

# An *ab initio* Study on the Molecular Elimination Reactions of Methacrylonitrile

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*Ab initio* quantum chemical molecular orbital calculations have been performed for the unimolecular decomposition of methacrylonitrile ( $\text{CH}_3\text{C}(\text{CN})=\text{CH}_2$ ), especially for HCN and  $\text{H}_2$  molecular elimination channels. Structures and energies of the reactants, products, and relevant species along the individual reaction pathways were determined by MP2 gradient optimization and MP4 single point energy calculations. Direct four-center elimination of HCN and three-center elimination of  $\text{H}_2$  channels were identified. In addition, H or CN migration followed by HCN or  $\text{H}_2$  elimination channels *via* the methylcyanoethylidene intermediate was also identified. Unlike the case of crotonitrile previously studied, in which the dominant decomposition process was the direct three-center elimination of HCN, the most important reaction pathway should be the direct three-center elimination of  $\text{H}_2$  in the case of methacrylonitrile.

**Key Words :** *Ab initio*, Molecular elimination, Methacrylonitrile

## Introduction

Photochemistry of ethylene and its derivatives has been paid much attention because dissociation of the molecule can take place in many ways. Although the reaction products may usually be classified into two, one as radical products, and the other as molecular elimination products, several different pathways are possible to reach the same product channel. In that sense, production of molecular hydrogen by either direct 1,1 three-center or 1,2 four-center elimination from ethylene may be a typical example.<sup>1-3</sup> Recent development of experimental techniques such as high resolution laser spectroscopy and molecular beams has made it possible to study the state-specific reaction dynamics of such reactions in detail. Branching ratios between the channels, reaction rates of individual channels and so forth can be experimentally measured and compared to those predicted by applying appropriate theories. *Ab initio* molecular orbital calculations have widely been employed to find out structures and energies of the molecules at the transition state and to elucidate detailed reaction mechanisms.

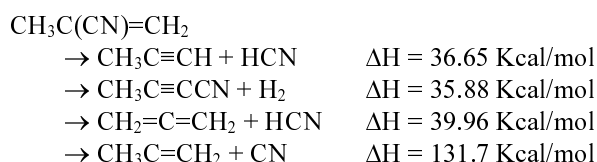
Being irradiated by 193 nm light, chloroethylene produces primary molecular products such as acetylene,  $\text{H}_2$ , and HCl mainly from vibrationally hot ground electronic state *via* internal conversion from the initial  $\pi\pi^*$  transition, which was extensively investigated by using photofragment translational spectroscopy and by resonance enhanced multiphoton ionization spectroscopy.<sup>4-8</sup> Detailed mechanisms of individual dissociation channels were also quantum chemically studied by *ab initio* molecular orbital calculations.<sup>9,10</sup> The molecular elimination channels were identified as the direct 1,1, 1,2 elimination, and H-migration and Cl-migration-elimination channels where corresponding transition states and potential energies along the reaction coordinates were calculated.

Acrylonitrile or vinyl cyanide is another prototype molecule that contains the C=C double bond, which undergoes unimolecular decomposition upon irradiation of the UV light. While the CN radical production channel was investigated by frequency-modulated diode laser absorption spectroscopy,<sup>11</sup> Blank *et al.* studied photofragment translational spectra of H, CN, HCN, and  $\text{H}_2$  primarily produced from acrylonitrile at 193 nm and concluded that the dissociation takes place on the ground electronic surface *via* internal conversion from the initial  $\pi\pi^*$  transition.<sup>12</sup> In addition, they found that the HCN molecular elimination channel with considerable recombination barrier is dominant over the CN radical production channel. Especially, the measured internal energy of the acetylene products was exceeding the predicted value by 1,1, three-center elimination, from which the concerted vinylidene production and isomerization to acetylene was suggested. An *ab initio* calculation was also performed to elucidate the detailed mechanisms of dissociation pathways observed in the experiment.<sup>13</sup>

In the dissociation of propylene derivatives where one more skeletal carbon atom is present, many more product channels can be opened and reaction mechanisms are much more complex than those in ethylene derivatives. However, the first electronic transition in UV still has mostly the  $\pi\pi^*$  character, from which the dissociation takes place. The CN production channels in allyl cyanide,<sup>14</sup> crotonitrile,<sup>15</sup> methacrylonitrile<sup>16</sup> photoexcited at 193 nm were investigated by using frequency-modulated transient absorption spectroscopy and laser induced fluorescence of CN. It was found that the elimination of CN occurs in the ground electronic state *via* rapid internal conversion from the initial  $\pi\pi^*$  transition. *Ab initio* calculations were performed for the decomposition of crotonitrile.<sup>17</sup> In the CN production channel, the H atom migration takes place prior to elimination producing allyl

and CN radicals rather than a propenyl radical product. The direct 1,1, 1,2 elimination of HCN or H<sub>2</sub>, and H or CN migration followed by HCN or H<sub>2</sub> elimination channels were identified where the direct 1,1 three-center HCN elimination was predicted to be the most important reaction channel.

The decomposition of methacrylonitrile produces following primary products.



