Ab Initio Studies of the Ring-Opening Reaction of the Cyclobutene Radical Cation

Olaf Wiest

Contribution from the Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received December 17, 1996. Revised Manuscript Received April 17, 1997[⊗]

Abstract: The ring-opening reaction of the cyclobutene radical cation was studied by using Hartree−Fock and density functional theory as well as various correlated MO methods. The species involved in three different mechanism—a concerted C_2-symmetric, a concerted C_1-symmetric, and a stepwise C_1-symmetric pathway— have been considered. It is shown that any symmetric pathway is dominated by state symmetry selection rules which determine the outcome of the reaction. The concerted C_2-symmetric pathway is subject to a pseudo-Jahn−Teller distortion and leads to *trans*-butadiene. This pathway is approximately 5 kcal/mol higher in energy than the concerted C_1-symmetric pathway, leading to *cis*-butadiene. Based on the results presented here, the stepwise C_1-symmetric or "nonelectrocyclic" pathway discussed in the literature is an artifact of an overestimation of the radical stability by MP2 and minimum basis set ab initio methods. It is therefore concluded that the ring opening of the cyclobutene radical cation proceeds via a concerted, unsymmetric pathway to *cis*-butadiene. The results from Becke3LYP calculations for geometries, energies, and isotropic hyperfine coupling constants are in good agreement with the available experimental data and with QCISD(T)/QCISD calculations. The results from the different methods are discussed with respect to the experimental data, and the implications of the data presented here for future computational studies of radical ion reactions are considered.

Introduction

The electrocyclic ring opening of cyclobutene **1** to *cis*-butadiene **2** is one of the most thoroughly studied reactions of organic chemistry.[1] The mechanistic analysis of this reaction within the framework of molecular orbital theory was one of the earliest successes of the Woodward−Hoffmann rules.[2] The concepts derived from this analysis were shown to be applicable to numerous other reactions and led to the firm establishment of pericyclic reactions as one of the most important reaction classes in organic chemistry.

The mechanism of the corresponding, electron-transfer-catalyzed pericyclic reactions, which proceed via the corresponding radical ions, is much less understood. This lack of basic understanding is not only unsatisfactory from a scientific point of view, but also hinders the synthetic application of electron-transfer catalysis (ETC). Because ETC can accelerate pericyclic reactions by many orders of magnitude over their neutral counterparts,[3] a better understanding of the mechanism is highly desirable. The development of rules that allow the prediction of substituent effects, stereochemistry, etc. would make a powerful method for the catalysis of slow or symmetry-forbidden pericyclic reactions widely available.

Although a large rate acceleration by ETC has been described for a number of substituted cyclobutenes[4] and the synthetic utility of this reaction has been shown,[5] there are very few mechanistic studies available, and the results of these studies are sometimes contradictory. The investigation of the conversion of the radical cation of cyclobutenedicarboxylic acid,[6] and

the corresponding methyl esters,[7] to the butadienes in the gas phase did not yield conclusive results about the reaction mechanism. A first estimate of the activation energy of ≤7 kcal/mol was reported by Gross et al.[8] It was also found by the same group that 1-substituted cyclobutenes have a higher activation energy, whereas substitution in the 3-position leads to a lower activation energy.[9] The observation that no ring opening occurs in frozen media at 90 K[10] implies that these estimates should be interpreted as a lower limit for the activation energy of the ring opening.

There are few data available for the activation energy in solution. From product studies of the competition between ring opening and oxygen addition to cyclobutene radical cations, it has been deduced that the ring opening is a relatively slow reaction in methylene chloride at −78 °C.[11] The most reliable value for the activation energy of the ring opening of a cyclobutene radical cation has been measured for 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene. By using several independent methods, the activation energy for this reaction has been determined to be ca. 16.5 kcal/mol.[12] Despite these discrep-

---

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

(1) For recent reviews, see: (a) Dolbier, W. R.; Koroniak, H.; Houk, K. N.; Sheu, C. M. *Acc. Chem. Res.* **1996**, *29*, 471. (b) Gajewski, J. J. *Hydrocarbon Thermal Rearrangement*; Academic Press: New York, 1981; p 47.

(2) (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 246. (b) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(3) (a) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307. (b) Dinnocenzo, J. P.; Conlon, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 2324.

(4) E.g.: (a) Faucitano, A.; Buttafava, A.; Martinotti, F.; Sustmann, R.; Korth, H.-G. *J. Chem. Soc., Perkin Trans. 1* **1992**, 865. (b) Takahaski, Y.; Kochi, J. K. *Chem. Ber.* **1988**, *121*, 253. (c) Marcinek, A.; Michalak, J.; Rogowski, J.; Tang, W.; Bally, T.; Gebicki, J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1353. (d) Gebicki, J.; Marcinek, A.; Michalak, J.; Rogowski, J.; Bally, T.; Tang, W. *J. Mol. Struct.* **1992**, *275*, 249.

(5) E.g.: (a) Takahashi, Y.; Miyamoto, K.; Sakai, K.; Ikeda, H.; Miyashi, T.; Ito, Y.; Tabohashi, K. *Tetrahedron Lett.* **1996**, *37*, 5547. (b) Pasto, D. J.; Yang, S.-H. *J. Org. Chem.* **1989**, *54*, 3544.

(6) Hoffmann, M. K.; Bursey, M. M.; Winter, R. E. K. *J. Am. Chem. Soc.* **1970**, *92*, 727.

(7) Mandelbaum, A.; Weinstein, S.; Gil-Av, E.; Leftin, J. H. *Org. Mass Spectrom.* **1975**, *10*, 842.

(8) Gross, M. L.; Russell, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 2082.

(9) (a) Dass, C.; Sack, T. M.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 5780. (b) Dass, C.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 5724.

