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Molecular Orbital Calculations of Ring Opening of the Isoelectronic Cyclopropylcarbinyl Radical, Cyclopropoxy Radical, and Cyclopropylaminium Radical Cation Series of Radical Clocks

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Detailed molecular orbital calculations were directed to the cyclopropylcarbinyl radical (**1**), the cyclopropoxy radical (**2**), and the cyclopropylaminium radical cation (**3**) as well as their ring-opened products. Since a considerable amount of data are published about cyclopropylcarbinyl radicals, calculations were made for this species and related ring-opened products as a reference for **2** and **3** and their reactions. Radicals **1**−**3** have practical utility as "radical clocks" that can be used to time other radical reactions. Radical **3** is of further interest in photoelectron-transfer processes where the back-electron-transfer process may be suppressed by rapid ring opening. Calculations have been carried out at the UHF/6-31G*, MP4//MP2/6-31G*, DFT B3LYP/6-31G*, and CCSD(T)/cc-pVTZ//QCISD/cc-pVDZ levels. Energies are corrected to 298 K, and the barriers between species are reported in terms of Arrhenius E_a and log A values along with differences in enthalpies, free energies, and entropies. The CCSD(T)-calculated energy barrier for ring opening of **1** is $E_a = 9.70$, $\Delta G^* = 8.49$ kcal/mol, which compares favorably to the previously calculated value of $E_a = 9.53$ kcal/mol by the G2 method, but is higher than an experimental value of 7.05 kcal/mol. Our CCSD(T)-calculated E_a value is also higher by 1.8 kcal/mol than a previously reported CBS-RAD//B3LYP/6-31G* calculation. The cyclopropoxy radical has a very small barrier to ring opening (CCSD(T), $E_a = 0.64$ kcal/mol) and should be a very sensitive time clock. Of the three series studied, the cyclopropylaminium radical cation is most complex. In agreement with experimental data, bisected cyclopropylaminium radical cation is not found, but instead a ring-opened species is found. A perpendicular cyclopropylaminium radical cation (**4**) was found as a transition-state structure. Rotation of the 2p orbital in **4** to the bisected array results in ring opening. The minimum onset energy of photoionization of cyclopropylamine was calculated to be 201.5 kcal/mol (CCSD(T)) compared to experimental values of between about 201 and 204 kcal/mol. Calculations were made on the closely related cyclopropylcarbinyl and bicyclobutonium cations. Stabilization of the bisected cyclopropylcarbinyl conformer relative to the perpendicular species is much greater for the cations (29.1 kcal/ mol, QCISD) compared to the radicals (3.10 kcal/mol, QCISD). A search was made for analogues to the bicyclobutonium cation in the radical series **1** and **2** and the radical cation series **3**. No comparable species were found. A rationale was made for some conflicting calculations involving the cyclopropylcarbinyl and bicyclobutonium cations. The order of stability of the cyclopropyl-X radicals was calculated to be $X = CH_2 \gg X = O > X = NH_2^+$, where the latter species has no barrier for ring opening. The relative rate of ring opening for cyclopropyl-X radicals X = CH_2 to X = O was calculated to be 3.1×10^6 s^{-1} at 298 K (QCISD).

Introduction

The cyclopropylcarbinyl radical has fascinated chemists for some time, and it has also found an important place as a radical clock.[1−3] In the latter context, various radical processes can be clocked by the competition of direct reaction with the cyclopropylcarbinyl radical (k_t) and opening of the radical **1** to the 1-buten-4-yl radical (k_r) followed by trapping as shown in Scheme 1. Relative rates (k_t/k_r) can be determined from yields of 4-X-1-butene and cyclopropylcarbinyl products as a function of the radical trap (X−Y) concentration. Absolute rate constants have been determined for a number of radicals with various radical traps by laser flash photolysis methods.[4] From these absolute rate constants, reasonably accurate values of k_t in Scheme 1 can be estimated, and with the relative rate (k_t/k_r), a value for k_r can be calculated. From the calibrated radical-clock reaction rate (k_r), rates (k_t)

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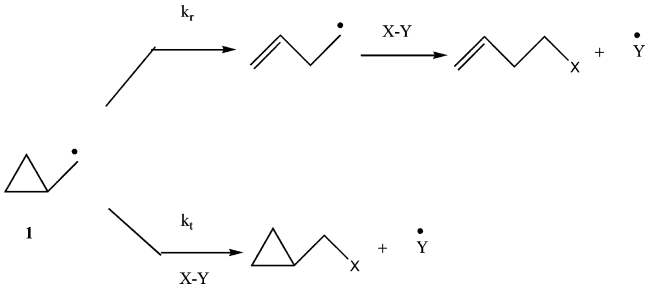
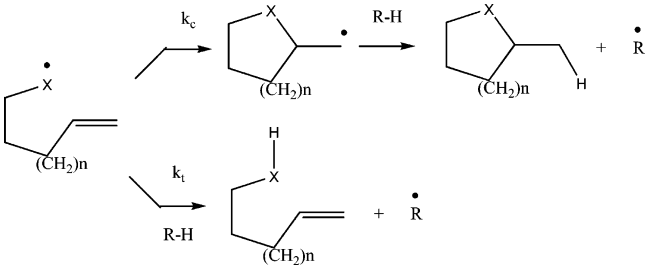
SCHEME 1



SCHEME 2

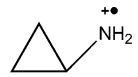


of other competing reactions involving **1** can be determined from relative rate data (k_t/k_r). A library of k_r for various substituted cyclopropylcarbinyl systems has been generated so that reactions covering a large span of k_t values can be determined.[2a,3,4] The radical-clock method provides an excellent means of determining lifetimes of various radicals and indeed if a radical process occurs. Of particular interest is the application to biooxidations such as those with non-heme monooxygenase,[5] methane monooxygenase,[6] and cytochrome P-450.[6ac,7]

In recent years there has been considerable interest in the synthetic application of radical cyclization reactions. Radical-clock studies have aided these synthetic strategies by providing rate constants (k_c) for various cyclization processes (Scheme 2). The rate of radical cyclization may be determined in a manner similar to that for ring opening by radical-clock methods. From k_t values estimated as described above and product ratios, rate constants of cyclization (k_c) have been determined for a variety of ring sizes and types of radicals.[8] Other useful radical clock molecules can be considered. For example, the cyclopropoxy radical (**2**), which is isoelectronically related to **1**, could be used to "clock" reactions involving alkoxy radicals. For example, the lifetime of the putative 1,4-dioxybutane biradical in the decomposition of 1,2-dioxetanes could be probed with such a clock molecule.[9] The radical clock **2** could also be used to study autoxidation reactions where alkoxy radicals are intermediates.[10] The 2,2-dimethylcyclopropoxy radical has been proposed as an intermediate in the mercuric acetate oxidation of 1-trimethylsiloxy-2,2-dimethylcyclopropane.[11]

2

A third molecule that is related isoelectronically to **1** and **2** is the cyclopropylaminium radical cation (**3**). Autoxidation and single-electron oxidation with tris(1,10-phenanthroline)iron(III) of *N*-phenylcyclopropylamine affected ring opening where a cyclopropylaminium radical cation is a possible intermediate.[12] It was pointed out that the ring-opening reaction could be of use in the study of heteroatom-oxidizing enzymes.[12] Photoinduced electron transfer, where the energy-wasting back-reaction is prevented, is of practical interest, for example, in photoimaging.[13] Rapid ring opening of radical cation **3** would avoid the energy-wasting back-reaction. During the course of this investigation, results from the photoionization of cyclopropylamine in the gas phase and calculations have provided evidence for **3** *not* being a minimum-energy species.[14] However, in another study, ESR spectra



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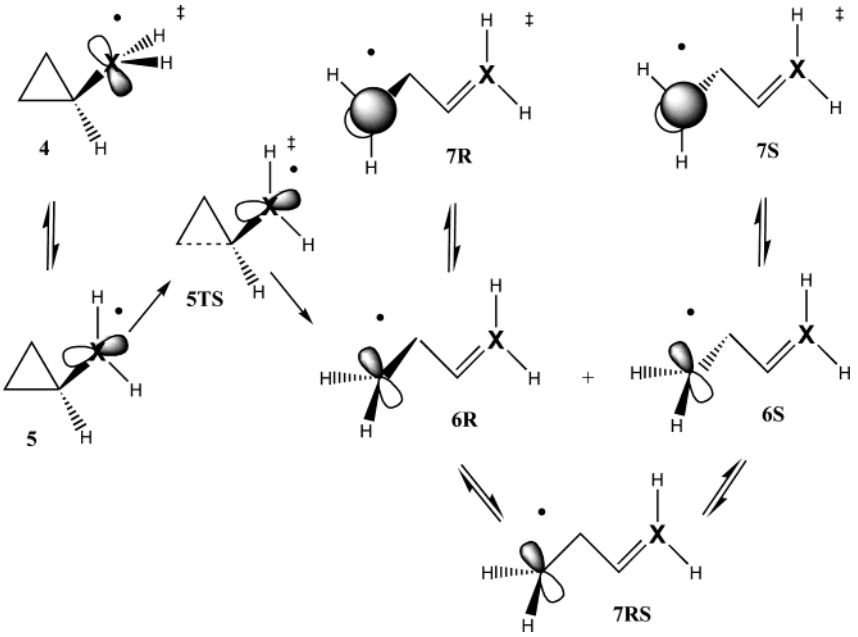
SCHEME 3