Unlike crotonitrile, either direct 1,1 three-center HCN elimination or 1,2 four-center H<sub>2</sub> elimination cannot occur from methacrylonitrile. Experimental measurements have not yet been performed for these molecular elimination reactions so far. However, the measured quantum yield for the CN radical production channel at 193 nm was 0.02, which implies the relative importance of the molecular elimination channels.<sup>16</sup>

In this article, results of *ab initio* molecular orbital calculations of the dissociation of methacrylonitrile, especially for the molecular elimination channels are presented. Structures and energies of the relevant species including the molecules at the transition states along the reaction coordinate leading to the individual product channels are calculated. By examining the energetics of the individual reaction pathways, the relative importance of each channel can be ascertained in this complex, competing reactions, which will be useful for analyses of the experimental results and for elucidation of the detailed mechanism of the reaction.

### Computation

The *ab initio* calculations were able to be performed somehow at high level because methacrylonitrile is a relatively small molecule with five heavy atoms. However, chemically distinct species that appear in the present unimolecular decomposition channels were so many that we might compromise between computational efficiency and accuracy, which was similarly applied in the studies of vinyl chloride<sup>9</sup> and vinyl cyanide.<sup>13</sup>

All the molecular geometries were first optimized by an energy gradient method at two different levels, RHF/6-31G(d) and MP2/6-31G(d,p) using the GAUSSIAN 98 package.<sup>18</sup> The energies were subsequently improved by using the single-point MP4/6-311+G(d,p) method for the structures obtained by the MP2 optimization. Vibrational frequencies were calculated at the MP2/6-31G(d,p) level for identification of the optimized stationary points and for the calculation of the zero point energy (ZPE), which was obtained by scaling the MP2 energy by 0.96.

In the Figures, all the drawings represent the structures

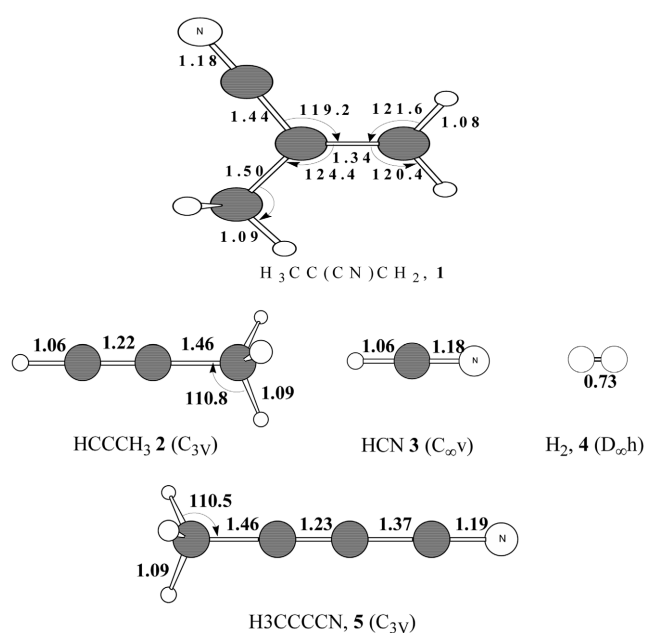
obtained by the MP2/6-31G(d,p) optimization except for the structures that could not be optimized by the MP2 calculations. In these drawings are also shown the point group of the structures and the values of the imaginary frequencies (in cm<sup>-1</sup>) for the transition states.

## Results and Discussion

**A. Reaction Energies.** Energies and structures of the reactant, methacrylonitrile (**1**) and the final products, propyne (**2**), HCN (**3**), H<sub>2</sub> (**4**), 2-butyne nitrile (**5**) from molecular elimination reactions were first calculated. The optimized structures and the energies are in Figure 1 and Table 1, respectively. These molecular elimination reactions are endothermic and the reaction enthalpies were calculated after the zero point energy correction as 36.65 and 35.88 kcal/mol for the HCN and H<sub>2</sub> eliminations, respectively. The energy difference between the two reaction pathways turns out to be very small just as in the case of vinyl cyanide.<sup>13</sup>

**B. Direct HCN and H<sub>2</sub> Elimination Reactions.** The direct 1,2 four-center HCN or HNC elimination can occur for the leaving CN with hydrogen atoms in the β position or in the methyl group since CN and the methyl group are attached to the same carbon atom. Unlike from crotonitrile, the direct 1,1 three-center H<sub>2</sub> elimination can only take place from methacrylonitrile. In the case of HCN or HNC elimination with H in the methyl group, allene (**6**) is formed, which may subsequently be isomerized to the more stable propyne but the isomerization barrier is high. HNC produced by the direct 1,2 elimination may also be isomerized to more stable HCN.

