Theoretical Kinetic Study of Thermal Unimolecular Decomposition of Cyclic Alkyl Radicals

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Received: June 26, 2008; Revised Manuscript Received: August 28, 2008

Whereas many studies have been reported on the reactions of aliphatic hydrocarbons, the chemistry of cyclic hydrocarbons has not been explored extensively. In the present work, a theoretical study of the gas-phase unimolecular decomposition of cyclic alkyl radicals was performed by means of quantum chemical calculations at the CBS-QB3 level of theory. Energy barriers and high-pressure-limit rate constants were calculated systematically. Thermochemical data were obtained from isodesmic reactions, and the contribution of hindered rotors was taken into account. Classical transition state theory was used to calculate rate constants. The effect of tunneling was taken into account in the case of C—H bond breaking. Three-parameter Arrhenius expressions were derived in the temperature range of 500−2000 K at atmospheric pressure, and the C—C and C—H bond breaking reactions were studied for cyclic alkyl radicals with a ring size ranging from three to seven carbon atoms, with and without a lateral alkyl chain. For the ring-opening reactions, the results clearly show an increase of the activation energy as the π bond is being formed in the ring (endo ring opening) in contrast to the cases in which the π bond is formed on the side chain (exo ring opening). These results are supported by analyses of the electronic charge density that were performed with Atoms in Molecules (AIM) theory. For all cycloalkyl radicals considered, C—H bond breaking exhibits larger activation energies than C—C bond breaking, except for cyclopentyl for which the ring-opening and H-loss reactions are competitive over the range of temperatures studied. The theoretical results compare rather well with the experimental data available in the literature. Evans−Polanyi correlations for C—C and C—H β-scissions in alkyl and cycloalkyl free radicals were derived. The results highlight two different types of behavior depending on the strain energy in the reactant.

1. Introduction

In recent years, many chemical kinetic studies have investigated the oxidation of straight or branched-chain alkanes. In comparison, little attention has been paid to cyclic alkanes and the chemistry involved in their oxidation.[1] However, cycloalkanes and alkylcycloalkanes (in particular, C_5 and C_6) are usually present in conventional fuels (up to 3% in gasoline and 35% in diesel fuel).[2] Under oxidative conditions, the reaction sequence starts from hydrogen abstraction by O_2 and/or from unimolecular dissociation. The latter leads to diradical species that are specific to the chemistry of cycloalkanes.[3] Hydrogen abstractions from the parent cycloalkane lead to cycloalkyl radicals. At low temperatures (between 650 and 850 K), the cyclic radical reacts with O_2 to produce a peroxycycloalkyl radical that isomerizes to form hydroperoxycycloalkyl radical. Several studies of these important low-temperature pathways have been conducted.[4−7] At high temperatures, cycloalkyl radicals decompose mainly through β-scission reactions. These processes are well-known for straight and branched alkyl radicals, but the rate constants are not well-known for cycloalkyl radicals because of complications due to ring strain. In a recent study, Orme et al.[8] examined the pyrolysis and oxidation of methylcyclohexane (MCH) over the temperature range of 1200−2100 K. They proposed a detailed chemical kinetic mechanism to simulate shock-tube and flow-reactor experiments. The high-temperature reactions of Orme et al.[8] were considered in a low-temperature mechanism, proposed by Pitz et al.,[4] to model the autoignition of MCH in a rapid compression machine. In these studies, the rate constants for the ring-opening reactions of cycloalkyl radicals were estimated from the reverse ring-closure process with rates equal to those reported by Matheu et al.[9] In fact, Matheu et al. had developed rules for ring closures or openings starting from model reactions listed by Newcomb[10] with rate parameters from the literature and calculated using quantum chemical methods for cyclobutyl endo ring opening, 1-penten-5-yl endo ring closure, and 1-hexen-6-yl endo ring closure. Even though theoretical and experimental studies have been carried out on the modeling of cyclohexane oxidation, no systematic study has been reported for other cycloalkanes and, in particular, alkylcycloalkanes that are commonly present in practical fuels. In general, the kinetic parameters of the ring opening of cycloalkyl radicals and their reverse, the internal addition of radical centers to a double bond, are still poorly known. The influence of the ring strain energy of a cyclic radical on the activation energy is poorly understood. Moreover, alkyl side chains tend to complicate the kinetics further.

The ring opening of small cyclic alkyl radicals has been investigated theoretically by several researchers. For example, the ring-opening reaction of cyclopropyl was studied at various ab initio and DFT levels of theory.[11,12] It represents a system small enough to be studied at a reasonably high level of theory. The reaction of cyclopropylcarbinyl radical to allyl radical was investigated.[13,14] The energy barriers for the ring opening of

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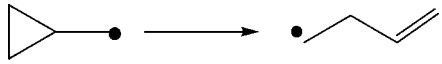
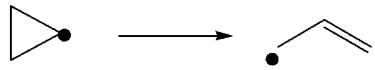
10.1021/jp805640s CCC: $40.75
Published on Web 10/29/2008

SCHEME 1: Exo and Endo Ring-Opening Reactions for Cyclopropylcarbinyl Radical and Cyclopropyl Radical



cyclopropylcarbinyl *exo* ring opening



cyclopropyl *endo* ring opening

the C_3 ring in these two systems are dramatically different: 21.9 kcal mol^{-1} for the cyclopropyl radical[12] vs 7.1 kcal mol^{-1} for the cyclopropylcarbinyl radical.[14] This large effect of a methyl group can be related to the endo and exo reaction types proposed by Newcomb.[10] Scheme 1 illustrates these two different ring-opening/-closing reactions. In exo ring opening, the radical center is located on the side chain, whereas in endo ring opening, the radical center is on the ring itself.

To obtain a deeper insight into ring-opening reactions, we studied C—C and C—H β-scissions for cycloalkyl radicals from C_3 to C_7 by quantum chemistry calculations. We compared the results to those obtained for straight (or unstrained) free radicals. The differences found are discussed in terms of endo and exo β-scissions. Moreover, to link the nature of the bonds created or broken in the transition state with those involved in the reactant and product, AIM[15] analyses were carried out. The effect of alkyl substitution on ring opening was also investigated systematically (a) by varying the size of the ring for a given alkyl side chain and (b) by varying the size of the alkyl side chain for a given ring size. In the same way, C—H bond breaking was examined accordingly with an emphasis on the branching ratio of C—C and C—H bond cleavage. Finally, an Evans—Polanyi correlation is proposed for C—C and C—H bond scissions of cyclic and straight-chain alkyl free radicals.

For all species considered in this study, thermochemical data were estimated, and the enthalpy of formation $\Delta_f H^\circ_{298\,K}$ was compared with experimental values when available or with estimates of group additivity methods when data were unavailable. Kinetic parameters were determined for all reactions involving C_4—C_6 rings. The results are compared with available values in the literature.

2. Computational Method

Calculations were performed with Gaussian 03.[16] The composite method CBS-QB3[17] was applied for all stationary geometries and transition states involved in the reaction schemes. Vibrational frequencies calculated at the B3LYP/cbsb7[18,19] level of theory confirm that all transition states (TSs) have exactly one imaginary frequency. The methodology used to obtain thermochemical and kinetic data was described elsewhere.[3] Thermochemical data were derived from CBS-QB3 energies and frequencies. Internal rotors were treated with the HinderedRotor option of Gaussian 03.[20] It must be stressed that the constrained torsions of the cyclic structure were treated as harmonic oscillators (including ring floppy motions) and the free alkyl groups as hindered rotations. Enthalpies of formation ($\Delta_f H^\circ$) were obtained using isodesmic reactions. The isodesmic reactions considered and the enthalpies of formation of the reference species used can be found in the Supporting Information.

Spin contamination was observed only for transition states at the CBS-QB3 level of theory ($0.8 < \langle s^2 \rangle < 1.2$). It must be noted that, in the CBS-QB3 method, an empirical correction for spin contamination is performed for the energy calculation.[17]

Rate constants for each elementary reaction were calculated using classical transition state theory (TST).[21] The effect of tunneling was taken into account for C—H bond breaking using the transmission coefficient of Wigner.[22] The enthalpies of activation involved in TST were calculated by taking into account the enthalpies of reaction calculated with isodesmic reactions in an elementary unimolecular reaction, reactant (R) → products (P), such as

$$\Delta H^{\ddagger}(\mathrm{R} \rightarrow \mathrm{P}) = \frac{1}{2}(\Delta H^{\ddagger}_{1(\mathrm{CBS\text{-}QB3})} + \Delta H^{\ddagger}_{-1(\mathrm{CBS\text{-}QB3})} + \Delta H_{\mathrm{r(isodesmic)}}) \quad (1)$$

and

$$\Delta H^{\ddagger}(\mathrm{P} \rightarrow \mathrm{R}) = \frac{1}{2}(\Delta H^{\ddagger}_{1(\mathrm{CBS\text{-}QB3})} + \Delta H^{\ddagger}_{-1(\mathrm{CBS\text{-}QB3})} - \Delta H_{\mathrm{r(isodesmic)}}) \quad (2)$$

where $\Delta H^{\ddagger}_{1(\mathrm{CBS\text{-}QB3})}$ and $\Delta H^{\ddagger}_{-1\ (\mathrm{CBS\text{-}QB3})}$ are the enthalpies of activation for the forward and back reactions, respectively, calculated at a temperature T (K). $\Delta H_{\mathrm{r(isodesmic)}}$corresponds to the enthalpy of reaction calculated at T (K) using the NASA polynomial obtained from calculated isodesmic enthalpies of formation and entropy at 298 K and heat capacities of reactants and products presented in Table 1.

