`A close up of a necklace

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**Scheme 1.** Structures of six low lying C4H6 isomers. Point groups and energies (kJ mol-1) relative to 1,3-butadiene are also shown. Energies were obtained from NIST.1-2

A flock of seagulls flying in the sky

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**Scheme 2.** Barrierless reactions of 1,3-butadiene with open shell reactants leading to key aromatic molecules: benzene (C6H6, D6h), phenyl (C6H5, C2v), pyridine (C5H5N, C2v) and 1,4-dihydronaphthalene (C10H10, C2v).

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**Scheme 3.** Reaction schematics for the reactions of (a) methylidyne-d (CD) with propylene (CH3CHCH2), (b) methylidyne (CH) with propylene-d6 (CD3CDCD2), and (c) methylidyne-d (CD) with propylene-3,3,3-d3 (CD3CHCH2), leading to H- and D- loss products. Successive dissociative electron impact ionization processes of the parent ions are represented in italics.

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**Figure 1.** Laboratory angular distribution (top) and time-of-flight (TOF) spectra (bottom) recorded at mass-to-charge ratio (m/z) of 53 for the reaction of the methylidyne radical (CH; C∞v; X2Π) with propylene (C3H6; Cs; X1A’). The directions of the methylidyne radical and propylene beams are defined as 0° and 90°, respectively. The red solid lines represent the best-fit derived from center-of-mass functions depicted in Figure 3 with black circles defining the experimental data.

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**Figure 2.** Time-of-flight (TOF) spectra for the reaction of (a) the methylidyne-d radical (CD; C∞v; X2Π) with propylene (C3H6; Cs; X1A’) recorded at mass-to-charge (m/z) ratios of 55 (C4H5D+) and 54 (C4H4D+/C4H6+), (b) the methylidyne radical (CH; C∞v; X2Π) with propylene-d6 (C3D6; Cs; X1A’) recorded at m/z 58 (C4D5+) and 59 (C4HD5+), (c) the methylidyne-d radical (CD; C∞v; X2Π) with propylene-3,3,3-d3 (CD3CHCH2; Cs; X1A’) recorded at m/z 58 (C4D4H2+) and 57 (C4D3H3+/C4D4H+), and (d) the methylidyne radical (CH; C∞v; X2Π) with propylene (C3H6; Cs; X1A’) recorded at m/z 54 (C4H6+) and 53 (C4H5+).

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**Figure 3.** Best-fit center-of-mass translational energy (*P(ET)*, upper) and angular (*T(θ)*, lower) flux distributions of the reaction of the methylidyne radical with propylene to form C4H6 molecule(s) plus atomic hydrogen. The red lines reveal the best fits; the shaded areas delimit the acceptable upper and lower error limits. *Emax*defines the maximum translational energy.

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Figure 4. Portion of the C4H7 PES following CH radical addition to the carbon-carbon double bond of propylene. Pathways leading to **p2** and **p3** are colored in red and blue, respectively.

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Figure 5. Portion of the C4H7 PES corresponding to CH radical insertion into the C-H bond the methyl and CH2 moieties of propylene.

A close up of a mans face

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Figure 6. Portion of the C4H7 PES corresponding to CH radical insertion into the C−H bond of the CH moiety of the vinyl group of propylene.

