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## H<sub>2</sub> Elimination and C-C Bond Cleavage of Propene: A Theoretical Research

Zahra Homayoon\*

Department of Chemistry, Marvdasht Branch, Islamic Azad University, Marvdasht, Fars, Iran

### Abstract

Propene dissociation channels were characterized by ab initio CCSD(T)/6-311++g(d,p) calculations. In this work the detailed mechanism of propene dissociation to C<sub>2</sub>H<sub>4</sub>+CH<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>+H+CH<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>+CH<sub>4</sub> and C<sub>3</sub>H<sub>3</sub>+H<sub>2</sub>+H have been investigated. According to our calculations, ten fragments can be classified into five dissociated channels. Our results point out that two mechanisms come into play in the H<sub>2</sub> elimination channels. These channels are responsible for the formation of CH<sub>2</sub>CCH. The C-C bonds rupture occur through three different channels.

**Keywords:** Propene; CCSD; H<sub>2</sub> Elimination

### 1. Introduction

Propene is a reagent for the formation of polypropene in industry, a natural fuel in combustion, and a photochemical species in atmosphere. Propene is an isomer of cyclopropane, the smallest cycloalkane, with an exothermicity of 8 kcal mol<sup>-1</sup> relative to cyclopropane.

In 2003 photodissociation dynamics of propene at 157.6 nm has been investigated in a molecular beam apparatus using the photofragment translational spectroscopic technique combined with the vacuum ultraviolet ionization method by Lee *et al* to determine kinetic energy distributions and branching ratios[1]. They detected eleven photofragments and ascribed them to eight dissociation channels: namely, C<sub>3</sub>H<sub>5</sub>+H, C<sub>3</sub>H<sub>4</sub>+H+H, C<sub>3</sub>H<sub>4</sub>+H<sub>2</sub>, C<sub>3</sub>H<sub>3</sub>+H<sub>2</sub>+H, C<sub>2</sub>H<sub>4</sub>+CH<sub>2</sub>,

C<sub>2</sub>H<sub>3</sub>+CH<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>+CH<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>+CH<sub>3</sub>+H.

Other researches of propene derivatives, Photodissociation dynamics of propyne at 157 nm[2], Photodissociation of propyne [2], Photodissociation of propyne allene at 193 nm[3], Photodissociation of the allyl radical[4],[5], Photodissociation dynamics of cyclopropane at 157 nm[6] and Ab Initio Direct Dynamics Study of Cyclopropyl Radical Ring-Opening[7], show the importance of title reaction. But surprisingly the theoretical dissociation of propene has drawn no attention.

It is important to reveal the in depth mechanism of propene dissociation because of importance of the alkanes reactions in the combustion and atmospheric chemistry. Since the photochemical rearrangements of propene and its related compound are useful,

we are curious about exactly how they occur and wanted detailed mechanistic knowledge in order to exercise greater control over them. Although the experimental results help in

\*Corresponding author

E-mail address: Homayoon.zahra@gmail.com

understanding the different products of propene systems, they are at present not capable of providing information about mechanistic detail. In fact, a detailed understanding of the photochemical reactions of propene is of interest not only for the advancement of basic science but also for further precise control of the total reaction process. Because of complication of mechanism in this work part of detailed dissociation of propene has been investigated by *ab initio* calculations. The aim of this paper is to generate the essential parts of the potential energy surfaces by quantum chemical calculations and to describe the consequences for the reaction mechanisms from such an explicit calculation of the reaction pathways. However, to the best of our knowledge, no theoretical investigations have yet been devoted to the study of this system.

