

Nature of Methyl and Silyl *Mesolytic* Dissociations in Substituted Cyclopropenyl Radical Cations and Anions. A CAS-MCSCF and CCSD(T) Theoretical Study

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Methyl- and silyl-cyclopropenyl radical charged systems are chosen to model the dissociative behavior of rigid and symmetric species. Dissociation of the radical cations in two fragments yields $c\text{-C}_3\text{H}_3^+$ and XH_3^+ moieties ($\text{X} = \text{C}, \text{Si}$), while, in the radical anions $c\text{-C}_3\text{H}_3^{\cdot-}$ and $\text{XH}_3^{\cdot-}$ fragments are produced. CAS-MCSCF C_s energy profiles show the presence of C–X bond cleavage saddle points in all four cases, separated from the resulting products by energy minima corresponding to electrostatic complexes. These features are retained in the coupled cluster C_s energy profiles, obtained by series of single-point calculations on CAS-MCSCF geometries, optimized at fixed C–X distances. However, at this theory level, the radical cation reactions are significantly more endoergic. The methyl system has a less unfavorable reaction energy than the silyl (16 vs 20 kcal mol⁻¹), and both saddle points prove to be slightly lower in energy than the dissociation limits (by ca. –4 and –2.5 kcal mol⁻¹, respectively). For the radical anions, a more pronounced endoergicity in the carbon case and a less unfavorable process for silicon are found (54 vs 39 kcal mol⁻¹). Moreover, while the C_s saddle point is lower in energy than the dissociation limit in the carbon case, it is higher for silicon (ca. –7 and +2 kcal mol⁻¹, respectively). It has to be pointed out, however, that even in the more endoergic radical anion fragmentations the process is easier than homolysis in the neutral parent molecules. The calculations carried out on C_s radical anions show the possible occurrence, in rigid systems, of real surface crossings, which open in principle the possibility of obtaining excited fragment products. However, it is clear that for more flexible systems a deformation of the structure along the dissociation pathway could generate a conical intersection. In this case the radical anions could certainly follow a lower-energy C_1 pathway in correspondence of an avoided crossing and bypass the real crossing.

Introduction

Organic radical cations and, less frequently, radical anions have been obtained by various methods from neutral precursors, and studied experimentally.¹ They can often undergo fragmentation into a radical and a charged species (Scheme 1).

Hyper- and hyponomers (these names designate species having one electron more or one electron less, respectively, than some precursor molecule)² are found to exhibit a more or less pronounced enhancement of reactivity (activation) with respect to their neutral parent molecules. For these processes, in which the cleavage of the weakened σ bond can have homolytic or heterolytic character, the word *mesolysis* has been proposed.³ Within

Scheme 1



a localized picture, the breaking σ bond is supposed to be weakened, and activated toward cleavage, by one extra electron or loss of one electron. Some possible ambiguity about the *formal* partitioning of (i) either two or three electrons (anion radical) or (ii) either two or one electrons (cation radical) pertaining to this bond seems to justify the introduction of a new word for this process.² Few theoretical studies on the cleavage of organic radical cations or anions have appeared so far. The following systems have been dealt with. The PhX radical anions, generated by $\text{Ph}^{\cdot} + \text{X}^{\cdot-}$ coupling ($\text{X} = \text{Me}, \text{F}^{\cdot-}, \text{Cl}^{\cdot-}$), that have been studied using the INDO and CNDO/2 methods.⁴ Then the C–C bond cleavage in $\text{PhEt}^{\cdot+}$ to give a benzyl cation and a methyl radical was studied by Hartree–Fock (HF)^{5a} and AM1^{5b} methods; in the latter paper the bibenzyl radical cation was also studied. Bond

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(1) Albini, A.; Mella, M.; Freccero, M. *Tetrahedron* **1994**, *50*, 575–607 (Tetrahedron Report No. 348) and references therein. Popielarz, R.; Arnold, D. R.; Du, X. *J. Am. Chem. Soc.* **1990**, *112*, 3068–3082. Arnett, E. M.; Venimadhavan, S. *J. Am. Chem. Soc.* **1991**, *113*, 6967–6975. Zhang, X.-M.; Bordwell, F. G.; Bares, J. E.; Cheng, J.-P.; Petrie, B. C. *J. Org. Chem.* **1993**, *58*, 3051–3059. Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 904–908. Ichinose, N.; Mizuno, K.; Otsuji, Y.; Tachikawa, H. *Tetrahedron Lett* **1994**, *35*, 587–590. Zhang, X.-M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2275–2279. Venimadhavan, S.; Amarnath, H.; Cheng, J.-P.; Arnett, E. M. *J. Am. Chem. Soc.* **1992**, *114*, 221–229. Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1992**, *114*, 9787–9792.

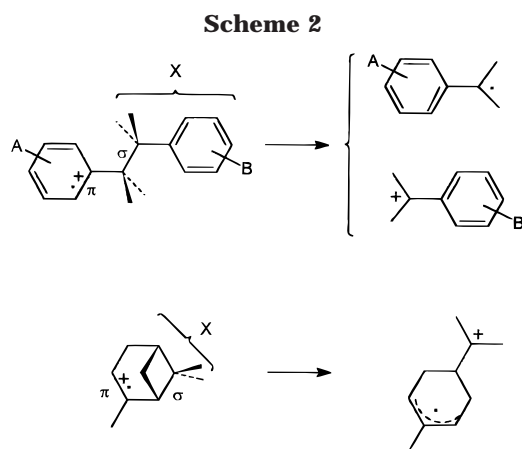
(2) Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193–6299 (Tetrahedron Report No. 280) and references therein.

(3) Maslak, P.; Vallombroso, T. M.; Chapman, W. H., Jr.; Narvaez, J. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 73–75 and references therein.

(4) Villar, H.; Castro, E. A.; Rossi, R. A. *Can. J. Chem.* **1982**, *60*, 2525–2527.

cleavage was also studied in the radical cations of 1-butene and 4,4-dimethyl-1-pentene by UHF optimizations followed by MP2 single-point calculations.⁶ Carbon-halogen bond breaking in radical anions has also been explored.⁷

The molecular systems studied experimentally are commonly made up by an aryl³ (or allylic)^{6,8} π subsystem, β to the σ bond involved in the fragmentation. This π subsystem is connected through the σ bond to another part of the molecule, X, which can be saturated as well as unsaturated (two examples of radical cation fragmentations involving aryl and allylic systems are shown in Scheme 2).



The purpose of the present study is to examine the nature of the C–C or C–Si σ bond cleavage process, which follows the generation of a radical cation (or anion) from a neutral precursor. The reasons for the “activation” observed in the hypo- or hypernomers with respect to their neutral precursors, as well as the differences in reactivity between the carbon and silicon cases, are analyzed in terms of (i) sign and magnitude of reaction energies and (ii) occurrence of avoided or real crossings of electronic states, taking place as the bond cleaves.

Method

The study of the model reactions discussed below was performed by determining, on the reaction energy hypersurfaces, the critical points corresponding to stable and transition structures. These were fully optimized using gradient optimization procedures⁹ at the CAS-MCSCF level of theory,¹⁰ with the polarized split-valence shell 6-31G(d)^{11a} and 6-31+G(d)^{11b} basis sets. This theory level is expected to take into account a large share of the structure-dependent (or nondynamical)

(5) (a) Takahashi, O.; Kikuchi, O. *Tetrahedron Lett.* **1991**, *32*, 4933–4936. Takahashi, O.; Morihashi, K.; Kikuchi, O. *Tetrahedron Lett.* **1990**, *31*, 5175–5178. (b) Camaioni, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 9475–9483.

(6) Du, X.; Arnold, D. R.; Boyd, R. J.; Shi, Z. *Can. J. Chem.* **1991**, *69*, 1365–1375. Arnold, D. R.; Du, X. *J. Am. Chem. Soc.* **1989**, *111*, 7666–7667.

