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ELECTRONIC SUPPLEMENTARY INFORMATION

FOR AN ARTICLE IN PCCP

**Kinetics and Branching Fractions of the Hydrogen Abstraction Reaction from Methyl Butenoates by H Atom**

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In this supporting information, we present:

**Table S1.** The enthalpies of activation (in kcal/mol) of the conventional transition states and the enthalpies of reaction (in kcal/mol), both at 0 K, for hydrogen abstraction reactions as computed by various quantum chemical methods. Single-point calculations were carried out based on the lowest-energy-structures optimized by M08-HX/MG3S, and zero point energies (ZPEs) were calculated using scaled harmonic frequencies with a scale factor of 0.973.

**Table S2.** The tunneling transmission coefficients for hydrogen abstraction reactions from methyl butenoate by H atom using small curvature tunneling, zero curvature tunneling, and the Eckart approximation.

**Table S3.** The rate constants ($cm^3\,mol^{-1}\,s^{-1}$) of R1~R8 by various kinetics methods.

**Table S4.** Calculated rovibrational partition functions of the transition state TS1.

**Table S5.** The fit parameters for the reverse rate constants of hydrogen abstraction reactions from methyl butenoate by H atom as calculated using MS-CVT/SCT.

**Figure S1.** The geometries and Cartesian coordinates of reactants, transition state and products of hydrogen abstraction reactions for methyl 3-butenoate and methyl 2-butenoate by hydrogen radical at the M06-2X/ma-TZVP level with integral grid of 99974 (coordinate units: Angstrom).

**Figure S2.** The branching fraction of the hydrogen abstraction from all sites of methyl 3-butenoate and methyl 2-butenoate by H atom by TST and CVT. Dotted lines: TST; dashed lines: CVT.

**Table S1.** The enthalpies of activation (in kcal/mol) of the conventional transition states and the enthalpies of reaction (in kcal/mol), both at 0 K, for hydrogen abstraction reactions as computed by various quantum chemical methods. Single-point calculations were carried out based on the lowest-energy-structures optimized by M08-HX/MG3S, and zero point energies (ZPEs) were calculated using scaled harmonic frequencies with a scale factor of 0.973.[a]

a) Methyl 3-butenoate

| Methods | R1 | | | R2 | | | R3 | | | R4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta H_0$ | $\Delta H_0^{\ddagger}$ | $\Delta H_{rev,0}^{\ddagger}$ | $\Delta H_0$ | $\Delta H_0^{\ddagger}$ | $\Delta H_{rev,0}^{\ddagger}$ | $\Delta H_0$ | $\Delta H_0^{\ddagger}$ | $\Delta H_{rev,0}^{\ddagger}$ | $\Delta H_0$ | $\Delta H_0^{\ddagger}$ | $\Delta H_{rev,0}^{\ddagger}$ |
| CCSD(T)-F12a/jun-cc-pVTZ | -5.0 | 10.2 | 15.2 | -22.8 | 5.4 | 28.1 | 5.2 | 14.1 | 9.0 | 7.4 | 15.8 | 8.4 |
| M06-2X/ma-TZVP | 0.1 | 0.7 | 0.6 | 0.6 | 0.9 | 0.3 | -0.5 | 0.3 | 0.9 | -0.2 | 0.4 | 0.6 |
| M06-2X/jul-cc-pVTZ | 0.0 | 0.7 | 0.7 | 0.3 | 0.9 | 0.5 | -0.8 | 0.1 | 0.9 | -0.5 | 0.3 | 0.7 |
| M06-2X/jun-cc-pVTZ | 0.0 | 0.8 | 0.7 | 0.4 | 0.9 | 0.5 | -0.7 | 0.2 | 0.9 | -0.4 | 0.3 | 0.7 |
| M06-2X/MG3S | 0.1 | 0.8 | 0.7 | 0.4 | 1.0 | 0.5 | -0.7 | 0.2 | 0.9 | -0.3 | 0.4 | 0.7 |
| M08-SO/MG3S | 0.0 | -0.6 | -0.6 | 0.6 | 0.1 | -0.5 | 1.2 | 0.1 | -1.1 | 1.5 | 0.2 | -1.2 |
| M08-HX/jun-cc-pVTZ | -0.6 | -0.6 | 0.0 | 0.9 | 0.4 | -0.4 | 0.8 | -0.4 | -1.2 | 1.0 | -0.2 | -1.2 |
| M08-SO/ma-TZVP | -0.1 | -0.7 | -0.6 | 0.7 | 0.1 | -0.5 | 1.1 | 0.0 | -1.1 | 1.5 | 0.2 | -1.3 |
| M08-HX/jul-cc-pVTZ | -0.6 | -0.6 | 0.0 | 0.9 | 0.4 | -0.5 | 0.8 | -0.5 | -1.3 | 1.0 | -0.3 | -1.3 |
| M08-HX/MG3S | -0.5 | -0.5 | 0.1 | 1.1 | 0.5 | -0.6 | 0.9 | -0.4 | -1.3 | 1.1 | -0.2 | -1.3 |
| PWB6K/jul-cc-pVTZ | 1.1 | 0.0 | -1.1 | -0.3 | -0.1 | 0.2 | 1.0 | 0.1 | -0.9 | 1.8 | 0.2 | -1.6 |
| M08-SO/jul-cc-pVTZ | -0.1 | -0.8 | -0.8 | 0.7 | -0.1 | -0.7 | 1.2 | 0.0 | -1.2 | 1.5 | 0.2 | -1.3 |
| M08-SO/jun-cc-pVTZ | 0.0 | -0.8 | -0.8 | 0.7 | -0.1 | -0.7 | 1.2 | 0.1 | -1.1 | 1.6 | 0.3 | -1.3 |
| PWB6K/jun-cc-pVTZ | 1.1 | 0.0 | -1.1 | -0.3 | -0.1 | 0.2 | 1.0 | 0.1 | -0.9 | 1.8 | 0.2 | -1.6 |
| PWB6K/MG3S | 1.2 | 0.2 | -1.0 | -0.3 | 0.1 | 0.3 | 1.0 | 0.1 | -0.9 | 1.8 | 0.3 | -1.5 |
| PWB6K/ma-TZVP | 1.2 | 0.1 | -1.1 | -0.2 | 0.0 | 0.2 | 1.1 | 0.2 | -0.9 | 1.9 | 0.3 | -1.6 |
| M11/MG3S | -0.7 | -1.0 | -0.3 | -0.5 | -0.6 | -0.1 | -1.3 | -1.7 | -0.4 | -0.4 | -1.4 | -1.0 |
| mPW1K/MG3S | 0.1 | -1.1 | -1.2 | -1.3 | -1.1 | 0.2 | -0.2 | -0.9 | -0.7 | 0.7 | -0.8 | -1.4 |
| M11/jul-cc-pVTZ | -0.8 | -1.0 | -0.2 | -0.6 | -0.6 | 0.0 | -1.3 | -1.8 | -0.5 | -0.4 | -1.5 | -1.1 |
| M11/jun-cc-pVTZ | -0.8 | -1.0 | -0.2 | -0.7 | -0.7 | 0.0 | -1.3 | -1.7 | -0.4 | -0.4 | -1.4 | -1.1 |
| mPW1K/ma-TZVP | 0.0 | -1.2 | -1.2 | -1.4 | -1.2 | 0.2 | -0.2 | -0.9 | -0.7 | 0.6 | -0.8 | -1.5 |
| mPW1K/jun-cc-pVTZ | 0.0 | -1.2 | -1.3 | -1.4 | -1.2 | 0.1 | -0.2 | -0.9 | -0.7 | 0.6 | -0.9 | -1.5 |
| mPW1K/jul-cc-pVTZ | 0.0 | -1.3 | -1.3 | -1.3 | -1.2 | 0.1 | -0.2 | -1.0 | -0.7 | 0.6 | -0.9 | -1.5 |
| M11/ma-TZVP | -0.3 | -1.2 | -0.9 | -0.3 | -0.9 | -0.6 | -1.0 | -1.7 | -0.8 | 0.0 | -1.5 | -1.4 |
| M08-HX/ma-TZVP | -0.3 | -0.6 | -0.3 | 1.4 | 0.4 | -1.0 | 1.2 | -0.4 | -1.7 | 1.5 | -0.3 | -1.7 |
| ωB97XD/MG3S | 0.0 | -1.0 | -1.0 | -0.7 | -0.3 | 0.4 | 0.0 | -1.7 | -1.7 | 0.7 | -1.6 | -2.2 |
| ωB97XD/ma-TZVP | 0.0 | -1.2 | -1.1 | -0.7 | -0.4 | 0.3 | 0.1 | -1.7 | -1.8 | 0.8 | -1.5 | -2.3 |
| ωB97X/jul-cc-pVTZ | 1.0 | 0.6 | -0.4 | 0.6 | 1.6 | 1.0 | 1.0 | -0.3 | -1.3 | 1.6 | -0.4 | -2.0 |
| ωB97X/jun-cc-pVTZ | 1.0 | 0.6 | -0.4 | 0.6 | 1.6 | 1.0 | 1.1 | -0.3 | -1.3 | 1.6 | -0.4 | -2.0 |
| ωB97XD/jun-cc-pVTZ | -0.1 | -1.2 | -1.1 | -0.7 | -0.5 | 0.3 | 0.0 | -1.7 | -1.8 | 0.7 | -1.6 | -2.3 |
| ωB97XD/jul-cc-pVTZ | -0.1 | -1.2 | -1.1 | -0.7 | -0.5 | 0.3 | 0.0 | -1.8 | -1.8 | 0.7 | -1.6 | -2.3 |
| ωB97X/MG3S | 1.1 | 0.8 | -0.2 | 0.5 | 1.8 | 1.2 | 1.0 | -0.3 | -1.3 | 1.6 | -0.4 | -2.0 |
| ωB97X/ma-TZVP | 1.1 | 0.7 | -0.4 | 0.7 | 1.7 | 1.0 | 1.1 | -0.2 | -1.3 | 1.7 | -0.3 | -2.0 |
| SOGGA11-X/jul-cc-pVTZ | 1.8 | -0.3 | -2.2 | -0.1 | -0.6 | -0.5 | 1.6 | 0.4 | -1.3 | 2.5 | 0.5 | -2.0 |
| SOGGA11-X/jun-cc-pVTZ | 1.8 | -0.3 | -2.2 | -0.1 | -0.6 | -0.5 | 1.7 | 0.4 | -1.3 | 2.5 | 0.5 | -2.0 |
| SOGGA11-X/MG3S | 2.0 | -0.1 | -2.1 | -0.1 | -0.4 | -0.3 | 1.8 | 0.5 | -1.3 | 2.6 | 0.6 | -2.1 |
| SOGGA11-X/ma-TZVP | 2.0 | -0.2 | -2.2 | 0.0 | -0.4 | -0.4 | 1.8 | 0.5 | -1.2 | 2.7 | 0.6 | -2.1 |
| M05-2X/jul-cc-pVTZ | 0.9 | 2.0 | 1.1 | -0.8 | 2.0 | 2.7 | 1.5 | 1.4 | -0.1 | 1.6 | 1.2 | -0.4 |
| M05-2X/ma-TZVP | 0.9 | 1.9 | 1.0 | -0.5 | 1.9 | 2.4 | 1.8 | 1.5 | -0.3 | 1.9 | 1.2 | -0.6 |
| M05-2X/jun-cc-pVTZ | 0.9 | 2.0 | 1.1 | -0.8 | 2.0 | 2.7 | 1.6 | 1.5 | -0.1 | 1.7 | 1.2 | -0.5 |
| M05-2X/MG3S | 1.0 | 2.1 | 1.1 | -0.6 | 2.1 | 2.7 | 1.6 | 1.5 | -0.1 | 1.8 | 1.3 | -0.5 |
| M06/ma-TZVP | 0.1 | -0.4 | -0.6 | -2.0 | -0.3 | 1.7 | -2.1 | -3.4 | -1.2 | -0.8 | -2.9 | -2.0 |
| M06/MG3S | 0.1 | -0.4 | -0.5 | -2.1 | -0.3 | 1.8 | -2.0 | -3.4 | -1.4 | -0.9 | -3.0 | -2.0 |
| M06/jun-cc-pVTZ | 0.0 | -0.7 | -0.7 | -2.0 | -0.5 | 1.4 | -2.0 | -3.4 | -1.4 | -0.9 | -2.9 | -2.1 |
| M06/jul-cc-pVTZ | 0.0 | -0.7 | -0.7 | -1.9 | -0.5 | 1.4 | -2.0 | -3.4 | -1.4 | -0.9 | -3.0 | -2.1 |
| ωB97/jul-cc-pVTZ | 1.8 | 2.1 | 0.3 | 1.7 | 3.2 | 1.4 | 1.9 | 0.8 | -1.1 | 2.3 | 0.6 | -1.7 |
| ωB97/jun-cc-pVTZ | 1.8 | 2.1 | 0.3 | 1.7 | 3.2 | 1.5 | 2.0 | 0.8 | -1.1 | 2.4 | 0.6 | -1.8 |
| ωB97/MG3S | 1.8 | 2.3 | 0.5 | 1.6 | 3.4 | 1.8 | 1.9 | 0.9 | -1.0 | 2.3 | 0.6 | -1.7 |
| ωB97/ma-TZVP | 1.9 | 2.2 | 0.3 | 1.8 | 3.4 | 1.6 | 2.0 | 0.9 | -1.1 | 2.5 | 0.7 | -1.8 |
| MN12-L/ma-TZVP | -0.7 | -1.5 | -0.9 | -4.9 | -2.3 | 2.5 | -3.9 | -1.5 | 2.4 | -2.0 | -0.3 | 1.7 |