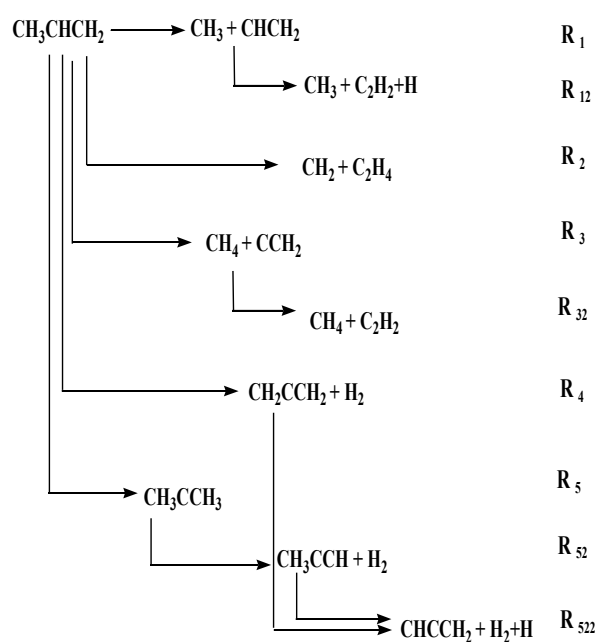
## 2. Electronic structure calculations

The *ab initio* molecular orbital calculations were performed using the Gaussian 03 software package [8]. All the geometries were fully optimized at CCSD level [9] of calculations using the standard 6-311G++(d,p) basis set. Every stationary point was characterized by its harmonic frequencies computed analytically at the MPWb1K/6-31+G(d,p) level. MPWb1K method is a very useful model designed for kinetics. The harmonic vibrational frequencies of all the stationary points were computed analytically to characterize them as minima (all frequencies are real) or transition states (only one imaginary frequency). For each transition state, an IRC (intrinsic reaction coordinate) calculation [10] has been performed as well to make sure that a transition structure connects with the expected minima. Accordingly, the products and reagents connected by the respective transition states have been unambiguously localized.

## 3. Result and Discussion

According to the *ab initio* results, the following mechanism is suggested for the title reaction.