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(8) Two recent papers deal with different cyclic radical cations. Bouchoux, G.; Alcaraz, C.; Dutuit, O.; Nguyen, M. T. *J. Am. Chem. Soc.* **1998**, *120*, 152–160. Herbertz, T.; Roth, H. D. *J. Am. Chem. Soc.* **1998**, *120*, 11904–11911.

(9) Schlegel, H. B. In *Computational Theoretical Organic Chemistry*; Csizmadia, I. G., Daudel, R., Eds.; Reidel Publ. Co.: Dordrecht, 1981; pp 129–159. Schlegel, H. B. *J. Chem. Phys.* **1982**, *77*, 3676–3681. Schlegel, H. B.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1984**, *80*, 1976–1981. Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214–218.

(10) Hegarty, D.; Robb, M. A. *Mol. Phys.* **1979**, *38*, 1795–1812.

correlation effects. In Figures 1–4 the optimum interatomic distances are reported in angstroms and angles in degrees. To obtain approximate reaction energy profiles (Figures 1–4) some extra points were defined by constrained optimizations in correspondence of fixed interfragment distances. Dynamic correlation effects on the reaction energetics were taken care of through a series of single-point coupled cluster calculations,¹² carried out for the cationic systems at the CCSD(T)/6-311G(d) level, and for all anionic systems at the CCSD(T)/6-311+G(d) level, within the default “frozen core” approximation (energy profiles in Figures 5 and 6). In these calculations CAS-MCSCF geometries were used, which had been obtained again by geometry optimizations with regard to fixed interfragment distances. All computations were executed by using the GAUSSIAN94 system of programs.¹³

Results and Discussion

The following points have been addressed, to which reference will be made in this Section.

(A) Is the estimate of the energy differences between the reactant and the resulting fragments sufficient to completely describe the dissociation process? Or will the expected intervention of an avoided crossing play an important role in contributing to the dissociation barrier and give rise to an energy overhead for the inverse process?

(B) Is it possible, in principle, not to obtain molecular fragments in their ground state?

(C) Fragmentation is expected to be more facile than in the neutral parent precursor for both cation and anion radicals: to which extent will it be activated by electron loss or gain?

(D) Which is the nature of the dissociation process in the hypo- and hypernomers? Do the wave function features in the vicinity of transition structure allow us to draw a comparison with typical homolytic or heterolytic processes taking place in neutral molecules?

A molecular model suitable to carry out the analysis of the cleavage process had to be chosen as simple as possible, having only one π bond and one σ bond in the β position, connecting a small X group (X = CH₃ or SiH₃):

(11) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294–301. (c) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4256–4266.

(12) (a) Coester, F.; Kümmel, H. *Nucl. Phys.* **1960**, *17*, 477. Cizek, J. *J. Chem. Phys.* **1966**, *45*, 650–654. Paldus, J.; Cizek, J.; Shavitt, I. *Phys. Rev. A* **1972**, *5*, 50–67. Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545–560. Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561–581. Cizek, J.; Paldus, J. *Phys. Scripta* **1980**, *21*, 251–254. Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359–401. Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910–1918. Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1988**, *89*, 7382–7387. Scuseria, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1989**, *90*, 3700–3703. (b) While CAS-MCSCF calculations are expected to provide qualitatively reliable geometries through the inclusion of a significant share of the structure-dependent (nondynamical) correlation energy, CCSD(T) energy evaluations should be more liable for assessing energy differences by inclusion of the dynamical contribution to the correlation energy. It must be prudently kept in mind, however, that performing single-point energy calculations, although usual, is in fact a rather rough probing of the higher-level energy hypersurface. This remark is particularly reasonable in the case of the transition structures.

(13) GAUSSIAN94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.;aghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. W.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

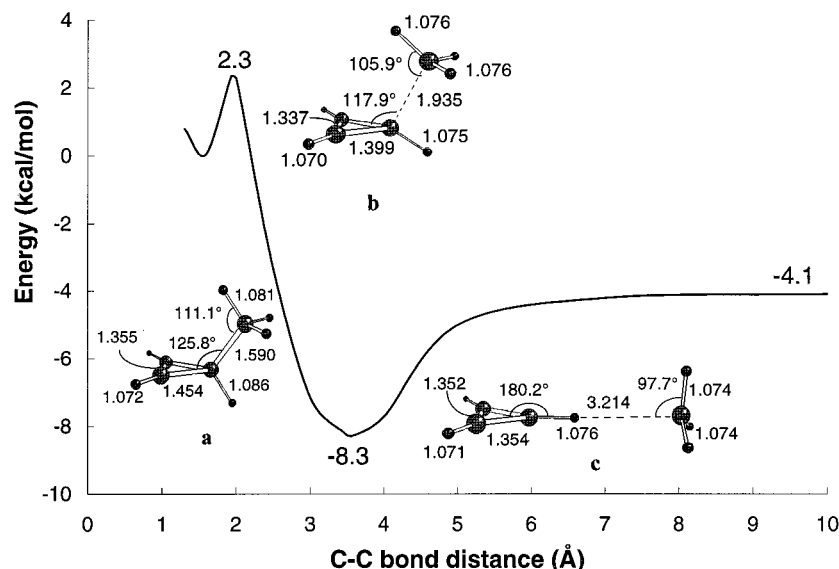
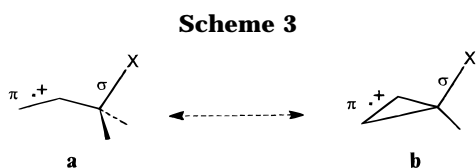


Figure 1. Dissociation energy profile for the methylcyclopropenyl radical cation (CAS-MCSCF theory level). Dashed line in the molecular structures: C¹-C "interfragment" distance.

this would turn out to be an X-substituted allylic system (in Scheme 3a a radical cationic system is shown).

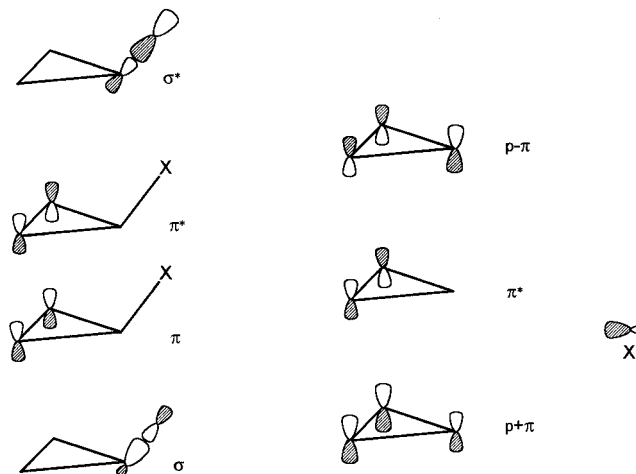


However, a model system similar to the allylic but endowed with a plane of symmetry (τ) has been set up in the present study to easily characterize as real crossings (between electronic states of different symmetry) interactions that would correspond to avoided crossings in systems of lower symmetry. How the overall picture so obtained could be altered in passing to open-chain systems will be explored in a subsequent paper. The symmetry was thus raised from C_1 (as in the allylic system) to C_s , by simply linking the C¹ and C³ atoms of the open system to yield a small cycle (Scheme 3b). The plane τ contains the central atom of X, the C¹ atom belonging to the cycle to which X is linked, and the midpoint of the C²-C³ bond.

Thus, the resulting systems are methyl- or silylcyclopropene (the neutral precursors); their hyponomers, methyl- and silylcyclopropenyl radical cations (**1** and **2**, respectively; numbers make reference to Figures 1 and 2); as well as their hyperomers, methyl- and silylcyclopropenyl radical anions (**3** and **4**; see Figures 3 and 4).