**Four-center HCN Elimination:** In Figure 2, structures and energies of the species involved in the two different direct 1,2 four-center HCN elimination pathways are

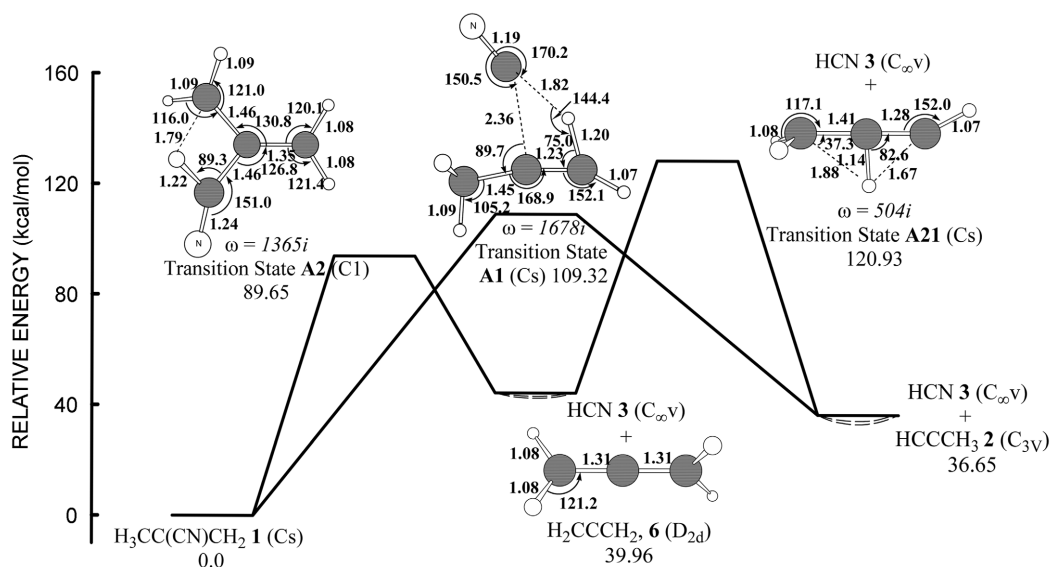


**Figure 1.** Optimized structures of the reactant and the products involved in the molecular elimination of methacrylonitrile.

**Table 1.** Total energies (in a.u.) of reference compounds involved in the molecular elimination of methacrylonitrile at various levels of calculation

Species	Label	Optimization		Single point <sup>a</sup>	ZPE <sup>b</sup>
		RHF/6-31G(d)	MP2/6-31G(d,p)	MP4/6-311+G(d,p)	
Methacrylonitrile	<b>1</b>	-208.807 619	-209.510 054	-209.655 580	48.35
Propyne	<b>2</b>	-115.864 318	-116.272 995	-116.362 565	33.81
HCN	<b>3</b>	-92.872 589	-93.166 172	-93.226 799	9.64
H <sub>2</sub>	<b>4</b>	-1.126 827	-1.157 661	-1.167 691	6.33
2-Butynenitrile	<b>5</b>	-207.599 574	-208.281 384	-208.416 950	33.39

<sup>a</sup>Single point calculations carried out using the MP2/6-31G(d,p) optimized geometry. <sup>b</sup>Zero-point energy (ZPE) calculated at the MP2/6-31G(d,p) level, scaled by 0.96 and given in kcal/mol.

**Figure 2.** Reaction path for the three-center elimination of HCN from methacrylonitrile.

presented. The elimination of CN with H in the  $\beta$  position directly produces propyne whereas the elimination with H in the methyl group produces allene as a primary product. In the case of propyne production, the transition state, **A1** is planar with one imaginary frequency of which the vibrational mode is associated with a' irreducible representation. Thus, the reaction would take place in the plane retaining the

Cs symmetry. The elimination of HCN with H in the methyl group takes place through an asymmetric transition state, **A2**, which primarily produces allene. Allene produced from the reaction may subsequently be isomerized to the more stable propyne through the transition state **A21**. The transition state **A21**, which belongs to the Cs point group, could only be optimized at the MP2 level, where the

**Table 2.** Energies (in kcal/mol), relative to the reactant **1**, of the structures involved in the molecular elimination of methacrylonitrile at various levels of calculation

Species	Label	Optimization		Single point <sup>a</sup>	ZPC <sup>b</sup>
		RHF/6-31G(d)	MP2/6-31G(d,p)	MP4/6-311+G(d,p)	
TS for $\alpha,\beta$ -elimination of HCN	<b>A1</b>	115.14	123.61	115.52	-6.2
TS for $\alpha,\beta'$ -elimination of HCN	<b>A2</b>	140.82	101.94	94.04	-4.39
TS for $\alpha,\beta$ -elimination of HNC	<b>A3</b>	126.89	121.83	115.54	-4.65
TS for $\alpha,\beta$ -elimination of HNC	<b>A3'</b>	c	124.22	114.03	-6.55
TS for $\alpha,\beta'$ -elimination of HNC	<b>A4</b>	141.14	104.22	95.84	-2.65
Allene + HCN	<b>6+3</b>	46.39	49.05	44.62	-4.66
TS for allene isomerization + HCN	<b>A21+3</b>	d	136.48	128.69	-7.76
HNC + Allene	<b>7+6</b>	57.22	69.12	60.52	-4.86
TS for HNC isomerization + Allene	<b>A31+6</b>	96.99	104.20	93.71	-7.58

<sup>a</sup>Single point calculations carried out using the MP2/6-31G(d,p) optimized geometry. <sup>b</sup>Zero-point energy (ZPE) correction relative to **1**. <sup>c</sup>**A3'** does not exist at the HF level. <sup>d</sup>See the text and figure.

