



Theoretical studies of the effects of substituents on the ring opening reactions for the cyclopropylcarbinyl radical

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ABSTRACT

DFT (U)B3LYP/6-31G(d,p), (U)B3LYP/6-31+G(d,p), and (U)B3LYP/6-311+G(d,p) calculations were carried out to investigate the ring opening reactions of the cyclopropylcarbinyl radical (leading to the 3-butenyl radical) and its mono-substituted analogues containing the methyl, ethyl, propyl, isopropyl, isobutyl, fluorine, chlorine, bromine, hydroxyl, methoxy, cyanogen, nitril, vinyl, and phenyl substituents on the ring (leading to the pseudo-secondary and primary radicals, respectively). The enthalpies of activation, rate constants, and reaction enthalpies for all ring opening reactions were calculated. The predicted enthalpy of activation, rate constant, and reaction enthalpy of the cyclopropylcarbinyl radical ring opening reaction are in excellent agreement with the corresponding experimental values. For the alkyl (methyl, ethyl, propyl, isopropyl, and isobutyl) substitutions, steric effects are found to be the dominating factor to affect the ring opening reactions, while for the rest substitutions, the stereoelectronic effects play the most important roles. Our calculations indicate that the cyanogen, nitril, vinyl, and phenyl substituents, which contain π bonds, have much larger effects on the ring opening reactions than the other substituents.

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1. Introduction

The ring opening of the cyclopropylcarbinyl radical to the 3-butenyl radical has attracted many experimental and theoretical research workers [1–13], because it is a fast radical rearrangement that holds a position of distinction in mechanistic studies involving ‘radical clocks’ and ‘mechanistic probes’ for the intermediacy radicals in both chemical [1,2] and biochemical [1,3,4] processes. Additionally, many biochemical processes have been suggested to involve such type reaction [5]. The rate constant of this ring opening at various temperature ranges was investigated experimentally by several groups [6–9]. Maillard et al. [6], Mathew and Warkentin [7], Beckwith et al. [8], and Newcomb and Glenn [9] determined the rate constant of the cyclopropylcarbinyl radical ring opening in the temperature ranges of 128–153 K, 303–363 K, 313–398 K, and 236–323 K, giving the temperature dependent functions of $\log k/s^{-1} = 12.48 \pm 0.85 - (5.94 \pm 0.57)/\theta$, $\log k/s^{-1} = 13.9 \pm 0.4 - (7.6 \pm 0.2)/\theta$, $\log k/s^{-1} = 13.3 - 7.4/\theta$, and $\log k/s^{-1} = (13.0 \pm 0.14) - (6.8 \pm 0.2)/\theta$, respectively, where $\theta = 2.3RT$ kcal/mol. The rate constants at 298 K were calculated from above equations to be 1.3×10^8 , 2.1×10^8 , 7.4×10^7 , and 1.0×10^8 s⁻¹ and Arrhenius activation energies to be 5.94 ± 0.57 , 7.6 ± 0.2 , 7.4 , and 6.8 ± 0.2 kcal/mol, respectively. By a equally weighted combination of

their data with the kinetic data from Maillard et al. [6] and Beckwith et al. [8], Newcomb and Glenn [9] obtained a quite reliable Arrhenius equation of $\log k/s^{-1} = 13.15 - 7.05/\theta$, where $\theta = 2.3RT$ kcal/mol, from which the rate constant at 298 K was calculated to be 9.4×10^7 s⁻¹ and Arrhenius activation energy to be 7.05 kcal/mol. Theoretically, the enthalpy of activation and reaction enthalpy for this ring opening were calculated by Hehre [10] using the UHF/STO-3G method, by Dewar et al. [11] using the MINDO/3 method, and by Martinez et al. [12] using the UHF/6-31G(d), UMP2/6-31G(d)//HF/6-31G(d), PMP2/6-31G(d)//HF/6-31G(d), QCISD/6-31G(d), and G2 [using HF/6-31G(d) geometry] methods. In 1998, Smith et al. [13] carried out the systematic studies on the cyclopropylcarbinyl radical ring opening. They performed geometry optimization calculations using the UHF, UPM2 (full), RMP2, B3LYP, and QCISD methods, all in conjunction with the 6-31G(d) basis set, and single-point energy calculations using the B3LYP/6-311+G(d,p), B3LYP/6-311+G(3df,2p), MP2/6-311+G(d,p), MP2/6-311+G(3df,2p), G2 and CBS methods and found that B3LYP/6-31G(d) performed well for geometry- and frequency-dependent quantities. All the calculated results mentioned above were summarized in Table 1.

The effects of several substituents on the cyclopropylcarbinyl radical ring opening reaction have been investigated experimentally [3,14–16]. The experimental results indicated that substituents have different effects on the ring openings, depending on the properties, positions, and numbers of substituents. For

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Table 1

The available calculated enthalpies of activation (ΔH^\ddagger) and reaction enthalpies (ΔH) for the cyclopropylcarbinyl radical ring opening reaction in the literature. The values are all given in kcal/mol.

| | HF ^a | MINDO/3 ^b | UHF ^c | UMP2 ^c | PMP2 ^c | QCISD ^c | G2 ^c | CBS-RAD ^d | B3LYP ^d | PMP2 ^d |
|---------------------|-----------------|----------------------|------------------|-------------------|-------------------|--------------------|-----------------|----------------------|--------------------|-------------------|
| ΔH^\ddagger | 21.6 | 12.5 | 10.6 | 15.5 | 8.3 | 10.4 | 7.9 | 7.87 | 7.34 | 8.68 |
| ΔH | | | -5.2 | -8.7 | -4.0 | -3.1 | -3.0 | -2.18 | -3.37 | 0.31 |

^a From Ref. [10].