In the text, we often assimilate the activation energy with the activation enthalpy calculated from the TST. This latter quantity is expressed as

$$\Delta^{\ddagger}H^\circ(T) = \Delta^{\ddagger}U^\circ(T) + \Delta^{\ddagger}nRT \quad (3a)$$

and

$$E_{\mathrm{exp}} = \Delta^{\ddagger}U^\circ(T) + RT \quad (3b)$$

where $\Delta^{\ddagger}U^\circ$ takes into account the electronic energy at 0 K; the zero-point energy (ZPE); and the thermal corrections due to translational, vibrational, and rotational contributions to the internal thermal energy. E_{exp} corresponds to the empirical activation energy (Arrhenius activation energy). In the case of the unimolecular reactions involved here ($\Delta^{\ddagger}n = 0$), $\Delta^{\ddagger}H^\circ$ differs from the classical Arrhenius activation energy by the quantity RT.

The kinetic parameters were obtained by fitting the rate constant values obtained from TST at several temperatures between 500 and 2000 K with the equation

$$k_\infty = AT^n \exp(-E/RT) \quad (4)$$

where A, n, and E are the parameters of the modified Arrhenius equation and k_∞ is the high-pressure-limit rate constant.

The AIM2000 program[24] was used to carry out the AIM analysis of the electronic charge density.

3. Thermochemical Data

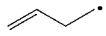
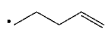
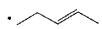
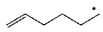
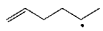
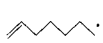
Thermochemical data ($\Delta_f H^\circ$, S°, C_p°) for all of the species considered in this study are collected in Table 1.

As mentioned previously, the enthalpies of formation, $\Delta_f H^\circ$ (column 2), were obtained from isodesmic reactions. The theoretical enthalpies of formation of molecular species are in good agreement with the experimental values.[25] The mean absolute deviation from experiment (MAD) given for CBS-QB3 calculations[17] (G2 set) is approximately equal to 0.9 kcal mol^{-1}. By comparison with the experimental enthalpies of formation,

TABLE 1: Ideal Gas-Phase Thermodynamic Properties for Species Considered in This Study and Computed at the CBS-QB3 Level[a]

Species	$\Delta H^{\circ}_{f,298}$	S°_{298}	$C^{\circ}_p(T)$ 300 K	400 K	500 K	600 K	800 K	1000 K	1500K	$\Delta_f H^{\circ}_{298K}$
	13.0	56.8	13.3	18.0	22.2	25.7	31.0	34.9	41.0	12.7±0.14[29]
	6.5	63.2	17.0	23.5	29.4	34.3	41.9	47.5	55.9	6.4
	-17.9	70.2	21.0	29.2	36.7	43.0	52.8	59.9	70.7	18.3±0.19[30]
	-29.4	71.5	25.4	35.3	44.3	52.0	63.9	72.5	85.7	-29.8[31]
	-2.2	73.5	23.1	31.0	37.9	440	53.0	59.7	70.2	*0.4*
	-25.7	81.6	27.2	36.7	45.2	52.5	63.9	72.2	85.0	-25.5[32]
	-30.5	90.0	32.5	41.5	53.5	61.9	75.0	84.6	99.2	-30.4±0.25[33]
	2.6	75.4	24.9	33.7	41.6	48.2	58.2	65.4	76.4	2.4[34]
	67.8	60.9	12.4	15.9	18.9	21.4	25.0	27.7	31.8	*66.0*
	38.8	62.7	15.5	21.0	25.9	29.9	35.9	40.2	46.7	37.5±0.4[35]
	8.3	69.7	19.4	26.7	33.1	38.5	46.7	52.6	61.5	8.5[34]
	-0.1	72.8	23.9	32.7	40.7	47.4	57.7	65.1	76.3	-1.0±0.23[36]
	-1.2	79.9	28.9	39.2	48.6	56.6	68.9	77.8	91.2	*-2.1*
	69.5	61.7	13.5	17.7	21.3	24.2	28.6	31.7	36.7	*66.9*
	54.0	68.8	17.9	23.7	28.9	33.2	39.7	44.5	51.7	*50.7*
	46.7	78.8	22.8	30.2	36.6	42.0	50.3	56.3	65.6	*48.5*
	46.6	76.9	23.9	31.1	37.4	42.7	50.8	56.7	65.9	*44.8*
	46.3	77.0	23.8	31.2	37.5	42.8	50.9	56.8	66.0	*44.8*
	44.1	78.8	22.4	29.4	35.9	41.4	50.0	56.2	65.7	*44.8*
	25.7	71.7	21.6	29.2	36.1	41.8	50.5	56.9	66.5	*23.9*
	23.7	85.5	26.9	35.9	43.9	50.7	61.1	68.7	80.4	*22.5*
	16.9	81.3	26.2	35.0	43.1	50.1	60.8	68.6	80.5	*16.8*
	18.8	79.2	27.7	36.8	44.7	51.4	61.7	69.2	80.7	*16.8*
	18.5	79.0	27.8	36.8	44.7	51.4	61.7	69.2	80.7	*16.8*
	12.0	90.2	31.6	42.0	51.5	59.5	71.8	80.9	94.6	*11.9*
	17.1	77.8	26.1	35.3	43.6	50.7	61.5	69.4	81.3	*18.0*
	15.3	84.5	31.0	42.3	52.4	60.8	73.7	82.9	96.7	*11.8*

TABLE 1: (Continued)

Species	$\Delta H^\circ_{f,298}$	S°_{298}	$C^\circ_p(T)$ 300 K	400 K	500 K	600 K	800 K	1000 K	1500K	$\Delta_f H^\circ_{298K}$
	39.1	63.1	14.9	18.8	22.0	24.7	28.75	31.8	36.6	40.9±0.7[37]
	49.6	75.7	21.1	26.4	31.0	34.7	40.4	44.8	51.5	*48.7*
	44.3	86.1	24.8	31.2	37.0	41.8	49.4	55.0	63.9	*43.7*
	43.7	85.0	25.3	31.9	37.7	42.5	49.8	55.3	64.0	*41.3*
	41.4	85.8	24.2	30.2	35.9	40.8	48.7	54.6	63.7	*41.5*
	41.8	84.5	25.9	31.6	37.0	41.7	49.2	54.9	63.8	*41.1*
	41.3	85.0	26.3	32.3	37.7	42.2	49.6	55.1	63.9	*40.0*
	37.2	93.6	31.6	39.5	46.3	52.0	61.0	67.7	78.3	*36.4*
	39.1	92.8	29.4	37.0	44.1	50.1	59.6	66.7	77.8	*38.7*
	36.0	91.4	31.7	39.5	46.6	52.7	62.3	69.4	80.6	*35.4*
	37.4	92.2	31.6	39.4	46.1	51.8	63.1	67.5	78.2	*37.6*
	36.9	91.6	30.1	37.4	44.2	50.1	59.5	66.6	77.8	*37.0*
	36.2	91.5	29.3	36.6	43.5	49.6	59.3	66.5	77.8	*36.5*
	37.2	93.6	31.6	39.5	46.3	52.0	61.	67.7	78.3	*36.4*
	33.9	101.8	35.6	44.6	52.9	59.9	70.9	79.2	92.1	*33.8*

[a] $\Delta H^\circ_{f,298\,K}$ in kcal mol^{-1} and $S^\circ_{298\,K}$ and $C^\circ_p(T)$ in cal mol^{-1} K^{-1}. The last column gives the experimental value of $\Delta H^\circ_{f,298\,K}$ from NIST[28] or estimated by the computer program Thergas[27] (in italics).

found in the literature for stable molecules (Table 1), we observed that the differences with CBS-QB3 calculations were always within this uncertainty.

For free radicals, our theoretical values are within a few kilocalories per mole of group additivity results[26] obtained using the computer program Thergas.[27] Of course, group additivity does not properly take into account the ring strain energy (RE) of the radical species for which experimental values are unavailable.

Hence, for branched cycloalkyl radicals, the same enthalpy of formation is obtained for isomers with a radical center located on the ring, in contrast to theoretical calculations. This result can be explained by the same bond dissociation energy used in Thergas for the latter free radicals. Notice also that the lowest $\Delta_f H^\circ_{298\,K}$ value is obtained for isomers with a radical center located on the tertiary carbon atom. This result is consistent with the variation of bond dissociation energy (BDE): BDE($C_{primary}$—H) > BDE($C_{secondary}$—H) < BDE($C_{tertiary}$—H).

4. β-Scission of Unbranched Cycloalkyl Radicals

4.1. Mechanism. The ring-opening reactions and C—H bond β-scissions are presented in Scheme 2, for cycloalkyl radicals from cyclopropyl to cycloheptyl.

