^{\bullet+}$

group.[74] The starting material **19**$^{\bullet+}$, the cyclopentene product of the rearrangement **20**$^{\bullet+}$, and pertinent intermediates on the potential energy hypersurface, together with several other potential rearrangement products, were studied at the QCISD(T)/6-31G*//QCISD/6-31G* and B3LYP/6-31G* levels of theory. The results of this study are summarized in Figure 5.

Starting material **19**$^{\bullet+}$ has two conformations, *syn* and *anti*. The *anti* conformation is calculated to be 2.4 kcal/mol more stable than the *syn*, and may be converted into the *syn* conformer by traversing a rotational barrier of 18.9 kcal/mol, caused by the interaction of the radical cation in the vinyl moiety with the Walsh orbitals of the cyclopropane. This rotational barrier is substantially higher than the value of ca. 3 kcal/mol for neutral **19** and also higher than the 13−17 kcal/mol estimated by Herbertz et al.[73a]

Synthetically, the most useful reaction of the vinylcyclopropane radical cation is the [1,3]-methylene shift to form **20**$^{\bullet+}$. This reaction, being exothermic by 13.3 kcal/mol at the QCISD(T) level, is 8.4 kcal/mol less exothermic than the corresponding neutral reaction at the B3LYP level.[69] This again reflects the stabilization of the radical cation with the cyclopropane Walsh orbitals. The reaction can occur either through ring-closure of the acyclic intermediate **22**$^{\bullet+}$ or by a concerted [1_a,3_s]-sigmatropic methylene shift in *syn*-**19**$^{\bullet+}$ via transition structure **21**$^{\bullet+}$, but not directly from *anti*-**19**$^{\bullet+}$.

The stepwise pathway involves the formation of the acyclic intermediate **22**$^{\bullet+}$, 18.9 kcal/mol less stable than *syn*-**19**$^{\bullet+}$, with an activation energy of 23.5 kcal/mol and a very late transition state, in accordance with the endothermicity of the reaction. The electronic structure of **22**$^{\bullet+}$ is best described as an allyl cation at $C^1-C^{1'}-C^{2'}$, connected to a methylene radical at C^2. With a dihedral angle $C^{1'}-C^1-C^3-C^2$ of 15°, the carbon framework is essentially planar. The carbon termini are more than 3 Å apart, indicating that there is no bonding interaction between them. Steric interactions of the *endo* hydrogen atoms at the carbon termini cause the *endo* hydrogen atom at C^2 to rotate out of plane by 36°. The calculated activation energy corresponds well to the observed rate enhancement by electron transfer catalysis, of more than 10^{13} compared to the thermal rearrangement of 2-anisyl-1,1′-dimethylvinylcyclopropane.[75] The second transition structure for the stepwise pathway, the closure of **22**$^{\bullet+}$ to **20**$^{\bullet+}$, has an activation energy of 3.5 kcal/mol. This is only slightly less than the barrier to reclosure to *syn*-**19**$^{\bullet+}$. Therefore, a significant amount of reclosure, possibly with stereoisomerization at C^2, can be expected.[76] In agreement with the high exothermicity of this step, this is a very early transition structure with an essentially planar carbon framework and a very long forming bond (of ca. 2.63 Å).

The concerted [1,3]-methylene shift proceeds through transition structure **21**$^{\bullet+}$, with an activation energy of 21.5 kcal/mol at the QCISD level of theory, and 21.0 kcal/mol at the B3LYP. Intrinsic reaction coordinate calculations at the B3LYP level show that **21**$^{\bullet+}$ indeed connects *syn*-**19**$^{\bullet+}$ to **20**$^{\bullet+}$ without involving any further intermediates. The activation energy of the concerted pathway is very close to that of the stepwise pathway and so makes the two competitive. The geometry of **21**$^{\bullet+}$ resembles the geometry of the corresponding transition structure of the [1,3]-methylene shift in neutral **21**;[69] at the QCISD level of theory the length of the breaking bond in **23**$^{\bullet+}$ is 2.495 Å, that of the forming bond is 3.239 Å, and C^2 − with a dihedral angle $C^{1'}-C^1-C^3-C^2$ of 64.3° − is almost perpendicular to the plane of the carbon atoms.