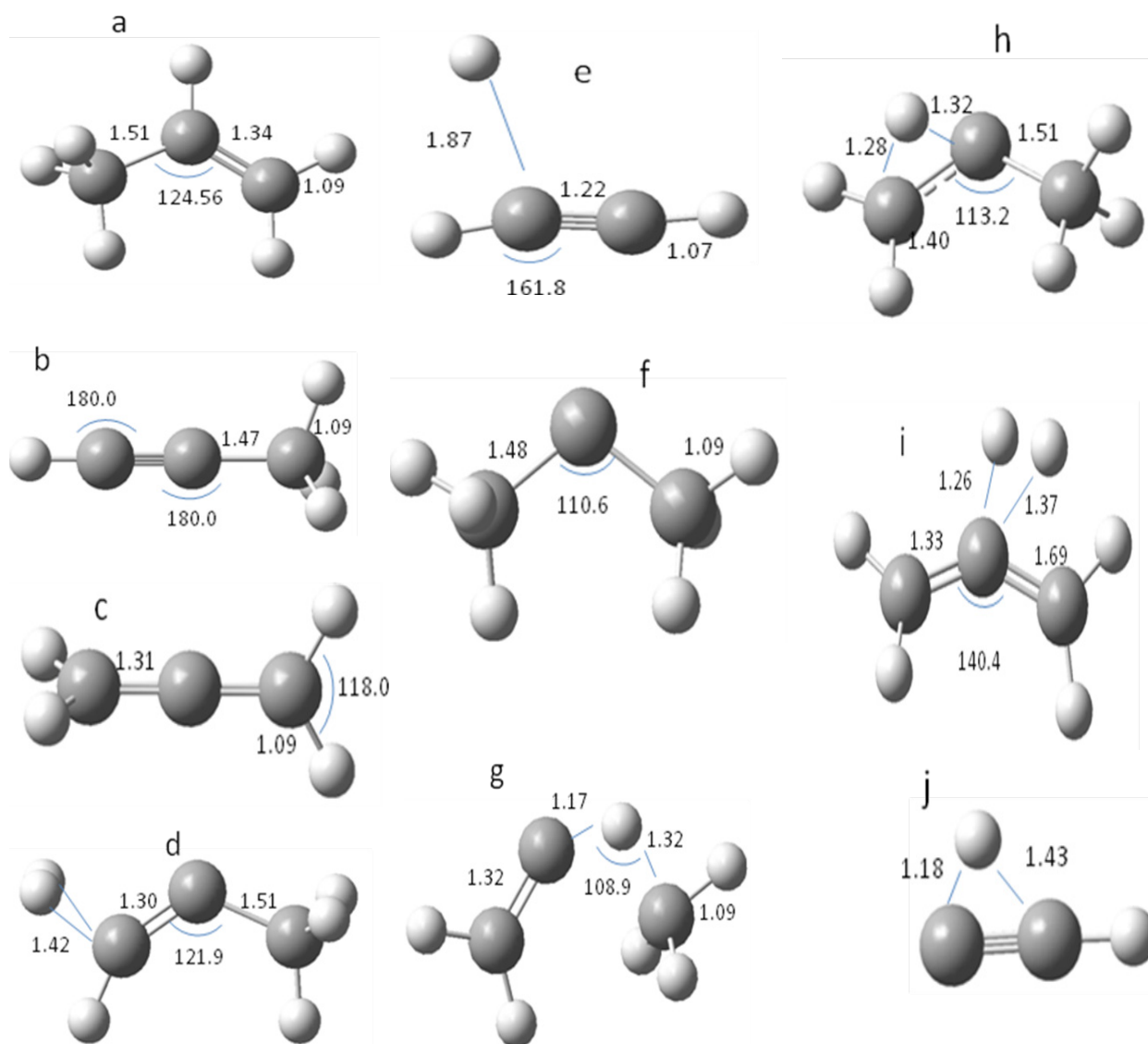
Figure 1 shows the optimized geometries



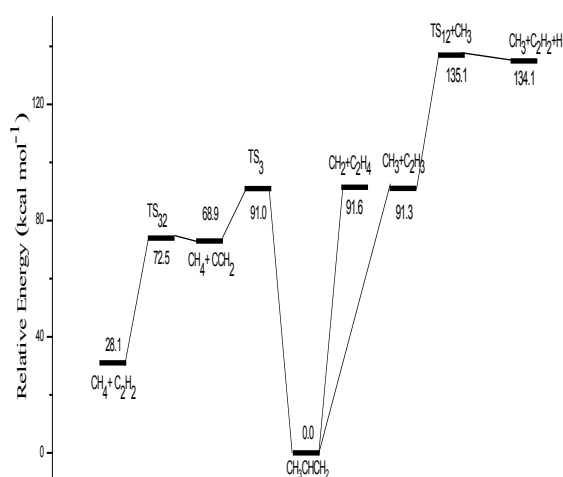
of all the stationary points at the CCSD/6-311G++(d,p) level of theory. A schematic potential energy diagram at the CCSD/6-311G++(d,p) level is presented in Figures 2 and 3 which include relative energies and zero-point energy contributions at the MPWb1K/6-31+G(d,p) level of theory. Vibrational term values for all species are listed in Table 1.

We divided our suggested mechanism to two parts. The first part (a) involves C-C bond dissociation of propene reactions. There are three different possible channels in this part. Two reactions for H<sub>2</sub> elimination are discussed in part b.