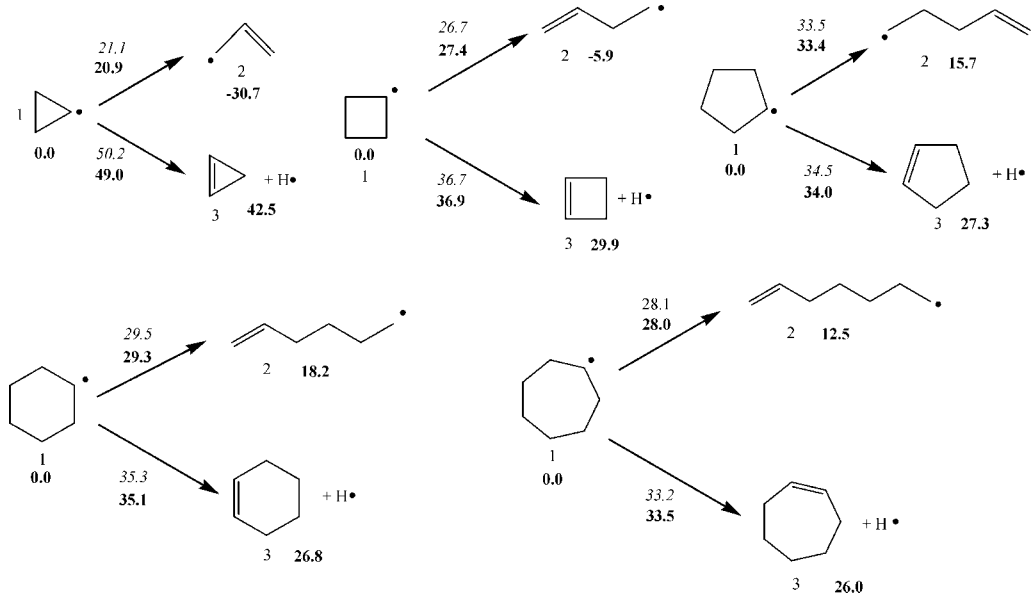
Table 2 summarizes the activation enthalpies obtained for the ring opening (and closure) of cycloalkyl radicals (Scheme 2) and the corresponding β-scission of straight-chain 1-alkyl radicals (eq 5) at the CBS-QB3 level of theory.

$$\bullet C_nH_{2n+1} \rightarrow C_2H_4 + \bullet C_{(n-2)}H_{2(n-2)+1} \quad \text{with } 3 \le n \le 7 \quad (5)$$

In general, CBS-QB3 activation energies are in good agreement with the literature values. The activation energy of cyclopropyl ring opening is close not only to the theoretical values of Olivella et al.[12] (21.9 kcal mol^{-1}), Arnold and Carpenter[11] (21.5 kcal mol^{-1}), and Greig and Thynne[38] (22.06 kcal mol^{-1}), but also to the experimental value given by Kerr and al.[39] (19.1 kcal mol^{-1}) at $P = 0.7$ bar and T ranging from 411 to 446 K. $\Delta H^{\ddagger}_{298\,K}$ for the ring opening of cyclobutyl is close to the value calculated by Matheu et al.[9] at the CBS-Q level of theory (25.9 kcal mol^{-1}). For cyclopentyl and cyclohexyl radicals, Matheu et al.[9] reported the activation energies for the reverse reactions. If we compare their activation energies with our values at 298 K, a good agreement is obtained (15.8 vs 14.7 kcal mol^{-1} for c-C_5H_9 and 6.4 vs 7.4 kcal mol^{-1} for c-C_6H_{11}).

As mentioned by Stein and Rabinovitch,[40] two opposite effects can be considered to explain ring-opening energetics.

SCHEME 2: β-Scissions of C_3-C_7 Cycloalkyl Radicals, Calculated at the CBS-QB3 Level of Theory[a]



[a] Gibbs free energies (in bold) and activation energies (in italic) are reported in kcal mol^{-1} at the standard state, in relation to the reference cycloalkyl radical.

TABLE 2: Activation Enthalpies and Enthalpies of Reaction ($\Delta_r H^\circ_{298\,K}$) of the Ring Opening of Cyclic Alkyl Free Radicals Described in Scheme *2* and Activation Enthalpies for the β-Scissions of the Corresponding Linear Alkyl Free Radicals Obtained at the CBS-QB3 Level of Theory[a]

reaction of cyclic radical	$\Delta H^{\circ\ddagger}_{298\,K}$ for ring opening	$\Delta H^{\circ\ddagger}_{298\,K}$ for ring closure	$\Delta_r H^\circ_{298\,K}$	$\Delta H^{\circ\ddagger}_{298\,K}$ for β-scission of unstrained *n*-alkyl[b]
c-$C_3H_5 \rightarrow C_3H_5$	21.1	51.4	−30.3	28.9
c-$C_4H_7 \rightarrow C_4H_7$	26.7	31.4	−4.7	27.8
c-$C_5H_9 \rightarrow C_5H_9$	33.5	14.7	18.8	28.2
c-$C_6H_{11} \rightarrow C_6H_{11}$	29.5	7.4	22.1	28.0
c-$C_7H_{13} \rightarrow C_7H_{13}$	28.1	11.0	18.0	28.0

[a] Values in kcal mol^{-1} at 298 K. [b] See text.

TABLE 3: Ring Strain Energies (REs, kcal mol^{-1}) of Cycloalkanes and Cycloalkenes[a] and Cylcloalkyl Radicals[b] for Species Containing 3−7 Carbon Atoms

number of carbon atoms in the cycle	RE cyclanes	RE cycloalkyl radicals	RE cycloalkenes
3	27.7	38.1	53.6
4	26.8	24.4	29.8
5	7.1	4.1	5.9
6	0.7	1.8	0.5
7	6.8	4.4	5.4

[a] From Cohen.[41] [b] Calculated here at the CBS-QB3 level.

The first is the ring strain energy being released in the TS leading to a reduced activation energy (E_a) as compared to unstrained radicals. The second is due to local orientation strain (steric effect) that tends to increase E_a. Because the ring strain energy varies from one cycloalkyl radical to another, as shown in Table 2, activation energies involved in ring opening differ greatly from one cycloalkyl radical to another. The lowest value is 21.1 kcal mol^{-1} for the C—C β-scission of cyclopropyl, whereas an activation energy of 33.5 kcal mol^{-1} is reached for cyclopentyl. On the other hand, the activation energy for C—C bond β-scissions in straight-chain alkyl radicals is found to be independent of the number of carbon atoms involved in the chain, as expected.

The difference between cyclic and noncyclic radicals is clearly associated with the release of ring strain energy (RE) in the former case. In the transition structure (TS) of cyclic radicals, RE is partially released, leading to a lower activation energy.

Some RE values for cycloalkanes and cycloalkenes are available in the literature,[41] but no value has been reported for the corresponding radicals. RE values for the molecules cannot be used for the radicals owing to geometry changes. In a previous work, we showed that CBS-QB3-calculated REs for cycloalkanes are in excellent agreement with experimental values.[3] Here, REs for the radicals were calculated by a similar approach. RE is obtained by calculating the difference between the enthalpy of formation of the cyclic radical and the sum of the contributions to the enthalpy of the different groups constituting the cyclic radical as deduced from unstrained structures. For example, in the case of cyclopentyl, RE is obtained from the calculation

$$\mathrm{RE} = \Delta_f H^\circ_{298\,K}(\text{cyclopentyl}) - 4\Delta_f H^\circ_{298\,K}(\mathrm{CH_2\ group}) - \Delta_f H^\circ_{298\,K}(\bullet\mathrm{CH\ group}) \quad (6)$$

The contribution to the enthalpy of the CH_2 group was obtained in a previous study,[3] whereas the contribution of a CH(•) group was obtained as the difference between the enthalpies of formation ($\Delta_f H°$) of *n*-hexane and pent-3-yl radical. $\Delta_f H°$ values were obtained from CBS-QB3 calculations and isodesmic reactions. Table 3 presents the results for the cycloalkyl radicals together with those reported by Cohen for cycloalkanes and cycloalkenes.[41]

The results show that the REs of cyclanes, cycloalkyl radicals, and cycloalkenes are similar for C_6 and C_7 species, whereas substantial variations are observed for smaller species, especially for C_3. It is worth noting that the RE of cyclopentyl is lower than that of cyclopentane or cyclopentene, which is consistent with the peculiar low reactivity of cyclopentane observed during its pyrolysis and oxidation.[42] The results in Table 3 also indicate that it is generally inaccurate to estimate the activation energy for the β-scission of a cyclic alkyl radical, even as a first approximation, by considering that the RE is completely released in the transition state. For example, this assumption yields an

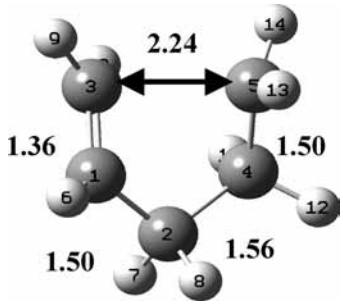


Figure 1. Structure of the transition state involved in the β-scission of the C—C bond of cyclopentyl radical at the CBS-QB3 level of calculation. Bond lengths are given in angstroms.

activation enthalpy of $27.8 - 24.4 = 3.4$ kcal mol^{-1} for c-C_4H_7, which is much smaller than the theoretical value (26.7 kcal mol^{-1}).

The TS involved in the ring opening of cyclopentyl radical is presented in Figure 1. All of the other TSs in Scheme 2 exhibit similar characteristics.

The TSs are generally tight. In Figure 1, the breaking C—C bond length is equal to 2.24 Å, only 1.4 times the initial bond length in the cyclopentyl radical. Consequently, part of the RE remains in the TS and does not help decrease the activation energy. On the other hand, the steric inhibition due to the formation of a π bond in the cyclic TS produces an increase in E_a. To form a π bond, the CH_2 group must rotate in the ring to bring the atoms into the same plane (here, atoms 1, 3, 6, 9, and 10). This effect is particularly important in the case of cyclopentyl. Its activation energy is 5.3 kcal mol^{-1} above that of the n-pentyl radical. Thus, the steric inhibition due to the nascent π bond strongly affects the activation energy of the ring opening of cyclopentyl radical, to an extent that is not compensated by the partial released of the RE.