Two other pathways, stereoisomerization and [1,2]-hydrogen shift, were also investigated. Species *syn*-**19**$^{\bullet+}$ can undergo bond homolysis to form the acyclic intermediate **22**$^{\bullet+}$, and subsequent rotation around a carbon−carbon bond and ring-closure can give a stereoisomer of **19**$^{\bullet+}$ with inversion at C^2. The isomerization of **22**$^{\bullet+}$ can proceed either through a [0,0] or a [90,0] transition state, with relative energies of 21.2 kcal/mol and 23.5 kcal/mol, respectively. Species *anti*-**19**$^{\bullet+}$ can form an acyclic intermediate, 17.5 kcal/mol higher than *anti*-**19**$^{\bullet+}$, and then undergo isomerization through a [90,0] transition state at 17.3 kcal/mol.

Intermediate **22**$^{\bullet+}$ can also undergo a [1,2]-hydrogen shift to form either the 1,3-pentadiene *syn*-**23**$^{\bullet+}$ or the 1,4-pentadiene *syn*-**24**$^{\bullet+}$. Although the **22**$^{\bullet+}$ → **23**$^{\bullet+}$ transition, which has a reaction energy of −26.6 kcal/mol, is more exothermic than the **22**$^{\bullet+}$ → **24**$^{\bullet+}$ transition, which has a reaction energy of −14.8 kcal/mol, it also has a larger activation energy: 26.0 kcal/mol vs. 23.6 kcal/mol, respectively. Species *anti*-**22**$^{\bullet+}$ can also undergo similar [1,2] hydrogen shifts, yielding *anti*-**23**$^{\bullet+}$ with an activation energy of 22.2 kcal/mol, or *anti*-**24**$^{\bullet+}$ with an activation energy of 19.7 kcal/mol.

The difference in activation energies calculated at the QCI level for the stepwise and the concerted processes is, at 1.9 kcal/mol, quite small. The preference for the concerted pathway at this level is reversed at the B3LYP level, presumably due to the tendency for B3LYP to overestimate conjugation.[10−12] Furthermore, the lowest energy pathway is the ring-opening of *anti*-**19**$^{\bullet+}$, followed by a [1,2]-hydrogen shift. This is in agreement with the observed experimental result of oxidizing **19** in gas phase.[77] Nevertheless, as the relevant transition states are only a few kcal/mol apart in energy, we feel that a definitive statement regarding the preferred pathway for the rearrangement of radical cationic vinylcyclopropanes is not possible. It can be expected that because of the small energy differences between the various pathways, dynamic, substituent, and solvent effects will be important for the determination of the product ratios. This is again analogous to the reaction of neutral **19**, in which the ratio of the stereoisomeric products was found to be determined by dynamic effects.[69c]

In light of the mechanistic ambiguity of the parent reaction, studies of substituted vinylcyclopropanes were also undertaken.[74] As an *anti* conformation of **19** precludes rearrangement to **20**, the effect of substituents at the vinyl moiety was investigated. It was found that a substituent as small as a methyl group is sufficient for a favorable *syn*/*anti* ratio.[70,74] This is particularly important in the case of the ETC reaction, because of the high barrier to isomerization in the radical cation. The electron distribution of the distonic intermediate **22**$^{\bullet+}$ can also be manipulated. Substitution by a *p*-anisol at the vinyl moiety produces the intermediate **25**$^{\bullet+}$, shown in Figure 6 on the left. Here, the radical is localized as a primary radical and the cation is delocalized over the aromatic moiety. Substitution by a *p*-anisol at the cyclopropane moiety leads to the intermediate **26**$^{\bullet+}$, in which the radical is delocalized as an allyl radical and the cation is again delocalized over the aromatic moiety. Species **26**$^{\bullet+}$ is substantially more stable than **25**$^{\bullet+}$, to the point that ring-opening of the vinylcyclopropane radical cation to form **26**$^{\bullet+}$ occurs in barrierless fashion, while formation of **25**$^{\bullet+}$ requires an activation energy of 19 kcal/mol. More detailed computational and experimental analysis of the hypersurfaces of substituted vinylcyclopropane radical cations and their exploitation in organic chemistry will be the subject of a further study.