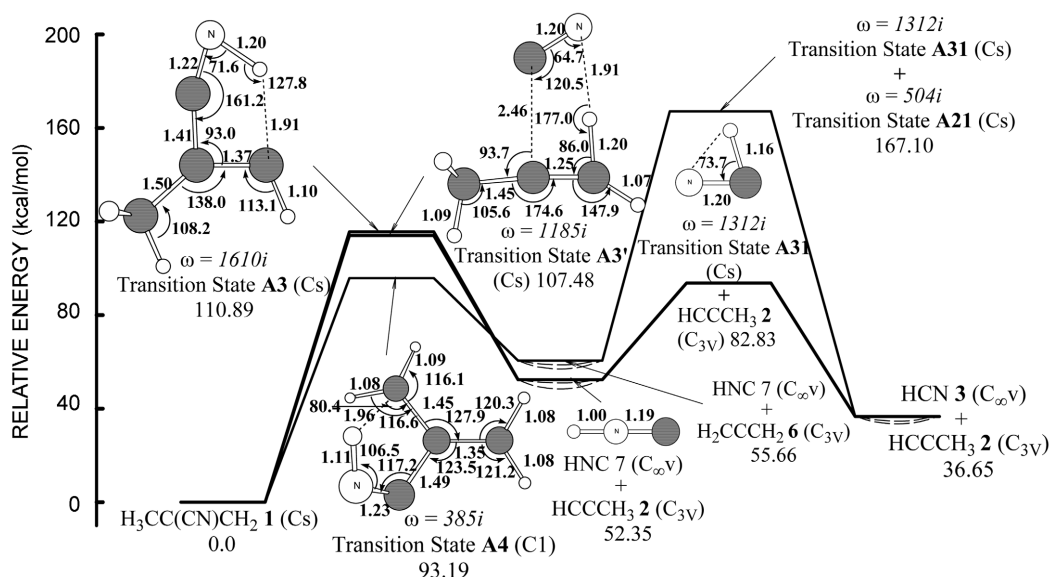


Figure 3. Reaction path for the three-center elimination of HCN from methacrylonitrile via HNC production.

migrating H is bridged between all three carbon atoms to form propyne.

After the zero point energy correction (ZPC), barriers for **A1** and **A2** are 109.32 and 89.65 kcal/mol relative to **1**, respectively (Table 2). Although the barrier for the allene formation through **A2** is lower than that for the direct propyne formation through **A1**, the transition state for the isomerization from allene to propyne has 120.93 kcal/mol in energy relative to **1**, which implies that the formation of propyne via **A2** should be much slower than the direct formation.

**Four-center HNC Elimination:** As in the case of 1,2 four-center elimination of HCN, the four-center elimination of HNC can take place through the transition states **A3**, **A3'**, and **A4** by removing CN with H in the  $\beta$  position or H in the methyl group (Fig. 3). In the case of HNC with H in

the  $\beta$  position, propyne is directly produced with HNC which can be further isomerized to the more stable HCN. In the case of elimination of HNC with H in the methyl group, allene and HNC are produced, which are subsequently isomerized to propyne and HCN, respectively. In the  $\beta$ -H elimination, the two transition states, **A3** and **A3'** were optimized, both of which belong to the Cs point group with one imaginary frequency associated with the  $a'$  vibrational mode, implying that the reactions proceed in the plane retaining the Cs symmetry. However, in the case of HNC elimination with H in the methyl, allene is first produced through the asymmetric transition state **A4**.

The transition states **A3** and **A3'** have energies 110.89 and 107.48 kcal/mol relative to **1**, respectively after ZPC. The energy of **A3'** is lower than that of **A3** but **A3'** cannot exist at the RHF level of calculation. The barrier for the elimination

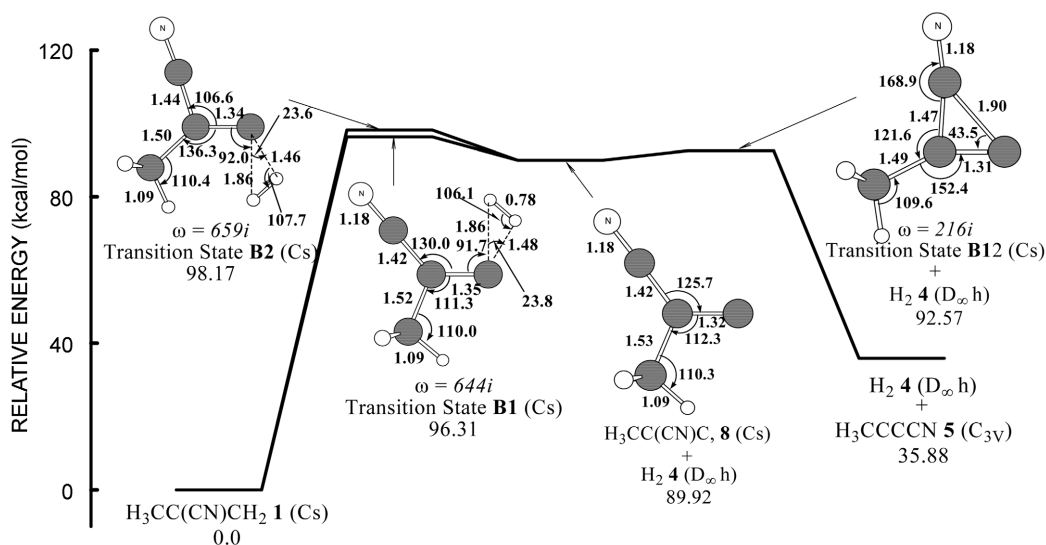


Figure 4. Reaction path for the three-center H<sub>2</sub> elimination from methacrylonitrile.

