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An MO Study of Fragmentation Mechanism of Ethane and Propane Radical Cations

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The decomposition mechanisms were studied for ionized species of ethane and propane in the low-energy region by using an ab initio molecular orbital method. Calculations show that rather complex fragmentation processes may occur in addition to a simple cleavage of C–C and C–H bonds. In order to examine the possibility of an elimination of H_2 or CH_4 from the radical cation of saturated hydrocarbons, the potential energy curves were calculated for both 1,1- and 1,2-eliminations. An energy barrier of 1,2-elimination was estimated to be small, but a 1,1-elimination can also possibly occur. It was also found that a single C–H bond scission of the parent radical cation may occur with the same order of energy for the H_2 loss. The present results are qualitatively in a good agreement with the experiments.

The mass spectra of saturated hydrocarbons give a complex pattern for the fragment species caused by ionization under electron bombardment,[1] although there are only two different kinds of bonds: C–C and C–H. Since saturated hydrocarbon molecules are fundamental organic molecules constructed with σ-frameworks, it is important to investigate the behavior of the ionized species produced by removing a σ-bonding electron in order to understand the fragmentation pattern of the mass spectra.

The unimolecular decomposition processes of radical cation species are strongly related to the electronic structure of the parent molecules. When molecules have a double bond or heteroatoms, a characteristic mass spectrum can be observed; this result can be effectively used for a molecular identification. In the case of saturated hydrocarbon, however, mechanistic studies have been very few, since various types of fragment ions are observed. In this respect, we carried out a quantum chemical investigation and theoretically explored the mechanism of the fragmentation processes for saturated hydrocarbon. In this paper, we look at for ethane and propane as the simplest system.

Theoretical Procedure

The molecular geometries of radical cations are calculated by using an analytical gradient method based on an unrestricted Hartree-Fock (UHF) method with STO-3G and 6-31G basis sets.[2] In order to determine whether the structures obtained by geometry optimization are located at equilibrium or a transition state, we carried out vibrational analysis by using an analytical second derivative method.[3]

Results and Discussion

Experimental data resulting from electron impact and photoionization studies for propane and butane show that cation species are mainly produced by a simple cleavage of the C–C bond in the high-energy region. In the low-energy region, however, it seems that there are rather complex processes, such as H_2 or CH_4 loss, or isomerization.[4,5] Before discussing the fragmentation mechanisms of propane, we consider the potential energy surfaces for the fragmentation processes of the ethane radical cation, especially in the lowest electronic state.

$C_2H_6^{+\cdot}$. The experimental data for ethane by electron impact shows that various kinds of fragment ions are produced and $C_2H_5^+$, $C_2H_4^{+\cdot}$, $C_2H_3^+$, $C_2H_2^{+\cdot}$, and CH_3^+ are observed in the electron energy from 10 to 23 eV.[6] It should be noted that the appearance potential of $C_2H_5^+$ (12.5 eV) is nearly the same as that of $C_2H_4^{+\cdot}$ (12.1 eV). This evidence is also shown by photoionization,[7] and suggests that the H_2 elimination competes with the hydrogen atom loss from an ethane radical cation.

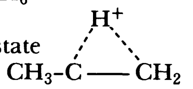
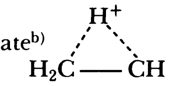
Unimolecular fragmentation takes place by breaking two C–H bonds which can be distinguished as 1,2-elimination and 1,1-elimination. The products are an ethylene radical cation $CH_2{=}CH_2^{+\cdot}$ and a methylcarbene radical cation $CH_3{-}CH^{+\cdot}$, respectively. Table 1 summarizes the energies of the parent ion $C_2H_6^{+\cdot}$ and fragments $C_2H_5^+$, $C_2H_4^{+\cdot}$, CH_3^+, etc. calculated at their equilibrium structures. Since the electron correlation effect is important for estimating the energy barrier, we also calculated the energies by using the MP3 method, as shown in Table 1. However, the qualitative feature of the product distribution for ionized species may be read from the SCF results.

Table 1 shows that the most stable fragments are $CH_2{=}CH_2^{+\cdot}{+}H_2$ and that the energy is 0.8 eV lower than that of $CH_3CH_2^{+}{+}H\cdot$. This result seems to be consistent with the fact that the appearance potential of $C_2H_4^{+\cdot}$ is lower than that of $C_2H_5^+$. However, we must consider the barrier height to dissociate two hydrogens from ethane radical cation.

