**Electronic Supporting Information**

**Elucidating the Chemical Dynamics of the Elementary Reactions of the 1‑Propynyl Radical (CH3CC; X2A1) with 2-Methylpropene**

**((CH3)2CCH2; X1A1)**

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# Discussion of the full potential energy surface (PES) of the reaction of 1-propynyl with 2‑methylpropene.

Reaction starts with an attack of 1-propynyl radical without any entrance barrier to one of the two chemically inequivalent carbon atoms C1 or C2 in 2-methylpropene via addition with its radical center to the C1=C2double bond. This leads to doublet radical intermediates **i1** and/or **i4**. Both intermediates can be interconverted through the three-carbon ring closure steps via **i2** and **i3** intermediates. **i4** canisomerize via two distinct [1,2-H] shifts: (1) from the CH3 group of the C4H8 moiety to **i5** or (2) from the CH2 group at the C1-position to form **i6**. The formation of **p1**–**p3** products is discussed in the main text of the manuscript (*4. Discussion*), here we will focus on the pathways to less important, according to the RRKM calculations (Table S1), products **cis/trans-p4** and **p7** – **p25** (Fig. S1–S5).

1.1 Acyclic products cis/trans-p4 and p7 – p10 (Fig. S1 and S2)

Products **p7** and **p8** (Fig. S1-S2) are formed from **i5** via propene and methyl loss channels, respectively. Intermediate **i6** leads to *cis-* and *trans-* isomers of hex-2-en-4-yne (**cis/trans-p4**) via methyl elimination and to 5-methylhexa-1,2,3-triene (**p9**) through the hydrogen elimination exit channels. The product **p10** only can be formed via an H-loss form **i2** or **i3**.

1.2 Cyclic products p11 – p20 containing a five-membered ring (Fig. S3 – S4)

The ‘bottle-neck’ step on the way to cyclic products is a five-membered ring closure in **i5** with an energy barrier of 76 kJ mol–1 that leads to **i9**. Further, **i9** can isomerize via two distinct [1,2-H] shifts: (1) from the CH2 group of the 2-methylpropene moiety to form **i10** or (2) from the methyl group of the 1-propynyl moiety to form **i14**. Starting from **i10** and **i14**, ten distinct products **p11** – **p20** containing five-membered rings can be formed via the pathways summarized below:

i10 → p11 + CH3;

i10 → p14/p15/p16 + H;

i10 → i13 → p12 + CH3;

i10 → i13 → p13/p15 + H;

i10 → i11 → i13 → p12 + CH3;

i10 → i11 → i13 → p13/p15 + H;

i10 → i11 → p16 + H;

i10 → i12 → p13/p14/p17 + H;

i14 → p16 + H;

i14 → i15 → p16/p17 + H;

i14 → i15 → p18 + CH3;

i14 → i15 → i16 → p17/p19/p20 + H.

1.3 Cyclic products p21 – p25 containing a six-membered ring (Fig. S5)

Intermediate **i10** can undergo a hydrogen shift from the methyl group of the 1-propynyl moiety to the five-membered ring (**i11**) followed by the ring expansion (**i11** → **i17**→ **i18**) that incorporates all the 1-propynyl carbon atoms into the newly formed six-membered ring. Isomers **p21 – p25** can be formed from **i18** via the pathways summarized below:

i18 → p24/p25 + H;

i18 → i19 → p21 + CH3;

i18 → i19 → p23/p25 + H;

i18 → i20 → p21 + CH3;

i18 → i20 → p22/p24 + H.

# Discussion of the probable sources of background signal at *m/z* 78, 79 and 80

Since the highly reactive 1-propynyl radical (CH3CC) has a molecular mass of 39 amu and the products of its recombination (C6H6) 78 amu. Contamination of the background signal at *m/z* = 78 and 79 most likely arises from products of 1-propynyl recombination (C6H6 – 78 amu) with the contribution of 13C-compounds (13CC5H6 – 79 amu). C6H6 isomers, according to the NIST database, show peaks at 78 – 80 *m/z* indicating the presence of up to two 13C atoms. Recombination of 1-propynyl most likely occurs during supersonic expansion in the "expansion region", on the stainless walls of the pulse valve (catalyzed by Fe2O3) or through a precursor decay (CH3CCI) during storage. In addition, mass 80 amu can have a contribution from ionized helium clusters He20, common in molecular beams of He1,2, which was used as a carrier gas for the CH3CCI precursor. The ionization energy used in the experiment (80 eV) is sufficient to ionize He clusters (He ionization potential is 24.6 eV).