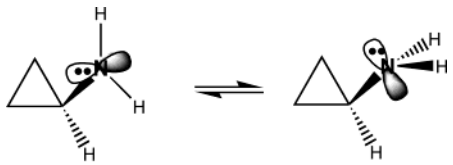


of cyclopropyldiisopropylamine and tricyclopropylamine radical cations were interpreted in terms of an intact cyclopropyl ring species.[15]

We set out to determine the viability of potential radical clocks **2** and **3** by computational methods. The ultimate goal would be to determine the lifetimes of these molecules. This entails a detailed knowledge of the potential energy surface near the transition state of the reaction.[16] To find the exact transition state is extremely computationally time-consuming, so we have settled for minimum-energy-path (MEP) activation energies. By this method the energy of the transition state is assumed to be the energy associated with the minimum-energy transition-state structure. From the MEP activation energies we can determine approximate relative rates for ring opening of molecules **1**−**3**. The reliability of the MEP method can be verified by comparison of calculated and experimental rates of ring opening of **1**.

Molecules on the reaction path for ring opening of **1**−**3** are given in general terms in Scheme 3, where XH_2 = CH_2, O, or NH_2^+, respectively. Two conformations of the cyclopropyl-XH_2 species are shown, where the 2p orbital bisects the cyclopropane (**5**) or is perpendicular to the ring (**4**). When XH_2 = O, structures **4** and **5** are equivalent. The transition-state structure **5TS** is shown leading to the lower energy *s-trans* acyclic enantiomers **6R** and **6S**. Calculations were not carried out for the higher energy *s-cis* enantiomers. The transition-state structures **7R** and **7S** represent rotation about the terminal $C_1(\bullet)-C_2$ carbon atoms for the particular enantiomer. Transition-state structure **7RS** represents rotation about the central C_2-C_3 bond and the barrier for racemization of **6R** and **6S**, which display axial chirality. Since **6R** and **6S** are enantiomers, their energies will be equal. Energies of enantiomers **7R** and **7S** will also be the same. Structure **7RS** is shown in Scheme 3 with idealized C_s symmetry. However, any deviation from this symmetry will produce *R,S*-enantiomers. The **7RS** designation was used for convenience even though C_s was not maintained. Calculations of the species in Scheme 3 for the cyclopropylcarbinyl radical (**1**) will be particularly useful to calibrate the results to experimental data[17] and other calculations.[18] Some time ago, calculations were made on the closure of radicals such as **6** (X = C and XH_2 = O) to the cyclopropane derivatives for comparison to experimental data.[19a] More recently, a CASSCF/6-31G* calculation was made on the cyclopropoxy radical.[19b] These results will be analyzed in light of our current calculations. To relate experimental photoionization of cyclopropylamine data to calculations of the species in Scheme 3 for X = NH_2^+, it was necessary to calculate the energies of the bisected and perpendicular conformers of cyclopropylamine, **3nb** and **3np**, respectively, in Scheme 4. From these two conformers, the vertical or Franck−Condon ionization energies of the corresponding radical cations related to **3** can be calculated and can be compared to the photoionization energy.

SCHEME 4



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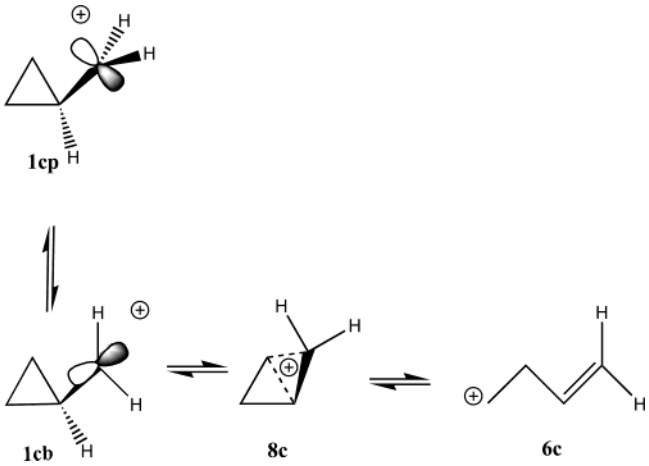
SCHEME 5



All three isoelectronic molecules **1**−**3** are related to the cyclopropylcarbinyl cation (**1c**) by possessing one additional electron. The particular species associated with **1c** are shown in Scheme 5, where **1cp** and **1cb** are the perpendicular and bisected cyclopropylcarbinyl cations, **8c** is the cyclobutonium cation, and **6c** is the homoallylic cation. The cyclopropylcarbinyl cations **1cp** and **1cb** and the cyclobutonium ion **8c** have a long history of experimental[20] and theoretical[21] studies. It is generally agreed that **1c** and **8c** are in rapid equilibrium along with **6c**. The lowest energy conformation of **1** is **1cb**, which is stabilized by overlap of the vacant 2p orbital with orbitals associated with the adjacent C−C bonds of cyclopropane.[21] Considering the relationship between these molecules and the isoelectronic series **1**−**3**, we wanted to compare calculated structures and relative energies. Since **1** and **2** are neutral, while **3** is positively charged, this provides an opportunity to compare the effect of charge on these properties.

Computational Methods

Ab initio molecular orbital calculations were carried out with the Gaussian suite of programs.[22] Typically, geometry optimizations were initiated at the HF or UHF level of theory with the 6-31G* basis set.[23] Higher level theory optimizations were started in each instance with the geometry of the preceding lower level of theory. In this manner, geometry optimizations were performed in the order MP2, DFT, and QCISD.[24] Single-point energies were determined at the MP4 level with MP2-optimized geometry and at the CCSD(T)[25] level with QCISD-optimized geometry. MP2 and MP4 calculations employed the 6-31G* basis set, while DFT used B3LYP/6-31G*. The QCISD and CCSD(T) methods used the Dunning double-ζ and triple-ζ basis sets cc-pVDZ and cc-pVTZ,[26] respectively. Spin-projected PMP2/6-31G* and PMP3/6-31G* energies were also calculated. Unless stated otherwise, the geometry optimizations were carried out in C_1 symmetry to avoid constraining the geometry. Frequency calculations were carried out at the MP2, DFT, and QCISD levels of theory and performed on all of the species to confirm convergence to appropriate local minima or saddle points on the energy surface. In all instances, transition-state structures gave one significant imaginary frequency,[27] while no significant imaginary frequencies were observed for the minimum-energy species. From the frequency calculations, corrections of the energy to 298 K were made, including zero-point energy corrections. Frequency calculations also provided entropies that were used to calculate log A and ΔS values. MEP Arrhenius activation barriers, enthalpies, and free energies are corrected to 298 K. Low frequencies were viewed in Molekel[28] for internal rotations. Contributions to internal rotations were subtracted from the thermal energy and entropy. Molekel was also used to view the imaginary normal-mode frequency associated with the transition-state structures. Absolute energies are available as Supporting Information (see below). From the absolute energies and the data mentioned above, the results are tabulated in the form of thermodynamic parameters.