4.2. AIM Analysis. The reaction coordinate can be viewed as a combination of the C—C σ bond breaking and the formation of a π bond. Roughly, one can consider that a decrease in RE is accompanied by the breaking of the σ bond and that the steric inhibition becomes significant as the π bond forms. To characterize this competition, we used AIM to analyze the electronic charge density.[15] This theory is based on a topological analysis of the electron density, ρ. Different critical points can be identified in a molecular structure. Bond critical point (BCPs) are localized on bond paths that connect two atoms. When bond paths connect atoms in a cycle, a ring critical point (RCP) is defined in AIM theory. The value of the electron density ρ at a BCP is characteristic of the bond type. Thus, electron densities of $\rho = 0.239$ and $\rho = 0.343$ at BCPs characterize a single bond and a double bond, respectively. Figure 2 presents the molecular graphs of the different species involved in the ring opening of the cyclopentyl radical.

The density values corresponding to C—C bonds are given in Table 4 for each structure. In cyclopentyl (Figure 2a), BCP 3 corresponds to a σ bond with a classical value of $\rho = 0.238$. The bonds located in the β position of the radical center (BCPs 2 and 4) have a lower density, showing that the bond is weakened; on the contrary, bonds located in the α position of the radical center (BCPs 1 and 5) have densities slightly higher than that of a classical σ bond. In the transition state (Figure 2b), the bond characterized by BCP 2 is clearly being broken.

The small electron density at this BCP ($\rho = 0.053$) indicates that a bonding character remains in the TS. The electron density of BCP 1 increases from 0.255 to 0.321, indicating the bond in the TS is close to that of a standard double bond. Thus, even though part of RE is released at the TS, a substantial structural deformation accompanying π-bond formation contributes to an increase in the activation energy (compared to β-scissions of straight-chain alkyl radicals). In a similar way, one can now explain why, for highly strained cycloalkyl radicals, such as cyclopropyl, for which the RE realeased is expected to dominate over the steric inhibition, the activation energy is smaller than that observed in the β-scission of the corresponding straight-chain alkyl radical (21.1 kcal mol^{-1} for cyclopropyl versus 28.9 kcal mol^{-1} for n-propyl).

We also performed a systematic AIM analysis for all cycloalkyl ring openings discussed in section 4 and for the β-scissions of the corresponding straight-chain 1-alkyl (eq 5). For each reaction, we were interested in the variations of the electron density at BCPs located on the α and β positions of the radical center. We introduce an empirical parameter, λ, defined as

$$\lambda = \frac{\rho[\mathrm{BCP}(\alpha)]}{\rho[\mathrm{BCP}(\beta)]} \tag{7}$$

For all the cycloalkyl and linear 1-alkyl radicals containing from four to seven carbon atoms, λ was calculated for both the reactants and the TSs (Table 5).

For 1-alkyl radicals, a perfect regularity of λ is observed for all of the reactants ($\lambda = 1.1$) and TSs ($\lambda = 7.2$). For cycloalkyl free radicals, one notes that λ is still equal to 1.1, independent of the ring size. These results indicate that the strengthening of the α bond and the destabilization of the β bond are similar for these radicals. For cyclic TSs, a bond character is always observed in the transition states $\{\rho[\mathrm{BCP}(\beta)] > 0\}$, but λ varies greatly from C_4 to C_7 species. In fact, the λ values of cyclobutyl and cyclopentyl radicals are smaller than those of their straight-chain analogues, which suggests that the TSs are close to the reactants and that a large part of the ring strain energy is retained. On the other hand, the λ values of cyclohexyl and cycloheptyl are similar to those of their straight-chain analogues, which can be explained by the similar reactivities exhibited by these radicals toward C—C bond cleavage, as mentioned above.

4.3. Kinetic Data. Kinetic parameters were calculated according to eq 4 for C_4—C_6 rings, which are the most relevant ones in pyrolysis and combustion. The results are presented in Table 6.

Only a few rate constant values are available in the literature for the ring opening of cycloalkyl radicals. In the following discussion, we compare our values with those found in the NIST kinetics database.[28] Figure 3 compares the calculated values of the cyclobutyl ring opening with those proposed by Matheu et al.[9] As shown, the rate constants of the two studies agree within a factor 1.2—1.7 in the range of 500—2000 K.

Figure 4a presents a comparison between the rate constant calculated for the ring opening of cyclopentyl radical and the experimental values reported by Hanford-Styring and Walker[43] and Gierczak et al.[44]

For ring opening, our rate constant is a factor 12 higher than the values of Handford-Styring and Walker[43] (derived from a complex mechanism). In a recent study on the mechanism of decomposition of pentenyl radicals and pressure effects, Tsang[44] proposed a high-pressure rate expression for the cyclic ring opening of cyclopentyl based on the values proposed by Handford-Styring and Walker. The same discrepancy is observed with values proposed by Tsang, 10 times lower than ours. An even larger discrepancy is observed with the work of Gierczak et al.,[44] in which case there is a difference of a factor greater than 100 between our values and those derived in that

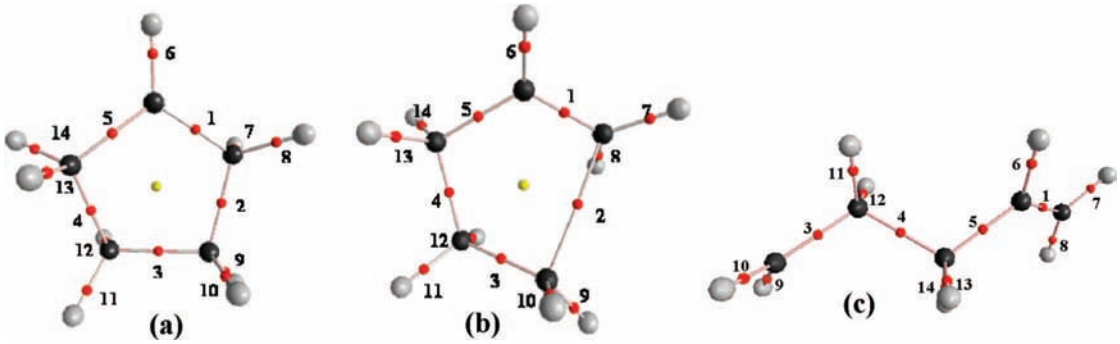


Figure 2. Molecular graphs obtained by AIM analysis[24] of (a) the cyclopentyl radical, (b) the transition state involved in the ring opening of cyclopentyl, and (c) 1-pentenyl. The bond paths appear in white, BCPs correspond to small dots, and the RCP is characterized by the central dot.

TABLE 4: Electron Densities, ρ, at Bond Critical Points (BCPs) for Structures in Figure 2

cyclopentyl (Figure 2a)		TS cyclopentyl (Figure 2b)		1-pentenyl (Figure 2c)	
BCP number	ρ	BCP number	ρ	BCP number	ρ
1	0.255	1	0.321	1	0.343
2	0.234	2	0.053	2	-
3	0.238	3	0.251	3	0.258
4	0.234	4	0.227	4	0.224
5	0.255	5	0.251	5	0.254

TABLE 5: Values of λ Calculated from Equation 7 for the Ring Openings and the β-Scissions of C_4-C_7 Species

	reactant			TS		
species	ρ [BCP(α)]	ρ [BCP(β)]	λ	ρ [BCP(α)]	ρ [BCP(β)]	λ
1-alkyl radicals (C_4-C_7)	0.257	0.229	1.1	0.326	0.045	7.2
cyclobutyl	0.253	0.227	1.1	0.309	0.067	4.6
cyclopentyl	0.255	0.234	1.1	0.321	0.053	6.1
cyclohexyl	0.257	0.235	1.1	0.327	0.045	7.3
cycloheptyl	0.254	0.232	1.1	0.326	0.046	7.1

TABLE 6: Rate Parameters for C—C and C—H Bond Breaking Obtained at the CBS-QB3 Level of Theory and Classical Transition State Theory for 500 $\leq T$ (K) $\leq$ 2000

reaction	A (s^{-1})	n	E (kcal mol^{-1})
c-$C_4H_7 \rightarrow C_4H_7$	4.36×10^{11}	0.539	26.84
c-$C_4H_7 \rightarrow c$-$C_4H_6 + H$	2.00×10^{11}	1.001	37.14
c-$C_5H_9 \rightarrow C_5H_9$	4.79×10^{12}	0.570	34.43
c-$C_5H_9 \rightarrow c$-$C_5H_8 + H$	2.95×10^{12}	0.847	35.42
c-$C_6H_{11} \rightarrow C_6H_{11}$	2.75×10^{12}	0.624	30.81
c-$C_6H_{11} \rightarrow c$-$C_6H_{10} + H$	8.91×10^{11}	0.834	36.34

work from chemical activation experiments and RRKM (Rice—Ramsperger—Kassel—Marcus) calculations employing both their own experimental data and literature data. In the low-temperature range considered in the study of Gierczak et al. (around 400 K), the estimated activation energy (approximately 3 kcal mol^{-1} greater than ours) and pre-exponential factor (2 times higher than that calculated by CBS-QB3) yield the large observed discrepancy. Matheu et al.[9] studied the reverse reaction, i.e., the internal addition $C_5H_9 \rightarrow c$-C_5H_9. Figure 4b presents a comparison of our rate constant for the latter reaction (Table 7) with that calculated by Matheu et al. As shown in Figure 4b, an excellent agreement is obtained, with a factor of 1—1.7 between the two rate constants.