| Methods | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| MN12-L/MG3S | -0.6 | -1.6 | -1.0 | -4.7 | -2.4 | 2.4 | -3.9 | -1.7 | 2.2 | -2.2 | -0.5 | 1.7 |
| MN12-L/jun-cc-pVTZ | -0.9 | -1.9 | -1.0 | -4.8 | -2.6 | 2.2 | -3.9 | -1.7 | 2.2 | -2.2 | -0.6 | 1.7 |
| MN12-L/jul-cc-pVTZ | -0.9 | -1.9 | -1.0 | -4.8 | -2.6 | 2.2 | -4.0 | -1.8 | 2.2 | -2.3 | -0.6 | 1.7 |
| MN12-SX/MG3S | -2.5 | -0.6 | 1.9 | -4.2 | -0.6 | 3.6 | -3.8 | -1.7 | 2.1 | -2.9 | -1.3 | 1.6 |
| MN12-SX/ma-TZVP | -2.5 | -0.4 | 2.2 | -4.3 | -0.4 | 3.9 | -3.7 | -1.5 | 2.3 | -2.8 | -1.1 | 1.7 |
| MN12-SX/jun-cc-pVTZ | -2.8 | -1.1 | 1.7 | -4.3 | -1.0 | 3.4 | -3.9 | -1.9 | 2.0 | -3.0 | -1.5 | 1.5 |
| MN12-SX/jul-cc-pVTZ | -2.9 | -1.1 | 1.8 | -4.3 | -1.0 | 3.4 | -3.9 | -1.9 | 2.0 | -3.1 | -1.5 | 1.5 |
| GAM/ma-TZVP | -1.6 | -3.4 | -1.8 | -3.9 | -3.8 | 0.1 | -2.7 | -4.1 | -1.5 | -1.3 | -3.8 | -2.5 |
| GAM/MG3S | -1.6 | -3.3 | -1.7 | -3.9 | -3.7 | 0.2 | -2.7 | -4.2 | -1.5 | -1.4 | -3.9 | -2.5 |
| GAM/jul-cc-pVTZ | -1.5 | -3.6 | -2.1 | -3.7 | -4.0 | -0.3 | -2.6 | -4.3 | -1.6 | -1.3 | -3.9 | -2.6 |
| GAM/jun-cc-pVTZ | -1.5 | -3.6 | -2.1 | -3.8 | -4.0 | -0.2 | -2.6 | -4.3 | -1.7 | -1.3 | -3.9 | -2.6 |
| MN15-L/jun-cc-pVTZ | -3.2 | -3.1 | 0.2 | -6.4 | -2.8 | 3.5 | -4.6 | -2.8 | 1.8 | -3.8 | -1.8 | 1.9 |
| MN15-L/jul-cc-pVTZ | -3.2 | -3.1 | 0.1 | -6.3 | -2.9 | 3.5 | -4.7 | -2.9 | 1.8 | -3.8 | -1.8 | 2.0 |
| MN15-L/ma-TZVP | -3.3 | -2.9 | 0.3 | -6.5 | -2.6 | 3.9 | -4.8 | -2.8 | 2.0 | -3.9 | -1.9 | 2.0 |
| MN15-L/MG3S | -3.3 | -2.9 | 0.4 | -6.5 | -2.6 | 3.9 | -4.9 | -2.8 | 2.1 | -4.0 | -1.8 | 2.1 |
| M11-L/ma-TZVP | -3.2 | -1.4 | 1.8 | -6.0 | -1.4 | 4.6 | -7.1 | -4.1 | 3.0 | -4.6 | -3.0 | 1.6 |
| B3LYP/MG3S | -4.1 | -5.1 | -0.9 | -6.1 | -5.0 | 1.1 | -4.1 | -5.4 | -1.2 | -2.9 | -5.2 | -2.2 |
| B3LYP/ma-TZVP | -4.1 | -5.2 | -1.0 | -6.1 | -5.1 | 1.0 | -4.1 | -5.4 | -1.2 | -2.9 | -5.2 | -2.3 |
| B3LYP/jun-cc-pVTZ | -4.1 | -5.2 | -1.1 | -6.2 | -5.2 | 1.0 | -4.1 | -5.4 | -1.3 | -2.9 | -5.2 | -2.3 |
| B3LYP/jul-cc-pVTZ | -4.1 | -5.2 | -1.1 | -6.1 | -5.2 | 1.0 | -4.1 | -5.4 | -1.3 | -3.0 | -5.3 | -2.3 |
| M11-L/MG3S | -3.7 | -1.5 | 2.2 | -6.2 | -1.5 | 4.7 | -7.5 | -4.4 | 3.1 | -5.1 | -3.2 | 1.9 |
| M11-L/jun-cc-pVTZ | -4.0 | -2.4 | 1.6 | -6.5 | -2.1 | 4.4 | -7.7 | -4.9 | 2.9 | -5.4 | -3.6 | 1.7 |
| M11-L/jul-cc-pVTZ | -4.0 | -2.4 | 1.6 | -6.6 | -2.2 | 4.4 | -7.9 | -5.0 | 2.9 | -5.5 | -3.7 | 1.8 |