# RRKM calculations results

Table S1. Statistical branching ratios (%) for the reaction of 2-methylpropene + propynyl with ***i1*** and ***i4*** as initial intermediates at different collision energies (*EC,* kJ mol–1)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ***i1*** | | ***i4*** | |
| *EC* | **0** | **38** | **0** | **38** |
| ***p1+H*** | 65.2 | 59.2 | 66.4 | 63.1 |
| ***p2+H*** | 8.7 | 12.2 | 8.8 | 13.0 |
| ***p3+CH3*** | 22.4 | 25.3 | 21.0 | 20.4 |
| ***cis-p4+CH3*** | 2.2 | 1.9 | 2.2 | 2.0 |
| ***trans-p4+CH3*** | 1.4 | 1.3 | 1.5 | 1.4 |
| ***p7+C3H6*** | 0.1 | 0.1 | 0.1 | 0.1 |
| ***p8+CH3*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p9+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p10+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p11+CH3*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p12+CH3*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p13+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p14+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p15+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p16+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p17+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p18+CH3*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p19+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p20+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p21+CH3*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p22+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p23+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p24+H*** | 0.0 | 0.0 | 0.0 | 0.0 |
| ***p25+H*** | 0.0 | 0.0 | 0.0 | 0.0 |

Table S2. RRKM calculated rate constants (*k(E)*, s–1) of the reaction of 2‑methylpropene + propynyl as functions of the internal energy (*E,* kJ mol–1) of the intermediate states for unimolecular reaction steps at different collision energies (*EC,* kJ mol–1)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ***EC*** | 0 | | 37 | | ***EC*** | 0 | | 37 | |
| **Reaction step** | *k(E)* | *E* | *k(E)* | *E* | **Reaction step** | *k(E)* | *E* | *k(E)* | *E* |
| ***i1 – i2*** | 3.35E+09 | 225 | 6.71E+09 | 263 | ***i10 – i11*** | 1.11E+06 | 399 | 4.22E+06 | 437 |
| ***i2 – i1*** | 1.95E+12 | 186 | 2.84E+12 | 224 | ***i11 – i10*** | 5.22E+07 | 321 | 1.39E+08 | 359 |
| ***i1 – p3*** | 1.83E+07 | 225 | 1.30E+08 | 263 | ***i11 – i17*** | 1.95E+10 | 321 | 2.66E+10 | 359 |
| ***i4 – i6*** | 1.02E+06 | 238 | 7.59E+06 | 276 | ***i17 – i11*** | 9.32E+11 | 302 | 1.18E+12 | 340 |
| ***i6 – i4*** | 7.47E+04 | 272 | 7.15E+05 | 310 | ***i14 – p16*** | 9.04E+07 | 386 | 3.11E+08 | 424 |
| ***i4 – p1*** | 1.80E+07 | 238 | 1.40E+08 | 276 | ***i14 – i15*** | 3.28E+06 | 386 | 1.17E+07 | 424 |
| ***i4 – p2*** | 2.40E+06 | 238 | 2.89E+07 | 276 | ***i15 – i14*** | 7.03E+07 | 330 | 1.95E+08 | 368 |
| ***i4 – i3*** | 1.09E+09 | 238 | 2.63E+09 | 276 | ***i15 – p18*** | 1.31E+09 | 330 | 3.54E+09 | 368 |