Results and Discussion

Ring Opening of the Cyclopropylcarbinyl Radical. Thermodynamic parameters are calculated and given in Table 1 for the ring-opening reaction of **1** as outlined in Scheme 3, where X = C. Thermal energy differences (ΔE_T), which include the zero-point energy correction and heat capacity correction to 298 K, are also given in Table 1. There is a small amount of spin contamination as measured by $\langle S^2 \rangle$ at the UHF level, but at higher levels of calculation this either disappears or is insignificant (cf. the footnotes in Table 1). Agreement between the DFT, QCISD, and CCSD(T) methods for the thermodynamic data is satisfactory. Experimental activation parameters for ring opening of **5** are reported to be E_a = 7.05 kcal/mol and log A = 13.15,[17a,b] while in another study values of E_a = 7.26 kcal/mol and log A = 13.31 are reported.[17c] At the highest level of the calculations (CCSD(T)), the calculated Arrhenius activation energy is about 2 kcal/mol higher than the experimental values. The calculated log A value is also greater than the experimental values at higher levels of theory. The activation energy and log A are interdependent with regard to a least-squares fit of experimental data in an Arrhenius plot. This slope−intercept interdependence results in increasing E_a with increases in log A. For example, with the experimental rate constant, calculated

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TABLE 1. Thermodynamic Parameters for Species Involved in the Ring Opening of 1[a,e,f]

method	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	E_a	log A	ΔE_T
		5 → 4				
UHF	0.71	−3.27	1.68	1.30	12.51	0.54
MP2(PMP2)	1.72	−3.27[b]	2.70	2.31	12.51[b]	0.54[b]
MP4//MP2(PMP3)	1.35	−3.27[b]	2.33	1.94	12.51[b]	0.54[b]
DFT	2.97	−0.18	3.02	3.56	13.18	0.02
QCISD	2.51	−0.09	2.54	3.10	13.20	−0.01
CCSD(T)//QCISD	2.67	−0.09[c]	2.69	3.26	13.20[c]	−0.01[c]
		5 → 5TS				
UHF	10.02	−0.97	10.31	10.61	13.01	−1.54
MP2(PMP2)	8.58	−0.97[b]	8.87	9.17	13.01[b]	−1.54[b]
MP4//MP2(PMP3)	8.99	−0.97[b]	9.28	9.58	13.01[b]	−1.54[b]
DFT	7.96	2.08	7.34	8.55	13.67	−0.40
QCISD	9.84	2.08	9.22	10.43	13.67	−0.58
CCSD(T)//QCISD	9.11	2.08[c]	8.49	9.70	13.67[c]	−0.58[c]
		6R → 7R, 6S → 7S				
UHF	0.00	−1.70	0.51	0.59	12.85	−0.66
MP2(PMP2)	−0.14	−1.70[b]	0.36	0.45	12.85[b]	−0.66[b]
MP4//MP2(PMP3)	−0.36	−1.70[b]	0.15	0.23	12.85[b]	−0.66[b]
DFT	0.01	−2.86	0.86	0.60	12.60	−0.63
QCISD	−0.17	−2.86[d]	0.69	0.42	12.60[d]	−0.63[d]
CCSD(T)//QCISD	−0.14	−2.86[d]	0.71	0.45	12.60[d]	−0.63[d]
		6R, 6S → 7RS				
UHF	0.55	−4.45	1.88	1.14	12.25	−1.68
MP2(PMP2)	1.89	−2.96	2.77	2.48	12.57	−0.84[d]
MP4//MP2(SDTQ)	1.49	−2.96	2.37	2.08	12.57	−0.84[d]
DFT	1.28	−2.96	2.16	1.87	12.57	−0.84

method	ΔH	ΔS	ΔG	ΔE_T
	5 → 6R, 6S			
UHF	−5.25	2.51	−6.00	−0.45
MP2(PMP2)	0.00	2.51[b]	−0.74	−0.45[b]
MP4//MP2(PMP3)	−1.68	2.51[b]	−2.43	−0.45[b]
DFT	−2.06	6.31	−3.94	0.22
QCISD	−3.24	6.31[d]	−5.12	0.22[d]
CCSD(T)//QCISD	−3.41	6.31[d]	−5.29	0.22[d]

[a] Kilocalories per mole at 298 K. [b] UHF. [c] QCISD. [d] DFT. [e] Imaginary frequencies (IMAG) (cm^{-1}): **4** (−194,[c] −206,[d] −73[b]), **5** (none[b,c,d,g,h]), **5TS** (−696,[c] −595,[d] −741[b]), **6R**, **6S** (none), **7R**, **7S** (−161,[c] −140,[d] −188[b]), **7RS** (−131,[b] −129[d]). [f] $\langle S^2\rangle = 0.75$ for a pure doublet. Calculated values of $\langle S^2\rangle$: **4** (0.762,[b] 0.750[c,d,g,h]), **5** (0.766,[b] 0.750[c,d,g,h]), **5TS** (0.943,[b] 0.758,[c] 0.750,[d] 0.756,[g] 0.757[h]), **6R**, **6S** (0.774,[b] 0.750,[c,d,h] 0.755[g]), **7R**, **7S** (0.751,[c] 0.750[b,d,g,h]), **7RS** (0.799,[b] 0.751,[h] 0.750[d,h]). [g] PMP2. [h] PMP3.

from the experimental activation parameters, and using the calculated log A value of 13.67, E_a is calculated to be 7.78 kcal/mol from the Arrhenius equation. By normalizing the log A parameter to 13.67, the recalculated experimental E_a value is now lower than the calculated value by about 1 kcal/mol. In terms of rate constants, the experimental value calculated from the activation parameters falls between[17] 9.7×10^7 and 9.9×10^7 s^{-1} at 298 K, while the values calculated from CCSD(T) and DFT data are 1×10^7 and 2.5×10^7 s^{-1}, respectively. For calculations to be within 1 kcal/mol or a factor of 10 is considered to be excellent. Agreement between the current and previous calculations is also good. In one previous calculation on the ring opening of **1** up to the G2 level with a 6-31G* basis set, the reaction barrier was calculated to be 9.53 kcal/mol.[18a] At the QCISD/6-31G* level the barrier was reported to be 10.41 kcal/mol compared to our values of 9.84 kcal/mol at the QCISD/cc-pVDZ level and 9.11 kcal/mol at the CCSD(T)/cc-pVTZ//QCISD/cc-pVDZ level. The enthalpy of reaction for the bisected cyclopropylcarbinyl radical **5** (X = C) to the 1-buten-4-yl radical **6** (X = C) is in good agreement with

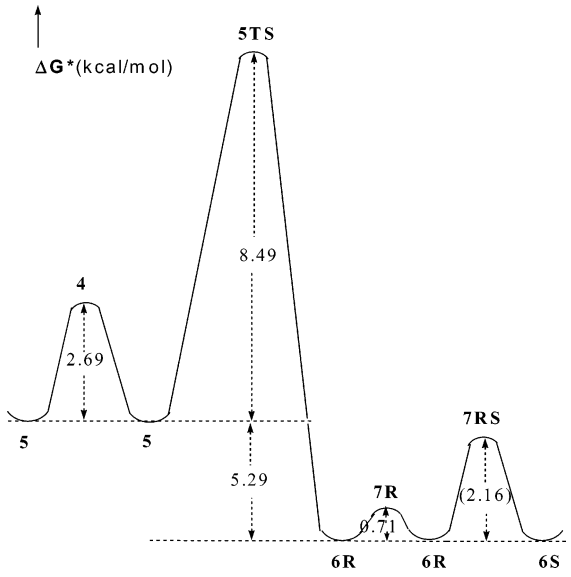


FIGURE 1. Energy diagram for the cyclopropylcarbinyl radical ring opening at the CCSD(T)/cc-pVTZ//QCISD/cc-pVDZ level, except for the **6R**, **6S** → **7RS** barrier, which is at the DFT level.

the previous calculations, which report a value of −2.96 kcal/mol at the G2/6-31G* level compared to our value of −3.41 kcal/mol at the CCSD(T)/cc-pVTZ//QCISD/cc-pVDZ level. In another study of the ring opening of **1**,[18c] the CBS-RAD method was used, which employs DFT B3LYP/6-31G* for geometry optimization and frequencies followed by a single-point energy calculation at the CCSD(T)/6-31G* level. This procedure[18c] gave somewhat better agreement with the experimental results. Compared to an experimental E_a value of 7.45 kcal/mol,[17a,b,18c] the CBS-RAD//B3LYP/6-31G* method gave 7.86 kcal/mol,[18c] while our B3LYP/6-31G* and CCSD(T)//QCISD/cc-pVDZ methods gave 8.36 and 9.69 kcal/mol, respectively, when all values were corrected to 0 K without zero-point corrections. The current calculations on the cyclopropylcarbinyl radical provide confidence for the calculations on the cyclopropoxy radical and the cyclopropylaminium radical cation as well as a link to experimental data. The energy diagram in Figure 1 summarizes the CCSD(T)/cc-pVTZ//QCISD/cc-pVDZ calculations for the cyclopropylcarbinyl radical ring opening. Geometries of the species in Figure 1 are given in Chart 1 at the QCISD/cc-pVDZ level. It is seen from the entries for **4** and **5** in Table 1 and in Figure 1 that there is a barrier to rotation about the $CH_2^{\bullet}-CH$ bond in the cyclopropylcarbinyl radical, where **4** is the transition-state structure for the rotation. The bisected radical **5** is then stabilized relative to the perpendicular radical **4**. This brings to mind the reported stabilization of the corresponding cationic species[21] and led us to calculate the rotational barrier between **1cp** and **1cb** in Scheme 5 at levels of theory comparable to those for the radical species. The results of these calculations are given in Table 2 along with those of **8c**. Chart 2 shows the geometries of these species at the QCISD/cc-pVDZ level. Agreement between the DFT and QCISD methods for the rotational barrier between **1cb** and **1cp** is excellent (Table 2). Frequency calculations (Table 2, footnote *c*) show that **1cp** is a transition-state structure while **1cb** is a minimum-energy species.