Figure 5 presents the rate constants for the ring-closure reaction leading to cyclohexyl radical, $C_6H_{11} \rightarrow c$-C_6H_{11}. For

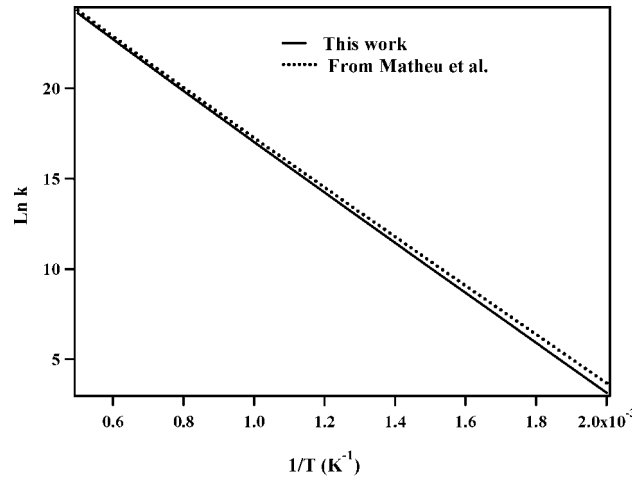


Figure 3. Comparison between of the rate constant for the reaction c-$C_4H_7 \rightarrow C_4H_7$ calculated at the CBS-QB3 level (this work) and that of Matheu et al.[9] at the CBS-Q level of theory.

comparison, the rate constants calculated by Matheu et al.[9] and estimated by Handford-Styring and Walker[43] are also presented.

In contrast to C_4 and C_5 rate constants, poor agreement is observed between our values and those calculated by Matheu et al.[9] In particular, at 500 K, their value is about 6 times higher than ours, and the slopes of the two curves are somewhat different. However, the deviation observed is not surprising because Matheu et al. used a lower computational level (B3LYP/ccp-VTZ) for the internal addition of 1-hexenyl than that used in the cases of cyclobutyl and cyclopentyl radicals (CBS-Q) and, consequently, their rate constant seems to be overestimated in the low-temperature range. The rate values obtained in our calculations are higher than those obtained by Handford-Styring and Walker[43] (derived from a complex mechanism) by a factor ranging from 5 to 10. It is worth noting that a large discrepancy exists between these two rate constants available in the NIST kinetic database[28] and that the kinetic parameters proposed by Matheu et al. have been used by several authors[4,8,46] in the modeling of cyclohexane combustion.

The ratio between C—C and C—H bond cleavage for species considered in Scheme 2 constitutes another interesting point. Because of the difference between energy barrier involved in the C—C and C—H bond scission of cyclopropyl and cyclobutyl and, to a lesser extent, of cyclohexyl and cycloheptyl, the ratio is always shifted toward the ring opening, even at high temperature. However, for cyclopentyl radical, the difference in activation energy observed for C—C and C—H rupture is relatively small, and the two channels have competitive rate constants, as shown in Figure 6.

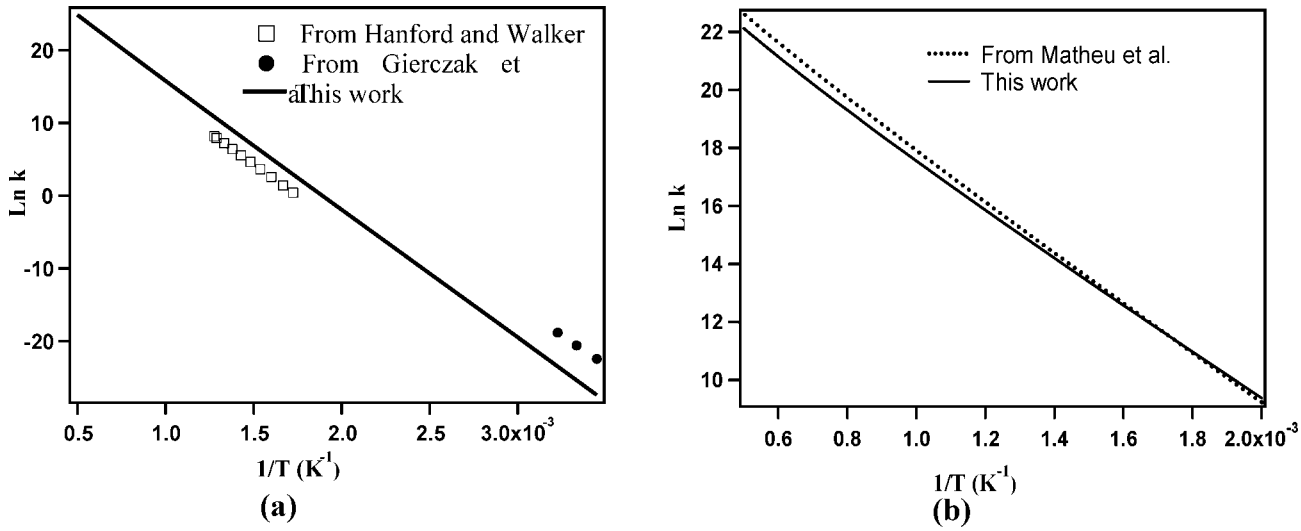


Figure 4. Comparison between rate constants of this work and (a) experimental data for the reaction c-$C_5H_9 \rightarrow C_5H_9$ and (b) values calculated by Matheu et al.[9] for the ring-closure reaction $C_5H_9 \rightarrow c$-C_5H_9.

TABLE 7: Rate Parameters for Internal Additions $C_5H_9 \rightarrow c$-C_5H_9 and $C_6H_{11} \rightarrow c$-C_6H_{11}, Obtained at the CBS-QB3 Level of Theory and Classical Transition State Theory for $500 \leq T$ (K) ≤ 2000

reaction	A (s^{-1})	n	E (kcal mol^{-1})
$C_5H_9 \rightarrow c$-C_5H_9	3.73×10^6	1.391	14.31
$C_6H_{11} \rightarrow c$-C_6H_{11}	5.31×10^4	1.921	6.67

It can be seen that, above 500 K, C—H β-scission is faster than C—C scission. A consequence of this result is that C_5 cyclic structures exhibit a different reactivity during combustion processes than other cyclic species such as cyclohexane.[42]

5. Branched Cycloalkyl Radical Decomposition

5.1. Methylcycloalkyl Decomposition Mechanism. As mentioned in the Introduction, the exo ring opening of cyclopropylcarbinyl has a lower activation energy than the endo ring opening of cyclopropyl radical: 7.06[14] vs 21.9[12] kcal mol^{-1}, respectively. In Scheme 1, only endo ring opening can be involved during the β-scission of the C—C bonds, and it would be interesting to add an alkyl group on the cycle to allow exo ring opening. The effect of methyl substitution on the ring is studied in detail here for methylcyclobutyl and methylcyclopentyl. The radical center can be located on the ring itself or on the methyl side chain. Radicals formed by hydrogen abstraction from methylcyclobutane and methylcyclopentane are presented in Schemes 3 and 4, respectively. The radicals formed by C—C bond breaking and the activation energies for the corresponding reactions are also displayed.

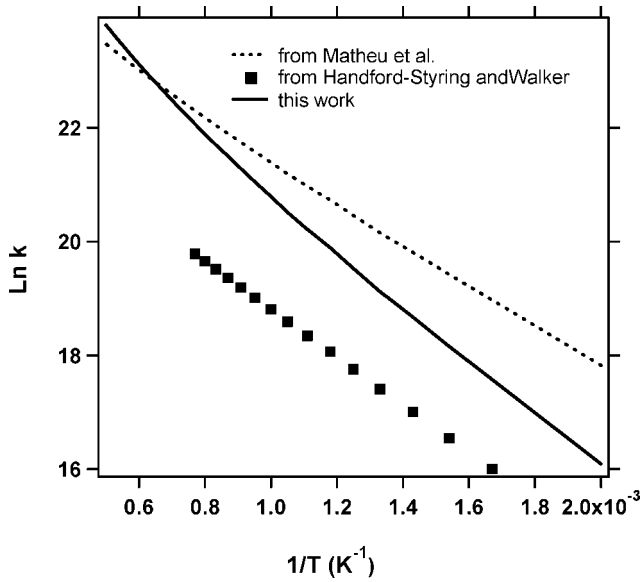


Figure 5. Comparison between rate constant calculated in this work and values in the literature for the reaction $C_6H_{11} \rightarrow c$-C_6H_{11}.