| ***i3 – i4*** | 3.03E+11 | 187 | 4.54E+11 | 225 | ***i15 – p17*** | 1.23E+08 | 330 | 3.83E+08 | 368 |
| ***i6 – p1*** | 3.06E+05 | 272 | 2.96E+06 | 310 | ***i10 – p16*** | 1.06E+08 | 399 | 3.73E+08 | 437 |
| ***i6 – trans-p4*** | 1.10E+07 | 272 | 7.47E+07 | 310 | ***i15 – i16*** | 1.09E+07 | 330 | 3.65E+07 | 368 |
| ***i6 – cis-p4*** | 1.68E+07 | 272 | 1.12E+08 | 310 | ***i16 – i15*** | 1.33E+06 | 338 | 4.60E+06 | 376 |
| ***i6 – p9*** | 1.76E+01 | 272 | 1.59E+03 | 310 | ***i16 – p17*** | 1.61E+08 | 338 | 4.86E+08 | 376 |
| ***i5 – p2*** | 5.11E+04 | 223 | 7.75E+05 | 261 | ***i16 – p19*** | 4.19E+08 | 338 | 1.09E+09 | 376 |
| ***i5 – p8*** | 5.61E+06 | 223 | 5.39E+07 | 261 | ***i16 – p20*** | 4.48E+07 | 338 | 1.59E+08 | 376 |
| ***i5 – p7*** | 2.59E+08 | 223 | 1.08E+09 | 261 | ***i17 – i18*** | 1.85E+11 | 302 | 2.51E+11 | 340 |
| ***i5 – i9*** | 1.51E+08 | 223 | 3.55E+08 | 261 | ***i18 – i17*** | 4.93E+09 | 340 | 8.10E+09 | 378 |
| ***i9 – i5*** | 2.29E+08 | 278 | 8.88E+08 | 316 | ***i18 – p24*** | 1.54E+08 | 340 | 4.53E+08 | 378 |
| ***i9 – i10*** | 3.42E+04 | 278 | 4.22E+05 | 316 | ***i18 – p25*** | 4.77E+08 | 340 | 1.38E+09 | 378 |
| ***i10 – i9*** | 1.55E+00 | 399 | 3.37E+01 | 437 | ***i19 – p25*** | 4.44E+08 | 339 | 1.29E+09 | 377 |
| ***i9 – i14*** | 1.53E+04 | 278 | 1.66E+05 | 316 | ***i19 – p21*** | 2.59E+09 | 339 | 6.36E+09 | 377 |
| ***i14 – i9*** | 3.20E+00 | 386 | 5.86E+01 | 424 | ***i19 – p23*** | 2.13E+08 | 339 | 5.91E+08 | 377 |
| ***i2 – i3*** | 1.51E+12 | 186 | 1.93E+12 | 224 | ***i20 – p24*** | 2.69E+07 | 400 | 9.43E+07 | 438 |
| ***i3 – i2*** | 2.29E+11 | 187 | 2.92E+11 | 225 | ***i20 – p22*** | 6.00E+06 | 400 | 2.09E+07 | 438 |
| ***i3 – p10*** | 2.04E+00 | 187 | 1.12E+03 | 225 | ***i20 – p21*** | 5.91E+08 | 400 | 1.64E+09 | 438 |
| ***i2 – p10*** | 1.20E+01 | 186 | 6.96E+03 | 224 | ***i13 – i11*** | 3.50E+06 | 337 | 1.25E+07 | 375 |
| ***i4 – i5*** | 1.93E+04 | 238 | 3.06E+05 | 276 | ***i11 – i13*** | 2.32E+06 | 321 | 7.63E+06 | 359 |
| ***i5 – i4*** | 1.87E+04 | 223 | 2.56E+05 | 261 | ***i11 – p16*** | 4.48E+07 | 321 | 1.31E+08 | 359 |
| ***i10 – i12*** | 3.34E+06 | 399 | 1.06E+07 | 437 | ***i12 – p14*** | 4.20E+08 | 358 | 1.13E+09 | 396 |
| ***i12 – i10*** | 1.87E+07 | 358 | 4.98E+07 | 396 | ***i12 – p17*** | 3.92E+08 | 358 | 1.25E+09 | 396 |
| ***i10 – p11*** | 4.39E+08 | 399 | 1.17E+09 | 437 | ***i12 – p13*** | 8.14E+08 | 358 | 2.13E+09 | 396 |
| ***i10 – p14*** | 3.71E+07 | 399 | 1.16E+08 | 437 | ***i15 – p16*** | 3.80E+08 | 330 | 1.11E+09 | 368 |
| ***i10 – p15*** | 9.65E+07 | 399 | 3.17E+08 | 437 | ***i18 – i19*** | 1.81E+07 | 340 | 6.32E+07 | 378 |
| ***i10 – i13*** | 9.95E+05 | 399 | 3.50E+06 | 437 | ***i19 – i18*** | 2.43E+07 | 339 | 8.46E+07 | 377 |
| ***i13 – i10*** | 7.09E+07 | 337 | 1.90E+08 | 375 | ***i18 – i20*** | 1.54E+08 | 340 | 3.86E+08 | 378 |
| ***i13 – p15*** | 1.67E+08 | 337 | 4.80E+08 | 375 | ***i20 – i18*** | 5.15E+06 | 400 | 1.67E+07 | 438 |
| ***i13 – p12*** | 3.84E+09 | 337 | 9.61E+09 | 375 |  |  |  |  |  |