CHART 1

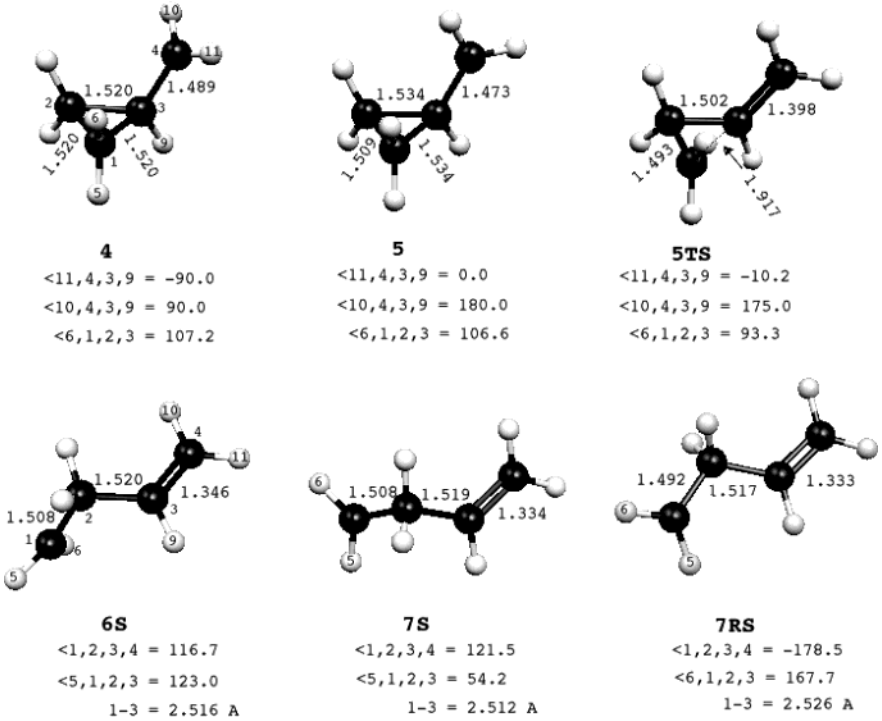


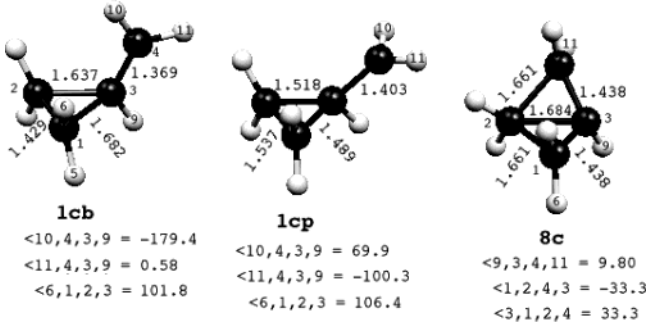
TABLE 2. Thermodynamic Parameters for 1cp, 1cb, and 8c[a,c]

method	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger\,b}$	$\Delta G^{\ddagger}$	E_a	log A	$\Delta E_T{}^b$
		1cb → 1cp				
MP2	33.21	−2.94	34.09	33.80	12.58	−2.94
MP4//MP2(SDTQ)	32.25	−2.94	33.12	32.84	12.58	−2.94
DFT	29.13	−2.94	30.00	29.72	12.58	−2.94
QCISD	29.07	−2.94	29.94	29.66	12.58	−2.94
method	ΔH	ΔS^b	ΔG			$\Delta E_T{}^b$
		1cb → 8c				
MP2	−1.30	−0.38	−1.19			0.46
MP4//MP2(SDTQ)	0.09	−0.38	0.20			0.46
DFT	1.96	−0.38	2.07			0.46
QCISD	0.50	−0.38	0.61			0.46
		1cp → 8c				
MP2	−37.91	2.56	−38.68			3.40
MP4//MP2(SDTQ)	−35.55	2.56	−36.32			3.40
DFT	−31.03	2.56	−31.80			3.40
QCISD	−31.97	2.56	−32.73			3.40

[a] Kilocalories per mole at 298 K. [b] DFT. [c] Imaginary frequencies (IMAG) (cm^{-1}): **1cp** (−662[b]), **1cp** (none[b]), **8c** (none[b]).

These two species have an interesting history. The bisected species was initially found to be at an energy minimum by frequency analysis at the HF/4-31G level.[29] The finding that **1cb** was a minimum-energy structure was supported by calculations at the MP2/6-31G* (6-31G**) level.[21e] An asymmetric bisected cyclopropylcarbinyl cation structure was also found in these two studies. Frequency analysis at the MP2/6-31G** level showed this species to be a transition-state structure, and it was proposed to link **1cb** to **8c**.[21e] The asymmetric bisected cyclopropylcarbinyl cation transition-state structure was located 0.5 kcal/mol above **1cb**.[21e] In another study, both the bisected structure **1cb** and the perpendicular structure **1cp** were found to have one imaginary frequency, which indicates both are transition-state structures.[21a] The energy difference between these two structures was reported to be 29.2 kcal/mol at the HF/6-311G** level at 0 K. This contrasts with our finding that **1cb** is a minimum-energy species while **1cp** is a transition-state structure. However, the reported[21a] energy difference between these structures is in good agreement with our calculations. The normal modes of the imaginary frequencies for **1cp** and **4** (X = C) are shown in Figure 2. The radical transition-state structure **4** involves rotation about the $C_1-CH_2^{\bullet}$ bond, while in **1cp** a 1,2-hydride shift to the carbinyl carbon atom is indicated with some rotation of the $C_1-CH_2^{+}$ bond. This normal mode vibration would lead to 1-methylcyclopropyl carbocation. We have not pursued a search for the transition-state structure that links the bisected cyclopropylcarbinyl cation (**1cb**) and **8c**. In previous studies[21d,e] an asymmetric bisected cyclopropylcarbinyl cation transition-state structure was located with an energy nearly the same as that of the bisected species corresponding to **1cb**. Exclusive of steric effects, **1cb** is stabilized relative to **1cp** by about 30 kcal/mol by the interaction of the 2p orbital with the orbitals of the adjacent C−C bonds in

CHART 2



(29) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5537.

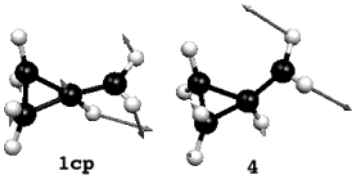


FIGURE 2. Normal mode of the imaginary frequency for transition-state structures **1cp** (−662 cm^{-1}) and **4** (X = C) (−206 cm^{-1}) at the DFT/B3LYP/6-31G* level.

the cyclopropane ring. Coming back to the cyclopropylcarbinyl radical, the corresponding stabilization is only about 3 kcal/mol as seen from Table 1 and Figure 1. This can be viewed as the difference in stabilization of a vacant 2p orbital compared to a singly occupied 2p orbital. A further comparison between the cyclopropylcarbinyl radical and the cation can be seen from geometries given in Charts 1 and 2. Changes in geometry between bisected and perpendicular species are most pronounced for the cations **1cb** and **1cp**. The cyclopropane ring of **1cb** is severely distorted where both the C_3-C_1 and C_3-C_2 bonds are lengthened at the expense of the C_1-C_2 bond. Some distortion of the cyclopropane ring is also seen in the perpendicular cationic species **1cp**. There is also a pronounced shortening of the C_3-C_4 bond in **1cb** compared to **1cp**. The distortions of the cyclopropane ring and shortening of the C_3-C_4 bond in **1cb** are consistent with stabilization of charge by interaction between the vacant 2p orbital of the methylene C_4 atom and the orbitals associated with the C_3-C_1 and C_3-C_2 cyclopropane bonds. Stabilization of the bisected cyclopropylcarbinyl cation along with geometric distortions has been studied and analyzed previously.[21a,30] In contrast to the cationic species, the radicals **4** and **5** (X = C) show little ring distortion or changes in the C_3-C_4 bond lengths, which is consistent with the small amount of stabilization of the bisected radical **5**. Spin densities in the HOMO support stabilization of **5**, where there is a small increase in spin density on the cyclopropane carbon atoms relative to those atoms in **4**. For the HOMOs of **4** and **5**, the spin densities from the DFT calculation are (**4**) (C_4) 0.116, (C_1) 0.016, (C_2) 0.016, and (C_3) −0.032 and (**5**) (C_4) 0.104, (C_1) 0.045, (C_2) 0.044, and (C_3) −0.032.