b) Methyl 2-butenoate

| Methods | R5 | | | R6 | | | R7 | | | R8 | | | MUD[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta H_0$ | $\Delta H_0^{\ddagger}$ | $\Delta H_{\text{rev},0}^{\ddagger}$ | $\Delta H_0$ | $\Delta H_0^{\ddagger}$ | $\Delta H_{\text{rev},0}^{\ddagger}$ | $\Delta H_0$ | $\Delta H_0^{\ddagger}$ | $\Delta H_{\text{rev},0}^{\ddagger}$ | $\Delta H_0$ | $\Delta H_0^{\ddagger}$ | $\Delta H_{\text{rev},0}^{\ddagger}$ | |
| CCSD(T)-F12a/jun-cc-pVTZ | -5.5 | 10.2 | 15.7 | 6.9 | 15.1 | 8.2 | 2.2 | 12.1 | 9.9 | -18.6 | 6.9 | 25.4 | |
| M06-2X/ma-TZVP | 0.0 | 0.5 | 0.5 | 0.1 | 0.7 | 0.6 | -0.7 | 0.3 | 1.1 | 0.8 | 0.7 | -0.1 | 0.5 |
| M06-2X/MG3S | -0.1 | 0.5 | 0.6 | 0.0 | 0.5 | 0.5 | -0.9 | 0.3 | 1.2 | 0.6 | 0.7 | 0.2 | 0.5 |
| M06-2X/jun-cc-pVTZ | -0.1 | 0.5 | 0.6 | -0.1 | 0.5 | 0.6 | -0.9 | 0.3 | 1.2 | 0.5 | 0.7 | 0.2 | 0.5 |
| M06-2X/jul-cc-pVTZ | -0.2 | 0.5 | 0.7 | -0.1 | 0.5 | 0.6 | -1.0 | 0.2 | 1.2 | 0.5 | 0.7 | 0.2 | 0.5 |
| mPW1K/MG3S | -0.1 | -0.8 | -0.8 | 0.7 | -0.5 | -1.1 | -0.2 | -1.1 | -0.9 | -0.1 | -1.1 | -1.0 | 0.8 |
| PWB6K/MG3S | 0.9 | 0.1 | -0.9 | 1.8 | 0.5 | -1.3 | 0.7 | 0.0 | -0.7 | 0.8 | 0.1 | -0.7 | 0.7 |
| mPW1K/ma-TZVP | -0.1 | -0.9 | -0.8 | 0.5 | -0.5 | -1.1 | -0.2 | -1.2 | -0.9 | -0.1 | -1.2 | -1.1 | 0.8 |
| PWB6K/jul-cc-pVTZ | 0.9 | 0.0 | -0.9 | 1.8 | 0.5 | -1.3 | 0.7 | -0.1 | -0.8 | 0.8 | -0.1 | -0.8 | 0.7 |
| PWB6K/jun-cc-pVTZ | 0.9 | 0.0 | -0.9 | 1.8 | 0.5 | -1.3 | 0.8 | -0.1 | -0.8 | 0.8 | -0.1 | -0.8 | 0.7 |
| PWB6K/ma-TZVP | 1.0 | 0.0 | -0.9 | 1.8 | 0.5 | -1.2 | 0.8 | 0.0 | -0.8 | 0.8 | 0.0 | -0.9 | 0.7 |
| mPW1K/jun-cc-pVTZ | -0.1 | -1.0 | -0.9 | 0.6 | -0.5 | -1.1 | -0.2 | -1.2 | -1.0 | -0.1 | -1.3 | -1.1 | 0.8 |
| mPW1K/jul-cc-pVTZ | -0.2 | -1.0 | -0.8 | 0.6 | -0.5 | -1.1 | -0.2 | -1.2 | -1.0 | -0.1 | -1.2 | -1.1 | 0.8 |
| M08-SO/ma-TZVP | -0.2 | -0.8 | -0.6 | 1.8 | 0.6 | -1.3 | 0.8 | -0.3 | -1.2 | 0.8 | -0.1 | -1.0 | 0.7 |
| M08-SO/MG3S | -0.1 | -0.7 | -0.6 | 1.9 | 0.6 | -1.3 | 0.9 | -0.2 | -1.1 | 0.8 | -0.2 | -0.9 | 0.7 |
| $\omega$B97XD/MG3S | -0.2 | -1.0 | -0.8 | 0.2 | -1.6 | -1.8 | -0.2 | -1.6 | -1.5 | 0.0 | -0.4 | -0.4 | 0.9 |
| $\omega$B97XD/ma-TZVP | -0.5 | -1.1 | -0.6 | -0.1 | -1.7 | -1.6 | -0.4 | -1.6 | -1.3 | -0.2 | -0.5 | -0.3 | 0.9 |
| $\omega$B97X/jul-cc-pVTZ | 1.0 | 0.7 | -0.3 | 1.5 | -0.2 | -1.7 | 0.8 | -0.2 | -1.0 | 1.0 | 1.4 | 0.4 | 0.9 |
| M08-HX/jun-cc-pVTZ | -0.8 | -0.7 | 0.0 | 1.9 | 0.4 | -1.4 | 0.7 | -0.6 | -1.3 | 1.2 | 0.2 | -1.0 | 0.8 |
| $\omega$B97X/jun-cc-pVTZ | 1.0 | 0.7 | -0.3 | 1.5 | -0.2 | -1.7 | 0.8 | -0.1 | -0.9 | 1.0 | 1.4 | 0.4 | 0.9 |
| $\omega$B97X/MG3S | 1.0 | 0.9 | -0.1 | 1.5 | -0.2 | -1.7 | 0.8 | -0.1 | -0.8 | 1.0 | 1.6 | 0.6 | 0.9 |
| M08-HX/jul-cc-pVTZ | -0.8 | -0.7 | 0.0 | 1.9 | 0.4 | -1.5 | 0.7 | -0.7 | -1.3 | 1.2 | 0.2 | -1.0 | 0.8 |
| $\omega$B97X/ma-TZVP | 1.1 | 0.8 | -0.3 | 1.5 | -0.2 | -1.7 | 0.9 | -0.1 | -0.9 | 1.1 | 1.5 | 0.4 | 0.9 |
| M08-SO/jun-cc-pVTZ | -0.2 | -1.0 | -0.8 | 1.9 | 0.6 | -1.3 | 0.9 | -0.3 | -1.2 | 0.8 | -0.3 | -1.1 | 0.8 |
| $\omega$B97XD/jun-cc-pVTZ | -0.3 | -1.2 | -0.9 | 0.1 | -1.7 | -1.8 | -0.2 | -1.7 | -1.5 | 0.0 | -0.5 | -0.5 | 0.9 |
| M08-SO/jul-cc-pVTZ | -0.2 | -1.0 | -0.8 | 1.9 | 0.5 | -1.3 | 0.9 | -0.3 | -1.3 | 0.8 | -0.3 | -1.1 | 0.8 |
| M08-HX/MG3S | -0.7 | -0.7 | 0.0 | 1.9 | 0.4 | -1.5 | 0.7 | -0.6 | -1.3 | 1.3 | 0.3 | -1.0 | 0.8 |
| $\omega$B97XD/jul-cc-pVTZ | -0.3 | -1.2 | -0.9 | 0.1 | -1.7 | -1.8 | -0.2 | -1.7 | -1.6 | 0.0 | -0.5 | -0.5 | 0.9 |
| M11/MG3S | -0.8 | -1.4 | -0.6 | -0.2 | -1.3 | -1.1 | -1.9 | -1.7 | 0.2 | -0.5 | -0.9 | -0.3 | 0.8 |
| M11/jul-cc-pVTZ | -0.9 | -1.3 | -0.5 | -0.2 | -1.3 | -1.1 | -1.9 | -1.7 | 0.2 | -0.5 | -0.9 | -0.4 | 0.9 |
| M11/jun-cc-pVTZ | -0.9 | -1.4 | -0.5 | -0.3 | -1.3 | -1.1 | -1.9 | -1.7 | 0.2 | -0.6 | -1.0 | -0.3 | 0.9 |
| M11/ma-TZVP | -0.4 | -1.6 | -1.2 | 0.2 | -1.3 | -1.4 | -1.6 | -1.8 | -0.2 | -0.2 | -1.2 | -0.9 | 0.9 |
| M08-HX/ma-TZVP | -0.4 | -0.7 | -0.3 | 2.3 | 0.4 | -1.9 | 1.1 | -0.6 | -1.7 | 1.7 | 0.2 | -1.5 | 1.0 |
| M06/ma-TZVP | -0.4 | -0.5 | -0.1 | -1.6 | -3.4 | -1.8 | -1.9 | -2.4 | -0.5 | -0.5 | -0.3 | 0.2 | 1.3 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M06/MG3S | -0.4 | -0.4 | 0.0 | -1.4 | -3.4 | -2.0 | -1.9 | -2.5 | -0.6 | -0.7 | -0.3 | 0.3 | 1.3 |
| SOGGA11-X/jul-cc-pVTZ | 1.5 | -0.1 | -1.6 | 2.2 | 0.7 | -1.5 | 1.6 | 0.1 | -1.5 | 1.1 | -0.5 | -1.6 | 1.2 |
| M05-2X/ma-TZVP | 0.7 | 1.7 | 1.0 | 2.0 | 1.5 | -0.6 | 1.1 | 1.3 | 0.3 | -0.3 | 1.6 | 1.9 | 1.2 |
| SOGGA11-X/jun-cc-pVTZ | 1.5 | -0.1 | -1.6 | 2.2 | 0.7 | -1.5 | 1.6 | 0.1 | -1.5 | 1.1 | -0.4 | -1.5 | 1.2 |
| M06/jun-cc-pVTZ | -0.5 | -0.7 | -0.2 | -1.4 | -3.4 | -2.0 | -1.8 | -2.5 | -0.7 | -0.6 | -0.5 | 0.0 | 1.3 |
| M06/jul-cc-pVTZ | -0.5 | -0.7 | -0.2 | -1.5 | -3.4 | -1.9 | -1.9 | -2.5 | -0.7 | -0.5 | -0.5 | 0.0 | 1.4 |
| SOGGA11-X/MG3S | 1.7 | 0.1 | -1.6 | 2.4 | 0.8 | -1.6 | 1.7 | 0.2 | -1.5 | 1.1 | -0.3 | -1.4 | 1.2 |
| M05-2X/jul-cc-pVTZ | 0.7 | 1.9 | 1.2 | 1.9 | 1.4 | -0.5 | 0.8 | 1.4 | 0.5 | -0.5 | 1.7 | 2.2 | 1.3 |
| SOGGA11-X/ma-TZVP | 1.7 | 0.1 | -1.6 | 2.3 | 0.8 | -1.5 | 1.8 | 0.3 | -1.5 | 1.2 | -0.2 | -1.5 | 1.2 |
| M05-2X/jun-cc-pVTZ | 0.7 | 1.8 | 1.1 | 1.9 | 1.5 | -0.5 | 0.8 | 1.4 | 0.6 | -0.5 | 1.7 | 2.2 | 1.3 |
| M05-2X/MG3S | 0.8 | 1.9 | 1.1 | 2.0 | 1.5 | -0.5 | 0.9 | 1.5 | 0.6 | -0.4 | 1.8 | 2.2 | 1.3 |
| $\omega$B97/jul-cc-pVTZ | 1.8 | 2.2 | 0.4 | 2.4 | 0.8 | -1.6 | 1.5 | 1.0 | -0.5 | 1.9 | 3.0 | 1.1 | 1.5 |
| $\omega$B97/jun-cc-pVTZ | 1.8 | 2.2 | 0.4 | 2.5 | 0.9 | -1.6 | 1.6 | 1.1 | -0.5 | 1.8 | 3.0 | 1.1 | 1.6 |
| $\omega$B97/MG3S | 1.9 | 2.4 | 0.5 | 2.4 | 0.9 | -1.6 | 1.5 | 1.1 | -0.4 | 1.8 | 3.2 | 1.4 | 1.6 |
| $\omega$B97/ma-TZVP | 1.9 | 2.4 | 0.4 | 2.5 | 0.9 | -1.5 | 1.7 | 1.2 | -0.5 | 1.9 | 3.1 | 1.2 | 1.6 |
| MN12-L/ma-TZVP | -1.6 | -2.0 | -0.4 | -3.4 | -1.3 | 2.0 | -3.9 | -2.0 | 1.9 | -2.3 | -1.9 | 0.3 | 2.0 |
| MN12-L/MG3S | -1.5 | -2.1 | -0.6 | -3.3 | -1.4 | 1.9 | -4.0 | -2.1 | 1.8 | -2.3 | -2.1 | 0.2 | 2.0 |
| MN12-L/jun-cc-pVTZ | -1.8 | -2.3 | -0.6 | -3.3 | -1.5 | 1.9 | -3.9 | -2.2 | 1.7 | -2.4 | -2.3 | 0.1 | 2.1 |
| MN12-L/jul-cc-pVTZ | -1.8 | -2.4 | -0.6 | -3.4 | -1.5 | 1.9 | -3.9 | -2.2 | 1.7 | -2.4 | -2.3 | 0.1 | 2.1 |
| MN12-SX/MG3S | -3.0 | -1.0 | 2.0 | -3.1 | -1.4 | 1.7 | -3.9 | -1.6 | 2.3 | -2.8 | -0.5 | 2.3 | 2.2 |
| MN12-SX/ma-TZVP | -3.0 | -0.6 | 2.4 | -3.1 | -1.3 | 1.8 | -3.8 | -1.4 | 2.4 | -2.8 | -0.2 | 2.6 | 2.2 |
| MN12-SX/jun-cc-pVTZ | -3.3 | -1.4 | 2.0 | -3.2 | -1.6 | 1.6 | -3.9 | -1.8 | 2.1 | -2.9 | -0.9 | 2.1 | 2.3 |
| MN12-SX/jul-cc-pVTZ | -3.4 | -1.4 | 2.0 | -3.3 | -1.7 | 1.6 | -4.0 | -1.9 | 2.1 | -2.9 | -0.9 | 2.1 | 2.3 |
| GAM/ma-TZVP | -2.6 | -3.3 | -0.6 | -3.2 | -4.8 | -1.6 | -2.5 | -4.2 | -1.6 | -1.5 | -3.4 | -1.9 | 2.6 |
| GAM/MG3S | -2.7 | -3.3 | -0.5 | -3.2 | -4.8 | -1.6 | -2.6 | -4.2 | -1.6 | -1.6 | -3.4 | -1.8 | 2.6 |
| GAM/jul-cc-pVTZ | -2.6 | -3.5 | -1.0 | -3.1 | -4.8 | -1.7 | -2.5 | -4.3 | -1.8 | -1.4 | -3.6 | -2.2 | 2.7 |
| GAM/jun-cc-pVTZ | -2.6 | -3.5 | -0.9 | -3.1 | -4.8 | -1.7 | -2.5 | -4.3 | -1.8 | -1.5 | -3.6 | -2.1 | 2.7 |
| MN15-L/jun-cc-pVTZ | -4.1 | -3.7 | 0.4 | -4.6 | -2.7 | 1.9 | -4.8 | -3.3 | 1.5 | -4.3 | -2.8 | 1.5 | 3.0 |
| MN15-L/jul-cc-pVTZ | -4.1 | -3.7 | 0.4 | -4.6 | -2.8 | 1.8 | -4.9 | -3.4 | 1.5 | -4.2 | -2.7 | 1.5 | 3.0 |
| MN15-L/ma-TZVP | -4.1 | -3.5 | 0.6 | -4.9 | -2.9 | 2.0 | -5.1 | -3.4 | 1.7 | -4.4 | -2.5 | 1.8 | 3.1 |
| MN15-L/MG3S | -4.2 | -3.5 | 0.6 | -4.9 | -2.8 | 2.1 | -5.2 | -3.4 | 1.8 | -4.4 | -2.5 | 1.9 | 3.1 |
| B3LYP/MG3S | -4.7 | -4.8 | -0.2 | -4.0 | -5.5 | -1.4 | -4.0 | -5.5 | -1.5 | -4.4 | -4.9 | -0.5 | 3.5 |
| B3LYP/ma-TZVP | -4.7 | -5.0 | -0.2 | -4.1 | -5.5 | -1.4 | -4.0 | -5.5 | -1.5 | -4.4 | -5.0 | -0.6 | 3.6 |
| B3LYP/jun-cc-pVTZ | -4.7 | -5.0 | -0.3 | -4.0 | -5.5 | -1.4 | -4.0 | -5.5 | -1.6 | -4.4 | -5.1 | -0.6 | 3.6 |
| M11-L/ma-TZVP | -4.2 | -1.6 | 2.6 | -6.3 | -4.3 | 1.9 | -6.8 | -3.6 | 3.2 | -3.8 | -0.9 | 2.9 | 3.5 |
| B3LYP/jul-cc-pVTZ | -4.7 | -5.0 | -0.3 | -4.0 | -5.5 | -1.5 | -4.0 | -5.6 | -1.6 | -4.4 | -5.1 | -0.7 | 3.6 |
| M11-L/MG3S | -4.7 | -1.8 | 2.9 | -6.6 | -4.5 | 2.1 | -7.2 | -3.8 | 3.3 | -4.1 | -1.0 | 3.1 | 3.8 |
| M11-L/jun-cc-pVTZ | -4.9 | -2.6 | 2.3 | -6.8 | -5.0 | 1.9 | -7.4 | -4.3 | 3.1 | -4.4 | -1.7 | 2.8 | 3.9 |
| M11-L/jul-cc-pVTZ | -5.0 | -2.6 | 2.4 | -7.0 | -5.1 | 1.8 | -7.6 | -4.5 | 3.1 | -4.4 | -1.7 | 2.7 | 4.0 |