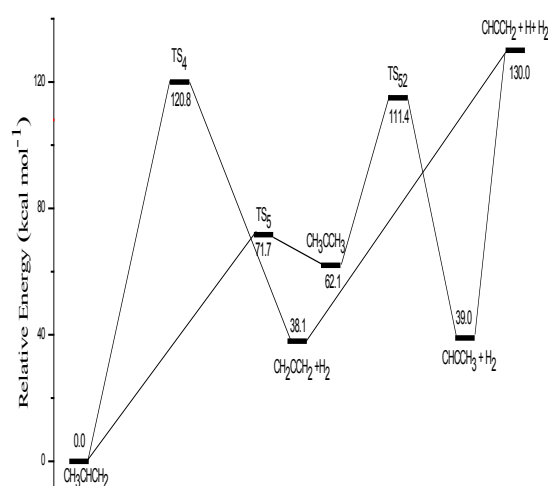
**Part a:** As shown in Figure 2 the first dissociation reaction of propene via a barrierless process forms CH<sub>3</sub> + CHCH<sub>2</sub>, which is 91.3 kcal mol<sup>-1</sup> more unstable than the total energy of propene at the CCSD/6-311G++(d,p) level of theory. This channel is followed by R<sub>12</sub>, which CHCH<sub>2</sub> can dissociate to more stable products, C<sub>2</sub>H<sub>2</sub> + H. This channel proceeds via TS<sub>12</sub> that is 1.5 kcal mol<sup>-1</sup> over products. Comparing with the result of Ref 1, at 157.6 nm CHCH<sub>2</sub> with enough internal energy can dissociate to C<sub>2</sub>H<sub>2</sub>. R<sub>2</sub> is the second barrierless dissociation channel of propene. By cleavage of C-C bond, propene can dissociate to CH<sub>2</sub> (triplet) + CHCH<sub>2</sub> which is 91.6 kcal mol<sup>-1</sup> over than propene. The



**Fig 1.** Optimized geometries of the stationary points at the CCSD/6-311++g(d,p) level. (a) Propene, (b) Propyne, (c) allene, (d)  $TS_{32}$ , (e)  $TS_{12}$ , (f)  $CH_3CCH_3$ , (g)  $TS_3$ , (h)  $TS_5$ , (i)  $TS_4$ , (j)  $TS_{32}$ .



**Fig2.** Relative energies of the stationary points at the CCSD/6-311++G(d,p) level in kcal mol<sup>-1</sup> for H<sub>2</sub> elimination channels. All values are corrected for the zero-point energies.



**Fig 3.** Relative energies of the stationary points at the CCSD/6-311++G(d,p) level in kcal mol<sup>-1</sup> for H<sub>2</sub> elimination channels. All values are corrected for the zero-point energies.

third C-C cleavage channel is  $R_3$ . By passing through  $TS_3$  propene dissociate to vinylidene and methane ( $CCH_2+CH_4$ ). The forward barrier height is 91 kcal mol<sup>-1</sup>. This channel followed by a rapid isomerization,  $TS_{32}$  with 3.6 kcal mol<sup>-1</sup> barrier height, of vinylidene to acetylene.

**Part b:** The first possible channel for  $H_2$  elimination is  $R_4$ , which proceeds via  $TS_4$  that lies 120.8 kcal mol<sup>-1</sup> above propene to form allene and  $H_2$ . Another possible path to form molecular hydrogen of this system is propyne formation that proceeds at two steps as follow. As can be seen in Figure 3, the propene isomerization process can take place via a transition state,  $TS_5$ . Vibrational frequency calculations show  $TS_5$  is a real transition state with one imaginary frequency (1115.8i cm<sup>-1</sup>) on the potential energy surface. Our CCSD calculation predicts for this process about 71.7 kcal mol<sup>-1</sup> barrier height, to form

$CH_3CCH_3$ . Then through  $TS_{52}$  with 49.3 kcal mol<sup>-1</sup> barrier height over  $CH_3CCH_3$ , propyne and molecular hydrogen will form. One of the products of Ref 1 is  $CHCCH_2+H_2+H$ . There are two different paths for this reaction based on our mechanism. Both allene and propyne can dissociate to propargyl ( $CHCCH_2$ ) and H. According to available energy of Ref 1 allene and propyne have enough energy, 143.3 and 142.4 kcal mol<sup>-1</sup>, for this path. As shown in Figure 3 both channels are barrierless.