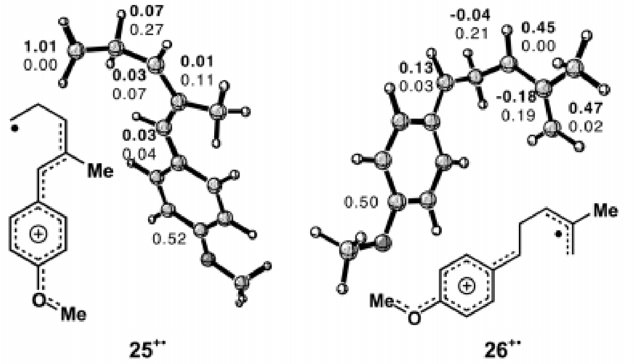

Figure 6. Distribution of spin and charge (B3LYP/6-31G*, CHELPG) in the substituted acyclic intermediates **25**$^{\bullet+}$ and **26**$^{\bullet+}$

Conclusions

There are a number of common features that evolved in the studies discussed above and are apparently rather general to pericyclic reactions of hydrocarbon radical cations. Firstly, the potential energy surfaces of all reactions discussed are extraordinarily flat. This causes low activation energies, in agreement with the frequently observed dramatic rate acceleration achieved by ETC. However, this is also the cause for many side reactions such as isomerizations, rearrangements of the carbon framework, and hydrogen shifts, opening many possible pathways and making the hypersurfaces rather complex, even for simple reactions. The actual pathway chosen by these charged, high energy-intermediates depends mostly on the relative energies of the intermediates involved and is strongly influenced by solvent, substituent, and dynamic effects. These influences, such as the stabilization of a charge at a given center by a substituent or over a number of atoms by delocalization, are much stronger than in the corresponding neutral reactions. Another consequence of the generally flat hypersurfaces is that the differences between the different computational methods are now large enough that the overall shape of the hypersurface strongly depends on the method chosen. Since all currently available methods have a bias, to different extents, towards localized or delocalized structures, geometrically similar stationary points can represent either minima, transition structures, or second-order saddle points on the hypersurface. Since the energy differences are small compared to other effects, these results should be analyzed in a qualitative rather than a quantitative fashion. Nevertheless, the analysis of the geometric and electronic structure of the species yields valuable information for understanding the reaction mechanism and how the reaction can be influenced.

Secondly, several of the stepwise pathways calculated closely resemble the corresponding stepwise, diradical pathways in the neutral pericyclic reactions. This is not only true for the Diels−Alder reaction and the vinylcyclopropane rearrangement discussed here, but also for the reaction of the 1,5-hexadiene radical cations[78] and, even though it was not realized at the time, for the cyclopropyl carbinyl radical cation, which also has a counterpart on the neutral, diradical hypersurface.[79] These findings can be rationalized by considering the effect of an electron transfer onto a generic pericyclic reaction, shown on the left in Figure 7. Here, the low-energy, concerted pathway goes through a transition state $\mathrm{TS_{conc}}$, which is stabilized by aromaticity. The stepwise pathway through $\mathrm{TS_{step}}$ is typically higher in energy, due to the initial bond homolysis required. The energy difference between the two pathways has been termed the "energy of concert". After electron transfer, this bond homolysis is much easier for the one-electron bond in the radical cation reaction through $\mathrm{TS_{step}}^{\bullet+}$. At the same time, $\mathrm{TS_{conc}}^{\bullet+}$ is no longer stabilized by aromaticity. If the energy of concert is small enough, the electron transfer will therefore lead to a stepwise pathway resembling the stepwise, diradical pathway of the neutral reaction.

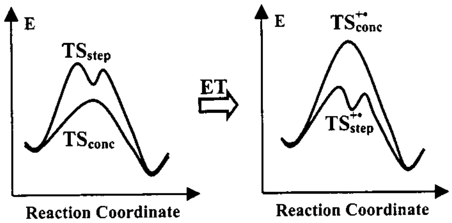

Figure 7. Schematic representation of the effect of an electron transfer on a pericyclic reaction

Thirdly, the unpaired electron has a profound effect on the reactions, which in the case of the neutral reactions would proceed through a symmetric transition state. In the case of the radical cations, the unpaired electron often produces a lowering of the symmetry, due to a first- and/or second-order Jahn−Teller distortion. This can lead either to structures of a lower symmetry, as in the case of the cyclobutane radical cation, or to completely asymmetric structures, as in the case of the ring-opening of cyclobutene. The later case also exhibits another effect unique to open-shell systems: the electronic state of the symmetric species on the hypersurface is now determined by the symmetry of the SOMO. This can, as in the case of the cyclobutene and the 1,3-butadiene radical cations, lead to a difference in the electronic states of the reactant and the product. Therefore, there cannot be a symmetry-preserving pathway between $\mathbf{1}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$. Instead, any symmetry-preserving pathway has to lead to the *trans*-1,3-butadiene radical cation $\mathbf{2}^{\bullet+}$.

Although the generality of these findings for the parent reaction will have to be tested on other systems in the future, they have already provided the foundation for several studies of larger, chemically more relevant systems as well as for an understanding of previous observations described in the literature.

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