[a] The values in the first line of each part of the table are enthalpies of activation and enthalpies of reaction computed by CCSD(T)-F12a/jun-cc-pVTZ// M08-HX/MG3S, and the other lines are differences from CCSD(T)-F12a/jun-cc-pVTZ. The density functionals are listed in order of ascending mean unsigned deviation (MUD) for the four reactions in a given part of a table (this reaction-specific MUD is not shown). All calculations and ZPEs in this table are computed at M08-HX/MG3S geometries with M08-HX/MG3 scaled frequencies.

[b] MUD: mean unsigned deviation for all eight reactions.

**Table S2.** The tunneling transmission coefficients for hydrogen abstraction reactions from methyl butenoate by H atom using small curvature tunneling, zero curvature tunneling, and the Eckart approximation.

a. SCT

| $T$(K) | R1 | R2 | R3 | R4 | R5 | R6 | R7 | R8 |
|---|---|---|---|---|---|---|---|---|
| 298 | 17.79 | 3.22 | 6.76 | 6.92 | 17.21 | 5.60 | 7.64 | 7.43 |
| 400 | 4.79 | 1.80 | 2.26 | 2.73 | 4.76 | 2.26 | 2.71 | 3.01 |
| 500 | 2.69 | 1.40 | 1.41 | 1.85 | 2.69 | 1.50 | 1.80 | 1.97 |
| 600 | 1.98 | 1.22 | 1.09 | 1.50 | 1.98 | 1.16 | 1.46 | 1.56 |
| 700 | 1.65 | 1.12 | 0.93 | 1.32 | 1.65 | 0.97 | 1.25 | 1.34 |
| 800 | 1.46 | 1.06 | 0.84 | 1.21 | 1.47 | 0.87 | 1.15 | 1.22 |
| 900 | 1.35 | 1.02 | 0.79 | 1.14 | 1.35 | 0.82 | 1.09 | 1.14 |
| 1000 | 1.27 | 0.99 | 0.75 | 1.09 | 1.27 | 0.80 | 1.05 | 1.08 |
| 1100 | 1.22 | 0.96 | 0.72 | 1.06 | 1.22 | 0.78 | 1.02 | 1.04 |
| 1200 | 1.18 | 0.95 | 0.71 | 1.02 | 1.18 | 0.78 | 1.00 | 1.01 |
| 1300 | 1.15 | 0.93 | 0.70 | 0.98 | 1.15 | 0.77 | 0.99 | 0.99 |
| 1400 | 1.13 | 0.92 | 0.69 | 0.95 | 1.13 | 0.77 | 0.97 | 0.97 |
| 1500 | 1.11 | 0.91 | 0.68 | 0.93 | 1.11 | 0.77 | 0.96 | 0.95 |
| 1600 | 1.10 | 0.90 | 0.68 | 0.92 | 1.10 | 0.77 | 0.95 | 0.94 |
| 1700 | 1.09 | 0.90 | 0.68 | 0.92 | 1.08 | 0.77 | 0.94 | 0.92 |
| 1800 | 1.08 | 0.89 | 0.68 | 0.91 | 1.07 | 0.78 | 0.94 | 0.91 |
| 1900 | 1.07 | 0.89 | 0.69 | 0.91 | 1.07 | 0.78 | 0.93 | 0.90 |
| 2000 | 1.06 | 0.88 | 0.69 | 0.91 | 1.06 | 0.78 | 0.93 | 0.89 |
| 2100 | 1.05 | 0.88 | 0.69 | 0.91 | 1.05 | 0.78 | 0.92 | 0.87 |
| 2200 | 1.05 | 0.88 | 0.70 | 0.91 | 1.05 | 0.79 | 0.92 | 0.86 |
| 2300 | 1.04 | 0.88 | 0.70 | 0.91 | 1.04 | 0.79 | 0.92 | 0.86 |
| 2400 | 1.04 | 0.87 | 0.71 | 0.91 | 1.04 | 0.79 | 0.91 | 0.85 |
| 2500 | 1.04 | 0.87 | 0.71 | 0.91 | 1.04 | 0.80 | 0.91 | 0.84 |