Ring Opening of the Cyclopropoxy Radical. Energies and thermodynamic parameters for the ring opening of **2** (Scheme 3, XH_2 = O) are given in Table 3. The energy barriers for ring opening of the cyclopropoxy radical **5** are in good agreement from MP2/6-31G* through CCSD(T)/cc-pVTZ methods. The UHF method, which is without electron correlation, shows considerable deviation from the higher level calculations. The spin-projected MP2(PMP2)/6-31G* method is clearly out of line from the higher level calculations where a negative activation barrier was found. Other thermodynamic parameters involving **5** and the MP2(PMP2) method are not out of line, so the problem is most likely in the MP2(PMP2) calculation of **5TS**. Although the transition-state structures show the largest spin contamination, $\langle S^2\rangle$ at the MP2(PMP2) level for **5TS** is 0.752 (cf. Table 3, footnote *h*). This is close to the theoretical expectation value of 0.750, so spin contamination does not seem a likely source of the discrepancy. A significant result of the cyclopropoxy ring opening is that the barrier is about 9 kcal/mol lower than that of the corresponding reaction for the cyclopropylcarbinyl radical at the higher level calculations. In fact, at the higher levels of theory, there is essentially no barrier for ring opening. Previous calculations at the MP3/6-31G*//UHF/3-21G[19a] and CASSCF/6-31G* [19b] levels show larger E_a barriers for ring opening of 3.6 and 2.8 kcal/mol at 0 K. It was pointed out by Houk and co-workers[19b] that "the CASSCF energies are known to lack some dynamic correlation, and therefore activation energies tend to be overestimated". In terms of the ring-closure reactions from species **6** and related conformers to **5TS**, in which Geise and coworkers[19a] were interested, they calculated the barrier for this closure reaction at 0 K to be about 15 kcal/mol for X = C and 19 kcal/mol for XH_2 = O in Scheme 3. Our calculations at the QCISD/cc-pVDZ level at 298 K give closure barriers of 13 and 16 kcal/mol, respectively, for X = C and XH_2 = O. Although the values of the barriers differ somewhat between the two calculations, the *difference* in the barriers is surprisingly close, i.e., 4 kcal/mol for the previous calculations[19a] and 3 kcal/mol for the current QCISD calculations.

Agreement is excellent between the DFT and QCISD methods for ring opening of **5** (XH_2 = O), where the calculated rate constants at 298 K are 5.2×10^{12} and 3.6×10^{12} s^{-1}, respectively. Another way of stating that the activation barrier is near zero is that the calculated rate

TABLE 3. Thermodynamic Parameters for Species Involved in the Ring Opening of 2[a,d,h]

method	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	E_a	log *A*	ΔE_T
			5 → 5TS			
UHF	4.93	1.45	4.50	5.52	13.54	−1.74
MP2(PMP2)	−3.44	1.45	−3.88	−2.85	13.54	−0.88
MP2(MP2)	0.70	1.45	0.27	1.29	13.54	−0.88
MP4//MP2(SDTQ)	0.75	1.45[b]	0.32	1.34	13.54[b]	−0.88[b]
DFT	0.30	0.68	0.09	0.89	13.37	−0.92
QCISD	0.71	0.68[c]	0.50	1.30	13.37[c]	−0.92[c]
CCSD(T)//QCISD	0.18	0.68[c]	−0.03	0.77	13.37[c]	−0.92[c]
			6R → 7R, 6S → 7S			
UHF	0.10	−0.05	0.11	0.69	13.21	−0.06
MP2(PMP2)	0.47	0.38[c]	0.35	1.06	13.30	−0.42[c]
MP2(MP2)	0.25	0.38[c]	0.14	0.84	13.30[c]	−0.42[c]
MP4//MP2(SDTQ)	0.50	0.38[c]	0.39	1.09	13.30[c]	−0.42[c]
DFT	0.65	0.38	0.53	1.24	13.30	−0.42
QCISD	0.20	0.38[c]	0.08	0.79	13.30[c]	−0.42[c]
			6R, 6S → 7RS			
UHF	−0.11	−1.57	0.36	0.48	12.88	−0.85
MP2(PMP2)	0.04	−0.34	0.14	0.63	13.15	−0.45
MP4//MP2(SDTQ)	0.07	−0.34[b]	0.17	0.66	13.15[b]	−0.45[b]
DFT	0.42	−1.13	0.75	1.01	12.97	−0.95

method	ΔH	ΔS	ΔG	ΔE_T
		5 → 6R, 6S		
UHF	−13.78	4.97	−15.26	−2.11
MP2(PMP2)	−15.90	3.59	−16.97	−1.46
MP4//MP2(SDTQ)	−15.83	3.59[b]	−16.90	−1.46[b]
DFT	−9.56	3.32	−10.55	−1.31
QCISD	−15.31	3.76	−16.43	−1.44
CCSD(T)//QCISD	−14.88	3.76[c]	−16.00	−1.44[c]

[a] Kilocalories per mole at 298 K. [b] MP2. [c] DFT. [d] Imaginary frequencies (IMAG) (cm^{-1}): **5** (none[c,e,f,g]), **5TS** (−535,[g] −428,[c] −749,[e] −622[f]), **6R**, **6S** (none[c,e,f,g]), **7R**, **7S** (−103,[e] −101,[c] −133[g]), **7RS** (−100,[c] −89[e]). [e] UHF. [f] PMP2. [g] QCISD. [h] $\langle S^2\rangle$ = 0.75 for a pure doublet. Calculated values of $\langle S^2\rangle$: **5** (0.778,[e] 0.750[c,f,g]), **5TS** (0.861,[e] 0.752,[f,g] 0.750[c]), **6R**, **6S** (0.763,[e] 0.750[c,f,g]), **7R**, **7S** (0.764,[e] 0.750[c,f,g]), **7RS** (0.764,[e] 0.750[c,f]).

(30) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 184.

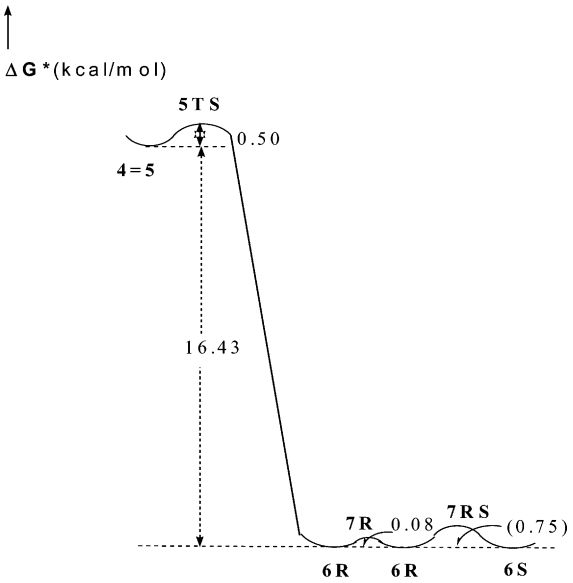


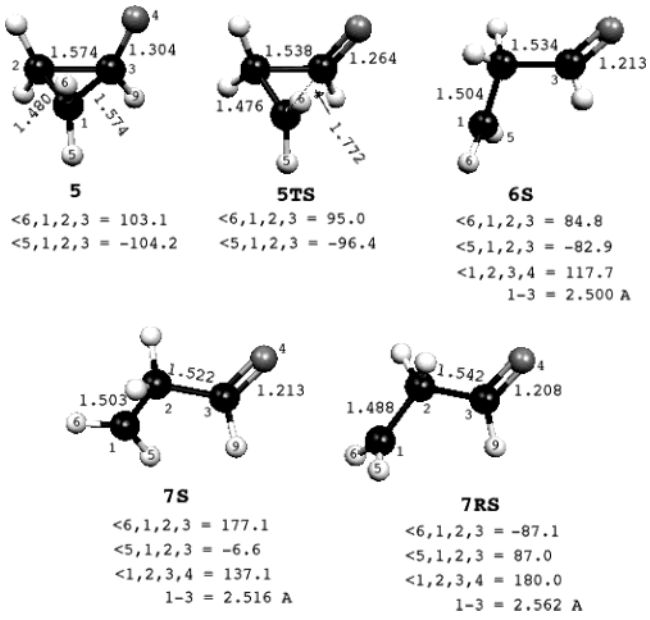
FIGURE 3. Energy diagram for the cyclopropyloxy radical ring opening based on the QCISD/cc-pVDZ calculation, except for the **6R** → **7RS** barrier, which is at the DFT level.

constants are approximately equal to the vibrational frequency associated with ring opening. This frequency from the QCISD calculation is −535 cm^{-1} (Table 3, footnote *d*) or a vibrational rate of 5.35×10^{12} s^{-1} or a lifetime ($\tau = 1/k$) of 2×10^{-13} s. Compared to the cyclopropylcarbinyl radical, the rate of ring opening for the cyclopropoxy radical is faster by a factor of 3.1×10^6 s^{-1} at 298 K (QCISD). The cyclopropoxy radical should then be an extremely sensitive radical clock and would be ideally suited to probing the question of a biradical intermediate in the decomposition of 1,2-dioxetanes. If such a 1,4-dioxybutane radical does exist in ring opening of 1,2-dioxetanes, it has a very short half-life.[9]

A qualitative argument can be made to rationalize the lower barrier of ring opening for the cyclopropoxy radical compared to the cyclopropylcarbinyl radical, namely, that a stronger π-carbonyl bond is forming in the transition state for ring opening of the oxy radical. The π-bond energy in ethylene is calculated to be 59.5 kcal/mol,[31] while that in formaldehyde is calculated to be 68.2 kcal/mol.[32] The energy diagram in Figure 3 summarizes the QCISD/cc-pVDZ calculations for the cyclopropoxy radical ring opening. Geometries of the species in Figure 3 are given in Chart 3 from the QCISD calculations.