Let us discuss the energy barrier for the H_2 loss via a 1,2-elimination:[8]

$$C_2H_6^{+\cdot} \rightarrow C_2H_4^{+\cdot} + H_2. \qquad (1)$$

Table 1. Total Energies (in Hartree) of Various Species Generated from the Ionization of Ethane and Propane[a)]

Method	HF	MP3	HF
Basis set	STO-3G	STO-3G	6-31G
C_3H_8 neutral ground state	−116.88642	−117.08059	−118.21617
$C_3H_8^{+\cdot}$ vertical ionized state			
C-C σ cation radical	−116.49155	—	−117.79739
π type C-H cation radical	−116.46667	—	−117.78382
$CH_3\text{-}CH_2\text{-}CH_3^{+\cdot}$	−116.54206	−116.72690	−117.85933
$CH_3\text{-}CH_2\text{-}CH_2^{+}$	−115.99633	−116.18340	−117.30797
$CH_3\text{-}CH\text{-}CH_3^{+}$	−116.02765	−116.21168	−117.33564
$CH_3\text{-}CH{=}CH_2^{+\cdot}$	−115.40747	−115.58188	−116.72748
$CH_3\text{-}CH_2\text{-}CH^{+\cdot}$	−115.34682	−115.51503	−116.65761
$CH_3\text{-}C\text{-}CH_3^{+\cdot}$	−115.38648	−115.55241	−116.69427
cyclo-$C_3H_6^{+\cdot}$	−115.38241	−115.56121	−116.69718
Tranisition state  $CH_3\text{-}C\overset{H^+}{\text{——}}CH_2$	−115.33808	−115.51734	−116.65693
C_2H_6 neutral ground state	−78.30618	−78.43054	−79.19757
$C_3H_6^{+\cdot}$ vertical ionized state			
C-C σ cation radical	−77.88165	—	−78.75330
π type C-H cation radical	−77.86100	—	−78.74363
$CH_3\text{-}CH_3^{+\cdot}$	−77.94048	−78.06046	−78.82031
$CH_3\text{-}CH_2^{+}$	−77.40806	−77.52825	−78.28072
$CH_3\text{-}CH_2\cdot$	−77.66300	−77.77419	−78.56873
$CH_2{=}CH_2^{+\cdot}$	−76.79755	−76.90882	−77.68118
$CH_3\text{-}CH^{+\cdot}$	−76.75790	−76.86099	−77.62983
Transition state[b)]  $H_2C\overset{H^+}{\text{——}}CH$	−76.73129	−76.84920	−77.61239
CH_4	−39.72686	−39.79712	−40.18055
CH_3^{+}	−38.77948	−38.83436	−39.21621
$CH_3\cdot$	−39.07701	−39.12706	−39.54666
$CH_2^{+\cdot}$	−38.11894	−38.15645	−38.55390
H_2	−1.11751	−1.13452	−1.12683
$H\cdot$	−0.46658	−0.46658	−0.49823

a) Equilibrium geometries are obtained by Hartree-Fock method (UHF method for radicals and RHF method for closed-shell molecules). The energies by MP3 method (third-order Møller-Plesset perturbation theory) are calculated at the geometries optimized by HF method with STO-3G basis set. b) Ref. 15.

In the case of a neutral ethane molecule, a reaction in which two hydrogens synchronously dissociate is known to be symmetry forbidden in the sense of the Woodward-Hoffmann rule. On the other hand, if one electron is removed from the system, one may expect that the barrier height of the 1,2-H_2 elimination for the ethane radical cation would be less than that in the case of a neutral molecule. Since an ethane radical cation is a potentially high energy species, the energy of a C-H bond dissociation of $C_2H_6^{+\cdot}$ has been calculated to be only 1.1 eV (6-31G). When we calculate the potential energy curve for a hydrogen abstraction reaction,

$$C_2H_5^{+} + H\cdot \rightarrow C_2H_4^{+\cdot} + H_2, \quad (2)$$

the reaction is found to be exothermic and to proceeds without an energy barrier. Therefore, we could estimate that the barrier height of a 1,2-H_2 elimination process,

$$C_2H_6^{+\cdot} \rightarrow [CH_3\text{-}CH_2\cdots H]^{+\cdot} \rightarrow [CH_2{=}CH_2]^{+\cdot} + H_2 \quad (3)$$

should not be greater than that of a two-step 1,2-H_2 elimination process:

$$C_2H_6^{+\cdot} \rightarrow [CH_3\text{-}CH_2]^{+} + H\cdot \rightarrow [CH_2{=}CH_2]^{+\cdot} + H_2. \quad (4)$$

Such an energy relation may explain why the appearance potential of $C_2H_4^{+\cdot}$ is slightly lower than that of $C_2H_5^{+}$ (see the dashed line in Fig. 2).