(10) (a) Haselbach, E.; Bally, T.; Gschwind, R.; Hemm, U.; Lanyiova, Z. *Chimia* **1979**, *33*, 405. (b) Haselbach, E.; Bally, T.; Lanyiova, Z. *Helv. Chim. Acta* **1979**, *62*, 577.

(11) Kirschenheuter, G. P.; Griffin, G. W. *J. Chem. Soc., Chem. Commun.* **1983**, 596.

ancies between the results for the activation energy from different sources, it is clear that the ring opening of cyclobutene radical cation is many orders of magnitude faster than the neutral reaction, which has an activation energy of 32.8 kcal/mol.[13]

This large acceleration of the reaction is combined with a high stereoselectivity of the reaction. It has been shown that the electron-transfer-catalyzed ring opening of 3,4-diarylcyclobutenes yields exclusively the product of the conrotatory ring opening.[14] A complete selectivity was also observed after irradiation of the cyclobutene radical cation in a matrix at 77 K, where only *trans*-butadiene **3** was found as a product.[15] This is in sharp contrast to the results for the neutral reaction, where isomerization to *trans*-butadiene occurs via the initial formation of *cis*-butadiene **2**, showing once more the often unique selectivity of radical cationic reactions.

Computational chemistry is particularly suitable for the study of this reaction, because the available experimental data are ambiguous and difficult to obtain. Accurate quantum mechanical studies can be used to clear some of these ambiguities and to evaluate the accuracy of computationally more efficient methods. This paper presents the first ab initio study of the ring-opening reaction of the cyclobutene radical cation at a high level of theory.

Theoretical Analysis

Given the success of the Woodward−Hoffmann rules for the description of pericyclic reactions of closed-shell molecules, it is not surprising that there have been a number of attempts to understand ETC reactions based on a FMO analysis and to correlate radical ion reactivity with the well-understood mechanisms of neutral molecules. In most of these studies, simple orbital correlation methods have been used to predict radical cationic reactions.[16] This simple FMO approach does not take into account the additional interactions of the singly occupied molecular orbital (SOMO) of the radical cation.[17] Furthermore, they do not consider possible stepwise or unsymmetric reaction pathways.[18] Consequently, their predictive powers have been limited, as exemplified by the "role selectivity" model that has been derived on the basis of FMO considerations[19] and was disproven experimentally.[20]

It was pointed out by Bally and co-workers[15] that the electronic state of open-shell species depends on the symmetry of the SOMO, and only allows reactions to occur where the electronic states of the reactants and products correlate. Figure 1 shows the state symmetry correlation diagram for the ring opening of the cyclobutene radical cation. It has been pointed out[15] that the electronic states of **1**[•+] and **2**[•+] do not correlate. Assuming a C_{2v} symmetry, **1**[•+] has a $^2B_1$ ground state. Upon preservation of the C_2-symmetry element, this state correlates with the first excited state of the C_{2v}-symmetric *cis*-butadiene
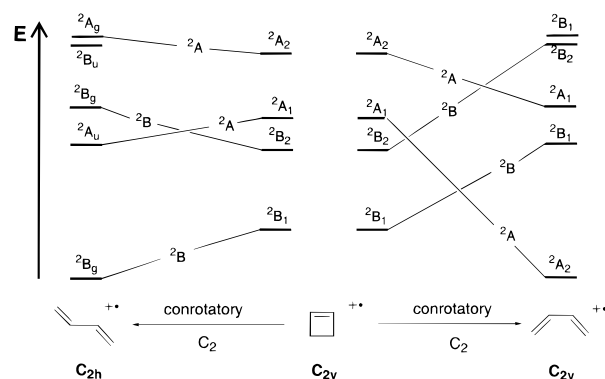
(12) (a) Kawamura, Y.; Thurnauer, M.; Schuster, G. B. *Tetrahedron* **1986**, *42*, 6195. (b) Brauer, B.-E.; Thurnauer, M. C. *Chem. Phys. Lett.* **1987**, *113*, 207.

(13) (a) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. (b) Carr, R. W.; Walters, W. D. *J. Phys. Chem.* **1965**, *69*, 1073.

(14) Miyashi, T.; Wakamatsu, K.; Akiya, T.; Kikuchi, K.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 5270.

(15) Aebischer, J. N.; Bally, T.; Roth, K.; Haselbach, E.; Gerson, F.; Qin, X.-Z. *J. Am. Chem. Soc.* **1989**, *111*, 7909.

(16) (a) Dunkin, I. R. *Tetrahedron*, **1985**, *41*, 145. (b) Bauld, N. L.; Cessac, J. *J. Am. Chem. Soc.* **1977**, *99*, 23. (c) Bishop, M. J.; Fleming, I. *J. Chem. Soc. (C)* **1969**, 1712.

(17) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley & Sons: New York, 1976; p 182.

(18) For some notable exceptions, compare: Dougherty, R. A.; *J. Am. Chem. Soc.* **1968**, *90*, 5780 and refs 10 and 15.

(19) (a) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665. (b) Bellville, D. J.; Bauld, N. L. *Tetrahedron* **1986**, *42*, 6167.

(20) Mlcoch, J.; Steckhan, E. *Tetrahedron Lett.* **1987**, *27*, 1081.

Figure 1. State symmetry analysis for the ring opening of the cyclobutene radical cation **1**[•+] to *cis*-butadiene **2**[•+] (right) and *trans*-butadiene **3**[•+] (left).
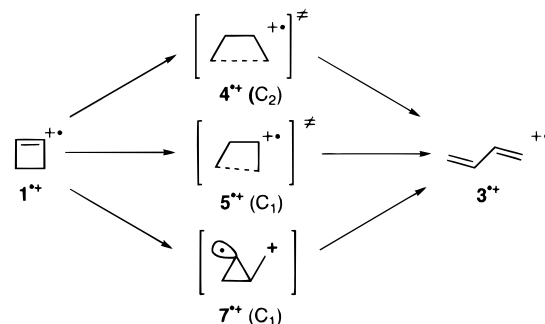

Figure 2. Possible reaction pathways for the ring opening of **1**[•+].