Ring Opening of the Cyclopropylaminium Radical Cation. Data for species associated with the ring opening of cyclopropylaminium radical cation are given in Table 4. These calculations were initially somewhat perplexing to interpret, since there was not a correspondence between the species associated with the

CHART 3



cyclopropylcarbinyl and cyclopropoxy radicals. We have listed the species associated with the cyclopropylaminium radical cation with the same numbering as before for convenience, and the relationships between the species will be discussed as we proceed.

At the MP2 level of theory, **5** and **6** have different energies and would appear to be different species. For example, the C_3-C_1 bond distance at the MP2 level is 1.707 Å in **5**, while it is 2.343 Å in **6**. The unusual C_3-C_1 bond distance in **5** is unique to the MP2 calculations, since at the UHF level, the bond distance is 2.433 Å in **5**. In the DFT calculations, **5** converges to **6** even though the geometry optimization of **5** was started with the MP2-optimized geometry. In the DFT calculations the C_3-C_1 bond distance in **6** is 2.264 Å. In a similar manner, **5TS** converges to **7R** (**7S**) at the MP2, MP4, and DFT levels. On the basis of the higher level calculations, we conclude that only species **4**, **6R**, **6S**, **7R**, **7S**, and **7RS** are unique species in the cyclopropylaminium radical cation series. Transition-state structure **7R** (or **7S**) represents rotation about the C_1-C_2 bond, while transition-state structure **7RS** represents rotation about the C_1-C_3 bond. The energy barrier for **5** (**6**) → **5TS** (**7R** or **7S**) in Table 4 is positive in E_a at the MP2/6-31G* level, but negative in $\Delta G^{\ddagger}$ (−0.31 kcal/mol). The MP4//MP2-6-31G* barrier is even more negative. Spin contamination should not be the cause of the erroneous negative activation energies, since $\langle S^2 \rangle$ is 0.750 (pure doublet) for the MP2 and MP4 calculations (cf. Table 4, footnote *h*). At higher levels of theory, this energy barrier is positive.

As mentioned in the Introduction, photoionization of cyclopropylamine has provided experimental data for comparison to calculations in the cyclopropylaminium radical cation series.[14] For this reason, calculations were made on the bisected (**3nb**) and perpendicular (**3np**) cyclopropylamine conformations. Photoionization of cyclopropylamine will be subject to the Franck−Condon principle,[34] where a vertical energy transition occurs

(31) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 63.

(32) The π-carbonyl bond energy was calculated by a method similar to that in ref 31 for the π-bond energy of ethylene. The heat of the reaction methoxy radical to formaldehyde and hydrogen atom is calculated to be 36.2 kcal/mol by the group additivity method of Benson.[31] With this value and the O−H bond dissociation energy of methanol of 104.4 kcal/mol,[33] one obtains 68.2 kcal/mol for the π-carbonyl bond energy in formaldehyde.

(33) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(34) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; p 45.

TABLE 4. Thermodynamic Parameters for Species Involved in the Ring Opening of 3[a,g,h]

method	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	E_a	log A	ΔE_T
		5 (6)[e] **→ 4**				
UHF	26.25	−2.21[b]	26.90	26.84	12.74[b]	−1.19[b]
MP2(PMP2)	20.65	−2.21	21.31	21.24	12.74	−1.19
MP4//MP2(SDTQ)	17.60	−2.21[b]	18.26	18.19	12.74[b]	−1.19[b]
DFT	19.74	−2.64	20.53	20.33	12.64	−1.46
QCISD	22.88	−2.64[c]	23.67	23.47	12.64[c]	−1.46[c]
CCSD(T)	22.77	−2.64[c]	23.56	23.36	12.64[c]	−1.46[c]
		5 (6)[e] **→ 5TS (7R** or **7S)**[f]				
UHF	1.13	2.17	0.48	1.72	13.69	−1.19[b]
MP2(PMP2)	−0.31	2.17	−0.96	0.28	13.69	−1.19
MP4//MP2(SDTQ)	−3.70	2.17[b]	−4.35	−3.11	13.69[b]	−1.19[b]
MP4//MP2(PMP3)	−3.25	2.17[b]	−3.90	−2.66	13.69[b]	−1.19[b]
DFT	3.28	1.38	2.87	3.87	13.52	−1.17
QCISD	1.21	0.33	1.11	1.80	13.29	−0.31
CCSD(T)	1.33	0.33[d]	1.23	1.92	13.29[d]	−0.31[d]
		6R → 7R, 6S → 7S				
UHF	4.25	1.43[b]	3.82	4.84	13.53[b]	−0.94[b]
MP2(PMP2)	3.91	1.43	3.48	4.50	13.53	−0.94
MP4//MP2(SDTQ)	3.85	1.43[b]	3.42	4.44	13.53[b]	−0.94[b]
MP4//MP2(PMP3)	3.65	1.43	3.22	4.24	13.53	−0.94[b]
DFT	3.28	1.38	2.87	3.87	13.52	−1.17
QCISD	1.21	0.33	1.11	1.80	13.29	−0.31
CCSD(T)//QCISD	1.33	0.33[d]	1.23	1.92	13.29[d]	−0.31[d]
		6R, 6S → 7RS				
UHF	2.59	2.26[b]	1.92	3.18	13.71[b]	2.02[b]
MP2(PMP2)	4.91	2.26	4.24	5.50	13.71	2.02
MP4//MP2(SDTQ)	4.64	2.26[b]	3.97	5.23	13.71[b]	2.02[b]
MP4//MP2(PMP3)	4.41	2.26[b]	3.73	5.00	13.71[b]	2.02[b]
DFT	4.48	3.14	3.54	5.07	13.91	−0.45

method	ΔH	ΔS	ΔG	ΔE_T
	5 (6)[e] **→ 6R, 6S**			
UHF	−1.90	0.74[b]	−2.12	−3.17[b]
MP2(PMP2)	−4.22	0.74	−4.44	−3.17
MP4//MP2(SDTQ)	−7.55	0.74[b]	−7.77	−3.17[b]
DFT	0.00	0.00	0.00	0.00
QCISD	0.00	0.00	0.00	0.00
CCSD(T)	0.00	0.00	0.00	0.00
	5TS (7R or **7S)**[f] **→ 7R,7S**			
UHF	1.22	0.00[b]	1.22	0.00[b]
MP2(PMP2)	0.00	0.00	0.00	0.00
MP4//MP2(SDTQ)	0.00	0.00[b]	0.00	0.00[b]
DFT	0.00	0.00	0.00	0.00
QCISD	0.00	0.00	0.00	0.00
CCSD(T)	0.00	0.00	0.00	0.00
	5 (6)[e] **→ 5** (C_s)			
QCISD	7.98	−3.97[g]	9.17	0.02[g]

[a] Kilocalories per mole at 298 K. [b] MP2/PMP2. [c] DFT. [d] UHF. [e] See the text; **5** when optimized in C_1 symmetry merges to **6**. If C_s symmetry is used, a transition-state structure is produced as seen by one imaginary frequency. [f] See the text; **5TS** merges to **7R** or **7S**. [g] Imaginary frequencies (IMAG) (cm^{-1}): **4** (−374,[i] −765,[c] −618[b]), **5** (none[b,c,d]), **5** (C_s) (−261[i]), **5TS** (−182,[c] −201[b]), **6R**, **6S** (none[b,c,d]), **7R**, **7S** (−219,[i] −182,[c] −201[b]), **7RS** (−125,[b] −147[c]). [h] $\langle S^2 \rangle$ = 0.75 for a pure doublet. Calculated values of $\langle S^2 \rangle$: **4** (0.750[b,c,i]), **5** (0.763,[d] 0.750[b,c,i]), **5** (C_s) (0.750[d]), **5TS** (0.750[b,c,i]), **6R**, **6S** (0.763,[d] 0.750[b,c,i]), **7R**, **7S** (0.750[b,c,i]), **7RS** (0.762,[d] 0.750[b,c,i]). [i] QCISD.

without nuclear motion. For the Franck−Condon states of the radical cation species, a single-point calculation was made on the radical cations at the same geometry as the cyclopropylamine conformers **3np** and **3nb**. These species are designated **4FC** and **5FC**, respectively. The energies of **4FC** and **5FC** were corrected to 298 K, and the differences in energies between these species and their corresponding amines **3np** and **3nb** were used to calculate the onset energy of photoionization. Calculated thermodynamic parameters for photoionization of cyclopropylamine are given in Table 5.