b. ZCT

| $T$(K) | R1 | R2 | R3 | R4 | R5 | R6 | R7 | R8 |
|---|---|---|---|---|---|---|---|---|
| 298 | 3.91 | 1.58 | 2.43 | 3.21 | 3.83 | 2.73 | 2.58 | 2.62 |
| 400 | 2.05 | 1.20 | 1.21 | 1.81 | 2.04 | 1.54 | 1.51 | 1.63 |
| 500 | 1.56 | 1.07 | 0.91 | 1.43 | 1.56 | 1.18 | 1.24 | 1.32 |
| 600 | 1.36 | 1.01 | 0.78 | 1.25 | 1.36 | 0.99 | 1.13 | 1.17 |
| 700 | 1.25 | 0.98 | 0.72 | 1.16 | 1.25 | 0.86 | 1.04 | 1.09 |
| 800 | 1.18 | 0.95 | 0.68 | 1.10 | 1.19 | 0.79 | 1.00 | 1.03 |
| 900 | 1.14 | 0.94 | 0.65 | 1.06 | 1.14 | 0.76 | 0.98 | 1.00 |
| 1000 | 1.11 | 0.92 | 0.64 | 1.03 | 1.11 | 0.75 | 0.96 | 0.97 |
| 1100 | 1.09 | 0.91 | 0.63 | 1.00 | 1.09 | 0.74 | 0.95 | 0.96 |
| 1200 | 1.08 | 0.90 | 0.63 | 0.98 | 1.08 | 0.74 | 0.94 | 0.94 |
| 1300 | 1.06 | 0.90 | 0.63 | 0.94 | 1.06 | 0.75 | 0.93 | 0.93 |
| 1400 | 1.06 | 0.89 | 0.63 | 0.92 | 1.05 | 0.75 | 0.93 | 0.92 |
| 1500 | 1.05 | 0.89 | 0.63 | 0.91 | 1.05 | 0.75 | 0.92 | 0.91 |
| 1600 | 1.04 | 0.88 | 0.63 | 0.90 | 1.04 | 0.75 | 0.92 | 0.90 |
| 1700 | 1.04 | 0.88 | 0.64 | 0.90 | 1.03 | 0.76 | 0.91 | 0.89 |
| 1800 | 1.03 | 0.87 | 0.64 | 0.90 | 1.03 | 0.76 | 0.91 | 0.88 |
| 1900 | 1.03 | 0.87 | 0.65 | 0.90 | 1.03 | 0.77 | 0.91 | 0.87 |
| 2000 | 1.03 | 0.87 | 0.66 | 0.90 | 1.02 | 0.77 | 0.91 | 0.86 |
| 2100 | 1.02 | 0.87 | 0.66 | 0.90 | 1.02 | 0.77 | 0.90 | 0.85 |
| 2200 | 1.02 | 0.87 | 0.67 | 0.90 | 1.02 | 0.78 | 0.90 | 0.85 |
| 2300 | 1.02 | 0.86 | 0.68 | 0.90 | 1.02 | 0.78 | 0.90 | 0.84 |
| 2400 | 1.02 | 0.86 | 0.68 | 0.90 | 1.01 | 0.78 | 0.90 | 0.83 |
| 2500 | 1.02 | 0.86 | 0.69 | 0.90 | 1.01 | 0.79 | 0.90 | 0.82 |

c. Eckart

| T(K) | R1 | R2 | R3 | R4 | R5 | R6 | R7 | R8 |
|------|------|-------|-------|------|-------|------|-------|-------|
| 298 | 18.05 | 11.71 | 10.13 | 8.09 | 18.45 | 7.42 | 10.78 | 18.45 |
| 400 | 4.17 | 3.77 | 3.25 | 2.84 | 4.22 | 2.81 | 3.34 | 4.61 |
| 500 | 2.41 | 2.32 | 2.09 | 1.91 | 2.42 | 1.91 | 2.12 | 2.60 |
| 600 | 1.83 | 1.80 | 1.66 | 1.56 | 1.83 | 1.57 | 1.68 | 1.94 |
| 700 | 1.56 | 1.54 | 1.45 | 1.39 | 1.56 | 1.39 | 1.47 | 1.63 |
| 800 | 1.41 | 1.40 | 1.34 | 1.29 | 1.41 | 1.29 | 1.34 | 1.45 |
| 900 | 1.31 | 1.31 | 1.26 | 1.22 | 1.31 | 1.23 | 1.27 | 1.35 |
| 1000 | 1.25 | 1.24 | 1.21 | 1.18 | 1.25 | 1.18 | 1.21 | 1.28 |
| 1100 | 1.20 | 1.20 | 1.17 | 1.15 | 1.20 | 1.15 | 1.18 | 1.23 |
| 1200 | 1.17 | 1.17 | 1.14 | 1.12 | 1.17 | 1.13 | 1.15 | 1.19 |
| 1300 | 1.14 | 1.14 | 1.12 | 1.10 | 1.14 | 1.11 | 1.13 | 1.16 |
| 1400 | 1.12 | 1.12 | 1.11 | 1.09 | 1.12 | 1.09 | 1.11 | 1.14 |
| 1500 | 1.11 | 1.11 | 1.09 | 1.08 | 1.11 | 1.08 | 1.10 | 1.12 |
| 1600 | 1.10 | 1.09 | 1.08 | 1.07 | 1.10 | 1.07 | 1.08 | 1.11 |
| 1700 | 1.09 | 1.08 | 1.07 | 1.06 | 1.09 | 1.06 | 1.08 | 1.09 |
| 1800 | 1.08 | 1.07 | 1.07 | 1.06 | 1.08 | 1.06 | 1.07 | 1.08 |
| 1900 | 1.07 | 1.07 | 1.06 | 1.05 | 1.07 | 1.05 | 1.06 | 1.08 |
| 2000 | 1.06 | 1.06 | 1.05 | 1.05 | 1.06 | 1.05 | 1.06 | 1.07 |
| 2100 | 1.06 | 1.06 | 1.05 | 1.04 | 1.06 | 1.04 | 1.05 | 1.06 |
| 2200 | 1.05 | 1.05 | 1.05 | 1.04 | 1.05 | 1.04 | 1.05 | 1.06 |
| 2300 | 1.05 | 1.05 | 1.04 | 1.03 | 1.05 | 1.04 | 1.04 | 1.05 |
| 2400 | 1.04 | 1.04 | 1.04 | 1.03 | 1.04 | 1.03 | 1.04 | 1.05 |
| 2500 | 1.04 | 1.04 | 1.04 | 1.03 | 1.04 | 1.03 | 1.04 | 1.05 |

**Table S3.** The rate constants ($cm^3\,mol^{-1}\,s^{-1}$) of R1~R8 by various kinetics methods.

R1:

| T(K) | TST | CVT | CVT/SCT | MS-LH-CVT/SCT | MS-CVT/SCT |
|---|---|---|---|---|---|
| 298 | 7.69E+04 | 7.48E+04 | 1.33E+06 | 2.69E+06 | 2.20E+06 |
| 400 | 9.81E+06 | 9.58E+06 | 4.59E+07 | 9.42E+07 | 7.77E+07 |
| 500 | 1.81E+08 | 1.77E+08 | 4.76E+08 | 9.83E+08 | 8.29E+08 |
| 600 | 1.34E+09 | 1.31E+09 | 2.60E+09 | 5.38E+09 | 4.67E+09 |
| 700 | 5.86E+09 | 5.76E+09 | 9.48E+09 | 1.97E+10 | 1.76E+10 |
| 800 | 1.84E+10 | 1.81E+10 | 2.65E+10 | 5.50E+10 | 5.09E+10 |
| 900 | 4.62E+10 | 4.55E+10 | 6.13E+10 | 1.27E+11 | 1.21E+11 |
| 1000 | 9.88E+10 | 9.72E+10 | 1.24E+11 | 2.57E+11 | 2.51E+11 |
| 1100 | 1.87E+11 | 1.84E+11 | 2.25E+11 | 4.67E+11 | 4.68E+11 |
| 1200 | 3.24E+11 | 3.19E+11 | 3.77E+11 | 7.82E+11 | 8.02E+11 |
| 1300 | 5.22E+11 | 5.14E+11 | 5.92E+11 | 1.23E+12 | 1.28E+12 |
| 1400 | 7.95E+11 | 7.82E+11 | 8.83E+11 | 1.83E+12 | 1.95E+12 |
| 1500 | 1.15E+12 | 1.14E+12 | 1.26E+12 | 2.61E+12 | 2.83E+12 |
| 1600 | 1.61E+12 | 1.59E+12 | 1.74E+12 | 3.59E+12 | 3.96E+12 |
| 1700 | 2.18E+12 | 2.14E+12 | 2.33E+12 | 4.79E+12 | 5.36E+12 |
| 1800 | 2.87E+12 | 2.82E+12 | 3.03E+12 | 6.23E+12 | 7.07E+12 |
| 1900 | 3.68E+12 | 3.62E+12 | 3.87E+12 | 7.93E+12 | 9.11E+12 |
| 2000 | 4.64E+12 | 4.56E+12 | 4.83E+12 | 9.90E+12 | 1.15E+13 |
| 2100 | 5.74E+12 | 5.64E+12 | 5.94E+12 | 1.22E+13 | 1.43E+13 |
| 2200 | 6.99E+12 | 6.86E+12 | 7.20E+12 | 1.47E+13 | 1.75E+13 |
| 2300 | 8.39E+12 | 8.24E+12 | 8.61E+12 | 1.76E+13 | 2.10E+13 |
| 2400 | 9.96E+12 | 9.78E+12 | 1.02E+13 | 2.07E+13 | 2.50E+13 |
| 2500 | 1.17E+13 | 1.15E+13 | 1.19E+13 | 2.42E+13 | 2.95E+13 |