**Table 3.** Energies (in kcal/mol), relative to the reactant **1**, of the structures involved in the molecular elimination of methacrylonitrile at various levels of calculation

Species	Label	Optimization		Single point <sup>a</sup>	ZPC <sup>b</sup>
		RHF/6-31G(d)	MP2/6-31G(d,p)	MP4/6-311+G(d,p)	
2-butyne nitrile + H <sub>2</sub>	<b>5+4</b>	50.96	44.56	44.51	-8.63
TS for $\beta,\beta$ -elimination of H <sub>2</sub>	<b>B1</b>	118.05	111.57	103.34	-7.03
TS for $\beta,\beta$ -elimination of H <sub>2</sub>	<b>B2</b>	118.89	113.12	104.99	-6.82
2-methylcyano vinylidene + H <sub>2</sub>	<b>8+4</b>	95.49	106.23	99.09	-9.17
TS for 2-methylcyano vinylidene isomerization + H <sub>2</sub>	<b>B12+4</b>	111.21	108.15	102.10	-9.53

<sup>a</sup>Single point calculations have been carried out using the MP2/6-31G(d,p) optimized geometry. <sup>b</sup>Zero-point energy (ZPE) correction relative to **1**.

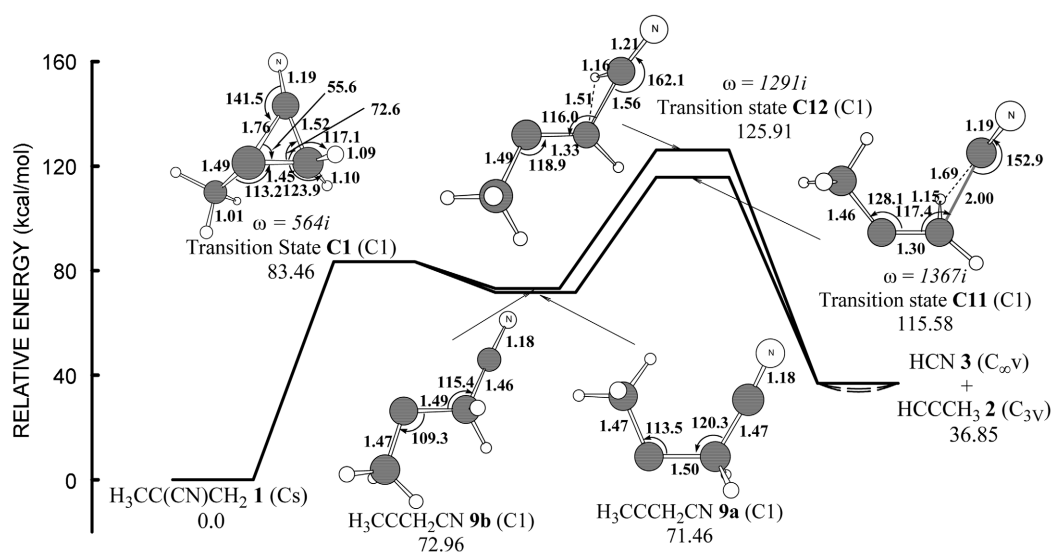
of HNC through **A4** is 93.19 kcal/mol, which is lower by some 15 kcal/mol than those through **A3** or **A3'** but the propyne formation from allene is supposed to be slow because the isomerization should overcome a substantial energy barrier.

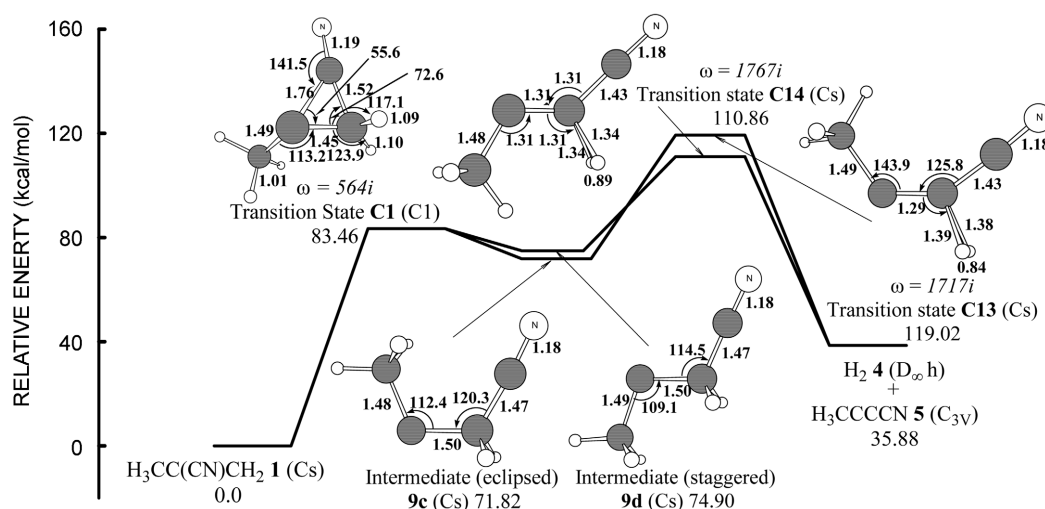
**Three-center H<sub>2</sub> Elimination:** The three-center H<sub>2</sub> elimination takes place through the transition state **B1** or **B2**, which produces 2-methylcyano vinylidene as an intermediate (Fig. 4). The transition states **B1** and **B2** belong to the C<sub>s</sub> point group where the leaving H<sub>2</sub> is either in the trans or *cis* position relative to the methyl group. The H<sub>2</sub> in the *cis* position has somewhat higher energy than that in the trans position, which might be due to the interaction with the methyl group. The 2-methylcyano vinylidene intermediate is then isomerized to the final product, 2-butyne nitrile with little barrier. After ZPC, the transition state **B1** and **B2** have 96.31 and 98.17 kcal/mol relative to **1**, respectively (Table 3). The barrier for isomerization from 2-methylcyano vinylidene to 2-butyne nitrile is 2.65 kcal/mol similar to the case of isomerization of vinylidene to acetylene whose barrier was reported to be  $\sim$ 3 kcal/mol from the coupled cluster calculations.<sup>19</sup> The energy barrier for the direct H<sub>2</sub> elimination is lower by some 10-15 kcal/mol than those for the direct HCN elimination, which implies the relative importance of the direct H<sub>2</sub> elimination channel.