The active space chosen in the CAS-MCSCF calculations consists of those orbitals that are more directly involved in bond reorganization: the π and π^* system of the double carbon-carbon bond and the σ , σ^* system of the bond to be cleaved (the first one mixed to some extent to the last two in the reactants). This choice corresponds, for the separated products, to the three-orbital π system of the resulting cyclopropenyl system and to either the σ_X hybrid of the X⁻ moiety (X = CH₃, SiH₃), or the corresponding p orbital of the X[•] moiety (Scheme 4). In the C_s cyclic systems, all these orbitals are symmetric (S) with respect to the τ plane of symmetry, with the exception of π^* , which is antisymmetric (A). Thus, any

Scheme 4



electronic state characterized by configurations having either zero or two electrons in the π^* orbital will be obviously S, while those electronic states whose configurations have a single electron in π^* will be A.

The active space is common to the computations carried out on neutrals, radical cations, and radical anions: the only difference lies in the number of electrons that populate them, in all possible ways, providing a complete CI. The first set of calculations, carried out at the CAS-MCSCF level of theory, has the purpose of providing easily readable wave functions, apt to support a qualitative description and interpretation of the cleavage processes. As the CAS-MCSCF calculations take care only of nondynamical correlation effects, a better assessment of the energy differences is achievable at the coupled cluster level of theory.^{12b}

Fragmentation in the Radical Cations. (a) CAS-MCSCF Results. The fragmentation of methylcyclopropenyl radical cation (Figure 1, structure **1a**) proceeds through the transition structure **1b**. An ion-dipole electrostatic complex, corresponding to an association of the cationic cycle with methyl radical (**1c**), is found as a well-defined minimum on the energy hypersurface (the real importance of this intermediate could only be defined

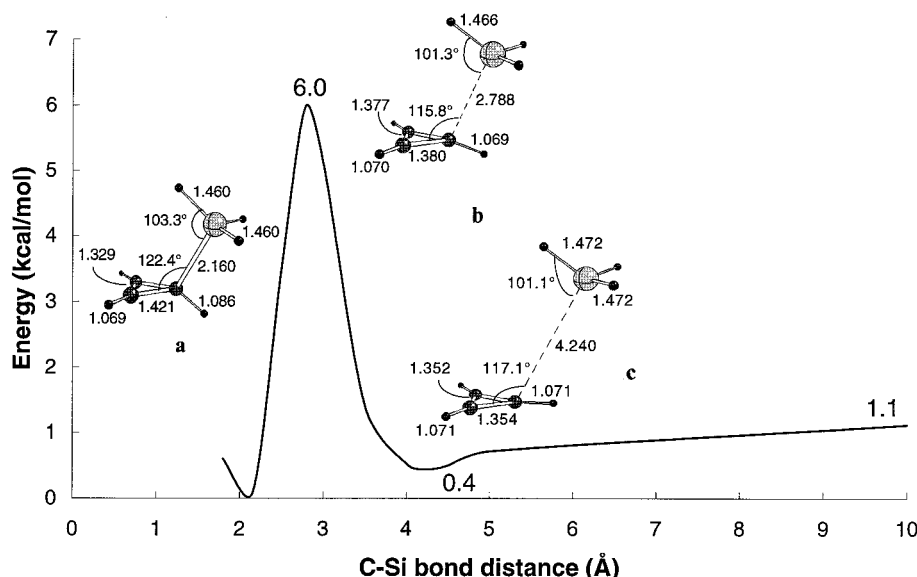


Figure 2. Dissociation energy profile for the silylcyclopropenyl radical cation (CAS-MCSCF theory level). Dashed line in the molecular structures: C¹-Si "interfragment" distance.

Table 1. Radical Cations. Total^a and Relative^b Energies of the Critical Points

X			CAS-MCSCF ^c		CCSD(T) ^d	
			<i>E</i>	ΔE	<i>E</i>	ΔE
CH ₃	reactant	1a	-154.578 931	0.0	-155.150 031	0.0
	TS	1b	-154.575 239	2.3	-155.131 530	11.6
	complex	1c	-154.592 124	-8.3	-155.132 882	10.8
	dissociation limit	1d	-154.585 338	-4.1	-155.124 945	15.7
SiH ₃	reactant	2a	-405.637 199	0.0	-406.169 341	0.0
	TS	2b	-405.627 661	6.0	-406.141 729	17.3
	complex	2c	-405.636 490	0.4	-406.142 940	16.6
	dissociation limit	2d	-405.635 403	1.1	-406.137 820	19.8

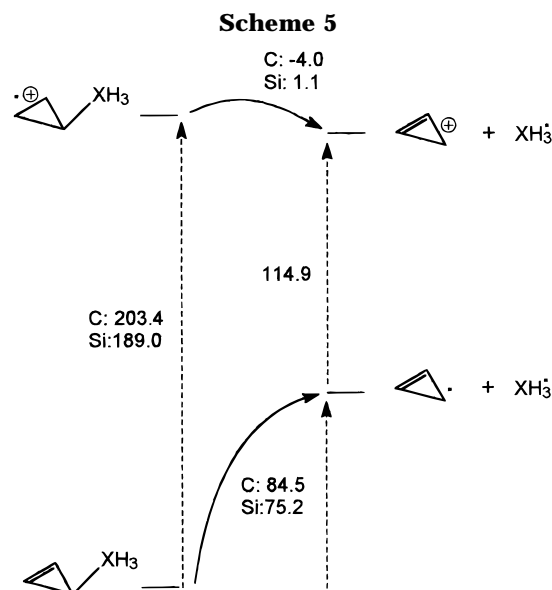
^a Hartree. ^b kcal mol⁻¹. ^c 6-31G(d) basis set. ^d 6-311G(d) basis set; the TS entries correspond to the maxima in the energy profiles.

by a molecular dynamics study). The analogous silicon system undergoes a similar evolution (Figure 2, structures **2a-c**).

CAS-MCSCF energies are collected in Table 1. Dissociation of the two hyponomers takes place by overcoming rather low energy barriers and is easier in methyl-substituted cyclopropenyl than in silyl (by 3.7 kcal mol⁻¹). The difference in barrier heights undoubtedly reflects to some extent the difference in reaction energies, as methyl dissociation is exoergic by 4.1 kcal mol⁻¹, while silyl dissociation is endoergic by 1.1. However, the energy profiles are obviously not entirely determined by the energy difference between the reactant and the two fragment products (point A). Indeed, the presence of an energy barrier in both cases clearly indicates the existence of an avoided crossing between the reactant and product states, which share the same symmetry and correspond to different bonding (spin coupling) situations. It is also apparent from these energy profiles that, even if the complex minima are disregarded, a barrier of 5–6 kcal mol⁻¹ for reassociation is present at this computational level. Moreover, given that reactant and products are related by an avoided crossing between states of the same symmetry, the lowest energy ground-state products are obtained (point B).