R2:

| T(K) | TST | CVT | CVT/SCT | MS-LH-CVT/SCT | MS-CVT/SCT |
|---|---|---|---|---|---|
| 298 | 1.29E+08 | 1.29E+08 | 4.14E+08 | 3.71E+08 | 4.06E+08 |
| 400 | 2.15E+09 | 2.15E+09 | 3.87E+09 | 3.62E+09 | 4.03E+09 |
| 500 | 1.20E+10 | 1.20E+10 | 1.67E+10 | 1.64E+10 | 1.85E+10 |
| 600 | 4.00E+10 | 3.96E+10 | 4.82E+10 | 4.94E+10 | 5.65E+10 |
| 700 | 9.90E+10 | 9.74E+10 | 1.09E+11 | 1.16E+11 | 1.34E+11 |
| 800 | 2.02E+11 | 1.97E+11 | 2.09E+11 | 2.30E+11 | 2.67E+11 |
| 900 | 3.62E+11 | 3.51E+11 | 3.57E+11 | 4.06E+11 | 4.73E+11 |
| 1000 | 5.91E+11 | 5.69E+11 | 5.62E+11 | 6.54E+11 | 7.64E+11 |
| 1100 | 8.98E+11 | 8.59E+11 | 8.28E+11 | 9.86E+11 | 1.15E+12 |
| 1200 | 1.29E+12 | 1.23E+12 | 1.16E+12 | 1.41E+12 | 1.65E+12 |
| 1300 | 1.78E+12 | 1.68E+12 | 1.56E+12 | 1.93E+12 | 2.26E+12 |
| 1400 | 2.37E+12 | 2.22E+12 | 2.04E+12 | 2.55E+12 | 3.00E+12 |
| 1500 | 3.06E+12 | 2.84E+12 | 2.59E+12 | 3.28E+12 | 3.85E+12 |
| 1600 | 3.85E+12 | 3.56E+12 | 3.22E+12 | 4.11E+12 | 4.83E+12 |
| 1700 | 4.76E+12 | 4.37E+12 | 3.92E+12 | 5.05E+12 | 5.95E+12 |
| 1800 | 5.78E+12 | 5.27E+12 | 4.70E+12 | 6.11E+12 | 7.18E+12 |
| 1900 | 6.91E+12 | 6.26E+12 | 5.56E+12 | 7.27E+12 | 8.55E+12 |
| 2000 | 8.15E+12 | 7.34E+12 | 6.49E+12 | 8.54E+12 | 1.00E+13 |
| 2100 | 9.50E+12 | 8.51E+12 | 7.50E+12 | 9.92E+12 | 1.17E+13 |
| 2200 | 1.10E+13 | 9.76E+12 | 8.58E+12 | 1.14E+13 | 1.34E+13 |
| 2300 | 1.25E+13 | 1.11E+13 | 9.73E+12 | 1.30E+13 | 1.53E+13 |
| 2400 | 1.42E+13 | 1.25E+13 | 1.10E+13 | 1.47E+13 | 1.73E+13 |
| 2500 | 1.60E+13 | 1.40E+13 | 1.22E+13 | 1.65E+13 | 1.94E+13 |

R3:

| T(K) | TST | CVT | CVT/SCT | MS-LH-CVT/SCT | MS-CVT/SCT |
|------|-----|-----|---------|---------------|------------|
| 298 | 5.34E+02 | 4.90E+02 | 3.31E+03 | 4.81E+03 | 3.69E+03 |
| 400 | 2.89E+05 | 2.82E+05 | 6.36E+05 | 9.18E+05 | 6.73E+05 |
| 500 | 1.25E+07 | 1.24E+07 | 1.75E+07 | 2.50E+07 | 1.75E+07 |
| 600 | 1.63E+08 | 1.63E+08 | 1.78E+08 | 2.51E+08 | 1.69E+08 |
| 700 | 1.07E+09 | 1.07E+09 | 1.00E+09 | 1.40E+09 | 9.10E+08 |
| 800 | 4.56E+09 | 4.56E+09 | 3.84E+09 | 5.30E+09 | 3.36E+09 |
| 900 | 1.45E+10 | 1.44E+10 | 1.13E+10 | 1.55E+10 | 9.56E+09 |
| 1000 | 3.72E+10 | 3.69E+10 | 2.77E+10 | 3.75E+10 | 2.27E+10 |
| 1100 | 8.21E+10 | 8.12E+10 | 5.88E+10 | 7.90E+10 | 4.70E+10 |
| 1200 | 1.61E+11 | 1.59E+11 | 1.12E+11 | 1.50E+11 | 8.76E+10 |
| 1300 | 2.89E+11 | 2.84E+11 | 1.97E+11 | 2.61E+11 | 1.51E+11 |
| 1400 | 4.81E+11 | 4.71E+11 | 3.24E+11 | 4.26E+11 | 2.43E+11 |
| 1500 | 7.56E+11 | 7.38E+11 | 5.05E+11 | 6.57E+11 | 3.71E+11 |
| 1600 | 1.13E+12 | 1.10E+12 | 7.51E+11 | 9.70E+11 | 5.43E+11 |
| 1700 | 1.62E+12 | 1.58E+12 | 1.08E+12 | 1.38E+12 | 7.66E+11 |
| 1800 | 2.25E+12 | 2.18E+12 | 1.49E+12 | 1.90E+12 | 1.05E+12 |
| 1900 | 3.04E+12 | 2.94E+12 | 2.01E+12 | 2.55E+12 | 1.39E+12 |
| 2000 | 3.99E+12 | 3.85E+12 | 2.65E+12 | 3.33E+12 | 1.82E+12 |
| 2100 | 5.14E+12 | 4.94E+12 | 3.42E+12 | 4.27E+12 | 2.31E+12 |
| 2200 | 6.48E+12 | 6.22E+12 | 4.34E+12 | 5.37E+12 | 2.90E+12 |
| 2300 | 8.04E+12 | 7.70E+12 | 5.40E+12 | 6.64E+12 | 3.58E+12 |
| 2400 | 9.83E+12 | 9.40E+12 | 6.63E+12 | 8.11E+12 | 4.35E+12 |
| 2500 | 1.19E+13 | 1.13E+13 | 8.04E+12 | 9.76E+12 | 5.22E+12 |

R4:

| T(K) | TST | CVT | CVT/SCT | MS-LH-CVT/SCT | MS-CVT/SCT |
|------|-----|-----|---------|---------------|------------|
| 298 | 2.00E+01 | 1.25E+01 | 8.65E+01 | 1.36E+02 | 1.12E+02 |
| 400 | 2.53E+04 | 1.89E+04 | 5.15E+04 | 8.91E+04 | 6.78E+04 |
| 500 | 1.79E+06 | 1.48E+06 | 2.74E+06 | 5.01E+06 | 3.57E+06 |
| 600 | 3.27E+07 | 2.89E+07 | 4.32E+07 | 8.20E+07 | 5.55E+07 |
| 700 | 2.72E+08 | 2.51E+08 | 3.31E+08 | 6.45E+08 | 4.17E+08 |
| 800 | 1.38E+09 | 1.31E+09 | 1.59E+09 | 3.16E+09 | 1.97E+09 |
| 900 | 5.03E+09 | 4.87E+09 | 5.57E+09 | 1.12E+10 | 6.78E+09 |
| 1000 | 1.45E+10 | 1.42E+10 | 1.55E+10 | 3.15E+10 | 1.86E+10 |
| 1100 | 3.49E+10 | 3.46E+10 | 3.65E+10 | 7.47E+10 | 4.31E+10 |
| 1200 | 7.39E+10 | 7.36E+10 | 7.52E+10 | 1.55E+11 | 8.76E+10 |
| 1300 | 1.41E+11 | 1.41E+11 | 1.38E+11 | 2.84E+11 | 1.59E+11 |
| 1400 | 2.48E+11 | 2.48E+11 | 2.35E+11 | 4.85E+11 | 2.67E+11 |
| 1500 | 4.08E+11 | 4.08E+11 | 3.80E+11 | 7.86E+11 | 4.28E+11 |
| 1600 | 6.37E+11 | 6.35E+11 | 5.86E+11 | 1.21E+12 | 6.54E+11 |
| 1700 | 9.48E+11 | 9.45E+11 | 8.67E+11 | 1.79E+12 | 9.59E+11 |
| 1800 | 1.36E+12 | 1.35E+12 | 1.24E+12 | 2.56E+12 | 1.36E+12 |
| 1900 | 1.89E+12 | 1.87E+12 | 1.71E+12 | 3.53E+12 | 1.86E+12 |
| 2000 | 2.54E+12 | 2.52E+12 | 2.30E+12 | 4.75E+12 | 2.49E+12 |
| 2100 | 3.35E+12 | 3.32E+12 | 3.03E+12 | 6.22E+12 | 3.25E+12 |
| 2200 | 4.31E+12 | 4.27E+12 | 3.89E+12 | 8.00E+12 | 4.16E+12 |
| 2300 | 5.46E+12 | 5.39E+12 | 4.92E+12 | 1.01E+13 | 5.23E+12 |
| 2400 | 6.79E+12 | 6.70E+12 | 6.12E+12 | 1.25E+13 | 6.47E+12 |
| 2500 | 8.32E+12 | 8.21E+12 | 7.50E+12 | 1.53E+13 | 7.89E+12 |

R5:

| T(K) | TST | CVT | CVT/SCT | MS-LH-CVT/SCT | MS-CVT/SCT |
|------|-----|-----|---------|---------------|------------|
| 298 | 8.89E+04 | 8.72E+04 | 1.50E+06 | 2.96E+06 | 2.35E+06 |

| T(K) | | | | | |
|------|------|------|------|------|------|
| 400 | 1.05E+07 | 1.03E+07 | 4.90E+07 | 9.56E+07 | 7.46E+07 |
| 500 | 1.84E+08 | 1.81E+08 | 4.88E+08 | 9.44E+08 | 7.41E+08 |
| 600 | 1.32E+09 | 1.30E+09 | 2.58E+09 | 4.97E+09 | 3.99E+09 |
| 700 | 5.67E+09 | 5.59E+09 | 9.23E+09 | 1.77E+10 | 1.47E+10 |
| 800 | 1.76E+10 | 1.73E+10 | 2.54E+10 | 4.85E+10 | 4.17E+10 |
| 900 | 4.35E+10 | 4.29E+10 | 5.80E+10 | 1.11E+11 | 9.89E+10 |
| 1000 | 9.21E+10 | 9.09E+10 | 1.16E+11 | 2.20E+11 | 2.05E+11 |
| 1100 | 1.73E+11 | 1.71E+11 | 2.09E+11 | 3.96E+11 | 3.82E+11 |
| 1200 | 2.98E+11 | 2.94E+11 | 3.48E+11 | 6.57E+11 | 6.58E+11 |
| 1300 | 4.78E+11 | 4.71E+11 | 5.43E+11 | 1.02E+12 | 1.06E+12 |
| 1400 | 7.24E+11 | 7.14E+11 | 8.06E+11 | 1.51E+12 | 1.62E+12 |
| 1500 | 1.05E+12 | 1.03E+12 | 1.15E+12 | 2.15E+12 | 2.36E+12 |
| 1600 | 1.46E+12 | 1.44E+12 | 1.57E+12 | 2.94E+12 | 3.32E+12 |
| 1700 | 1.97E+12 | 1.94E+12 | 2.10E+12 | 3.90E+12 | 4.53E+12 |
| 1800 | 2.58E+12 | 2.54E+12 | 2.73E+12 | 5.05E+12 | 6.01E+12 |
| 1900 | 3.31E+12 | 3.25E+12 | 3.47E+12 | 6.41E+12 | 7.79E+12 |
| 2000 | 4.16E+12 | 4.09E+12 | 4.32E+12 | 7.96E+12 | 9.89E+12 |
| 2100 | 5.13E+12 | 5.04E+12 | 5.31E+12 | 9.74E+12 | 1.23E+13 |
| 2200 | 6.24E+12 | 6.13E+12 | 6.42E+12 | 1.17E+13 | 1.52E+13 |
| 2300 | 7.48E+12 | 7.35E+12 | 7.66E+12 | 1.40E+13 | 1.83E+13 |
| 2400 | 8.87E+12 | 8.70E+12 | 9.04E+12 | 1.64E+13 | 2.19E+13 |
| 2500 | 1.04E+13 | 1.02E+13 | 1.06E+13 | 1.91E+13 | 2.59E+13 |