**C. H and CN Migration-elimination Reactions.** As another type of molecular elimination from methacrylonitrile, CN or H migration followed by HCN or H<sub>2</sub> elimination would be considered. Upon CN migration, 1-methylcyanoethylidene is formed as an intermediate from which the HCN or H<sub>2</sub> elimination would occur whereas the H<sub>2</sub> elimination can only take place through 2-methyl-2-cyanoethylidene by the  $\beta$ -H migration.

**Reactions Involving 1-Methylcyanoethylidene (HCN and H<sub>2</sub> elimination):** As shown in Figure 5 and Figure 6, conformers of 1-methylcyanoethylidene, **9a**, **9b**, **9c**, and **9d**, are produced from the CN migration through the transition state **C1**. Among the 1-methylcyanoethylidene conformers, **9a** is at the global minimum where the C-C-C-C dihedral angle is 8.7° while **9b** is at a local minimum with the dihedral angle of 157.9°. The conformers, **9c** and **9d** are in the eclipsed and the staggered form, respectively, both of which are in the C<sub>s</sub> symmetry. Other conformers resulting from internal rotation of the methyl group irrelevant to the present molecular elimination reactions are not presented.

The transition state, where the moving CN is bridged between the two carbon atoms has 83.46 kcal/mol of energy relative to **1** (after ZPC). The energy of the transition state, **C1** is higher than the conformers, **9a**, **9b**, **9c**, and **9d** (Table 4), which implies that the 1-methylcyanoethylidene inter-

**Figure 5.** Reaction path for the HCN elimination *via* 1-methylcyanoethylidene intermediate produced by CN migration.



**Figure 6.** Reaction path for the H<sub>2</sub> elimination *via* 1-methylcyanoethylidene intermediate produced by CN migration.

mediate would be kinetically stable judging from the fact that the barriers for the subsequent molecular elimination reactions are very high. The barriers for this CN shift are lower by approximately 20 kcal/mol than those in the direct HCN and H<sub>2</sub> elimination reactions mentioned above, which implies the importance of the reactions involving the 1-methylcyanoethylidene intermediate for the molecular elimination reactions of methacrylonitrile.

The three-center molecular elimination of HCN can take place from **9a** and **9b** through the transition states **C11** and **C12**, respectively, producing propyne (Fig. 5). The difference between the two reaction pathways is in a manner of producing HCN. In **C11**, the C-CN bond is almost broken (2.00 Å) but the leaving H is still in the vicinity of the central carbon atom whereas in **C12**, the H-CN bond is almost formed (1.16 Å) but CN is still close to the central carbon atom. This difference may be due to the adjacent methyl group keeping the leaving hydrogen from moving freely in space in **C11**. After the zero point energy corrections, **C11** has the barrier of 44.12 kcal/mol relative to **9a** while **C12** has 52.95 kcal/mol relative to **9b**. Thus, it can be expected that the reaction through **C11** would be favored over the

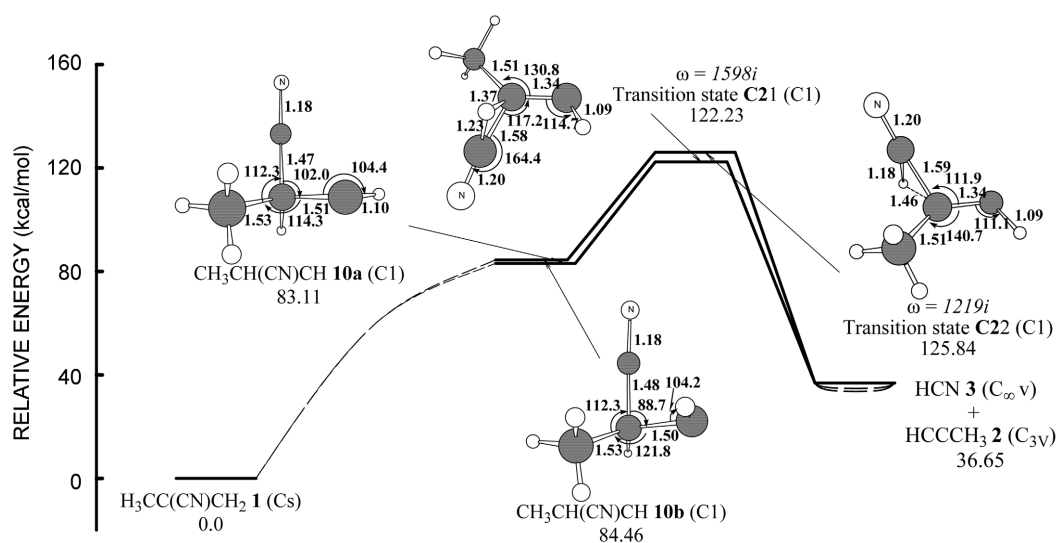
reaction through **C12** in the HCN elimination reactions involving 1-methylcyanoethylidene.