The other possibility of H_2 loss is a 1,1-elimination in which two hydrogens are removed from one carbon atom of ethane. Although a methylcarbene radical cation, being a product, seems to be a very unstable species, the energy of $CH_3CH^{+\cdot}+H_2$ is calculated to be only 0.6 eV higher than that of $CH_3CH_2^{+}+H\cdot$. This means that a 1,1-elimination can also occur. While electron-impact experiments for CH_3CD_3 at 70 eV show that $C_2H_2D_2^{+\cdot}$, $C_2H_3D^{+\cdot}$, and $C_2D_3H^{+\cdot}$ are all observed,[9)] experimental evidence for such mechanisms has not been reported in the low-energy region. The present calculation strongly suggests evidence for the formation of a carbene radical cation due to a H_2 or D_2 loss from $CH_3CD_3^{+\cdot}$. Such species have been men-

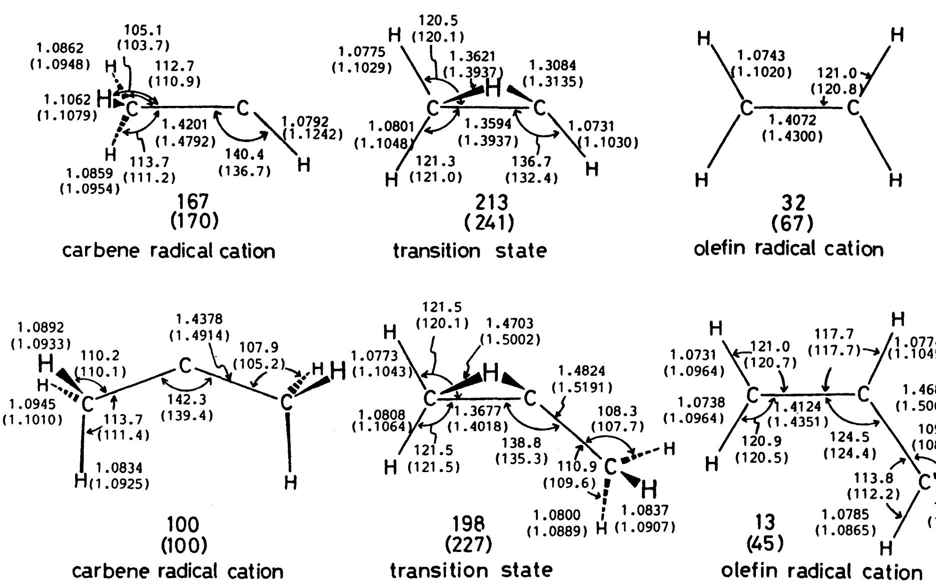


Fig. 1. The structures of methylcarbene radical cation and dimethylcarbene radical cation and their transition states of hydrogen migration calculated by using the UHF method with 6-31G (STO-3G) basis set. The units of bond lengths and bond angles are in Angstrom and degrees. The values shown in each geometry are the relative energies (kJ mol^{-1}) from the energy of the radical cation of ethane or propane at equilibrium structure. The values in parentheses are obtained with STO-3G basis set.

tioned as non-symmetric ethylene ions by von Koch[10] as the major precursor of acetylene ions. The methylcarbene radical cation may isomerize to a more stable ethylene radical cation; this energy barrier has been calculated to be ca. 0.5 eV. Figure 1 shows the geometries of the carbene radical cation and its transition state to an ethylene radical cation. The energy profile of this isomerization is shown by the curved line in Fig. 2. Most of the structures of other species have already been published elsewhere.[11,12,15]

Figure 2 summarizes the energy relations of the species formed by the ionization of ethane, as is discussed in this section. The ground state of an ethane radical cation was calculated to be a C-C σ-type radical cation which diabatically correlates to the cleavage of a C-C bond. The dissociation reaction of a C-C bond, however, requires more energy than the loss of H$\cdot$ or H_2. Since the energy of a C-C σ-type radical cation is very close to that of a C-H pseudo π-type radical cation, it would be expected that internal energy dispensation should rapidly occur during decomposition reactions.

$C_3H_8^{+\cdot}$. We have shown that there are two possibilities for removing two hydrogens from an ethane radical cation: 1,1- and 1,2-eliminations. In the case of propane, there are $CH_3\cdot$ and CH_4 losses as well as H$\cdot$ and H_2 losses. Table 1 also summarizes the energies of the possible fragments generated from propane. The potential energy surfaces are illustrated for H$\cdot$ and H_2 losses from $C_3H_8^{+\cdot}$ in Fig. 3(a) and for $CH_3\cdot$ and CH_4 losses in Fig. 3(b).