Table S3. Statistical branching ratios (%) for the reaction of *trans*-but-2-ene + propynyl with ***i7*** as an initial intermediate at different collision energies (*EC,* kJ mol–1)

|  |  |  |
| --- | --- | --- |
|  | ***i7*** | |
| *EC* | **0** | **38** |
| ***trans-p4+CH3*** | 97.4 | 95.8 |
| ***cis-p5+H*** | 2.3 | 3.5 |
| ***p6+H*** | 0.3 | 0.7 |

Table S4. Statistical branching ratios (%) for the reaction of *cis*-but-2-ene + propynyl with ***i8*** as an initial intermediate at different collision energies (*EC,* kJ mol–1)

|  |  |  |
| --- | --- | --- |
|  | ***i8*** | |
| *EC* | **0** | **38** |
| ***cis-p4+CH3*** | 96.8 | 94.4 |
| ***trans-p5+H*** | 3.0 | 5.1 |
| ***p6’+H*** | 0.2 | 0.5 |

# Full potential energy surface for the bimolecular reaction of the 1-propynyl radical (CH3CC; X2A1) with 2-methylpropene ((CH3)2CCH2; X1A') calculated at the CCSD(T)-F12/cc-pVTZ-F12//ωB97X-D/6-311G(d,p) level of theory

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**Figure S1.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical (CH3CC; X2A1) with 2-methylpropene ((CH3)2CCH2; X1A') calculated at the CCSD(T)-F12/cc-pVTZ-F12//ωB97X-D/6-311G(d,p) level of theory. Relative energies are given in kJ mol–1. Part I.



**Figure S2.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical (CH3CC; X2A1) with 2-methylpropene ((CH3)2CCH2; X1A') calculated at the CCSD(T)-F12/cc-pVTZ-F12//ωB97X-D/6-311G(d,p) level of theory. Relative energies are given in kJ mol–1. Part II.



**Figure S3.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical (CH3CC; X2A1) with 2-methylpropene ((CH3)2CCH2; X1A') calculated at the CCSD(T)-F12/cc-pVTZ-F12//ωB97X-D/6-311G(d,p) level of theory. Relative energies are given in kJ mol–1. Part III.



**Figure S4.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical (CH3CC; X2A1) with 2-methylpropene ((CH3)2CCH2; X1A') calculated at the CCSD(T)-F12/cc-pVTZ-F12//ωB97X-D/6-311G(d,p) level of theory. Relative energies are given in kJ mol–1. Part IV.



**Figure S5.** Potential energy surface for the bimolecular reaction of the 1-propynyl radical (CH3CC; X2A1) with 2-methylpropene ((CH3)2CCH2; X1A') calculated at the CCSD(T)-F12/cc-pVTZ-F12//ωB97X-D/6-311G(d,p) level of theory. Relative energies are given in kJ mol–1. Part V.

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