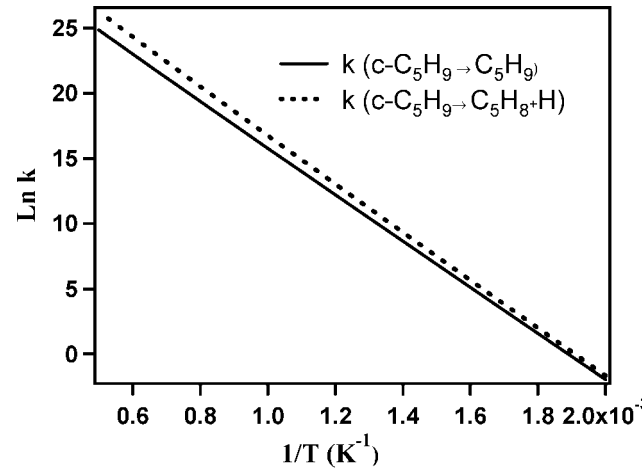
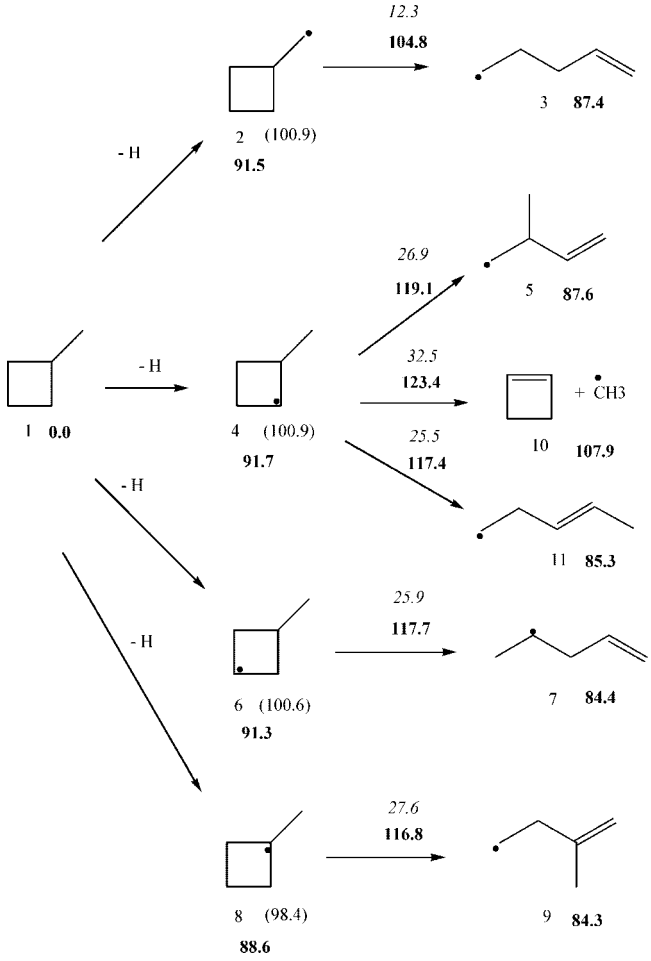


Figure 6. Comparison between the rate constants of C—C and C—H β-scission for cyclopentyl radical (see Scheme 2 and Table 5).

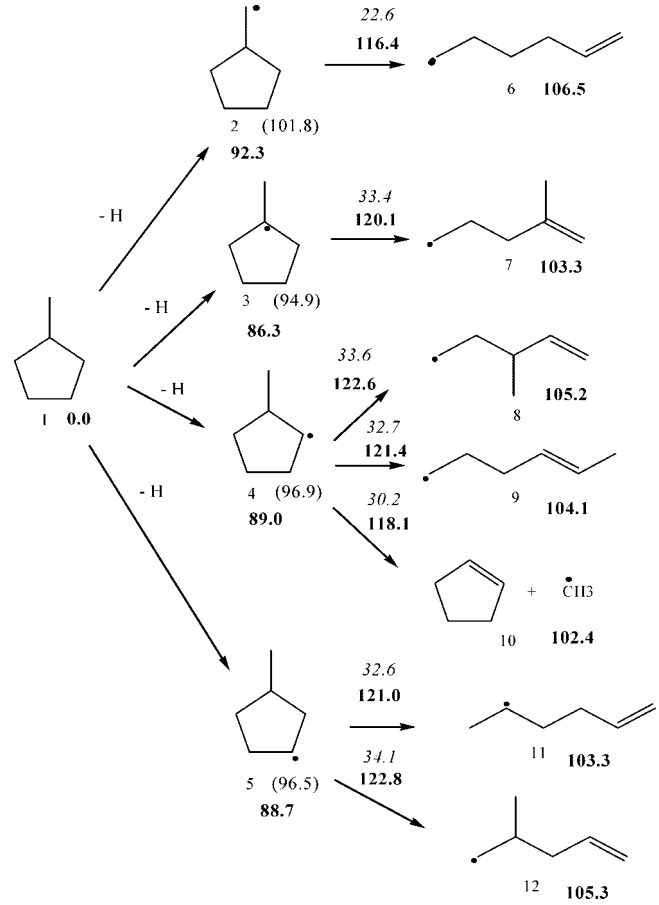
The enthalpies of reaction displayed in Schemes 3 and 4 correspond to the C—H bond dissociation energies (BDEs). For methylcyclobutane, BDEs found for the secondary carbon atoms (radicals **4** and **6** in Scheme 3) are close to the value proposed by Tumanov and Denisov[47] and equal to 100.0 kcal mol^{-1}. For the primary carbon atom (radical **2** in Scheme 3), our value is close to the BDE recommended by Luo[48] for primary C—H bonds in n-butane (100.7 kcal mol^{-1}). For a tertiary carbon atom (radical **8** in Scheme 3), our value is 3 kcal mol^{-1} higher than the BDE of a tertiary C—H bond in isobutane (95.7 kcal mol^{-1}),[48] which could be used, by analogy, to model this BDE in methylcyclobutane. In the case of methylcyclopentane (Scheme 4), our calculations reproduce the classical stability of C—H bonds in primary, secondary, and tertiary carbon atoms that is observed in linear alkyl radicals.[48] Thus, for the primary carbon atom (radical **2**, Scheme 4), our BDE is close to that

SCHEME 3: β-Scissions for the Different Isomers of Methylcyclobutyl Radicals[a]



[a] Gibbs free energies (in bold), activation enthalpies (in italics), and bond dissociation energies (in parentheses) at 298 K are reported in kcal mol^{-1} and are relative to the reference cycloalkane.

SCHEME 4: β-Scissions of the Different Isomers of Methylcyclopentyl Radicals[a]



[a] Gibbs free energies (in bold), activation enthalpies (in italics), and bond dissociation energies (in parentheses) at 298 K are reported in kcal mol^{-1} and are relative to the reference cycloalkane.

given for a primary C—H bond in *n*-pentane (100.2 kcal mol^{-1}),[48] and the BDE values for the two secondary carbon atoms (radicals 4 and 5 in Scheme 4) agree with those for cyclopentane (95.6 kcal mol^{-1}).[48] For the tertiary C—H bond (radical **3** in Scheme 4), the BDE is close to that observed for isobutane.[48]

In Schemes 3 and 4, three types of C—C bond dissociation are considered for methylcyclobutyl and methylcyclopentyl radicals: (1) the β-scission of the methyl group, leading to the formation of cycloalkene and CH_3 radical (reaction **4** → **10** in Schemes 3 and 4); (2) the endo β-scission, which corresponds to the ring opening with the π bond being formed within the ring (reactions **4** → **5**, **4** → **11**, **6** → **7**, and **8** → **9** in Scheme 3 and reactions **3** → **7**, **4** → **8**, **4** → **9**, **5** → **11**, and **5** → **12** in Scheme 4) (these reactions are similar to those considered in section 4, where no alkyl substitution was considered); and (3) the exo β-scission, which corresponds to the ring opening with the π bond being formed out of the ring (reaction **2** → **3** in Scheme 3 and reaction **2** → **6** in Scheme 4).

Consider the activation energies involved in the first series of reactions. We note that the values obtained are relatively close to the one reported for the β-scission of a CH_3 group in alkyl free radicals (31 kcal mol^{-1}, Buda et al.[49]) and that the ring structure does not strongly affect the cleavage of the alkyl side chain. An interesting feature concerns the activation energy differences between endo and exo β-scissions. Indeed, endo β-scissions require greater activation energies than exo β-scissions (11 kcal mol^{-1} for methylcyclopentyl and 15 kcal mol^{-1} for methylcyclobutyl). Figure 7 illustrates the TS geometries obtained at the B3LYP/cbsb7 level of theory for β-scissions in methylcyclobutyl radical: an endo β-scission (reaction **4** → **5** in Scheme 3) and an exo β-scission (reaction **2** → **3** in Scheme 3).

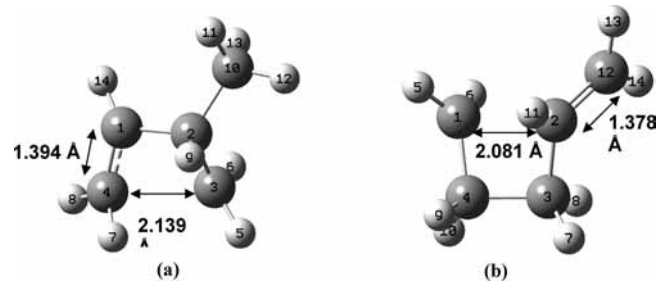
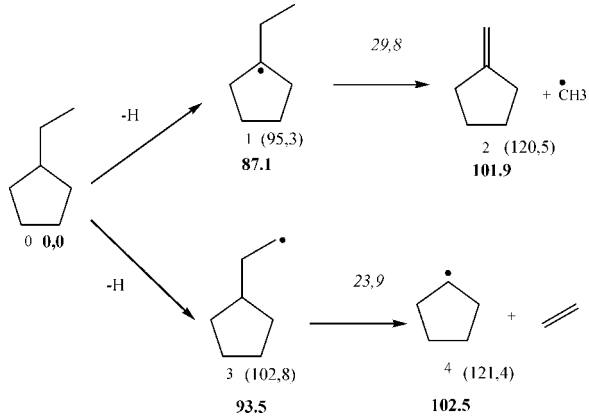


Figure 7. Geometries of the TSs in the β-scissions of methylcyclobutyl radicals, obtained at the B3LYP/cbsb7 level of calculation: (a) endo ring opening (**4** → **5** in Scheme 3) and (b) exo ring opening (**2** → **3** in Scheme 3).