TABLE 5. Thermodynamic Parameters for Photoionization of Cyclopropylamine[a,c,d]

method	ΔH	ΔS[b]	ΔG	ΔE_T[b]
	3nb → 3np			
DFT	−2.71	−2.20	−2.05	−0.85
QCISD	−2.72	−2.20	−2.06	−0.85
CCSD(T)//QCISD	−2.64	−2.20	−1.98	−0.85
	3nb → 5FC			
DFT	193.20	0.74	192.98	−1.70
QCISD	201.49	0.74	201.27	−1.70
CCSD(T)//QCISD	201.71	0.74	201.49	−1.70
	3np → 4FC			
DFT	202.29	2.20	201.63	0.85
QCISD	213.85	2.20	213.19	0.85
CCSD(T)//QCISD	215.22	2.20	214.56	0.85
	5FC → 4FC			
DFT	6.38	−0.74	6.60	1.70
QCISD	9.65	−0.74	9.87	1.70
CCSD(T)//QCISD	10.87	−0.74	11.09	1.70
	4 → 5FC			
DFT	2.09	0.71	1.88	0.23
QCISD	8.79	0.71	8.58	0.23
CCSD(T)//QCISD	8.01	0.71	7.80	0.23
	3np → 6R, 6S			
DFT	173.38	4.87	171.93	−0.59
QCISD	171.85	4.87	170.39	−0.59[b]
CCSD(T)//QCISD	172.88	4.87	171.43	−0.59[b]

[a] Kilocalories per mole at 298 K. [b] DFT. [c] Imaginary frequencies (IMAG) (cm^{-1}): **3nb** (none[b]), **3np** (none[b]), **4FC** (−1038[b]), **5FC** (none[b]). [d] $\langle S^2 \rangle$ = 0.75 for a pure doublet. Calculated values of $\langle S^2 \rangle$: **4FC** (0.750[b,e]), **5FC** (0.750[b,e]). [e] QCISD.

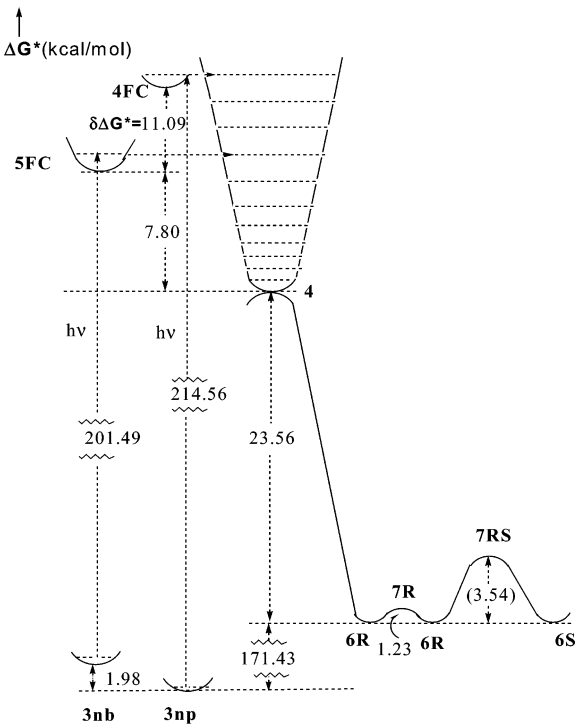
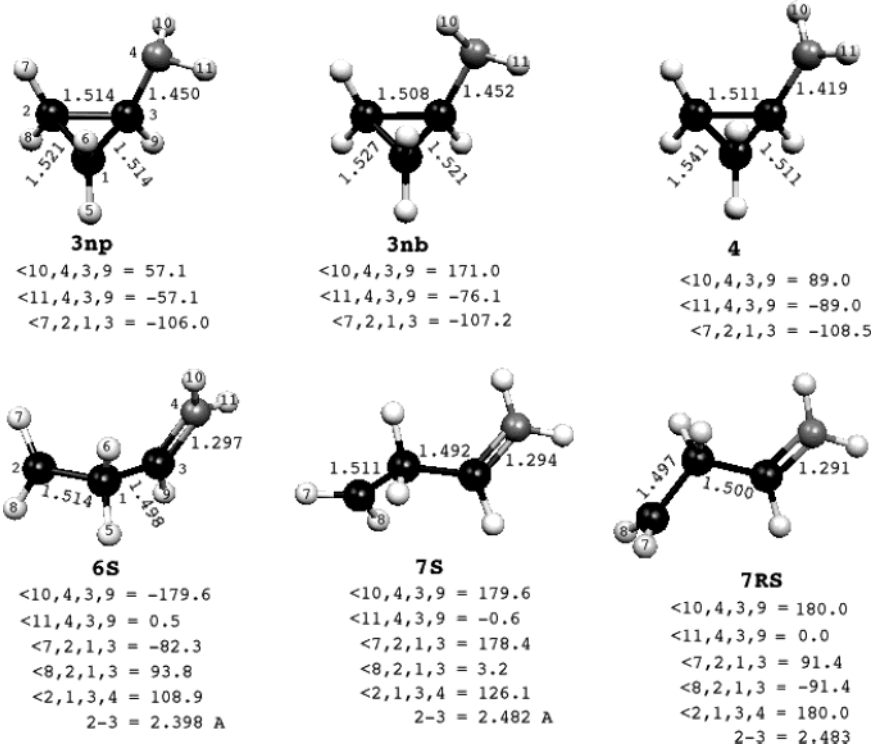


FIGURE 4. Energy diagram for the cyclopropylaminium ring opening at the CCSD(T)/cc-pVTZ//QCISD/cc-pVDZ level, except for the **6R → 7RS** barrier, which is at the DFT level.

Figure 4 presents an energy diagram for the unique species associated with the cyclopropylaminium radical cation and cyclopropylamine. Chart 4 gives the structures of these species at the QCISD/cc-pVDZ level. To compare

CHART 4



the vertical energies of **3np** to **4FC** and **3nb** to **5FC** to the experimentally determined onset of ionization of cyclopropylamine, the fraction of cyclopropylamine molecules that are photoionized to **4FC** and **5FC** must be calculated. The fraction of **5FC** ($\mathbf{F_{5FC}}$) is determined from the relative velocities for the formation of these species (v_{5FC}/v_{4FC}) by $F_{5FC} = (v_{5FC}/v_{4FC})/[(v_{5FC}/v_{4FC}) + 1]$. The Curtin−Hammett Principle[37] states that v_{5FC}/v_{4FC} is determined only by the difference between the energies of **4FC** and **5FC**, where $v_{5FC}/v_{4FC} = e^{\delta\Delta G^*/RT}$. From Figure 4, $\delta\Delta G^* = 11.09$ kcal/mol so that $v_{5FC}/v_{4FC} = 3.36 \times 10^3$ and $\mathbf{F_{5FC}} = 1.00$ at 298 K. The only path that needs to be considered is then **3nb** to **5FC**, for which the energy is calculated to be 201.49 kcal/mol at the CCSD(T)// QCISD level. The calculated value compares favorably with the range of experimental values: 8.78 eV (202.5 kcal/mol),[14b] 8.7 eV (200.6 kcal/mol),[35] 8.85 eV (204.1 kcal/mol).[36] Once formed, **5FC** crosses to a higher vibrational energy state of **4**, and then an exothermic reaction to **5** follows as seen from Figure 4.

The amine radical cation series **3** is unique compared to the carbon and oxygen radical analogues **1** and **2** in that series **3** has no closed-ring species corresponding to **5**. Furthermore, the bisected array in the cyclopropylcarbinyl cation **1cb** has a stabilizing effect on the closed-ring species, while the bisected array in the cyclopropylaminium radical cation effects ring opening. This is seen dramatically by the effect of rotation about the C_3−N bond in the closed-ring species **4** (X = N). The normal modes associated with the imaginary frequency of **4** (X = N) correspond to translation along the reaction coordinate with ring opening as seen in Figure 5, which leads to **6** (X = N). If the cyclopropylaminium radical cation symmetry is constrained to C_s, the ring remains closed (cf. **5** (C_s) in Table 5). The difference in energy of about 9 kcal/mol between **5** (C_s) and **6** in C_1 symmetry provides a measure of the cost of maintaining the ring intact. Even though the bisected 2p orbital is singly occupied and nitrogen is positively charged, the corresponding stability of the bisected cyclopropyl ring array found for **1cb** is not found for the nitrogen analogue **5** (X = N).