The CAS-MCSCF/6-31G(d) data reported in Tables 1 and 3 and displayed in Figures 1 and 2, show that both reactions are remarkably activated with respect to the similar homolytic process in the neutral systems (point C). Homolysis of methylcyclopropene and silylcyclopro-

pene requires very large energies: both dissociation profiles are entirely determined by the reaction energies and do not show a barrier for the inverse process. Considering the energetics of these dissociations, it can be seen, on one hand, that the hyponomers are higher in energy than the neutrals by a large amount (Scheme 5),

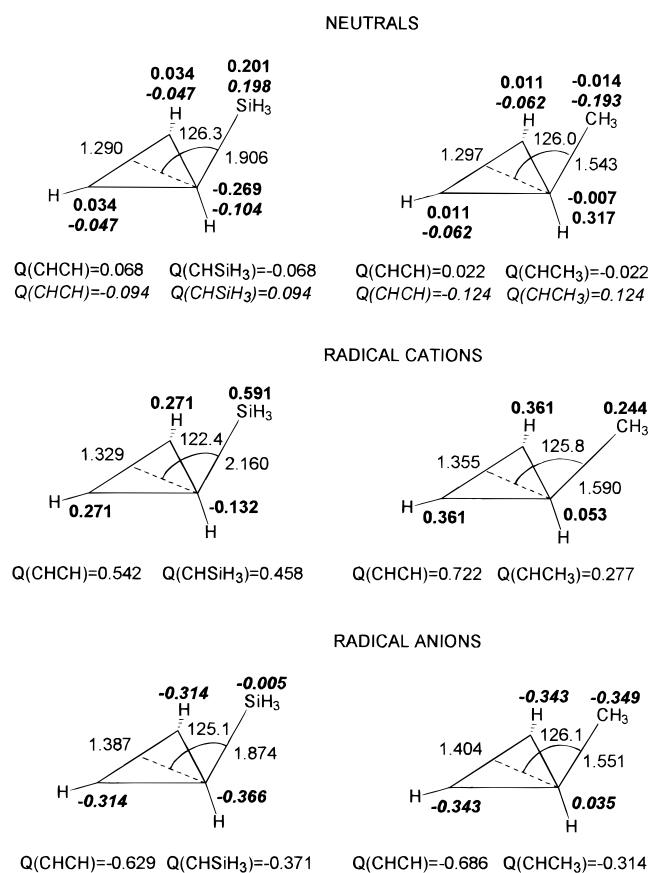


estimated, at the same computational level, as 203.4 kcal mol⁻¹ (methyl) and 189.0 kcal mol⁻¹ (silyl). On the other

hand, the dissociation limits (radical cations vs neutrals) are separated by 114.9 kcal mol⁻¹, i.e., by the energy difference between c-C₃H₃⁺ (a two-electron cycle) and c-C₃H₃[•]. Thus, an important contribution to cleavage activation comes from the fact that the reactant energy is raised by removal of one electron, but the cyclic product is destabilized to a lesser extent.

The silyl hyponomer is less destabilized than the methyl, with respect to the neutral, by ca. 14 kcal mol⁻¹. This characteristic of the reactants brings about a less advantageous dissociation energy for the silyl. The reason for this feature could be tentatively traced back to an energetically stabilizing hyperconjugative overlap between the singly occupied π_{CC} molecular orbital and the σ_{CSi} orbital of the bond to be cleaved. This effect implies some electron density transfer to the π_{CC} and is expected to be easier (from the point of view of the σ_{CX} energy levels involved) in the silicon case. It is revealed by a comparison of the geometrical characteristics of the two radical cations (Scheme 6). In the silicon radical cation,

Scheme 6



three prominent geometrical features can be discussed. (1) A slightly shorter central C²–C³ bond (–0.032 Å) with respect to its carbon analogue is observed. The C²–C³ bond length increases with respect to the relevant neutrals are 3% and 4.5% for the Si and C radical cations, respectively. Thus, the carbon radical cation reveals a more pronounced depopulation of the π_{CC} orbital. (2) A rather long C–Si bond is also observed. The elongation with respect to the neutral is +13%, while the analogous C–CH₃ distance undergoes only a 3% increase. This feature is complementary to the preceding one and indicates a larger electron density transfer, in the Si radical cation, from the σ_{CSi} molecular orbital to the π_{CC}

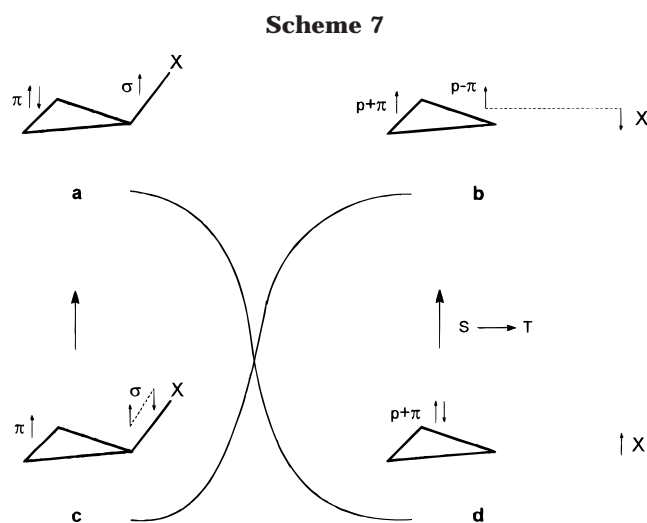
orbital. (3) The angle defined by the midpoint of the C²–C³ bond, C¹, and X, explicitly indicated in Scheme 6, concurs with its smaller value to emphasize the presence of a hyperconjugative overlap. Besides, group charges (bold numbers) provide complementary information, by showing in the silicon case a larger share of positive charge on the groups connected by the bond to be cleaved (below the structure, right), with respect to those connected by the original double bond (below the structure, left). It is interesting to note how this hyperconjugative effect, though implying an elongation of the bond to be cleaved, translates into some charge delocalization and a relative stabilization of the reactant. It can be anticipated that in the two radical anions, in which a π^*_{CC} is populated with an extra electron, this delocalization cannot be operative, because of the different symmetry of the π^*_{CC} orbital and the two orbitals pertaining to the σ_{CX} bond, which implies zero overlap (Scheme 6, bottom).

The analysis of the CI wave function (Ψ) can be carried out in terms of coefficients of the lowest eigenvector, or, equivalently, of populations of the active orbitals (γ_i). A single configuration dominates Ψ all along the reaction pathway in both cases (for instance, the highest coefficient is larger than 0.98 in both transition structures). These data are reflected in fractional populations γ_i rather close to 0, 1, and 2 for the four active orbitals (Scheme 4). For instance, in the transition structure **1b** $\gamma_1 = 1.953$, $\gamma_2 = 0.992$, $\gamma_3 = 0.032$, $\gamma_4 = 0.022$. Orbitals 1 and 2 are in-phase and out-of-phase combinations of π_{CC} and σ_{CX} orbitals and, at the transition structure, the electron distribution switches approximately toward a $\pi_{CC}^2\sigma_{CX}^1$ situation (cleavage of a singly occupied σ bond). This picture points out that the dissociation process, which can be formally thought of as homolytic, is basically different in nature (point D). Indeed, in the neutral molecules, changes in Ψ are significantly different from the radical cation case. In the C–X distance range 3.0–3.8 Å, two large coefficients are observed in the lowest CI eigenvector: they vary from –0.461 to –0.626 for one configuration and from 0.855 to 0.755 for the other. Correspondingly, the populations of the active orbitals vary in the ranges $\gamma_1 = 1.906$ –1.934, $\gamma_2 = 0.452$ –0.812, $\gamma_3 = 1.533$ –1.180, $\gamma_4 = 0.108$ –0.074. These data, which sharply contrast those for the radical cations, are typical of a homolytic process.

(b) Qualitative Discussion of the Avoided Crossings. Two factors concur to determine the barrier heights: the destabilization of the bonding situation of the reactants, which grows up in the first part of the reaction pathway, and the sign and magnitude of the reaction energy. Both are also expected to influence the earlier or later occurrence of the dissociation transition structures. Inspection of the energy profiles reported in Figures 1–6 reveals the extent to which their relative importance can be different in the cases just examined. The moderate CAS-MCSCF exothermicity of the methyl system **1** compares with the very modest endothermicity of the silyl system **2** (Table 1): the two reaction energies differ by 5 kcal mol⁻¹. Also, the difference between the two dissociation energy barriers is not large, less than 4 kcal mol⁻¹, whereas the barriers to reassociation differ by only 1.5 kcal mol⁻¹. On the whole, the energy profiles of the two radical cation reactions appear to be rather similar.