As shown in Figure 7a, in the endo ring opening, the formation of the π bond requires a rotation of the CH_2 group (atoms 4, 7, and 8) around the 1—4 bond to bring these atoms into the same plane as atoms 1 and 14. As discussed above, this rotation is hindered by the cyclic structure of the TS. In contrast, in the exo β-scission (Figure 7b), formation of the π

SCHEME 5: β-Scissions of Two Isomers of Ethylcyclopentyl Radicals[a]



[a] Gibbs free energies (in bold), activation enthalpies (in italics), and enthalpies of reaction (in parentheses) at 298 K are reported in kcal mol^{-1} and are relative to the reference cycloalkane.

bond involves the rotation of the CH_2 group linked to the ring (atoms 12−14), which can be carried out quite easily. Not surprisingly, exo β-scission exhibits a lower activation energy than endo β-scission. The C—C distances in Figure 7 also show that the distance between carbons 4 and 3 (d = 2.139 Å) in endo ring opening is greater than that between carbons 1 and 2 (d = 2.081 Å) in exo ring opening. It is seen that, in endo ring opening, the deformation of the cyclic structure to create a double bond is significant. It is worth noting that, even in the exo β-scission, the ring strain energy is not completely released in the TS. In the case of the cyclobutyl radical, the activation energy would be 3.4 kcal mol^{-1} if all of the RE had been released in the TS, whereas the value obtained for reaction **2** → **3** in Scheme 3 is equal to 12.3 kcal mol^{-1}. This result confirms that the TS in the exo β-scission of methylcyclobutyl radical is tight and has a pronounced cyclic character.

Another interesting comment can be made by comparing the activation energies and those obtained in the β-scission of straight-chain alkyl radicals. In the case of methylcyclobutyl radicals, the activation energies obtained are always lower, even for endo β-scissions, than those found for alkyl radicals (about 28 kcal mol^{-1}). The release of a large part of the RE involved in cyclobutyl (RE = 24.4 kcal mol^{-1}) balances the steric inhibition created by the π-bond formation. Conversely, for methylcyclopentyl radicals, the RE is much smaller (4.1 kcal mol^{-1}), and the partial recovery of the RE is not sufficient to compensate the steric inhibition in the case of the endo β-scission. As a consequence, the activation energies obtained for endo ring openings are greater than the activation energies of straight-chain alkyl radicals.

5.2. Influence of the Size of the Lateral Alkyl Chain: Ethylcyclopentyl Decomposition. For ethylcyclopentyl, one observes the formation of the same type of products as for the methylcyclopentyl radical, except for two new elementary processes presented in Scheme 5. These new processes correspond to the rupture of the alkyl side chain and lead to the formation of cyclopentane methylene and cyclopentyl radical. For reaction **1** → **2**, the activation energy is close to that for the β-scission of the CH_3 group in a straight-chain alkyl radical,[50] whereas the value obtained for the reaction **3** → **4** (23.9 kcal mol^{-1}) is smaller. The less stable primary center in **3** is certainly responsible for the lowered activation energy as compared to the more stable tertiary radical in **1**.

As mentioned previously, all other reactions involved in the decomposition scheme of ethylcyclopentyl radicals lead to the same types of products with activation energies similar to those of methylcyclopentyl radicals. Thus, the size of the alkyl side chain does not impact the activation energy for a given class of β-scission reactions, i.e., endo or exo ring opening. The detailed scheme for ethylcyclopentyl can be found in the Supporting Information.

TABLE 8: Rate Parameters for the C—C Bond Breaking of Methylcyclobutyl Radicals in Scheme 3 for 500 ≤ *T* (K) ≤ 2000

reaction	A (s^{-1})	n	E (kcal mol^{-1})
2 → **3**	1.51×10^{10}	0.899	12.84
4 → **5**	1.82×10^{12}	0.331	27.86
4 → **10** + CH_3	3.31×10^{11}	0.810	33.02
4 → **11**	6.31×10^{12}	0.235	26.62
6 → **7**	3.16×10^{14}	−0.282	27.93
8 → **9**	1.44×10^{11}	0.702	28.83

TABLE 9: Rate Parameters for the C—C Bond Breaking of Methylcyclopentyl Radicals in Scheme 4 for 500 ≤ *T* (K) ≤ 2000

reaction	A (s^{-1})	n	E (kcal mol^{-1})
2 → **6**	2.75×10^{9}	0.991	23.26
6 → **2**	7.93×10^{4}	1.951	6.45
3 → **7**	1.86×10^{12}	0.419	34.37
4 → **8**	3.47×10^{10}	0.959	33.91
4 → **9**	4.27×10^{12}	0.404	33.71
4 → **10** + CH_3	4.57×10^{11}	0.843	30.53
5 → **11**	1.44×10^{13}	0.277	33.74
5 → **12**	6.76×10^{11}	0.692	35.45

TABLE 10: Rate for Parameters the C—C Bond Breaking of Ethylcyclopentyl Radicals in Scheme 5 for 500 ≤ *T* (K) ≤ 2000

reaction	A (s^{-1})	n	E (kcal mol^{-1})
1 → **2**	8.51×10^{9}	1.485	30.30
3 → **4**	5.01×10^{8}	1.286	24.05

5.3. Rate Parameters. Kinetic parameters are presented in Tables 8 −10. It is interesting to note that the pre-exponential factors for exo β-scissions are lower than those for endo β-scissions. This can be explained by an entropic effect given that, in the former case, the internal rotation of the CH_3 group is lost in the TS (as a result of the formation of the double bond) whereas, in the latter case, the rotation of the CH_3 group contributes to the entropy of the TS.

Very few rate constants are available in the literature for the β-scissions in methylcyclobutyl and methylcyclopentyl. Rate rules for cycloalkyl ring closures or openings were listed by Newcomb.[10] A rate constant for the exo ring opening of methycyclobutyl radical (reaction **2** → **3** in Scheme 3) is proposed in an experimental study of Walton.[51] Figure 8 compares the values obtained here for the rate constant with those proposed by Walton.

This comparison shows that the rate constant calculated in our work has a higher activation energy. However, the rate values are within a factor 0.5−3 of each other from 500 to 2000 K. For the exo β-scission of methylcyclopentyl, Newcomb[10] proposed a rate constant related to the inverse reaction, i.e., the ring closure of 1-hexen-6-yl radical, with rate parameters derived from room-temperature experiments of Chatgilialoglu et al.[52] and estimation of the pre-exponential factor based on analogous ring-closure reactions. Figure 9 compares the values obtained with the rate constant suggested by Newcomb and that from our CBS-QB3 calculations for the reaction **6** → **2** related to Scheme 4.

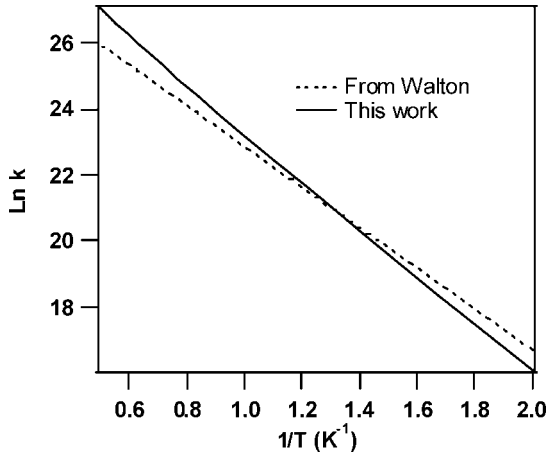


Figure 8. Comparison between the rate constant proposed by Walton[51] and that obtained from our CBS-QB3 calculations for the exo ring opening of methylcyclobutyl free radical (reaction **2** → **3** in Scheme 3) at temperatures in the range $500 \leq T\,(\mathrm{K}) \leq 2000$.

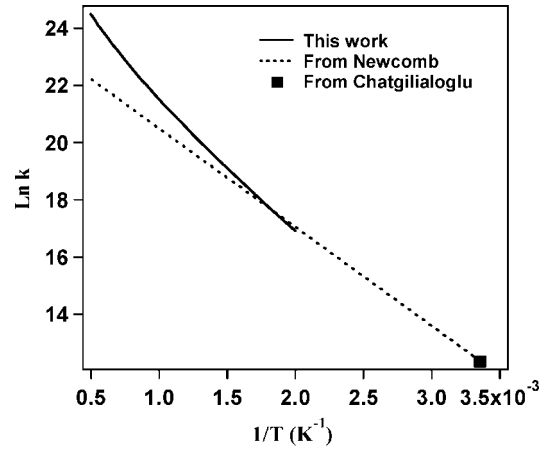


Figure 9. Comparison between the rate constant proposed by Newcomb[10] and that obtained from our CBS-QB3 calculations (Table 9) for the ring closure of 1-hexen-6-yl radical (reaction **6** → **2** in Scheme 4) at temperatures in the range $500 \leq T\,(\mathrm{K}) \leq 2000$.

As can be seen, the rate constants are in good agreement at around 800 K. At 2000 K, a factor of 10 difference is reached. Because the rate expression of Newcomb[10] was derived from the room-temperature experiments of Chatgilialoglu et al.,[52] as shown in Figure 9, the discrepancy at high temperature is not surprising.