The three-center molecular elimination of H<sub>2</sub> takes place from **9c** and **9d** through the transition states **C13** and **C14**, respectively, producing 2-butyne nitrile (Fig. 6). At the transition states, for each reaction pathway, an imaginary vibrational frequency for the normal mode associated with the a' irreducible representation was found implying that the reactions would proceed in the plane retaining the Cs symmetry. After the zero point corrections, the barrier for **C13** is 47.2 kcal/mol relative to **9c** while the barrier for **C14** is 35.96 kcal/mol relative to **9d**. The barrier to form the eclipsed 1-methylcyanoethylidene (**9c**) is lower than that to form the staggered 1-methylcyanoethylidene (**9d**) whereas the barrier for the subsequent three-center H<sub>2</sub> elimination reaction from **9d** is lower than that from **9c**. In addition, from 1-methylcyanoethylidene, the barriers for the H<sub>2</sub> elimination are lower than those for the HCN elimination, which implies that the H<sub>2</sub> elimination is favored over the HCN elimination in the reactions involving 1-methylcyanoethylidene intermediate produced from the CN shift in methacrylonitrile.

**Table 4.** Energies (in kcal/mol), relative to the reactant **1**, of the structures involved in the molecular elimination of methacrylonitrile at various levels of calculation

Species	Label	Optimization		Single point <sup>a</sup>	ZPC <sup>b</sup>
		RHF/6-31G(d)	MP2/6-31G(d,p)	MP4/6-311+G(d,p)	
TS for CN shift in <b>1</b>	<b>C1</b>	94.21	89.94	85.46	-2.00
1-methylcyanoethylidene from <b>C1</b>	<b>9a</b>	66.03	79.98	73.69	-2.23
1-methylcyanoethylidene from <b>C1</b>	<b>9b</b>	66.84	81.50	75.16	-2.20
Intermediate(eclipsed) of <b>9a</b>	<b>9c</b>	66.39	80.95	74.39	-2.57
Intermediate(staggered) of <b>9b</b>	<b>9d</b>	68.51	84.59	77.74	-2.84
TS for HCN elimination from <b>9a</b>	<b>C11</b>	142.81	130.47	120.79	-5.21
Ts for HCN elimination from <b>9b</b>	<b>C12</b>	147.62	138.04	130.77	-4.86
TS for H <sub>2</sub> elimination from <b>9c</b>	<b>C13</b>	135.96	132.99	124.72	-5.59
TS for H <sub>2</sub> elimination from <b>9d</b>	<b>C14</b>	130.56	124.88	117.04	-6.18

<sup>a</sup>Single point calculations have been carried out using the MP2/6-31G(d,p) optimized geometry. <sup>b</sup>Zero-point energy (ZPE) correction relative to **1**.



**Figure 7.** Reaction path for the HCN elimination via 2-methyl-2-cyanoethylidene intermediate produced by H migration.

**Table 5.** Energies (in kcal/mol), relative to the reactant **1**, of the structures involved in the molecular elimination of methacrylonitrile at various levels of calculation

Species	Label	Optimization		Single point <sup>c</sup>	ZPC <sup>b</sup>
		RHF/6-31G(d)	MP2/6-31G(d,p)	MP4/6-311+G(d,p)	
TS for trans H shift in <b>1</b>	<b>C2</b>	86.14	c	–	–
TS for cis H shift in <b>1</b>	<b>C3</b>	87.43	c	–	–
2-methyl-2-cyanoethylidene from <b>C2</b>	<b>10a</b>	69.81	92.91	85.40	-2.29
2-methyl-2-cyanoethylidene from <b>C3</b>	<b>10b</b>	75.43	92.76	86.18	-1.72
TS for HCN elimination from 10a	<b>C21</b>	141.15	135.43	127.11	-4.99
TS for HCN elimination from 10b	<b>C22</b>	148.23	138.65	130.82	-4.98

<sup>a</sup>Single point calculations have been carried out using the RHF/6-31G(d,p) optimized geometry. <sup>b</sup>Zero-point energy (ZPE) correction relative to **1**. <sup>c</sup>Geometries of **C2** and **C3** do not exist at the MP2/6-31G(d,p) level.