2[•+] through a transition state with a ^2B state.[21] The ^2A ground state of **2**[•+] correlates with the second excited state of **1**[•+]. Thus, there is no connection between the ground states of **1**[•+] and **2**[•+]. The electrocyclic ring opening is, however, not invariably state symmetry forbidden, as claimed earlier.[15] A correlation of the electronic states can be achieved between **1**[•+] and the C_{2h}-symmetric *trans*-butadiene **3**[•+], as shown in Figure 1 on the left. In this case, the $^2B_1$ state of **1**[•+] correlates through a transition state, thus preserving the C_2 symmetry element state to the ^2B_g state of **3**[•+].[22] Hence, the structure of the product depends on the symmetry and therefore the electronic state of the reactant.

Alternatively, the reactant could lose all symmetry along the reaction path to proceed from a reactant of one electronic state to a product of a different, noncorrelating electronic state. Such a C_1-symmetric reaction pathway could be concerted through the transition state **5**[•+] or a stepwise mechanism involving the intermediate **7**[•+]. Figure 2 summarizes these three distinct possibilities to convert **1**[•+] to **3**[•+].

Computational Methodology

The adequate treatment of electron correlation is crucial for the accurate treatment of radical ions.[23] On the basis of a theoretical analysis of the cyclobutene ring opening similar to the one presented here, multireference methods have been suggested for the study of the isomerization of **2**[•+] and **3**[•+].[15] However, the choice of the active space for the reaction studied here is problematic, because the differences between σ- and π-orbitals vanished in polyene radical cations. Instead, we used QCISD(T) single-point calculations on QCISD-optimized

(21) Preservation of the C_s-symmetry element in a disrotatory pathway is less favorable; compare ref 15.

(22) Herzberg, G. *Molecular Spectra and Molecular Structure*; vanNostrant: New York, 1966.

(23) (a) Murray, C. W.; Handy, N. C. *J. Chem. Phys.* **1992**, *97*, 6509. (b) Handy, N. C.; Ma, N. L.; Smith, B. J.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1991**, *113*, 7903. (c) Clark, T.; *Top. Curr. Chem.* **1996**, *177*, 1.

Ring-Opening Reaction of the Cyclobutene Radical Cation

J. Am. Chem. Soc., Vol. 119, No. 24, 1997 5715

Table 1. Selected Geometric and Energetic Parameters for $1^{\bullet+}-3^{\bullet+}$

	cyclobutene radical cation $1^{\bullet+}$				*trans*-butadiene radical cation $3^{\bullet+}$			*cis*-butadiene radical cation $2^{\bullet+}$		
	E_{SCF} [h]	R_{C1-C2} [Å]	R_{C2-C3} [Å]	R_{C3-C4} [Å]	E_{rel} [kcal/mol]	R_{C1-C2} [Å]	R_{C2-C3} [Å]	E_{rel} [kcal/mol]	R_{C1-C2} [Å]	R_{C2-C3} [Å]
UHF	−154.51975	1.409	1.500	1.561	−27.5	1.386	1.396	−23.4	1.386	1.403
MP2	−154.99115	1.428	1.486	1.563	−17.8	1.384	1.408	−13.6	1.382	1.418
QCISD(T)//QCISD	−155.05675	1.427	1.494	1.568	−21.6	1.391	1.408	−17.9	1.391	1.416
Becke3LYP	−155.55811	1.427	1.487	1.573	−23.8	1.390	1.410	−20.2	1.388	1.419
BLYP	−155.47757	1.438	1.494	1.587	−25.4	1.399	1.422	−21.8	1.398	1.431

geometries (QCISD(T)//QCISD)[24] to obtain reference values for the evaluation of other methods, including nonlocal (BLYP) and hybrid (Becke3LYP) DFT methods. There are a number of cases known in the literature where QCI methods including triple excitations were able to describe multireference problems quite accurately.[25,26]

All calculations were performed with the G94 series of programs[27] running on IBM SP1/SP2 parallel computers at the Office of Information Technologies at the University of Notre Dame and at the Maui High Performance Computing Complex. All geometry optimizations and energy calculations were performed with the 6-31G* basis set.[28] The cc-pCVTZ basis set[29] was used for the calculation of the isotropic hyperfine coupling constants. The standard grids have been used for the integration of the electron density in the density functional theory (DFT) calculations. The geometries reported for the UHF, MP2, and DFT calculations have been fully optimized and characterized by harmonic frequency analysis. All energies reported are corrected for zero-point vibrational energies obtained at the same level of theory except for the QCISD(T) results, where the zero-point energies form Becke3LYP calculations have been used.

Results and Discussion

The Radical Cations of Cyclobutene and Butadiene. As a first step in the investigation of the ring-opening reaction of the cyclobutene radical cation, the reactant and product radical cations have been studied. Table 1 summarizes the results for the radical cations $1^{\bullet+}-3^{\bullet+}$, shown in Figure 3. Because of their instability, there is relatively little experimental data available for the radical cations $1^{\bullet+}-3^{\bullet+}$. The ESR spectra of $1^{\bullet+}$ and $3^{\bullet+}$ in different matrices have been measured at 77 K. The isotropic hyperfine coupling constants are extremely sensitive to geometry and were, therefore, calculated at the Becke3LYP geometry with the Becke3LYP/cc-pCVTZ method. It has been shown earlier that DFT methods yield acceptable results for the isotropic hyperfine coupling constants.[30] The values computed for $1^{\bullet+}-3^{\bullet+}$ are summarized in Table 2.