The origin of the reaction energy barrier can in both cases be essentially traced back mainly to the avoided

crossing of two electronic states of the reactant (or of the products). The nature of the two interacting states is the same in the C and Si cases and is determined by the bonding (spin coupling) in the reactant and products. Both states are symmetric with respect to the symmetry plane τ . The two-state scheme is obviously an approximation because more than two states of this symmetry are allowed to mix. The intended crossing is sketched in Scheme 7, in which the dominant configurations are



indicated for each state. The ground state of the reactant is shown in Scheme 7c: in the more important configuration two electrons populate the σ_{CX} orbital, while the π_{CC} orbital of the cycle is singly occupied. This state correlates (crossing curves in Scheme 7) with an excited state of the two resulting fragments (Scheme 7b), which can be described as the lowest triplet of the cyclopropenyl cation, coupled with the ground doublet of the methyl or silyl radical to an overall doublet (dashed lines symbolize spin coupling).¹⁴ The ground state of the products (Scheme 7d) corresponds to the cyclopropenyl cation (two electrons in the $p + \pi$ orbital) plus methyl or silyl radical (X). It correlates in turn, in a backward process, with an excited state of the reactant (Scheme 7a). In the more important configuration of this state two electrons are spin-coupled and populate the π_{CC} orbital, while a single electron populates the σ_{CX} orbital. The reactant excited state **7a** would need, to be generated from the ground state **7c**, a σ to π one-electron transfer, with spin recoupling (left vertical arrow). This implies that, as dissociation takes place, the increasing importance of the mixing of the two reactant states would translate into σ_{CX} bond depopulation. On the other hand, the product excited state **7b** can be generated from the ground state **7d** via a singlet ($p + \pi$)² to triplet ($p + \pi$)¹($p - \pi$)¹ excitation and spin recoupling (right vertical arrow).

The intended curve crossing just discussed is at the origin of the energy barrier, originated by the fact that

the crossing between these two reactant and product S states is avoided. One evident limit of the present discussion is that it plainly leaves out of consideration the stabilization brought about by state mixing along the reaction pathway. This stabilization concurs to determine the actual position and height of the energy maximum along the reaction energy profile. Both the excited state of the reagent (correlating with the ground state of the products) and the excited state of the products (correlating with the ground state of the reagent) are characterized by dominant configurations that can be seen, in either the C or Si case, as differing from the ground-state dominant configuration by promotion of a single electron. Also the reaction energy factor obviously concurs to determine the actual reaction energy profile (the lower barrier is found for the exoergic reaction, the higher for the endoergic; see Table 1), but, in determining the CAS-MCSCF energy profiles, it does not dominate. As will be presently seen in the subsection dealing with the coupled cluster results, dynamical correlation effects tend to emphasize the role of the reaction energies and provide a modified picture of the two dissociation energy profiles, characterized by a larger endoergicity. This is parallel to imagining the right-hand side of Scheme 7 dragged up at higher energies and strongly suggests that extending the present curve crossing scheme beyond the purpose of providing a simple qualitative analysis of the nature of the avoided crossing is not appropriate. The qualitative description of the changes in bonding situations due to the curve crossing is, however, still valid and superimposed to the reaction energy datum.

Fragmentation in the Radical Anions. (a) CAS-MCSCF Results. In contrast with the features of the radical cation dissociations just discussed, the ground state of both reactant radical anions is of symmetry different from that of the ground state of the product fragments. This is due to the different occupation of the π^* orbital in the reagent (one electron) and in the products (empty). As a consequence, if symmetry is strictly maintained, a real crossing occurs between the two electronic states, and fragmentation of the ground-state reactants cannot yield ground-state products. Therefore, two energy hypersurfaces were probed (Figures 3 and 4): one, labeled A (antisymmetric), contains the reactant as its lowest minimum point, from which methyl or silyl dissociation was studied; the other, labeled S (symmetric), is relevant to the ground-state products. On surface A, the fragmentation of methyl and silylcyclopropenyl radical anions (structures **3a** and **4a**) proceeds through the C_s maximum energy structures **3b** and **4b** (see Figures 3 and 4), which correspond to first-order saddle points in the C_s subspace and will be hereafter loosely called *transition structures*. The dissociation so described always preserves the C_s symmetry of the reacting system (energies reported under pathway A in Table 2). Again, past **3b** or **4b**, ion-dipole electrostatic complexes are found as well-defined minima on the energy hypersurface, corresponding to associations of the radical cycle with a methyl or silyl anion (structures **3c** and **4c**). At large distances the cyclic fragment is found to be in an excited state. On the other hand, the S pathway was explored starting from the two ground-state products at large distance and proceeding backward toward the reagent, with the purpose of defining the position of the curve crossing.¹⁵ The real crossing between

(14) Compare the configuration mixing scheme of Shaik and Pross, which is formulated in VB terms, e.g., in: Pross, A. *Theoretical and Physical Principles of Organic Reactivity*, John Wiley & Sons: New York, 1995; pp 109–121 (and references therein). Shaik, S. S.; Hiberty, P. C. *Adv. Quantum Chem.* **1995**, *26*, 99–163. See also, for instance: Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692–3701. Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1989**, *111*, 4306–4312. Shaik, S. S.; Dinnocenzo, J. P. *J. Org. Chem.* **1990**, *55*, 3434–3436. Shaik, S.; Reddy, A. C. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1631–1642. The description provided here derives, of course, from the results of the CAS-MCSCF calculations, which are in MO terms.

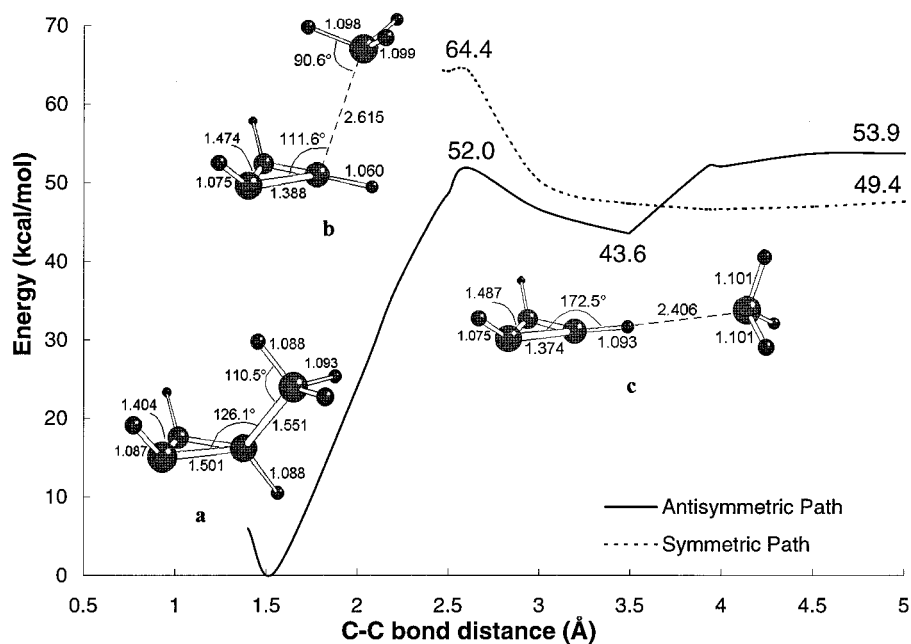


Figure 3. Dissociation energy profile for the methylcyclopropenyl radical anion (CAS-MCSCF theory level). Dashed line in the molecular structures: C¹-C "interfragment" distance.