R6:

| T(K) | TST | CVT | CVT/SCT | MS-LH-CVT/SCT | MS-CVT/SCT |
|------|------|------|---------|---------------|------------|
| 298 | 4.41E+01 | 3.26E+01 | 1.82E+02 | 3.60E+02 | 4.09E+02 |
| 400 | 4.65E+04 | 4.09E+04 | 9.26E+04 | 1.78E+05 | 1.97E+05 |
| 500 | 2.96E+06 | 2.83E+06 | 4.25E+06 | 7.94E+06 | 8.58E+06 |
| 600 | 5.01E+07 | 4.97E+07 | 5.79E+07 | 1.05E+08 | 1.12E+08 |
| 700 | 3.95E+08 | 3.95E+08 | 3.82E+08 | 6.78E+08 | 7.18E+08 |
| 800 | 1.93E+09 | 1.91E+09 | 1.65E+09 | 2.87E+09 | 3.03E+09 |
| 900 | 6.78E+09 | 6.63E+09 | 5.43E+09 | 9.25E+09 | 9.75E+09 |
| 1000 | 1.90E+10 | 1.83E+10 | 1.45E+10 | 2.43E+10 | 2.56E+10 |
| 1100 | 4.48E+10 | 4.26E+10 | 3.33E+10 | 5.48E+10 | 5.79E+10 |
| 1200 | 9.31E+10 | 8.74E+10 | 6.78E+10 | 1.10E+11 | 1.16E+11 |
| 1300 | 1.75E+11 | 1.62E+11 | 1.25E+11 | 2.00E+11 | 2.11E+11 |
| 1400 | 3.03E+11 | 2.78E+11 | 2.15E+11 | 3.37E+11 | 3.58E+11 |
| 1500 | 4.93E+11 | 4.48E+11 | 3.46E+11 | 5.35E+11 | 5.69E+11 |
| 1600 | 7.60E+11 | 6.85E+11 | 5.29E+11 | 8.07E+11 | 8.59E+11 |
| 1700 | 1.12E+12 | 1.00E+12 | 7.76E+11 | 1.17E+12 | 1.24E+12 |
| 1800 | 1.59E+12 | 1.41E+12 | 1.10E+12 | 1.63E+12 | 1.74E+12 |
| 1900 | 2.19E+12 | 1.93E+12 | 1.50E+12 | 2.21E+12 | 2.36E+12 |
| 2000 | 2.94E+12 | 2.57E+12 | 2.01E+12 | 2.91E+12 | 3.11E+12 |
| 2100 | 3.84E+12 | 3.34E+12 | 2.62E+12 | 3.75E+12 | 4.01E+12 |
| 2200 | 4.93E+12 | 4.25E+12 | 3.35E+12 | 4.74E+12 | 5.07E+12 |
| 2300 | 6.20E+12 | 5.32E+12 | 4.20E+12 | 5.89E+12 | 6.30E+12 |
| 2400 | 7.67E+12 | 6.55E+12 | 5.19E+12 | 7.20E+12 | 7.70E+12 |
| 2500 | 9.37E+12 | 7.96E+12 | 6.33E+12 | 8.69E+12 | 9.29E+12 |

R7:

| T(K) | TST | CVT | CVT/SCT | MS-LH-CVT/SCT | MS-CVT/SCT |
|------|------|------|---------|---------------|------------|
| 298 | 1.18E+04 | 1.17E+04 | 8.92E+04 | 9.29E+04 | 1.02E+05 |
| 400 | 2.77E+06 | 2.77E+06 | 7.53E+06 | 7.84E+06 | 8.68E+06 |
| 500 | 7.35E+07 | 7.35E+07 | 1.32E+08 | 1.36E+08 | 1.52E+08 |

| | | | | |
|---|---|---|---|---|
| 600 | 6.94E+08 | 6.93E+08 | 1.01E+09 | 1.02E+09 | 1.16E+09 |
| 700 | 3.61E+09 | 3.59E+09 | 4.50E+09 | 4.50E+09 | 5.15E+09 |
| 800 | 1.29E+10 | 1.27E+10 | 1.47E+10 | 1.45E+10 | 1.68E+10 |
| 900 | 3.57E+10 | 3.50E+10 | 3.83E+10 | 3.74E+10 | 4.35E+10 |
| 1000 | 8.24E+10 | 8.04E+10 | 8.47E+10 | 8.18E+10 | 9.59E+10 |
| 1100 | 1.66E+11 | 1.61E+11 | 1.65E+11 | 1.59E+11 | 1.87E+11 |
| 1200 | 3.04E+11 | 2.93E+11 | 2.93E+11 | 2.80E+11 | 3.30E+11 |
| 1300 | 5.11E+11 | 4.91E+11 | 4.84E+11 | 4.59E+11 | 5.42E+11 |
| 1400 | 8.07E+11 | 7.71E+11 | 7.50E+11 | 7.10E+11 | 8.38E+11 |
| 1500 | 1.21E+12 | 1.15E+12 | 1.11E+12 | 1.05E+12 | 1.23E+12 |
| 1600 | 1.74E+12 | 1.65E+12 | 1.57E+12 | 1.48E+12 | 1.74E+12 |
| 1700 | 2.41E+12 | 2.27E+12 | 2.15E+12 | 2.02E+12 | 2.38E+12 |
| 1800 | 3.24E+12 | 3.04E+12 | 2.85E+12 | 2.69E+12 | 3.16E+12 |
| 1900 | 4.25E+12 | 3.97E+12 | 3.70E+12 | 3.49E+12 | 4.08E+12 |
| 2000 | 5.44E+12 | 5.07E+12 | 4.70E+12 | 4.43E+12 | 5.17E+12 |
| 2100 | 6.84E+12 | 6.35E+12 | 5.86E+12 | 5.53E+12 | 6.43E+12 |
| 2200 | 8.45E+12 | 7.82E+12 | 7.18E+12 | 6.79E+12 | 7.87E+12 |
| 2300 | 1.03E+13 | 9.48E+12 | 8.69E+12 | 8.22E+12 | 9.51E+12 |
| 2400 | 1.24E+13 | 1.13E+13 | 1.04E+13 | 9.83E+12 | 1.13E+13 |
| 2500 | 1.47E+13 | 1.34E+13 | 1.23E+13 | 1.16E+13 | 1.34E+13 |

R8:

| T(K) | TST | CVT | CVT/SCT | MS-LH-CVT/SCT | MS-CVT/SCT |
|---|---|---|---|---|---|
| 298 | 1.41E+07 | 1.38E+07 | 1.03E+08 | 2.01E+08 | 1.68E+08 |
| 400 | 3.96E+08 | 3.79E+08 | 1.14E+09 | 2.18E+09 | 1.94E+09 |
| 500 | 2.99E+09 | 2.80E+09 | 5.54E+09 | 1.03E+10 | 9.78E+09 |
| 600 | 1.22E+10 | 1.12E+10 | 1.75E+10 | 3.18E+10 | 3.19E+10 |
| 700 | 3.48E+10 | 3.15E+10 | 4.23E+10 | 7.57E+10 | 7.97E+10 |
| 800 | 7.92E+10 | 7.05E+10 | 8.60E+10 | 1.52E+11 | 1.66E+11 |
| 900 | 1.55E+11 | 1.35E+11 | 1.54E+11 | 2.69E+11 | 3.05E+11 |
| 1000 | 2.70E+11 | 2.33E+11 | 2.53E+11 | 4.35E+11 | 5.08E+11 |
| 1100 | 4.34E+11 | 3.70E+11 | 3.87E+11 | 6.57E+11 | 7.88E+11 |
| 1200 | 6.54E+11 | 5.52E+11 | 5.59E+11 | 9.41E+11 | 1.15E+12 |
| 1300 | 9.38E+11 | 7.82E+11 | 7.73E+11 | 1.29E+12 | 1.61E+12 |
| 1400 | 1.29E+12 | 1.06E+12 | 1.03E+12 | 1.71E+12 | 2.16E+12 |
| 1500 | 1.72E+12 | 1.40E+12 | 1.33E+12 | 2.19E+12 | 2.81E+12 |
| 1600 | 2.22E+12 | 1.80E+12 | 1.68E+12 | 2.74E+12 | 3.56E+12 |
| 1700 | 2.81E+12 | 2.25E+12 | 2.07E+12 | 3.36E+12 | 4.40E+12 |
| 1800 | 3.48E+12 | 2.76E+12 | 2.50E+12 | 4.04E+12 | 5.33E+12 |
| 1900 | 4.24E+12 | 3.32E+12 | 2.98E+12 | 4.78E+12 | 6.35E+12 |
| 2000 | 5.09E+12 | 3.95E+12 | 3.49E+12 | 5.57E+12 | 7.45E+12 |
| 2100 | 6.02E+12 | 4.63E+12 | 4.05E+12 | 6.43E+12 | 8.64E+12 |
| 2200 | 7.05E+12 | 5.36E+12 | 4.64E+12 | 7.34E+12 | 9.90E+12 |
| 2300 | 8.16E+12 | 6.15E+12 | 5.26E+12 | 8.29E+12 | 1.12E+13 |
| 2400 | 9.36E+12 | 6.99E+12 | 5.92E+12 | 9.29E+12 | 1.26E+13 |
| 2500 | 1.07E+13 | 7.88E+12 | 6.60E+12 | 1.03E+13 | 1.41E+13 |