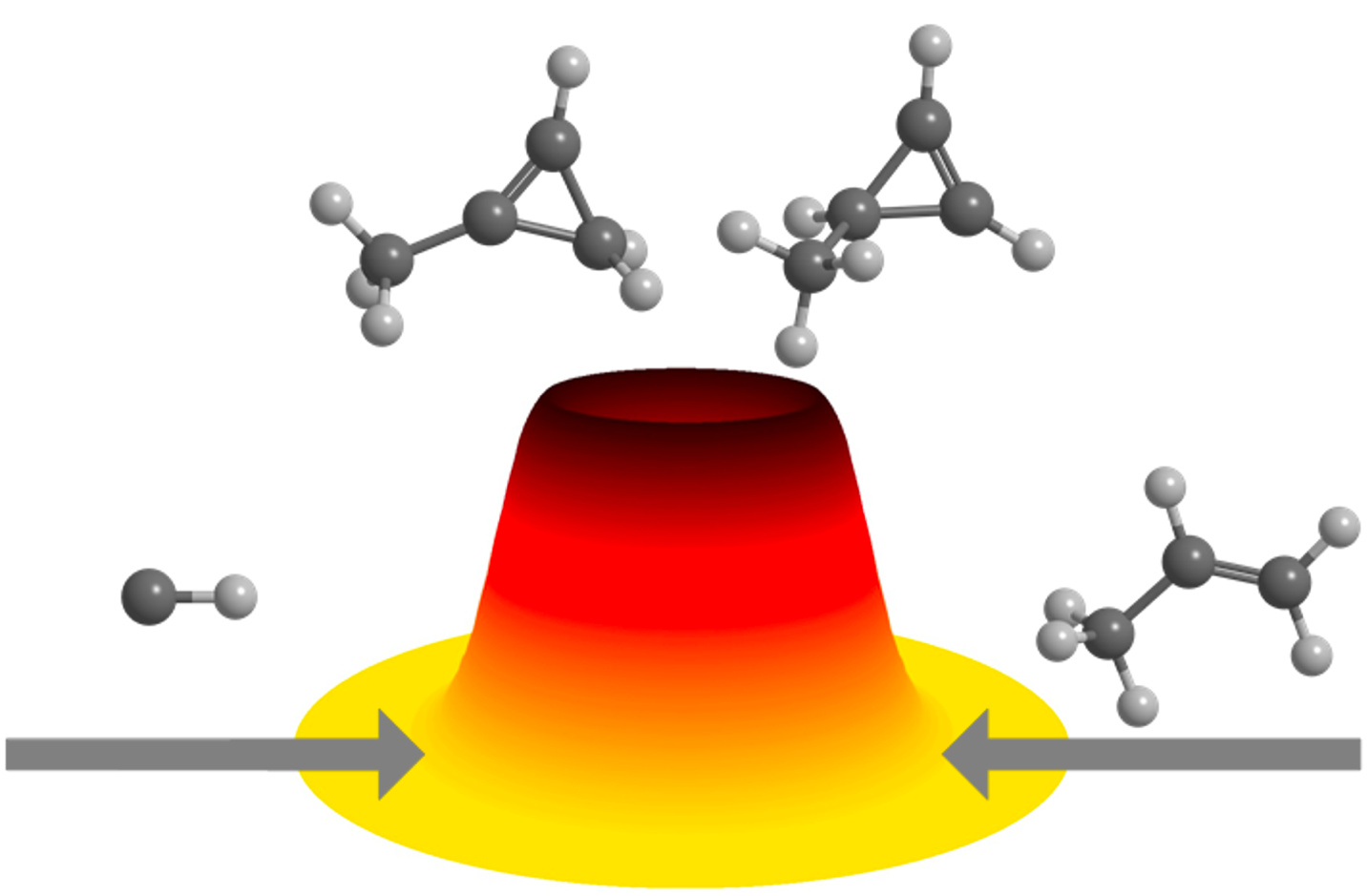
**Table 1**. Peak velocities (*v*p) and speed ratios (*S*) of the methylidyne (CH), propylene (C3H6), propylene-d6 (C3D6), methylidyne-d (CD) beams along with the corresponding collision energies (*E*C) and center-of-mass angles (ΘCM) for each reactive scattering experiment.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Beam | *v*p  (m s−1) | *S* | *E*C  (kJ mol−1) | ΘCM  (degree) |
| CH (X2Π) | 1782 ± 29 | 13.8 ± 1.6 | 19.3 ± 0.4 | 56.7 ± 0.3 |
| C3H6 (X1A’) | 840 ± 10 | 11.0 ± 0.2 |
| C3D6 (X1A’) | 820 ± 10 | 7.8 ± 1.0 | 19.7 ± 0.4 | 59.5 ± 0.3 |
| CD (X2Π) | 1841 ± 15 | 13.9 ± 0.8 |  |  |
| C3H6 (X1A’) | 840 ± 10 | 11.0 ± 0.2 | 21.5 ± 0.4 | 53.9 ± 0.3 |
| CD3CHCH2 (X1A’) | 830 ± 10 | 11.0 ± 0.2 | 21.8 ± 0.4 | 55.4 ± 0.3 |

**Table 2**. Statistical branching ratios (%) for the reaction of the methylidyne (CH) radical with propylene (CH3CHCH2) at collision energy *EC* = 19.3 kJ mol-1.*a*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **i1**  100 | **i2**  100 | **i3**  100 | **i4**  100 | **i5**  100 | **i6**  100 |
| **p1** | 1.2796 | 1.0229 | 0.0243 | 0.0246 | 0.0007 | 0.0025 |
| **p2** | 0.0701 | 0.0559 | 0.0013 | 0.0014 | 0.2155 | 0.0002 |
| **p3** | 0.2114 | 0.2008 | 0.0049 | 0.0049 | 0.0002 | 0.0005 |
| **p4** | 0.0094 | 0.0070 | 0.0010 | 0.0010 | 1.6341 | 0.0073 |
| **p5** | 83.4638 | 83.5392 | 80.4935 | 80.4319 | 0.087 | 16.1737 |
| **p6** | 1.4382 | 1.4335 | 1.0402 | 1.376 | 0.0030 | 0.1642 |
| **p7** | 12.7444 | 12.9762 | 17.4795 | 17.2215 | 0.1958 | 78.6169 |
| **p8** | 0.4653 | 0.4717 | 0.6431 | 0.59 | 0.0058 | 4.5521 |
| **p9** | 0.0812 | 0.0821 | 0.1129 | 0.142 | 0.0089 | 0.2873 |
| **p10** | 0.0145 | 0.0147 | 0.0199 | 0.0196 | 0.0002 | 0.1786 |
| **p11** | 0.0156 | 0.0157 | 0.022 | 0.0226 | 0.0 | 0.0015 |
| **p12** | 0.0949 | 0.0687 | 0.0022 | 0.0023 | 95.0226 | 0.0048 |
| **p13** | 0.1116 | 0.1115 | 0.1552 | 0.1623 | 2.8262 | 0.0106 |
|  |  |  |  |  |  |  |

*a*Here, **p1**-**p13** are cyclopropene, 1-methylcyclopropene, 3-methylcyclopropene, methylenecyclopropane, 1,3-butadiene, 1,2-butadiene, ethylene, acetylene, 1-butyne, cyclobutene, 2-butyne, allene and propyne.



**TOC GRAPHIC**

CM velocity flux contour maps for the reactions of methylidyne radical (CH; X2Π) with propylene (CH3CHCH2; X1A’)for the atomic hydrogen loss channel leading to C4H6 isomers 1-methylcyclopropene and 3-methylcyclopropene. The contour lines connect points of constant fluxes (white, minimum intensity; black, maximum intensity); the direction of the methylidyne radical beam is defined as 0° and of the propylene beam as 180°.

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(2) Wiberg, K. B.; Fenoglio, R. A. Heats of Formation of C4H6 Hydrocarbons. *J. Am. Chem. Soc.* **1968,** *90*, 3395-3397.