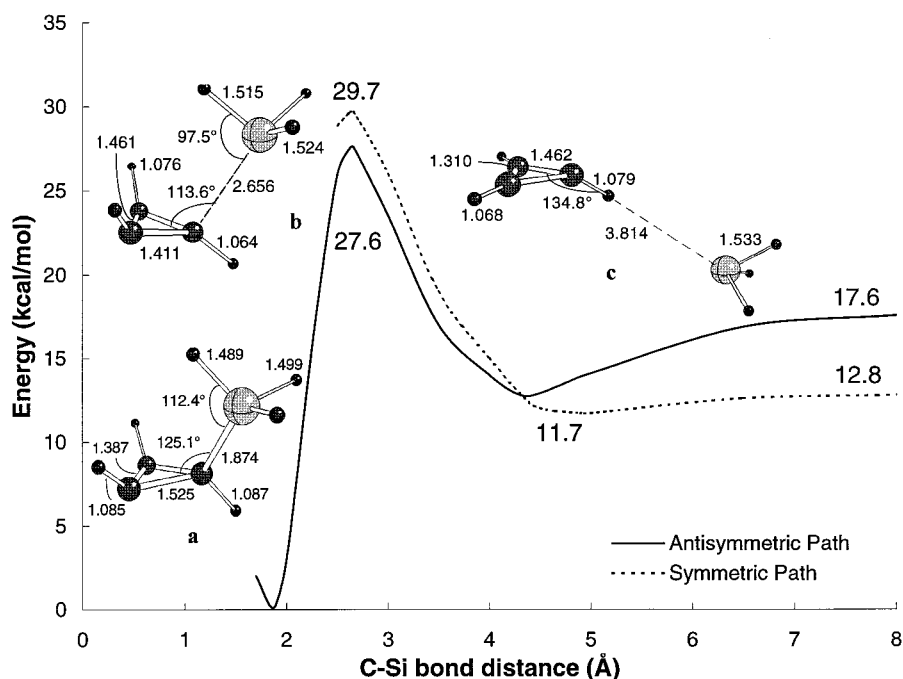


Figure 4. Dissociation energy profile for the silylcyclopropenyl radical anion (CAS-MCSCF theory level). Dashed line in the molecular structures: C¹-Si "interfragment" distance.

the A and S curves is found to occur past the A *transition structure* along the approximate dissociation coordinate.

The radical anionic systems show fragmentation energy barriers of much larger magnitude than the radical cations: 52.0 and 27.6 kcal mol⁻¹, for methyl and silyl dissociation, respectively (CAS-MCSCF/6-31+G(d) results, Table 2). In the methyl case, the A dissociation limit (separated from the *transition structure 3b* by the complex **3c**) is located at a higher energy than the

transition structure itself: 53.9 kcal mol⁻¹. In the silyl case, the A dissociation limit is much lower, and results lower than the *transition structure 4b*: 17.6 kcal mol⁻¹ (see point A at the beginning of the Results). The indication provided by this finding is that in some cases (sufficiently symmetric and rigid molecules) fragmentation could yield non-ground-state products (point B). However, if the symmetry were lowered to C₁, the lowest dissociation limit would be directly attained. This could occur either by operating a substitution, in which case the real crossing would simply become an avoided crossing, or through a deformation of the system along the dissociation pathway, in which case a conical intersection

(15) The reactant geometry in the excited S state was determined only with the 6-31G(d) basis set; with the addition of sp diffuse functions (6-31+G(d) basis set), the MCSCF procedure failed to converge in the reactant zone (distance < 2.4 Å).

Table 2. Radical Anions: Total^a and Relative^b Energies of the Critical Points

X			CAS-MCSCF ^c				CCSD(T) ^d	
			pathway A		pathway S		E	ΔE
			E	ΔE	E	ΔE		
CH ₃	reactant	3a	-154.800 368	0.0			-155.412 674	0.0 (A)
	TS	3b	-154.717 554	52.0	-154.697 698	64.4	-155.336 867	47.6 (A)
	complex	3c	-154.730 819	43.6	-154.725 853	46.8	-155.341 443	44.7 (A)
	dissociation limit	3d	-154.714 485	53.9	-154.721 663	49.4	-155.325 958	54.4 (S)
SiH ₃	reactant	4a	-405.852 745	0.0			-406.448 772	0.0 (A)
	TS	4b	-405.808 758	27.6	-405.805 354	29.7	-406.383 912	40.7 (A)
	complex	4c	-405.832 355	12.8	-405.834 140	11.7	-406.393 438	34.7 (A)
	dissociation limit	4d	-405.824 649	17.6	-405.832 274	12.8	-406.386 695	38.9 (S)

^a Hartree. ^b kcal mol⁻¹; relative to the ground-state reactant. ^c 6-31+G(d) basis set. ^d 6-311+G(d) basis set; the TS entries correspond to the maxima in the energy profiles.

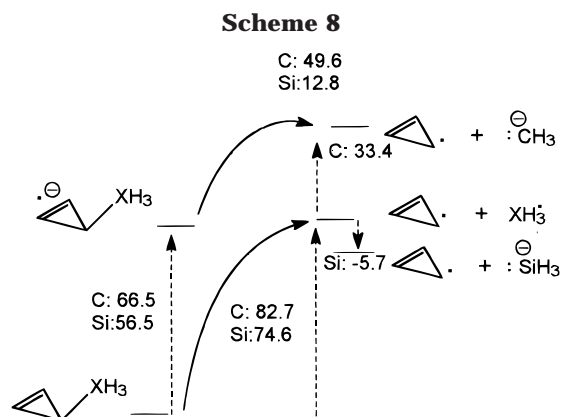
Table 3. Neutral systems. Total^a and Relative^b Energies of Reactants and Dissociation Limits

X			CAS-MCSCF/6-31G(d)		CAS-MCSCF/6-31+G(d)	
			E	ΔE	E	ΔE
CH ₃	reactant		-154.903 102	0.0	-154.906 332	0.0
	dissociation limit		-154.768 469	84.5	-154.774 578	82.7
SiH ₃	reactant		-405.938 402	0.0	-405.942 429	0.0
	dissociation limit		-405.803 839	84.4	-405.823 655	74.5

^a Hartree. ^b kcal mol⁻¹.

would be generated, and the real crossing could be consequently bypassed.¹⁶ If this case is contemplated, reference can be made, for the reaction energies, to the values of the S dissociation limit in the C_s case: these are 49.4 and 12.8 kcal mol⁻¹ for methyl and silyl dissociation, respectively.

The CAS-MCSCF/6-31+G(d) results reported in Tables 2 and 3, and displayed in Figures 3 and 4, show that also in the hypernomers the fragmentation reactions are activated with respect to the similar homolytic process in the neutral systems (point C). Homolysis of methylcyclopropene and silylcyclopropene requires, as already observed, a very large energy and does not show a barrier for the reassociation process (Table 3, rightmost columns). The hypernomers are higher in energy than the neutrals by 66.5 kcal mol⁻¹ (methyl) and 56.5 kcal mol⁻¹ (silyl), as illustrated in Scheme 8. These quantities are



about one-third of those calculated for the hypernomers. The dissociation limits are separated from the homolytic ones (neutrals) by 33.4 (methyl radical favored over methide) and -5.8 kcal mol⁻¹ (silide favored over silyl radical). The first result shows that the dissociation limit is destabilized by half the amount computed for the

reactant in passing from the neutral to the radical anion, leaving some 33 kcal in favor of the radical anion process. In the second case, almost 6 kcal mol⁻¹ are gained in having a silyl anion instead of the radical, and this quantity adds to the 56 relative to the reactants and favoring the radical anion process (Scheme 8). The process involving silicon is thus expected, on these grounds, to be easier than that involving carbon. Indeed, as in the case of the radical cations, the reactant energy is raised by addition of one electron but the fragmentation products are not as destabilized (in the case of C) or even stabilized to some extent (Si). This allows a more favorable energy balance and, therefore, contributes to cleavage activation. However, the two hypernomer dissociations are not activated to the extent of those involving the hypernomers. In the case of the radical anions, the contributions to dissociative activation coming from the gross reaction-energy differences are 33 kcal mol⁻¹ (C, 66-33 kcal mol⁻¹ from Scheme 8) and 62 (Si, 56+6 kcal mol⁻¹ from Scheme 8). These figures compare with the more favorable quantities estimated for the radical cations, 88 kcal mol⁻¹ for C (derived from 203-115 kcal mol⁻¹ from Scheme 5) and 74 kcal mol⁻¹ for Si (derived from 189-115 kcal mol⁻¹ from Scheme 5). In the case of the radical cations, differential destabilizations of reactant and products put C and Si almost on the same ground, in contrast with what is found for the radical anions, as only the contribution to activation for silyl is comparable to those of the radical cations.