The experiment by Chupka and Berkowitz[7] shows that $C_3H_7^+$, $C_3H_6^{+\cdot}$, $C_2H_5^+$, and $C_2H_4^{+\cdot}$ are observed

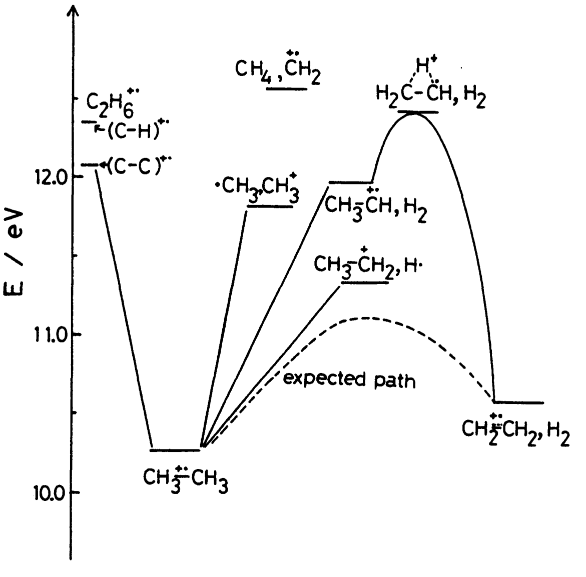


Fig. 2. The energy relations of the radical cation species caused by the ionization of ethane in the lowest state. The energies are calculated by UHF method at the optimized geometries with 6-31G basis set relative to the neutral ethane molecule.

over a narrow range: 11.3—11.9 eV. This means that losses of H$\cdot$, H_2, $CH_3\cdot$, and CH_4 from $C_3H_8^{+\cdot}$ occur at almost the same energy.[13]

As demonstrated in Fig. 3, the most stable product is an isopropyl cation. Due to the strong hyperconjugation by two methyl groups, the cation center prefers the central carbon to the terminal one. From Table 1, the dissociation of the central C-H bond in $C_3H_8^{+\cdot}$ is

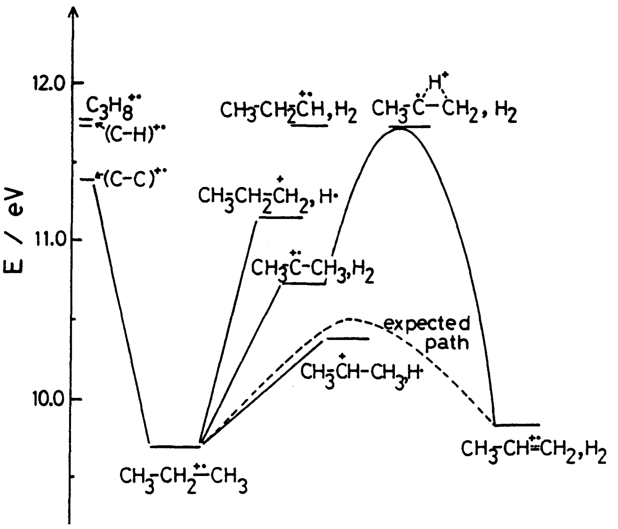


Fig. 3(a). The energy relations for H· and H_2 elimination from propane radical cation.

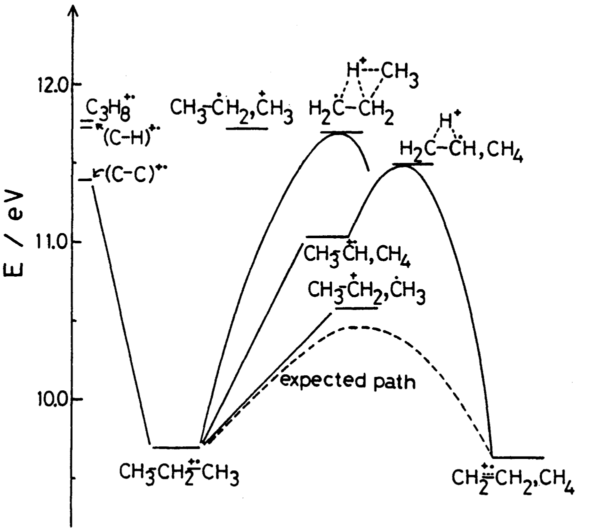


Fig. 3(b). The energy relations for CH_3· and CH_4 elimination from propane radical cation.

calculated to be only 0.7 eV (6-31G), while 1.4 eV is obtained for a terminal C-H bond dissociation.