(24) (a) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968. (b) Gauss, J.; Cremer, D. *Chem. Phys. Lett.* **1988**, *150*, 280.

(25) (a) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072. (b) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 334.

(26) (a) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1907. (b) Wierschke, S. G.; Nash, J.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11958. (c) Lindh, R.; Perrson, B. J. *J. Am. Chem. Soc.* **1994**, *116*, 4963.

(27) Gaussian 94, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh: PA, 1995.

(28) The 6-311+G** basis set was also tested, but did not give significantly different results for either the DFT or the HF calculations.

(29) This basis set offers a more balanced description of the core electrons than the similar cc-pVTZ basis set: (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Woon, D.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572.

(30) E.g.: (a) Engels, B.; Erikson, L. A.; Lunell, S. *Adv. Quantum Chem.* **1996**, *27*, 297. (b) Batra, R.; Giese, B.; Spichty, M.; Gescheidt, G.; Houk, K. N. *J. Phys. Chem.* **1996**, *100*, 18371.
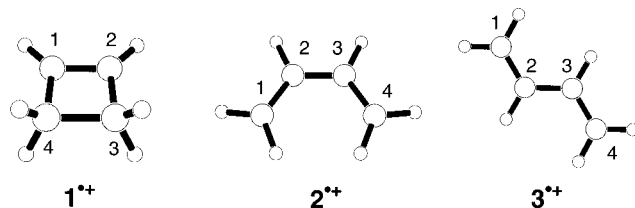
Figure 3. Becke3LYP/6-31G* structures of the radical cations of cyclobutene $1^{\bullet+}$ (left), *cis*-butadiene $2^{\bullet+}$ (middle), and *trans*-butadiene $3^{\bullet+}$ (right).

Table 2. Experimental and Calculated Isotropic Hyperfine Coupling Constants for $1^{\bullet+}-3^{\bullet+}$

compd	proton	exptl [G][a]	calcd [G][b]
$1^{\bullet+}$	H_1; H_2	11.1	−10.5
	H_3; H_4	28.0	28.9
$3^{\bullet+}$	H_1; H_4(exo)	11.2	−10.3
	H_1; H_4(endo)	10.5	−10.0
	H_2; H_3	2.8	−1.4
$2^{\bullet+}$	H_1; H_4(exo)		−10.4
	H_1; H_4(endo)		−9.8
	H_2; H_3		−2.0

[a] In $CFCl_3$, ref 31. [b] Becke3LYP/cc-pCVTZ//Becke3LYP/6-31G*.

As expected, the removal of an electron from the HOMO of **1** leads to a lengthening of the C_1-C_2 double bond as compared to neutral **1**. This effect is relatively small at the UHF level of theory, but larger for the correlated methods. Similar to the results from other studies, the BLYP method is found to consistently overestimate the bond lengths as compared to the QCISD geometry. For the other geometric parameters, the differences between the results from the various methods are very small.

The calculated isotropic hyperfine coupling constants calculated for the hydrogens in $1^{\bullet+}$ are in excellent agreement with the experimentally observed values.[31] It should be noted that the experimental values are subject to strong matrix effects. The change from $CFCl_3$ to CF_3CCl_3 as the matrix leads to a distortion of the molecule, and different hyperfine coupling constants for the protons at C3 and C4. Despite the small differences between the experimental and calculated values and the experimental difficulties, the assignment of the hyperfine coupling constants to the protons is still unambiguous.

For $3^{\bullet+}$, a totally delocalized structure is obtained at all levels of theory used here. The central C−C single bond in $3^{\bullet+}$ is only 0.02 Å longer than the formally olefinic bonds. This difference is much smaller than in neutral **3** and confirms the earlier notion that in small polyene radical cations such as $2^{\bullet+}$ or $3^{\bullet+}$, single and double bonds are essentially indistinguishable.[32] For the reaction of $1^{\bullet+}$ to $3^{\bullet+}$, reaction energies of −27.5 and −25.4 kcal/mol were calculated at the BLYP and HF levels

(31) Gerson, F.; Qin, X.-Z.; Bally, T.; Aebischer, J.-N. *Helv. Chim. Acta* **1988**, *71*, 1069.

(32) E.g.: (a) Tang, W.; Zhang, X.-L.; Bally, T. *J. Phys. Chem.* **1993**, *97*, 4373. (b) Cave, R. J.; Johnson, J. L. *J. Phys. Chem.* **1992**, *96*, 5332.

Table 3.   Selected Data for the C_2-Symmetric Transition Structure $4^{\bullet+}$

	E_{rel} [kcal/mol]	R_{C3-C4} [Å]	$\varphi_{C1-C2-C3-C4}$ [deg]	ν_{imag} [cm^{-1}]
UHF	31.0	2.211	27.8	$-1231; -348$
MP2	30.4	2.224	29.1	-538
QCISD(T)//QCISD	23.4	2.215	27.9	$-2131; -808; -132$
Becke3LYP	23.9	2.196	26.7	$-617; -450$
BLYP	20.2	2.194	25.7	$-570; -441$

of theory, respectively. The reaction is therefore considerably more exothermic than the neutral reaction, for which reaction energies of $\Delta E_{react} = -15.1$ and -13.7 kcal/mol have been calculated at the same levels of theory.[33] The UHF calculations give the largest reaction energy of -27.5 kcal/mol, and the MP2 calculations give the smallest value of -17.8 kcal/mol. This large difference can be explained by the fact that the UHF method does not describe electron correlation appropriately, whereas MP2 calculations are known to overestimate this factor in a number of systems.[34] The QCISD(T)//QCISD and Becke3LYP calculations yield relatively similar results, -21.6 and -23.8 kcal/mol, respectively, for the reaction energy, and the values obtained by the BLYP calculations are only slightly higher. The increase in reaction energy and the almost identical bond lengths of the formal single and double bonds reflect the increased stabilization of the polyene radical cation as compared with the cyclobutene radical cation through complete delocalization of the radical cationic character.