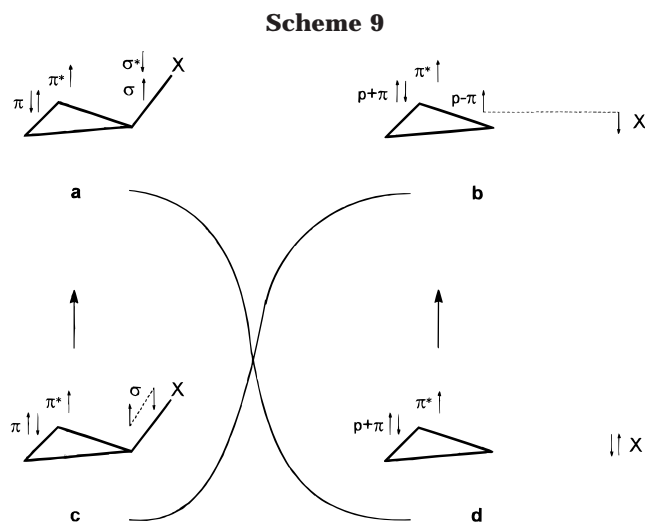
As was the case for the two radical cations, Ψ is dominated by one configuration all along the reaction pathway A in both cases (the highest CI eigenvector coefficient is larger than 0.97 in the two dissociation transition structures). The same is true for that part of the S surface that has been investigated in order to define the real crossing position.¹⁵ While the dominant configuration in the reactant has, as mentioned above, a single electron in the π^* orbital (A), in the ground-state cyclopropenyl radical the unpaired electron is located in the out-of-phase p- π combination (S) (Scheme 4). The fractional populations γ_i of the four active orbitals in the transition structures convey the same information. These

(16) Salem, L. *Electrons in Chemical Reactions. First Principles*; J. Wiley & Sons: New York, 1982; pp 141-143 and 148-151.

are, in the methyl dissociation A transition structure **3b** $\gamma_1 = 1.995$ (σ_{CX} , polarized toward X), $\gamma_2 = 1.924$ ($\pi_{CC} + \sigma^*_{CX}$, or, equivalently, $(\pi + p)$ out of phase with σ_X , the bonding hybrid on the X fragment), $\gamma_3 = 1.000$ (π^*_{CC}), $\gamma_4 = 0.081$ ($\pi_{CC} - \sigma^*_{CX}$, or, equivalently, $(p - \pi)$ out of phase with σ_X). Similarly, in the silyl dissociation A transition structure **4b**: $\gamma_1 = 1.989$, $\gamma_2 = 1.925$, $\gamma_3 = 1.000$, $\gamma_4 = 0.086$. These data contrast those for the homolytic dissociation of the parent neutral molecules, already discussed for the radical cations, and convey the information that the process basically shares the features of a heterolytic cleavage (point D).

(b) Qualitative Discussion of the Avoided Crossings. In the case of the methylcyclopropenyl radical anion the reaction energy determines the features of the reaction profile (Table 2). Even if the symmetry were broken and the lowest dissociation limit attained, the resulting overhead would only be ca. 2 kcal mol⁻¹. However, for the similar silylcyclopropenyl system the transition structure is higher in energy than the A dissociation limit by 10 kcal mol⁻¹, which would become ca. 15 if the S dissociation limit could be attained. Particularly for this last system, a qualitative discussion of the nature of the avoided crossing to which the energy barrier is related, similar to that elaborated for the radical cations, could be worthwhile. It will be developed with the same purpose and within the same limits mentioned in that subsection. Indeed, as will be discussed in the following subsection, dynamical correlation effects furnish again more endoergic dissociation profiles. Two cases will be contemplated: (1) dissociation in a rigid system, maintaining the C_s symmetry, for which only A configurations are considered (Scheme 9); and (2) breaking down of the symmetry constraint, resulting in the attainment of the lowest energy fragments (Scheme 10).

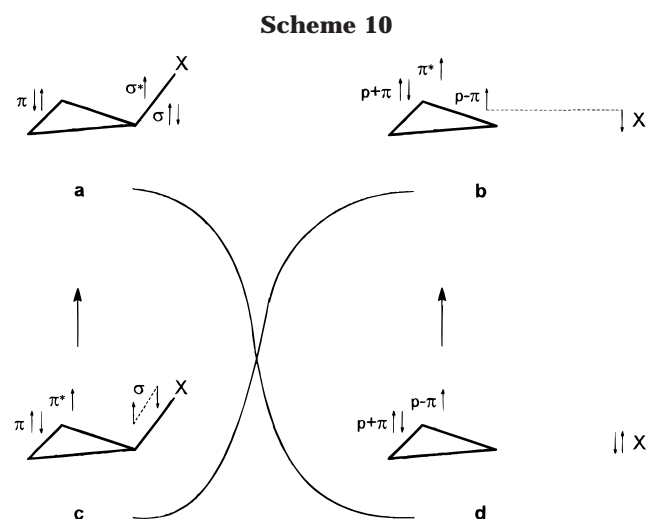
In the radical anion reactants one electron is always located in the π^*_{CC} orbital of the cycle (energy profile A). Thus, the reactant ground state (Scheme 9c) differs from



that of the radical cation (Scheme 7c) by having two more electrons, and the dominant configuration is $\pi_{CC}^2 \pi^*_{CC} \sigma_{CX}^2$ (A). The avoided crossing on the A surface is associated with two A states of the product fragments: both are excited states. The lower, as regards the cycle, has dominant configuration $(\pi + p)^2 \pi^{*1}$, as shown in Scheme 9d. The higher, which correlates with **9c**, can be described as the lowest triplet of the cyclopropenyl anion, coupled

with the ground doublet of the methyl or silyl radical to an overall doublet (Scheme 9b; dashed lines symbolize again spin coupling). The second excited state of the fragments is thus related to the first one through an electron transfer from $:XH_3^-$ to the $(p - \pi)$ orbital of the cycle, to get a four-electron π -system (right vertical arrow). Moreover, the cycle must be in a triplet state to allow the spin coupling between the two moieties, which is characteristic of the σ_{CX} bond involved in the cleavage (as depicted in **9c**). The remaining three electrons are spin-coupled in a way corresponding to the reactant three-electron π -system, found in correspondence of the double bond (Scheme 9c). On the other hand, the excited state of the reactant (Scheme 9a) that correlates with the lowest excited state of the products **9d** has, as more important configurations, $\pi_{CC}^1 \pi^*_{CC} \sigma_{CX}^2 \sigma^*_{CX}^1$ and $\pi_{CC}^2 \pi^*_{CC} \sigma_{CX}^1 \sigma^*_{CX}^1$ (only the last one indicated in Scheme 9). Therefore, the ground-state dominant configuration of the reactant **9c** needs to undergo a one-electron σ_{CX} to σ^*_{CX} or π_{CC} to σ^*_{CX} promotion to be transformed into **9a** (left vertical arrow).

If the symmetry were broken, and the lowest dissociation limit attainable, this excitation of the reagent would be substituted by a π^*_{CC} to σ^*_{CX} excitation (Scheme 10) to correlate with the lowest product state, whose dominant configuration in the cycle is $(p + \pi_{CC})^2 (p - \pi_{CC})^1$.



Final Assessment of the Energy Fragmentation Profiles. Although the CAS-MCSCF approach has the merit of providing results that allow a qualitative reading of the wave function and interpretation of the process underway, a quantitatively sound assessment of the reaction energetics is not to be expected. By taking into account only the structure-dependent correlation contribution, they seem to provide an unbalanced description of the separated fragments with respect to the reactant, although to different extents in the four cases studied in this paper.