Bicyclobutonium Radicals and Radical Cations. We now pursue the possibility of species analogous to **8c** for the cyclopropylcarbinyl radical, cyclopropoxy radical, and cyclopropylaminium radical cation series. These hypothetical analogues are shown in Chart 5. Geometry

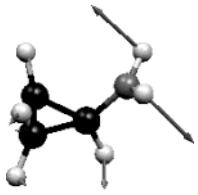
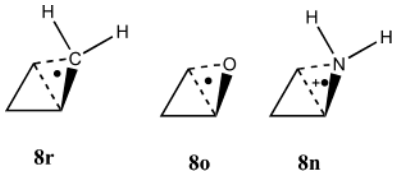


FIGURE 5. Normal-mode vibration of the imaginary frequency (−765 cm^{-1}) for transition-state structure **4** (X = N) at the DFT/B3LYP/6-31G* level.

CHART 5



8r **8o** **8n**

(35) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17 (Suppl. 1)*.

(36) Aue, D.; Bowers, M. T.; Eds. *Gas-Phase Ion Chemistry*; Academic Press: New York, 1979; Vol. 2, p 23.

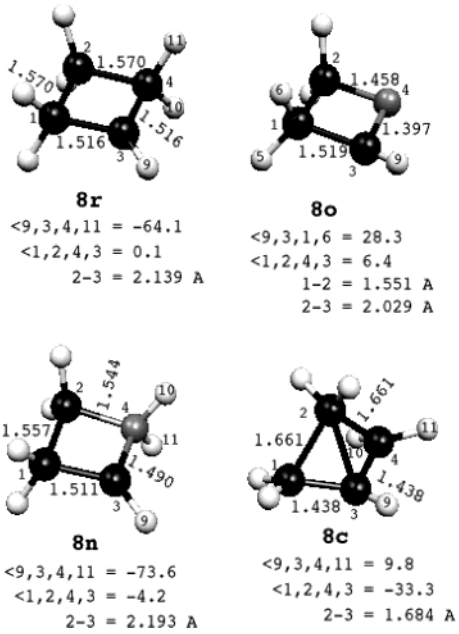
(37) Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: New York, 1985; p 293.

TABLE 6. Thermodynamic Parameters Related to 8c and Analogues 8r, 8o, and 8n Compared to the Corresponding Cyclopropyl-X Species[a,d,e]

method	ΔH	ΔS[b]	ΔG	ΔE_T[b]
Bicyclobutonium Cation, 1cb → 8c				
MP2	−1.26	−0.40	−1.15	0.50
DFT	2.00	−0.40	2.11	0.50
QCISD	0.54	−0.40	0.66	0.50
Bicyclobutonium Radical, 5 → 8r				
MP2(PMP2)	1.37	−0.57	1.54	0.28
DFT	−0.32	−0.57	−0.15	0.28
QCISD	−0.20	−0.57	−0.03	0.28
Oxybicyclobutonium Radical, 5 → 8o				
MP2(PMP2)	4.86	−0.86	5.11	0.80
DFT	8.95	−0.86	9.20	0.80
QCISD	6.49	−0.86	6.74	0.80
Azabicyclobutonium Radical Cation,[c] **6 → 8n**				
MP2(PMP2)	12.67	−1.63	13.16	0.79
DFT	16.02	−1.63	16.51	0.79
QCISD	14.56	−1.63	15.04	0.79

[a] Kilocalories per mole at 298 K. [b] DFT. [c] Comparison to **6** for X = N, since there is no closed-ring **5** species in this series. [d] Imaginary frequencies (IMAG) (cm^{-1}): **8r, 8o, 8n** (none[b]). [e] $\langle S^2 \rangle = 0.75$ for a pure doublet. Calculated values of $\langle S^2 \rangle$: **8r** (0.750[b,f,g]), **8o** (0.750[b,f,g]), **8n** (0.750[b,f,g]). [f] PMP2. [g] QCISD.

CHART 6



optimization was carried out for **8c**, and that geometry for the four-membered ring was used to start geometry optimizations for the analogues **8r**, **8o**, and **8n**. Thermodynamic parameters for these analogues and **8c** are given in Table 6. There was no evidence for the hypothetical analogues **8r**, **8o**, and **8n** shown in Chart 5 to **8c**. Instead, geometry optimization led to cyclobutyl radical structures **8r**, **8o**, and **8n** as shown in Chart 6 along with **8c** for comparison, at the QCISD level. Addition of one electron to **8c** to give the corresponding radical **8r** results in a nearly planar cyclobutane ring compared to the puckered ring in **8c**. There is no evidence for cross-ring bonding between the C_2 and C_3 atoms in **8r** (2.139 Å) compared to **8c**, where cross-ring bonding shortens the C_2-C_3 bond (1.684 Å). Similarly, the four-membered rings in **8o** and **8n** are only slightly out of the plane (−1,2,4,3 = 6.4° and −4.2°, respectively) compared to that in **8c** (−33.3°). The cross-ring bond distances in **8o** and **8n** are also long (C_2-C_3 = 2.029 and 2.193 Å, respectively) compared to that in **8c** (1.684 Å). Cationic charge in **8n** then does not encourage cross-ring bonding and a cyclobutonium cation type of structure.

The interplay between three- and four-membered rings in terms of energies is interesting. For comparison purposes the thermochemical data for these species are given relative to the corresponding molecules **5**, **6** (X = N), and **1cb** in Table 6. As seen from the higher level calculations in Table 6, **1cb** is slightly lower in energy than **8c**. This trend is reversed for the corresponding radical, where **8r** is slightly lower in energy than the bisected cyclopropylcarbinyl radical **5** (X = C). There is nothing in the geometry of **8r** to suggest cross-ring bonding as the source of the slightly lower energy of **8r** compared to the bisected radical **5** (X = C) at the higher level calculations. The interplay between three- and four-membered rings in the oxygen series (**5** (XH_2 = O) and **8o**) shows a clear preference for the three-membered ring species **5** (XH_2 = O), where the energy difference between **5** (XH_2 = O) and **8o** is 6.49 kcal/mol (QCISD). Since the ring strain in oxetane (25.7 kcal/mol) is slightly less than in cyclobutane (26.2 kcal/mol),[38] the 6.49 kcal/mol cannot be attributed to ring strain differences. Another possibility is that an oxy radical is more stable than a carbon radical, since the radical center changes from oxygen to carbon in **5** (XH_2 = O) proceeding to **8o**. A comparison of the heats of formation of the isomeric radicals $CH_3CH_2O^\bullet$ (−4 kcal/ mol) and $CH_3OCH_2^\bullet$ (−2 kcal/mol)[38] does support this trend, but accounts for only 2 kcal/mol of the 6.49 kcal/mol. Considering both the differences in radical stabilities and ring strain, one is left to account for 5 kcal/mol favoring **5** (XH_2 = O) over **8o**. A remaining possibility is that the cyclopropane ring stabilizes the oxy radical in **8o** by 5 kcal/mol, in a manner similar to that by which the bisected cyclopropylcarbinyl radical **5** is stabilized relative to the perpendicular species **4** by 3 kcal/mol (cf. Table 1).

Conclusions

Thermodynamic parameters were calculated at the CCSD(T)/cc-pVTZ//QCISD/cc-pVDZ level for ring opening of isoelectronic molecules **1**−**3**. Calculations on the ring-opened products as shown in Scheme 3 were also made. Relative rates at 298 K were calculated to be **1** (1.0) ≪ **2** (3.1×10^6) < **3**, where loss of an electron from cyclopropylamine causes an immediate ring opening. An minimum-energy bisected cyclopropylaminium radical cation (X = N) was not found at higher levels of theory. The perpendicular conformer **4** (X = N) was found to be a transition-state structure, which leads to ring opening. Ring opening of **1** provided a calibration to reported experimental values, and agreement was excellent. Agreement between the reported photoionization of cyclopropylamine and the calculated value was excellent as well. Relationships between species associated with ring opening of the cyclopropylcarbinyl radical and the correspond-

(38) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; Appendix.

ing cation were explored. The possibility of analogues to the bicyclobutonium cation in the isoelectronic series **1**−**3** was investigated. On the basis of the geometry and energy of these analogues, there was no evidence for bicyclobutonium cation like species. The bisected cyclopropylcarbinyl radical **5** (X = C) was stabilized relative to the perpendicular conformer **4** (X = C) by about 3 kcal/mol. This stabilization is dwarfed by the stabilization in the corresponding cation species of about 29 kcal/mol. The alkoxy radical may be stabilized by the cyclopropane ring in the cyclopropoxy radical **5** by about 5 kcal/mol.

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Supporting Information Available: Cartesian coordinates of the structures, calculated at the highest level of theory, and absolute energies for all of the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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