The computed isotropic hyperfine coupling constants for $3^{\bullet+}$ are again in excellent agreement with the experimental values. The calculated values for the endo and exo protons deviate by only 0.5 and 0.9 G, respectively. This unusually small deviation might be fortuitous, and the error of 1.4 G calculated for the protons attached to C_2 and C_3 is probably a better estimate of the errors that can be expected in these calculations. It is nevertheless clear that the Becke3LYP/cc-pCVTZ//Becke3LYP/6-31G* is a promising method for the calculation of isotropic hyperfine coupling constants and that, using trends rather than absolute numbers, an unequivocal assignment of the protons will be possible in most cases.
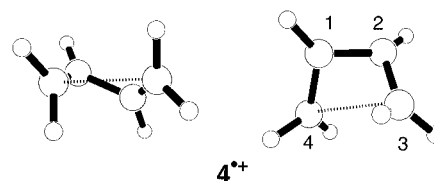
The *cis*-butadiene $2^{\bullet+}$ also stabilizes the radical cation by complete delocalization in the π-system, resulting in a planar structure with very similar C−C and C=C bond lengths. This stabilization is strong enough to overcome the steric repulsion of the endo hydrogens. In neutral **2**, this C_{2v} symmetric structure is a transition state for the interconversion of two gauche structures, and is 3.5 kcal/mol higher in energy than *trans*-butadiene.[35] This value provides an estimate of the steric repulsion and is in good agreement with the energy difference between $2^{\bullet+}$ and $3^{\bullet+}$ of 3.6 and 3.7 kcal/mol calculated at the Becke3LYP and QCISD(T)//QCISD levels of theory, respectively. The steric repulsion also leads to a widening of the $C_1-C_2-C_3$ bond angle in $2^{\bullet+}$ to 125.5° at the Becke3LYP level.

No experimental data for the isotropic hyperfine coupling constants of $2^{\bullet+}$ are available. The theoretical predictions show however a distinct pattern with the endo protons on the carbon termini having slightly smaller coupling constants than the protons in the exo positions. The computed values for the protons at C_2 and C_3 in $2^{\bullet+}$ are ~2 G, smaller than the values for the terminal hydrogens.

Figure 4. C_2-symmetric transition state $4^{\bullet+}$ for the ring opening of the cyclobutene radical cation $1^{\bullet+}$.

The Concerted, C_2-Symmetric Pathway. The stationary point $4^{\bullet+}$, which is very similar to the conrotatory transition structure for the ring opening of neutral **1**, is shown in Figure 4. Selected results for $4^{\bullet+}$ are summarized in Table 3. The C−C bond distance computed for the breaking bond varies very little with the computational method used. The bond length of ~2.2 Å is 0.05−0.08 Å longer than the one calculated for the neutral transition structure because of the removal of an electron from the binding HOMO. As a result of the decreased conjugation in $4^{\bullet+}$, dihedral angles between 25.7° and 29.1° are calculated. This makes the carbon skeleton in $4^{\bullet+}$ even more twisted than the corresponding neutral transition structure.

The calculated activation energies are considerably lower than the energies for the neutral reaction. The largest difference in activation energy between the neutral[13] and the radical cation ring opening is 16.4 kcal/mol, calculated at the UHF level. This is in part due to the well-known overestimation of the activation energy of the neutral reaction. The MP2 method gives the smallest decrease in activation energy because this method is known to underestimate the activation energy of the neutral reaction.[36] It has been found earlier by our group[37] and others[38] that both methods are not suitable for the calculation of radical ions because the UHF wave function of radical cations is often severely spin contaminated. The effect of spin contamination on the energies calculated by the QCISD(T) method is much smaller. DFT methods, including hybrid DFT methods, are on the other hand known to give $\langle S^2 \rangle$ values very close to the expectation values.[39] The BLYP and Becke3LYP functionals predict a lowering of the activation energy by electron transfer of 9.6 and 10.0 kcal/mol, respectively. There are no QCISD-(T) results available for the ring opening of neutral **1**, and a comparison of the neutral and the radical cationic ring opening is therefore not possible. However, it is gratifying to note that the results for geometries and energies obtained by the Becke3LYP method are very close to the results from the computationally much more demanding QCISD(T) method. The activation energies computed by this and the DFT methods are close to the values of 0.9 eV estimated as an upper limit by Haselbach et al. for a concerted, conrotatory pathway based on photoelectron spectroscopy data.[10]

(33) Wiest, O.; Houk, K. N.; Black, K. A.; Thomas, B., IV *J. Am. Chem. Soc.* **1995**, *117*, 8594.

(34) Wiest, O.; Houk, K. N. *Top. Curr. Chem.* **1996**, *183*, 1 and references cited therein.

(35) Murko, M.; Castejon, J.; Wiberg, K. B. *J. Phys. Chem.* **1996**, *100*, 16162. A recent experimental study in the gas phase gave a barrier of 4.0 kcal/mol: Kofranek, M.; Karpfen, A.; Lischka, H. *Chem. Phys. Lett.* **1992**, *189*, 281.

(36) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682. (b) Raghavachari, K.; Anderson, J. B. *J. Phys. Chem.* **1996**, *100*, 12960.

(37) Wiest, O. *J. Mol. Struct (THEOCHEM)* **1996**, *368*, 39.

(38) (a) Ma, N. L.; Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1992**, *193*, 386. (b) Nobes, R. H.; Moncrieff, D.; Wong, M. W.; Radom, L.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *182*, 216.