^b From Ref. [11].

^c From Ref. [12].

^d From Ref. [13].

example, the rate constants of the ring openings for the methyl substituted radicals at 310 K were determined to range from $8.0 \times 10^7 \text{ s}^{-1}$ for 1-methylcyclopropylcarbinyl radical to $4.7 \times 10^9 \text{ s}^{-1}$ for pents-methylcyclopropylcarbinyl radical by Bowry et al. [14], while that of the phenyl substituted radicals at 298 K to be $3 \times 10^{11} \text{ s}^{-1}$ for the *trans*-(2-phenylcyclopropyl) carbinyl, $4 \times 10^{11} \text{ s}^{-1}$ for the *cis*-(2-phenylcyclopropyl) carbinyl, and $5 \times 10^{11} \text{ s}^{-1}$ for the (2,2-diphenylcyclopropyl) carbinyl by Newcomb et al. [15].

In the present work, we selected the 14 substituents (methyl, ethyl, propyl, isopropyl, isobutyl, fluorine, chlorine, bromine, hydroxyl, methoxy, cyanogen, nitril, vinyl, and phenyl) as our objects to investigate the effects of the substituents on the structure and reactivity of the cyclopropylcarbinyl radical theoretically and only a single substituent on the ring was considered. For the mono substitution on the ring, there exist two conformations (*cis* and *trans* relative to carbinyl moiety) and for both conformations there are two nondegenerate channels for ring cleavages (the cleavages of the proximal and distal bonds). Therefore, there are four possible reactions (reactions q1–q4, see Fig. 1) for each substituted radical.

To the best of our knowledge, among the 14 substituents, only the methyl and phenyl substituted radical ring openings were investigated experimentally (see above). Theoretically, the ring openings of the methyl, fluorine, methoxy, and vinyl substituted cyclopropylcarbinyl radicals were studied [12,17–18]. Martinez et al. [12,18] studied the effects of the methyl, vinyl, and methoxy substituents on the cyclopropylcarbinyl radical ring opening at the PMP2/6-31G(d)//UHF/6-31G(d) level. For the mono methyl substitution on the ring, they computed the enthalpies of activation and relative rates to the unsubstituted radical ring opening for reactions a1–a4 (see Fig. 1), the former being evaluated to be 7.45, 6.91, 7.51, and 7.97 kcal/mol and the latter to be 1.8, 5.1, 2.0, and 1.2, respectively, and they concluded that the steric effect was the dominating influence for the ring opening [12]. For the mono methoxy and vinyl substitutions on the ring [18], they calculated the enthalpies of activation and the reaction enthalpies for reactions j1–j4 and m1–m4 (see Fig. 1) and obtained the enthalpies of activation of 7.01, 6.53, 6.84, and 6.20 kcal/mol for the methoxy substitution and 8.70, 1.20, 10.00, and 0.52 kcal/mol for the vinyl substitution, respectively, and the reaction enthalpy values of

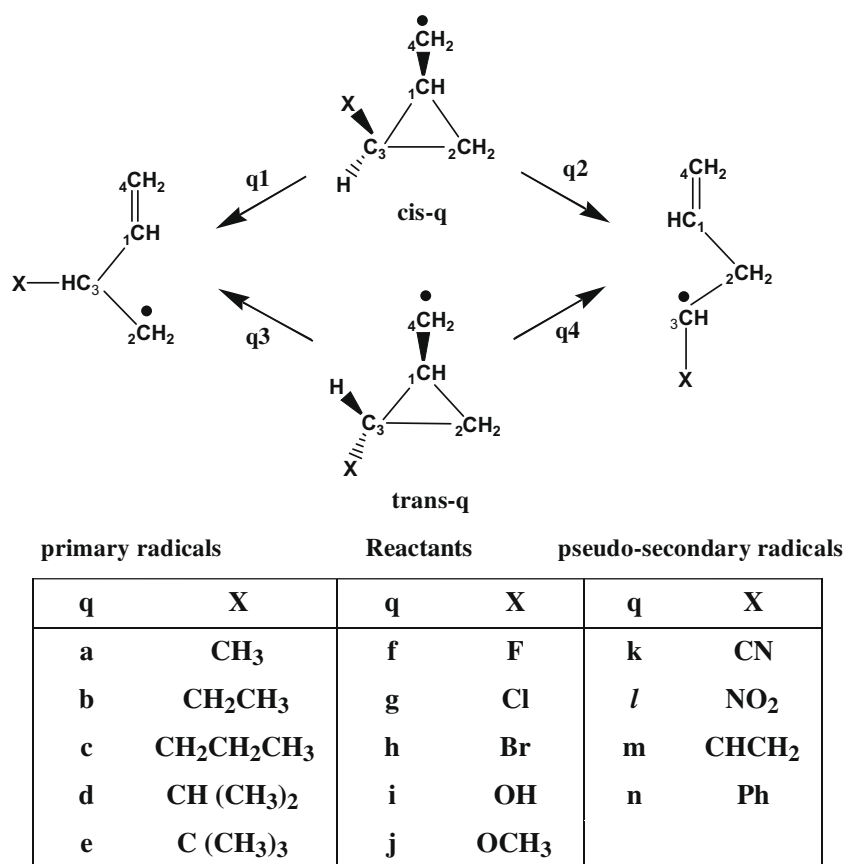


Fig. 1. The four possible reactions of X- substituted cyclopropylcarbinyl radicals, leading to the pseudo-secondary and primary radicals.

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