**Reaction Involving 2-Methyl-2-cyanoethylidene (HCN elimination):** The  $\beta$ -H shift in methacrylonitrile produces a 2-methyl-2-cyanoethylidene intermediate from which the HCN elimination takes place. As shown in Figure 7, the transition states for this H migration could not be located at the MP2 level but the bridged H structures between the two carbon atoms were obtained at the RHF level. In crotonitrile, the energy difference between 2-methyl-2-cyanoethylidene and the transition state for the CN migration to form 2-methyl-2-cyanoethylidene is  $\sim 1.5$  kcal/mol,<sup>17</sup> which is similar to the present case. The intermediates, **10a** and **10b** are at local minima representing the C1 symmetry and especially, CN in **10b** is somewhat closer to the lone pair electrons at the terminal carbon atom.

2-methyl-2-cyanoethylidene, **10a** and **10b** produce HCN and propyne by three-center elimination through the transition states **C21** and **C22**, respectively. The transition state structures are asymmetric (C1 symmetry) where in **C21**, H is bridged between the central carbon atom and the leaving CN. As in **C21**, the hydrogen atom is moved toward the leaving CN but in **C22**, the H-CN bond is almost formed (1.18 Å) at the transition state. After the zero point corrections, the barrier for **C21** is 39.12 kcal/mol relative to

**10a** while the barrier for **C22** is 41.38 kcal/mol relative to **10b**. As in the case of 1-methylcyanoethylidene intermediate, the lower barrier for producing the 2-methyl-2-cyanoethylidene intermediate than those for the direct HCN or H<sub>2</sub> elimination implies the relative importance of the H migration-elimination channels.

## Summary

The HCN or H<sub>2</sub> molecular elimination reactions from methacrylonitrile were theoretically investigated by *ab initio* molecular orbital calculations. The direct four-center HCN or HNC elimination (1), the direct three-center H<sub>2</sub> elimination (2), the CN migration followed by HCN or H<sub>2</sub> elimination through 1-methylcyanoethylidene intermediate (3), and the H migration followed by HCN elimination through 2-methyl-2-cyanoethylidene intermediate (4) channels were identified. Among them, the direct three-center H<sub>2</sub> elimination, (2) would be the most important reaction channel with the lowest overall energy barrier. The H<sub>2</sub> elimination produces 2-butyne nitrile while the HCN or HNC elimination produces propyne as final products. However, allene would be a final product in the direct four-

center HCN or HNC elimination judging from the high energy barrier for the isomerization to propyne.

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### References

1. Balko, B. A.; Zhang, J.; Lee, Y. T. *J. Chem. Phys.* **1992**, *97*, 935.
  2. Cromwell, E. F.; Stolow, A.; Vrakking, M. J. J.; Lee, Y. T. *J. Chem. Phys.* **1992**, *97*, 4029.
  3. Jensen, J. H.; Morokuma, K.; Gordon, M. S. *J. Chem. Phys.* **1994**, *100*, 1981.
  4. Reilly, P. T. A.; Xie, Y.; Gordon, R. J. *J. Chem. Phys. Lett.* **1991**, *178*, 511.
  5. Mo, Y.; Tonokura, K.; Matsumi, Y.; Kawasaki, M.; Sato, S.; Arikawa, T.; Reilly, P. T. A.; Xie, Y.; Yang, Y.; Huang, Y.; Gordon, R. J. *J. Chem. Phys.* **1992**, *97*, 4815.
  6. He, G.; Yang, Y.; Huang, Y.; Gordon, R. J. *J. Phys. Chem.* **1993**, *97*, 2186.
  7. Tonokura, K.; Daniels, L. B.; Suzuki, T.; Yamashita, K. *J. Phys. Chem.* **1997**, *101*, 7754.
  8. Blank, D. A.; Sun, W.; Suits, A. G.; Lee, Y. T.; North, S. W.; Hall, G. E. *J. Chem. Phys.* **1998**, *108*, 5414.
  9. Riehl, J. F.; Morokuma, K. *J. Chem. Phys.* **1994**, *100*, 8976.
  10. Riehl, J. F.; Musaev, D.; Morokuma, K. *J. Chem. Phys.* **1994**, *101*, 5942.
  11. North, S. W.; Hall, G. E. *Chem. Phys. Lett.* **1996**, *263*, 148.
  12. Blank, D. A.; Suits, A. G.; Lee, Y. T.; North, S. W.; Hall, G. E. *J. Chem. Phys.* **1998**, *108*, 5784.
  13. Derecskei-Kovacs, A.; North, S. W. *J. Chem. Phys.* **1999**, *110*, 2862.
  14. Oh, C. Y.; Shin, S. K.; Kim, H. L.; Park, C. R. *Chem. Phys. Lett.* **2001**, *342*, 27.
  15. Li, R.; Derecskei-Kovacs, A.; North, S. W. *Chem. Phys.* **2000**, *254*, 309.
  16. Oh, C. Y.; Shin, S. K.; Kim, H. L.; Park, C. R. *J. Phys. Chem. A* **2003**, *107*, 4333.
  17. Oh, C. Y.; Kim, H. L. *J. Chem. Phys.* Submitted for publication.
  18. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Perderson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; RaghavaChari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nagayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian Inc.: Pittsburgh, PA, 1998.
  19. Gallo, M. M.; Hamilton, T. P.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1990**, *112*, 8714.
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