(39) E.g.: (a) Erikson, L. A.; Malkina, O. L.; Malkin, V. G.; Salahub, D. R. *J. Chem. Phys.* **1994**, *100*, 5066. (b) Wang, J.; Becke, A. D.; Smith, V. H., Jr. *J. Chem. Phys.* **1995**, *102*, 3477. (c) Laming, G. J.; Handy, N. C.; Amos, R. D. *Mol. Phys.* **1993**, *80*, 1121.
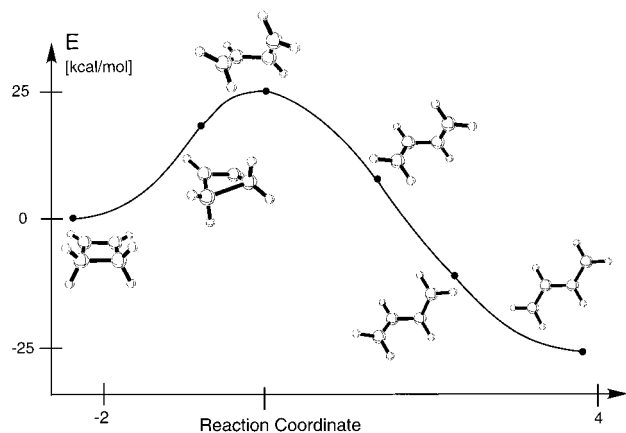
Ring-Opening Reaction of the Cyclobutene Radical Cation

J. Am. Chem. Soc., Vol. 119, No. 24, 1997 5717

Figure 5. IRC calculation starting from $\mathbf{4^{•+}}$.

Figure 6. C_1-symmetric transition state $\mathbf{5^{•+}}$ for the ring opening of the cyclobutene radical cation $\mathbf{1^{•+}}$.

Table 4. Selected Data for the C_1-Symmetric Transition Structure $\mathbf{5^{•+}}$

	E_{rel} [kcal/mol]	R_{C3-C4} [Å]	$\varphi_{C1-C2-C3-C4}$ [deg]
UHF	24.6	2.115	13.4
QCISD(T)//QCISD	18.6	2.165	13.7
Becke3LYP	18.1	2.186	10.9
BLYP	14.8	2.174	10.4

Although these results appear to be reasonable, the frequency analysis of $\mathbf{4^{•+}}$ at the UHF, QCISD, and DFT levels of theory reveals that this stationary point is a second-order saddle point and therefore not a true transition structure. The first imaginary frequency is unusually strong and corresponds to the antisymmetric motion of the hydrogens attached to the terminal carbons. This symmetry-breaking mode is caused by a pseudo-Jahn–Teller distortion of the C_2-symmetric transition structure $\mathbf{4^{•+}}$. This effect is caused by the degeneracy of the SOMO and leads to an increase in the activation energy for the symmetric pathway. As the reaction coordinate approaches the transition state region the orbitals become degenerate. A pseudo-Jahn–Teller effect then leads to a sharp energy increase for the symmetry-preserving pathway. Similar results have been obtained earlier for the ring opening of the cyclopropyl radical cation.[40] The MP2 method does not predict this effect, even though this method gives a higher activation energy than either the QCISD(T) or the DFT methods. This indicates that the MP2 method does not give reliable results for this radical cation system. The second, smaller negative vibration calculated by the UHF, QCISD, Becke3LYP, and BLYP methods corresponds to the expected reaction coordinate. The computed frequencies of 450 and 441 cm^{-1} at the Becke3LYP and BLYP levels of theory are typical values for a relatively long, breaking C–C bond in the transition state. The absolute values calculated for the QCISD method are less reliable because only a numerical evaluation of the frequency is possible at this level of theory.[41]

In order to gain further insight into this reaction path, and to ensure that $\mathbf{4^{•+}}$ does indeed connect the reactants and the products of the reaction, the second imaginary mode was followed by an intrinsic reaction coordinate (IRC) calculation. Figure 5 shows the results of the IRC calculations at the Becke3LYP level of theory, together with 6 structures out of a total of 54 calculated points. Starting from $\mathbf{4^{•+}}$, the reaction path connects in the backward direction to the cyclobutene radical cation $\mathbf{1^{•+}}$. In accordance with the conservation of the electronic state symmetry discussed above, the computed reaction path leads to *trans*-butadiene $\mathbf{3^{•+}}$ without the involvement of the *cis*-isomer. This is in contrast to the IRC for the electrocyclic ring opening of neutral cyclobutene which connected $\mathbf{1}$ with *gauche* butadiene.[42] Due to the higher exothermicity of the radical cation reaction, a considerably earlier transition structure is obtained here.

The Concerted, C_1-Symmetric Pathway. If the first imaginary mode in $\mathbf{4^{•+}}$ is followed, the first-order saddle point $\mathbf{5^{•+}}$ shown in Figure 6 is obtained. $\mathbf{5^{•+}}$ is a true transition structure with one imaginary frequency corresponding to an asymmetric, bond-breaking mode of the terminal carbons. The length of the breaking carbon–carbon bond calculated at the UHF level of theory is substantially shorter in $\mathbf{5^{•+}}$ than in the C_2-symmetric transition structure $\mathbf{4^{•+}}$. The values calculated for $\mathbf{5^{•+}}$ by the DFT methods are essentially identical with the ones obtained for $\mathbf{4^{•+}}$, whereas the QCISD calculation predict a bond shortening by 0.05 Å. The carbon skeleton in $\mathbf{5^{•+}}$ is considerably less twisted than the one in either $\mathbf{4^{•+}}$ or the transition structure for the ring opening of neutral $\mathbf{1}$. The MO-based methods predict a dihedral angle of $\sim$13.5°, whereas the two DFT methods yield a value of $\sim$10.5°. Overall, the geometric and electronic structure of $\mathbf{5^{•+}}$ resembles that of a methylene radical attached to an allyl cation. The steric interactions between one of the terminal carbons and the hydrogen pointing inward lead to the calculated distortion from planarity and a decreased conjugation between the two moieties. It is also noteworthy that $\mathbf{5^{•+}}$ could not be located at the MP2 level of theory. All attempts to do so led to one of the structure $\mathbf{6^{•+}}-\mathbf{8^{•+}}$ discussed below.