6. Evans−Polanyi Correlation for the β-Scission of Cycloalkyl and Linear Alkyl Free Radicals

Our theoretical study on the ring opening of cycloalkyl radicals highlights the roles of the ring strain energy and the π-bond formation in the transition state. We showed that three types of reactions can occur during the decomposition of cycloalkyl radicals: endo and exo ring opening and β-scission of an alkyl group. It is interesting to compare the activation energies involved in the three elementary β-scission processes with the enthalpies of reaction, i.e., to build an Evans−Polanyi plot at 298 K. The plot was constructed by considering all of the reactions included in Schemes 2−4. We also included further calculations of the activation energies for all possible ring-opening processes (endo and exo) in methylcyclopropyl and ethylcyclopentyl isomers, as well as β-scissions of the alkyl side chain. All of these results were obtained at the CBS-QB3 level of calculation.

TABLE 11: Reaction Enthalpies and Activation Enthalpies Obtained at the CBS-QB3 Level of Calculation for the β-Scissions of C−C and C−H Bonds of Acyclic Radicals Used in the Evans−Polanyi Plot ($T = 298$ K)

reactions considered in the Evans−Polanyi correlation	$\Delta_r H°$ (kcal mol^{-1})	$\Delta H^{\ddagger\circ}_{298\,\mathrm{K}}$ (kcal mol^{-1})
$\bullet C_3H_7 \rightarrow \bullet CH_3 + C_2H_4$	22.8	28.9
$\bullet C_4H_9 \rightarrow \bullet C_2H_5 + C_2H_4$	22.0	27.8
$\bullet C_5H_{11} \rightarrow \bullet C_3H_7 + C_2H_4$	22.8	28.2
$\bullet C_6H_{13} \rightarrow \bullet C_4H_9 + C_2H_4$	22.7	28.0
$\bullet C_7H_{15} \rightarrow \bullet C_5H_{11} + C_2H_4$	22.7	28.0
1-hexen-6-yl → 1-buten-4-yl + C_2H_4	22.8	27.8
1-hexen-3-yl → buta-1.3-diene + $\bullet C_2H_5$	15.7	25.0
1-penten-5-yl → $\bullet C_3H_5 + C_2H_4$	7.4	19.2
$\bullet C_3H_7 \rightarrow C_3H_6 + H$	32.0	34.0
$\bullet C_4H_9 \rightarrow C_4H_8 + H$	32.6	34.4
$\bullet C_5H_{11} \rightarrow C_5H_{10} + H$	32.5	34.4
$\bullet C_6H_{13} \rightarrow C_6H_{12} + H$	32.4	34.4
$\bullet C_7H_{15} \rightarrow C_7H_{14} + H$	32.4	34.2

To compare the activation energies involved in the β-scissions of cycloalkyls with those of linear alkyl free radicals in an Evans−Polanyi plot, we also considered the ruptures of C−C and C−H bonds for several linear alkyl radicals presented in Table 11.

Figure 10 shows the results obtained for the Evans−Polanyi plot at 298 K and for all of the reactions mentioned above. Activation energies for β-scissions of alkyl groups, C−H ruptures, and exo ring openings of cycloalkyl radicals correlate well with C−C and C−H bond breaking of linear alkyl radicals, except for β-scissions 1−3 (Figure 10). These last reactions correspond to exo β-scissions of methyl cyclopropyl radicals (1, 2) and the C−H bond scission of cyclopropyl (3).

These results are not surprising given that the REs in cyclopropyl and cyclopropene are very important and can lead to particular behavior. The activation energy obtained for endo ring opening in the C_6 cycloalkyl radical is also in good agreement with the previous values. The latter result can be explained by the low ring strain energy involved in this structure, associated with a moderate steric inhibition effect when the π bond is being formed in the TS. For C_7 ring opening, the agreement is a little worse, and the activation energy obtained was not included in the correlation.

For endo ring opening of C_3−C_5 cycloalkyl radicals, the activation energies are clearly not correlated with β-scissions of straight-chain alkyl radicals. However, we note that, for a given size of the cyclic structure, the effect of alkyl substitution is relatively weak and, at a first approximation, the same activation energy can be used in this case. The Evans−Polanyi correlation (eq 8) was obtained by including all reactions considered in this study except those of endo ring opening of C_4, C_5, and C_7 cycloalkyl radicals and all C−C and C−H bond cleavages of C_3 cyclic structures

$$E_a\,(\mathrm{kcal\ mol^{-1}}) = 14.3\,(\pm 0.6) + [0.60\,(\pm 0.02)]\Delta_r H^{\circ}_{298\,\mathrm{K}}\,(\mathrm{kcal\ mol^{-1}}) \quad (8)$$

The latter simplification was made in order to obtain a more accurate Evans−Polanyi correlation but also because of the practical importance of C_4−C_6 cyclic structures.

For endo ring opening of C_4 and C_5 cycloalkyl free radicals, the rate parameters given in Table 6 can be used as estimates in mechanism construction.

7. Conclusion

In this work, the unimolecular decomposition of cycloalkyl radicals with and without an alkyl side chain were investigated

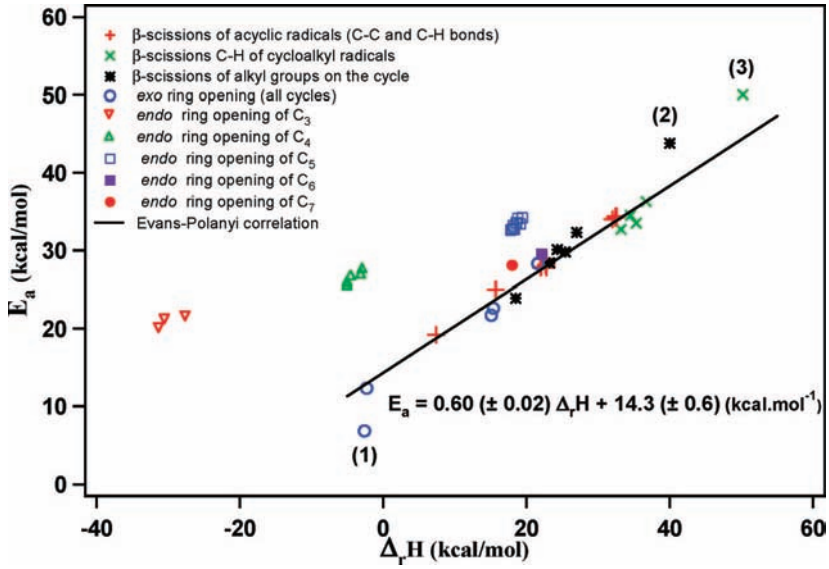


Figure 10. Evans−Polanyi correlation for the β-scissions of linear and cyclic alkyl free radicals at $T = 298$ K. Values obtained at the CBS-QB3 level of calculation.

at the CBS-QB3 level of theory. The study of unsubstituted cycloalkyl radicals revealed the importance of two opposite effects on the activation energy (E_a). The first effect tends to decrease the energy barrier and is related to the ring strain energy (RE) in the reactants. In general, only part of the RE is released at the saddle point. The second effect tends to increase E_a and is related to π-bond formation in the TS, which introduces steric hindrance. This effect is particularly important in the case of the cyclopentyl ring: E_a for this reaction is as high as 33.5 kcal mol^{-1}. Different methylcycloalkyl radicals were also investigated. The radical center is located either on a ring carbon atom or on the alkyl side chain. If the radical center is in the ring, two types of reaction can occur: (a) an endo ring opening, which presents the same characteristics as the equivalent process in unsubstituted cycloalkyl radicals, and (b) the removal of the alkyl side chain. If the radical center is on the methyl side chain, exo ring openings can occur that proceed with lower E_a's than endo ring openings. This can be explained by the fact that, in exo ring opening, the formation of the π bond occurs out of the ring, involving lower steric inhibition. Increasing the size of the alkyl side chain from methyl to ethyl leads to additional pathways involving the fragmentation of the alkyl chain. The ring opening in branched cycloalkyl radicals appears to be independent of the size of the alkyl side chain. The C−H bond breakings for cycloalkyl radicals were also studied, and it was found that the C−H β-scission rate is close to that of a strain-free alkyl.

Finally, an Evans−Polanyi correlation was proposed for β-scissions of straight-chain alkyl radicals, exo ring opening in C_4-C_7, C−H and alkyl chain ruptures of C_4-C_6 cycloalkyl radicals, and endo C_6 ring opening. For endo ring opening in C_3-C_5 cycloalkyl radicals, the Evans−Polanyi diagram shows that a lateral alkyl side chain does not affect the activation energy of β-scissions strongly. The Evans−Polanyi correlation derived in this work constitutes an interesting contribution in the field of cyclic alkane reactivity, as it allows the estimation of the activation energies of C−C and C−H bond β-scissions involving not only linear alkyl radicals but also any cyclic alkyl radicals with a ring size ranging from C_4 to C_6, with or without alkyl substitution.

Acknowledgment. We thank Professor A. Hocquet (Laboratoire de Chimie Physique Macromoléculaire of Nancy Universités, France) for helpful discussions concerning AIM analyses. The Centre Informatique National de l'Enseignement Supérieur (CINES) is gratefully acknowledged for the allocation of computational resources.

Supporting Information Available: Full list of authors in ref 16, structural parameters for all of the species investigated in this study, energies and zero-point energies, isodesmic reactions, and vibrational frequencies. Detailed decomposition schemes of methylcyclopropyl and ethylcyclopentyl. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP805640S