#### 4. Conclusions

Ab initio CCSD/6-311G++(d,p) calculations for complicated mechanism of dissociation of propene had been done. Possible channels for ten photofragments reported by Lee et al [1] were characterized. For  $CH_2CCH+H_2+H$  two different channels exist. As shown in Figure 2 and 3 all transition states are below the available

**Table1.** Vibrational Term Values of Different Species Calculated at the MPWb1K/6-31+G(d,p) Level

species	frequencies (cm <sup>-1</sup> )
$CH_3CHCH_2$	206.8, 431.3, 603.3, 959.8, 961.8, 976.1, 1049.4, 1093.3, 1219.4, 1350.5, 1435.1, 1481.8, 1508.9, 1524.9, 1782.6, 3109.2, 3176.1, 3205.5, 3226.5, 3237.2, 3323.4
$CH_3CCH_3$	214.1, 206.9, 364.4, 546.3, 620.9, 924.8, 934.1, 1085.2, 1184.7, 1232.8, 1269.1, 1304.4, 1314.9, 1423.5, 1424.6, 2978.6, 2982.4, 3051.4, 3051.4, 3168.5, 3170.1
$TS_{12}$	510.6i, 313.8, 542.2, 593.7, 726.8, 761.8, 1959.5, 3352.7, 439.8
$TS_4$	1520.9i, 285.8, 407.8, 556.2, 594.9, 686.9, 813.0, 869.8, 904.4, 1037.2, 1061.6, 1152.7, 1206.1, 1364.9, 1454.3, 1778.3, 2092.1, 3188.5, 3210.1, 3307.2, 3313.6
$TS_5$	1115.8i, 268.3, 351.2, 507.0, 903.0, 940.0, 954.5, 987.3, 1107.0, 1278.3, 1308.3, 1385.5, 1394.3, 1425.3, 1485.2, 2265.9, 2999.6, 3003.7, 3129.0, 3167.4, 3193.0
$TS_{32}$	1246.6i, 120.6, 151.3, 258.8, 484.1, 640.9, 764.1, 954.9, 961.5, 1026.7, 1113.9, 1303.9, 1310.9, 1413.3, 1418.6, 1783.7, 3037.2, 3126.6, 3151.4, 3264.5, 3274.5
$TS_3$	812.1 i, 273.5, 308.8, 352.4, 645.9, 680.6, 790.3, 806.4, 957.2, 1047.1, 1112.8, 1332.7, 1382.7, 1384.9, 1640.1, 2530.7, 3116.1, 3162.1, 3246.0, 3247.8, 3308.5
$TS_{32}$	988.8 i, 479.2, 821.8, 1914.7, 2664.0, 3425.3
$C_2H_2$	446.3, 446.3, 663.7, 663.7, 2113.8, 3468.8, 3573.2
$C_2H_4$	843.5, 1005.9, 1010.8, 1083.1, 1259.8, 1411.5, 1498.3, 1756.5, 3225.7, 3244.1, 3311.2, 3336.7
$C_2H_3$	597.2, 698.9, 799.7, 965.5, 1314.5, 1673.9, 3119.7, 3222.3, 3306.4
$CH_2$	1096.2, 3222.2, 3462.2
$CH_3$	382.6, 1336.9, 1336.9, 3175.8, 3367.7, 3367.7
$CCH_2$	272.1, 582.8, 1116.2, 1739.3, 3188.9, 3278.1
$CH_4$	1266.7, 1266.7, 1266.7, 1506.6, 1506.6, 3083.3, 3215.5, 3215.5, 3215.5
$CH_3CCH$	367.8, 367.8, 689.1, 689.1, 979.6, 1073.1, 1073.1, 1442.5, 1508.8, 1508.8, 2302.3, 3125.2, 3207.8, 3207.8, 3558.9
$CH_2CCH_2$	386.3, 386.3, 899.1, 903.1, 903.2, 1035.1, 1035.1, 1143.1, 1449.3, 1516.8, 2126.2, 3227.7, 3230.5, 3316.2, 3316.2

energy of Ref 1(181.4 kcal mol<sup>-1</sup>). The mechanism for other fragments reported in Ref 1 can be recognized. More theoretical research such as RRKM calculations and quasiclassical calculations can help to recognize the more important channels of products.

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