The activation energies calculated for the C_1-symmetric pathway by the different methods are consistently lower by approximately 5 kcal/mol as compared with the C_2-symmetric pathway, thus providing an estimate for the energetic effect of the pseudo-Jahn–Teller distortion. Similar to the results obtained for $\mathbf{4^{•+}}$, the UHF method predicts the highest E_a and the BLYP calculations predict the lowest activation energy. These results are also in line with the findings for the ring opening of neutral $\mathbf{1}$. The Becke3LYP results are, again, very close to the QCISD(T)/QCISD values, establishing once more that hybrid DFT methods are an efficient and reliable alternative to the computationally much more demanding correlated MO method. The activation energies calculated at this level are in reasonable agreement with the experimental values of $\sim$16 kcal/mol measured for 3,3,4,4-tetramethyl-1,2-diphenylcyclobutene,[12] but much higher than the value of $\sim$7 kcal/mol obtained by mass spectroscopic techniques for $\mathbf{1}$.[9]

The Becke3LYP method was also used to follow the intrinsic reaction coordinate for the C_1-symmetric reaction pathway, shown in Figure 7. Since there are no state-symmetry constrains, the IRC now connects $\mathbf{5^{•+}}$ to the reactant $\mathbf{1^{•+}}$ and to *cis*-butadiene $\mathbf{2^{•+}}$. This confirms the importance of symmetry effects on the reaction. Because of the steric repulsion of the endo hydrogens, the reaction is less exothermic by 3.6 kcal/

(40) (a) Bischoff, P. *J. Am. Chem. Soc.* **1977**, *99*, 8145. (b) Compare also: Skanke, A. *J. Phys. Chem.* **1995**, *99*, 13886. (c) Olivella, S.; Sole, A.; Bofill, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2160 and literature cited therein.

(41) This is presumably also the reason for the presence of a third, weak imaginary frequency in the QCISD/6-31G* calculations.

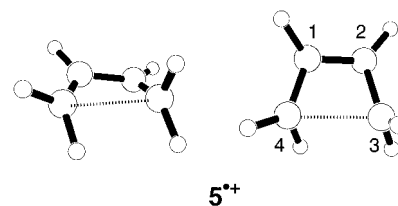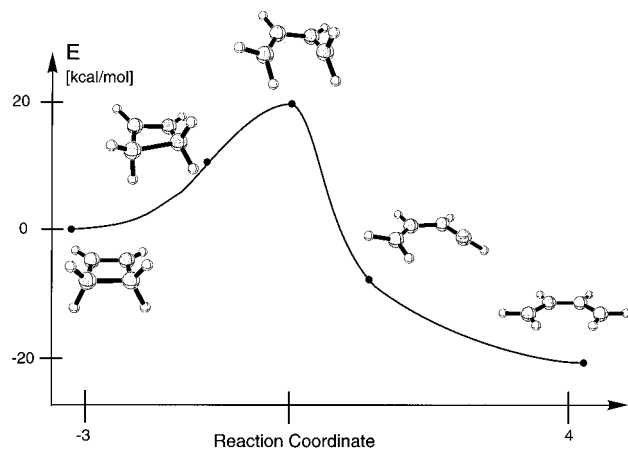(42) Deng, L.; Ziegler, T. *J. Phys. Chem.* **1995**, *99*, 612.

Figure 7. IRC calculation starting from **5•+**.

Table 5. Selected Data for the Stepwise Pathway Involving **6•+−8•+** (MP2/6-31G*)

	E_{rel} [kcal/mol]	R_{C1-C3} [Å]	R_{C3-C4} [Å]	$\varphi_{C1-C2-C3-C4}$ [deg]
6•+	18.0	1.716	2.394	80.6
7•+	17.4	1.693	2.553	98.2
8•+	21.4	1.885	2.529	69.6
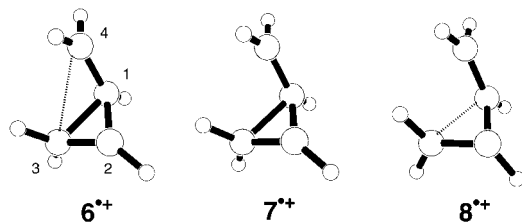
Figure 8. First transition structure **6•+** (left), intermediate **7•+** (middle), and second transition structure **8•+** (right) for the stepwise pathway.

mol, making **5•+** a slightly later transition structure than **4•+**. The IRC also shows that **5•+** enforces the conrotatory pathway observed experimentally, even though it lacks the C_2-symmetry element. This can be explained with the decreased steric repulsion for this mode of rotation. The disrotatory mode would lead to a closer contact between the two inward pointing terminal hydrogens, thus increasing the energy of the transition structure. Therefore, the experimentally observed stereochemistry can be attributed to steric rather than electronic factors in the transition structure.

The Stepwise, C_1-Symmetric Pathway. A C_1-symmetric, stepwise pathway for the ring opening of **1•+** was first suggested by Bellville et al.[43] and later supported by Bally and co-workers.[15] In this "nonelectrocyclic" pathway, **1•+** rearranges to a cyclopropylcarbinyl-type intermediate **7•+**,[44] which then opens to form **3•+**. By using UHF/6-31G* single-point calculations on geometries obtained by UHF/STO-3G and semiempirical MINDO/3 calculations, an activation energy of ~20 kcal/mol was obtained for this pathway.[43] The intermediate **7•+** and the two transition structures **6•+** and **8•+** connecting the intermediate to the reactant and the product, respectively, have been optimized at the MP2 level of theory. Selected results of these calculations are summarized in Table 5 and the structures **6•+−8•+** are shown in Figure 8.