(a) Coupled Cluster Results for the Radical Cations. The effects of dynamic correlation on the energies are large, and in both cases the cyclic reactant is much more stabilized than the products. The more important variation with respect to the CAS-MCSCF energy differences is displayed by reaction energies. A significantly more pronounced endothermicity results (by ca. +20 kcal mol⁻¹) in both methyl and silyl reactions. The reaction energy remains less unfavorable for the methyl system, by 4 kcal mol⁻¹. A series of single-point CCSD(T) calcula-

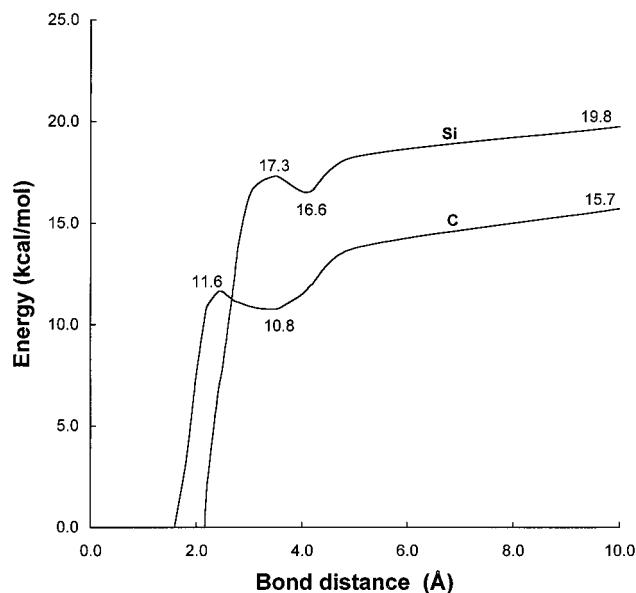


Figure 5. Dissociation energy profiles for the methyl and silyl cyclopropenyl radical cations (CCSD(T) theory level).

tions, performed on the CAS-MCSCF geometries obtained by constrained optimizations at several fixed interfragment distances, allowed us to define an approximate energy profile (Figure 5).

Both methyl and silyl radical cations still dissociate by passing through an energy maximum followed by an energy dip, which corresponds to an electrostatic complex between the two fragments. This is, however, encountered at larger distances than those corresponding to the CAS-MCSCF transition structures. The methyl maximum is at ca. 2.4 Å, while the CAS-MCSCF TS was encountered at a distance of 1.9 Å. That of the silyl profile is found at ca. 3.5 Å, to be compared with the 2.8 Å distance in the CAS-MCSCF TS. It is noteworthy that both these maxima lie below the dissociation limits. It is also to be observed that single-point calculations, if carried out on the critical point geometries alone, would completely miss the energy profile features.

(b) Coupled Cluster Results for the Radical Anions. In the radical anions, the effects of dynamic correlation on the energies are large in the silicon case, not much so for carbon, although the effect is in the same direction. The reaction energy was computed in both cases by taking the lowest dissociation limit as a reference, on the basis of the above considerations on the possible intervention of conical intersections.

Again, the cyclic reactant is more stabilized than the products, with an impressive increase in reaction energy (+26 kcal mol⁻¹) for the silicon dissociation. The reaction energy remains, however, less unfavorable for the silyl system, by more than 15 kcal mol⁻¹. As observed for the radical cations, an estimate of possible energy barriers (or their very detection) is possible only by drawing approximate energy profiles. These were defined as done for the cations. Both methyl and silyl radical anions dissociate by passing through energy sags corresponding to electrostatic complexes between the two moieties. Accordingly, this depression implies the existence of an energy maximum preceding it. This is encountered at larger distances than those corresponding to the CAS-MCSCF transition structures, as already observed for the radical cations. In fact, both maxima are found at ca. 3.0

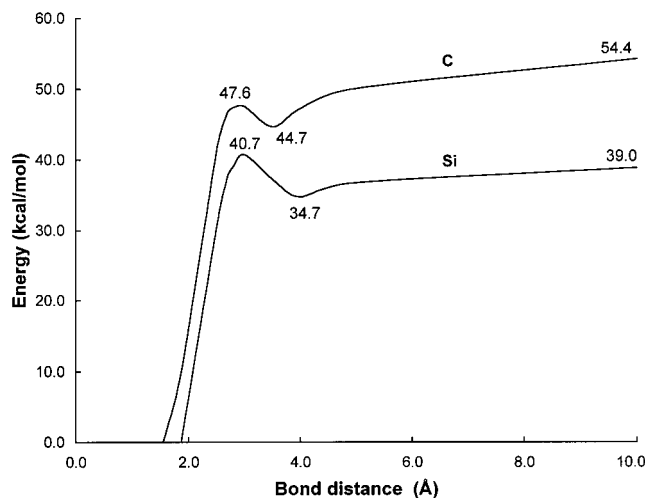


Figure 6. Dissociation energy profiles for the methyl and silyl cyclopropenyl radical anions (CCSD(T) theory level).

Å, while the CAS-MCSCF saddle points were encountered at a distance of 2.6 Å. It is notable that, while the methyl maximum lies some 6 kcal mol⁻¹ below the relevant dissociation limit, the silyl maximum is 1.7 kcal mol⁻¹ above. The role of dynamic correlation appears to be of the utmost importance in determining the overall description of all dissociation process.

Conclusions

This study, intentionally carried out on very simple and rather rigid systems, outlines how the questions raised at the beginning can be answered.

(A) The relative stabilities of neutral reactants and charged radical reactants, compared with the relative stabilities of the resulting fragments, can provide a reliable estimate of the more or less pronounced feasibility of the fragmentation process, but only if the role of avoided crossings giving a contribution to the energy barrier is modest. From the CAS-MCSCF data collected here it would appear that it cannot generally be so: a significant energy overhead for the inverse process is found in the majority of cases (the smallest is that of the carbon radical anion). However, the higher level coupled cluster calculations tend to minimize the role of avoided crossings, leaving reaction energies as a major factor. It is noted that dynamic correlation has consequences of variable importance: it heavily affects the reaction energies of both radical cations, as well as that of the silicon radical anion, but it provides just a small refinement to the value determined for the carbon radical anion. In all cases, energy maxima are present on the CCSD(T) profiles, due to the presence of a dip corresponding to a complex between the two fragments. Only in one case, that of the silicon radical anion, does the avoided crossing result in an energy barrier that is slightly above the dissociation limit. In summary, the final answer to question A can be that the energy difference between reactant and dissociated fragments is a major factor in the four cases considered.

(B) The study of methyl and silyl separation from methyl- and silylcyclopropenyl radical anions shows that it is possible, in principle, to obtain molecular fragments that are not in their ground state. This may occur if symmetry is preserved in sufficiently rigid systems

during the bond cleavage process. For more flexible systems, due to the presence of a conical intersection, the radical anions would follow a lower-energy C_1 pathway in correspondence of an avoided crossing, which would lead to the ground-state products.¹⁶

(C) Fragmentation is easier than in the neutral parent precursor not only for the cation radical (hyponomer) but also for the anion radical (hypernomer). This "activation" of the system toward bond cleavage occurs to different extents in the two cases. While gross activations of 88 and 74 kcal mol⁻¹ are estimated (at the CAS-MCSCF level) for methyl and silyl dissociations in the radical cations, on the sole basis of reaction energies, the related radical anions have analogous contributions to dissociative activation of 33 and 62 kcal mol⁻¹. On these data, the effect of the avoided crossings is at this level certainly superimposed.

(D) The analysis of the wave function at the transition structures indicates that the description of the cleavage

in the radical cations, although formally germane to a homolytic process, is at variance with this model. For the radical anions the process fundamentally reveals the characteristics of heterolytic cleavage.

How the overall picture obtained in the present paper could change in simple open-chain systems (as the allyl system shown in Scheme 3) will form the subject of a follow-up study.

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