Although an olefin π radical cation is energetically more stable, there is an energy barrier to be formed from a saturated hydrocarbon radical cation. It should be noted that the energy of the hydrogen atom loss of an ethane radical cation (1.1 eV) is in the middle of those of the central and terminal H· losses of $C_3H_8^{+\cdot}$ (0.7 eV and 1.4 eV). When the energy barrier of the H_2 loss of $C_3H_8^{+\cdot}$ is comparable to that in the case of $C_2H_6^{+\cdot}$, one can expect that the H· loss occurs more easily than the H_2 loss for $C_3H_8^{+\cdot}$. This expectation is in accord with the experimental results.[7]

Moreover, one can not neglect the two processes in which CH_4 or H_2 eliminates from the same carbon atom (1,1-elimination) and a different carbon atom (1,2-elimination). It is interesting that the energy of a dimethylcarbene radical cation is located between the energies of an isopropyl cation and a propyl cation. The molecular structure of a dimethylcarbene radical cation is illustrated in Fig. 1. Although the equilibrium geometry takes a C_2 symmetry, two methyl groups almost freely rotate internally. Since the carbene radical cation center is stabilized by two methyl groups, the energy barrier of the 1,2-hydrogen shift is calculated to be much higher than in the case of a methylcarbene radical cation. The dimethylcarbene radical cation is one of the strong candidates for a H_2 loss of the propane radical cation.

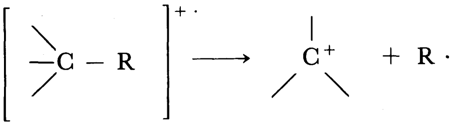
Molecular Orbitals and Ionization Potentials. The I.P. (ionization potential) from the high-lying occupied molecular orbitals of ethane is observed at 12.0—13.5 eV.[14] The degenerate C-H pseudo π-type bonding orbital ($1e_g$) and the C-C σ-type bond orbital ($3a_g$) are included in this energy region; these orbitals are energetically very close. Similar patterns of I.P. were measured at 11.5—12.6 eV in the case of propane. Although the highest occupied molecular orbitals of ethane and propane were assigned to be a C-H π-type molecular orbital through an RHF calculation,[14] a UHF calculation shows that the energy of a C-C σ-type radical cation is slightly lower than that of a C-H pseudo π-type radical cation. The energies of the vertical ionized states of ethane were estimated to be 12.1 eV for the C-C σ orbital and 12.4 eV for C-H π-type MO with the present UHF calculation.

As a result of geometry optimization, the lowest state of the ionized parent molecule was found to be a C-C σ-type radical cation for both ethane and propane. Since the energy difference is very small between C-C σ and C-H pseudo π-type radical cations, the electronic coupling between them becomes large through a geometrical relaxation. This fact would lead to the complex fragmentation profiles of ethane and propane radical cations.

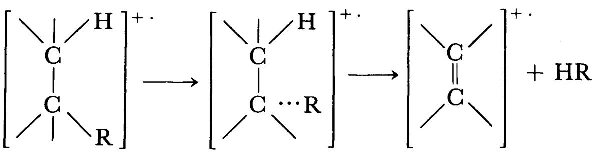
Concluding Remarks

The fragmentation mechanisms of the saturated hydrocarbon in the low-energy region may be summarized as follows:

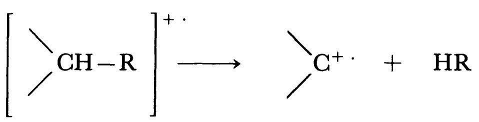
1) Hydrogen or alkyl radical (R·) elimination



2) 1,2-HR elimination



3) 1,1-HR elimination



where R=H or CH_3. Mechanism 1 is a simple bond cleavage process. Mechanism 2 proceeds with a small energy barrier. Although a reverse 2+2 type reaction is symmetry forbidden in the case of a neutral system, the energy barrier is substantially reduced for the HR loss of a radical cation. The 1,2-HR elimination process is expected to compete with a simple C-R bond scission, since the expected transition-state energy of mechanism 2 is very close to the energy of the product by mechanism 1 (see Figs. 2 and 3). Our calculation also shows that a carbene radical cation could be produced via HR loss by 1,1-elimination in the low-energy region.

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8) We can exclude two-step elimination of hydrogen atoms

$$C_2H_6^{+\cdot} \rightarrow C_2H_5^{+} + H\cdot \rightarrow C_2H_4^{+\cdot} + 2H\cdot \qquad (A1)$$

because this process needs high energy (3.9 eV from $C_2H_6^{+\cdot}$ with 6-31G basis set).

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