The calculations yield a very product-like transition structure **6•+**, where the $C_3−C_4$ bond is essentially broken and the $C_1−$

C_3 bond has a length of 1.71 Å, i.e. it is almost completely formed. The exocyclic carbon C_4 in **6•+** is rotated out of plane by 80.6° into a bisecting conformation. This allows the interaction of the empty p-orbital at C_4 with the filled Walsh orbitals of the cyclopropyl ring, stabilizing the positive charge. The bisected conformation is therefore the most stable for all three structures **6•+−8•+**, and has been observed experimentally for a number of cyclopropylcarbinyl cations.[45]

The intermediate **7•+** is only 0.6 kcal/mol lower in energy than the transition structure **6•+**. The $C_3−C_4$ bond is fully broken, and the $C_1−C_3$ bond is 1.69 Å, only ~10% longer than a typical carbon−carbon single bond. This bond breaks in the rate-determining step to form **3•+**, involving transition state **8•+**, which is only 4 kcal/mol higher in energy than **7•+**. The geometry of **8•+** is, in accordance with the high exothermicity of 35.2 kcal/mol for the reaction of **7•+** to **8•+**, closely related to the structure of **7•+**. Similar to the Hartree−Fock results of Bellville et al., but in contrast to the semiempirical calculations, there is significant pyramidilization at C_2 in **6•+−8•+**, indicating that the radical character is localized at this center.[43]

The result that the hypersurface for the "nonelectrocyclic" pathway is extraordinarily flat, and that the intermediate lies in a very shallow minimum, raises some serious doubts about the existence of this minimum. Numerous attempts to locate **6•+− 8•+**, using any of the other methods discussed in this study, starting from either the MP2 optimized structures or those described by Bellville et al.,[43] have not been successful. Instead, the bicyclobutene radical cation was obtained as the only minimum. This, together with the geometries obtained for **6•+− 8•+**, shows that the species calculated for the "nonelectrocyclic" pathway result from the well-documented bias of either MP2 or minimum basis set Hartree−Fock calculations to overestimate the stability of localized radicals and distonic radical cations.[46] An analysis of the electronic structure of **6•+−8•+** indeed shows that the radical is mainly localized at C_2, whereas the positive charge is largely located at C_4. This favors the nonelectrocyclic species over the concerted pathways discussed above. It can therefore be concluded that the "nonelectrocyclic" stepwise mechanism involving a cyclopropylcarbinyl-like radical cation as an intermediate is not a viable pathway for the ring opening of **1•+** but an artifact of the bias of the computational methods used.

Conclusions

Three different mechanisms for the ring opening of the cyclobutane radical cation **1•+** have been studied with a variety of theoretical methods. The reaction is dominated by symmetry effects, which lead to state symmetry selection rules and a pseudo-Jahn−Teller distortion of the C_2-symmetric pathway. This enforces a concerted reaction mechanism with a C_1-symmetric transition structure. The stepwise mechanism proposed in the literature was found to be a result of the overestimation of the stability of localized radicals. Although further pathways are conceivable,[47] the results for the C_1-symmetric pathway presented here are in good agreement with the available experimental data.

The findings described here are further evidence that hybrid DFT methods are promising tools for the study of radical ion

(43) Bellville, D. J.; Chelsky, R.; Bauld, N. L. *J. Comp. Chem.* **1982**, *3*, 548.

(44) This intermediate has first been proposed for the decomposition of 1,3-butadiene: Russell, D. H.; Gross, M. L.; van der Greef, J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1979**, *101*, 2086.

(45) Childs, R. F.; Faggiani, C. J.; Lock, C. L.; Mahendran, M.; Zweep, S. D. *J. Am. Chem. Soc.* **1986**, *108*, 1692.

(46) E.g.: (a) Ma, N. L.; Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1992**, *193*, 386. (b) Houk, K. N.; Gonzales, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81.

(47) Prof. Bally kindly provided information about a computational study of alternative pathways performed in his laboratories.

and other open-shell reactions. The agreement of the DFT results with the available experimental data and with the QCISD-(T) calculations presented here indicates that these computationally efficient methods could also be used in future investigations of larger, chemically more realistic model systems of radical cationic pericyclic reactions.

The dominating influence of the electronic state on the outcome of the reaction has a number of interesting implications. Depending on the electronic state of a radical ion and the number of electrons involved in the bond reorganization process, the Woodward−Hoffmann rules and the state-symmetry selection rules may lead to opposite predictions about the stereochemistry of the reaction. This is the case for the ring opening the of 1,3-cyclohexadiene radical cation. Orbital-symmetry consideration predicts a disrotatory process, whereas the state-symmetry selection rules require a conrotatory process for the symmetry-preserving pathway. This opens the possibility to change the ring-opening mode of this reaction by using either thermal or electron transfer conditions. Furthermore, the increased stabilization of the radical cationic character in hexatriene is likely to revert the thermochemistry of the reaction. In addition, the preference of a C_1-symmetric pathway for the ring opening of $\mathbf{1^{•+}}$ is a consequence of the degeneracy of the orbitals in the C_2-symmetric transition structure $\mathbf{4^{•+}}$ and the resulting pseudo-Jahn−Teller effect. For substituted cy-clobutene radical cations, this effect should disappear and the transition structure might be closer to $\mathbf{4^{•+}}$. Investigations of the ring opening of 1,3-cyclohexadiene and 1,3,5-cyclooctatriene as well as various substituted cyclobutenes are currently in progress and will be reported in due course.

Supporting Information Available: Energies, zero-point energies, imaginary frequencies, and Cartesian coordinates of all structures reported (8 pages). See any current masthead page for ordering and Internet access instructions.

JA964334T