**Table S4.** Calculated rovibrational partition functions of the transition state TS1.

| T/K | SS-HO | SS-T | MS-LH | MS-T | $Q^{MS-T}/Q^{SS-T}$ |
|---|---|---|---|---|---|
| 298 | 6.35E-47 | 5.68E-47 | 3.97E-46 | 3.22E-46 | 5.67 |
| 400 | 6.25E-32 | 6.03E-32 | 4.41E-31 | 3.83E-31 | 6.34 |
| 500 | 9.00E-23 | 9.15E-23 | 6.87E-22 | 6.29E-22 | 6.87 |
| 600 | 2.36E-16 | 2.49E-16 | 1.91E-15 | 1.82E-15 | 7.31 |
| 700 | 1.63E-11 | 1.75E-11 | 1.38E-10 | 1.35E-10 | 7.69 |
| 800 | 1.13E-07 | 1.22E-07 | 9.88E-07 | 9.79E-07 | 8.03 |
| 900 | 1.63E-04 | 1.76E-04 | 1.48E-03 | 1.47E-03 | 8.33 |
| 1000 | 7.76E-02 | 8.31E-02 | 7.20E-01 | 7.17E-01 | 8.62 |
| 1100 | 1.61E+01 | 1.70E+01 | 1.53E+02 | 1.51E+02 | 8.89 |
| 1200 | 1.76E+03 | 1.83E+03 | 1.72E+04 | 1.68E+04 | 9.15 |
| 1300 | 1.17E+05 | 1.19E+05 | 1.16E+06 | 1.12E+06 | 9.39 |
| 1400 | 5.17E+06 | 5.14E+06 | 5.25E+07 | 4.94E+07 | 9.63 |
| 1500 | 1.63E+08 | 1.58E+08 | 1.69E+09 | 1.56E+09 | 9.86 |
| 1600 | 3.91E+09 | 3.69E+09 | 4.13E+10 | 3.72E+10 | 10.08 |
| 1700 | 7.38E+10 | 6.77E+10 | 7.93E+11 | 6.96E+11 | 10.29 |
| 1800 | 1.14E+12 | 1.01E+12 | 1.24E+13 | 1.06E+13 | 10.50 |
| 1900 | 1.47E+13 | 1.27E+13 | 1.63E+14 | 1.36E+14 | 10.70 |
| 2000 | 1.62E+14 | 1.36E+14 | 1.83E+15 | 1.48E+15 | 10.90 |
| 2100 | 1.56E+15 | 1.27E+15 | 1.80E+16 | 1.41E+16 | 11.09 |
| 2200 | 1.34E+16 | 1.05E+16 | 1.56E+17 | 1.19E+17 | 11.28 |
| 2300 | 1.02E+17 | 7.81E+16 | 1.21E+18 | 8.96E+17 | 11.46 |
| 2400 | 7.12E+17 | 5.26E+17 | 8.54E+18 | 6.12E+18 | 11.64 |
| 2500 | 4.53E+18 | 3.24E+18 | 5.50E+19 | 3.83E+19 | 11.81 |

**Table S5.** The fit parameters for the reverse rate constants of hydrogen abstraction reactions from methyl butenoate by H atom as calculated using MS-CVT/SCT.

| | $B(cm^3\ mol^{-1}\ s^{-1}\ K^{-n})$ | $n$ | $E$ (kcal/mol) |
|---|---|---|---|
| R1 | 1.61E+02 | 2.90 | 10.799 |
| R2 | 3.92E+06 | 1.86 | 25.157 |
| R3 | 7.06E+00 | 3.27 | 4.061 |
| R4 | 4.34E+02 | 2.94 | 4.342 |
| R5 | 9.18E+02 | 2.74 | 11.153 |
| R6 | 3.30E+02 | 2.88 | 4.229 |
| R7 | 4.53E+02 | 2.87 | 6.297 |
| R8 | 9.54E+09 | 0.84 | 24.380 |

**Figure S1.** The geometries and Cartetian coordinates of reactants, transition state and products of hydrogen abstraction reactions for methyl 3-butenoate and methyl 2-butenoate by hydrogen radical at the M06-2X/ma-TZVP level with integral grid of 99974 (coordinate units: Angstrom)

- Reactants
a) Methyl 3-butenoate
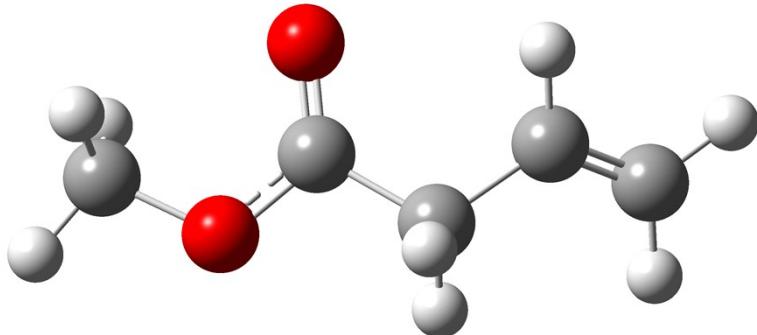
Coordinates

| | | | |
|---|---|---|---|
| C | 0.79398300 | -0.59662900 | 0.44161700 |
| C | 2.00924600 | 0.24475000 | 0.21128200 |
| H | 0.82932500 | -1.52666600 | -0.12555300 |
| H | 0.71765300 | -0.87879200 | 1.49798400 |
| C | 3.07548000 | -0.17027900 | -0.45304300 |
| H | 1.97685400 | 1.24659000 | 0.62469000 |
| H | 3.93882400 | 0.46750900 | -0.58762700 |
| H | 3.12208100 | -1.16262800 | -0.88728700 |
| C | -0.48827700 | 0.13411000 | 0.11894300 |
| O | -0.60310900 | 1.32234800 | 0.00495500 |
| O | -1.51474700 | -0.71954000 | 0.00327000 |
| C | -2.78178300 | -0.11764600 | -0.25648100 |
| H | -2.75069300 | 0.43973300 | -1.19138600 |
| H | -3.05076700 | 0.56171500 | 0.55105000 |
| H | -3.49232700 | -0.93576100 | -0.32158200 |

b) Methyl 2-butenoate
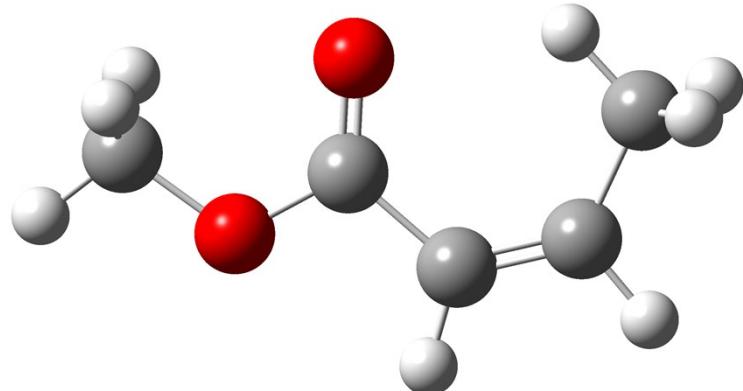
Coordinates

| | | | |
|---|---|---|---|
| C | 1.99061800 | 0.68607300 | -0.00011400 |
| C | 0.69346000 | 0.98854600 | 0.00005300 |
| H | 0.38121300 | 2.02420900 | 0.00000400 |
| C | -0.41392500 | 0.00761700 | 0.00033800 |
| O | -0.33037700 | -1.19339100 | 0.00011200 |
| O | -1.59702000 | 0.64766900 | 0.00002000 |
| C | -2.74397900 | -0.19606100 | -0.00016800 |
| H | -3.60295900 | 0.46801100 | -0.00040700 |
| H | -2.74907600 | -0.82995500 | 0.88563300 |
| H | -2.74869100 | -0.83009200 | -0.88587200 |
| H | 2.67682000 | 1.52897500 | -0.00027900 |
| C | 2.63664600 | -0.65817900 | -0.00008900 |
| H | 3.28497100 | -0.74839000 | -0.87515100 |

| H | 1.91474500 | -1.46673800 | 0.00009000 |
| H | 3.28522900 | -0.74823100 | 0.87479900 |

- Transition state

a) TS1
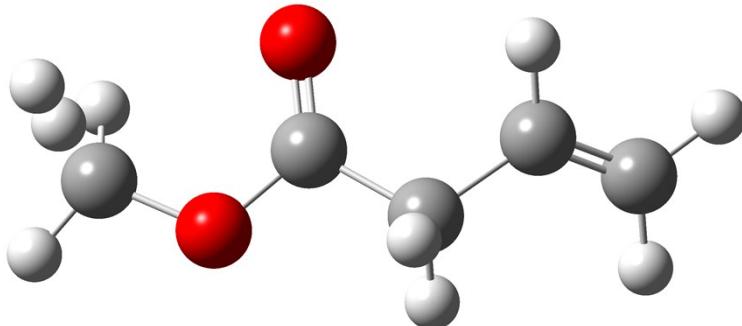


Coordinates

| C | 0.84534000 | -0.58678000 | 0.43981900 |
| C | 2.06319300 | 0.26080300 | 0.24968900 |
| H | 0.91457100 | -1.52749700 | -0.10706400 |
| H | 0.71876000 | -0.85142500 | 1.49584300 |
| C | 3.15965500 | -0.15685200 | -0.36125500 |
| H | 2.00722300 | 1.26804900 | 0.64705700 |
| H | 4.02428900 | 0.48451100 | -0.46699100 |
| H | 3.23107800 | -1.15497300 | -0.77847600 |
| C | -0.42300400 | 0.12361700 | 0.03926700 |
| O | -0.54201700 | 1.29497500 | -0.16854000 |
| O | -1.45588500 | -0.74799200 | -0.03752200 |
| C | -2.70026400 | -0.20666300 | -0.34336600 |
| H | -2.66560800 | 0.58181100 | -1.08916000 |
| H | -3.14019900 | 0.40923700 | 0.75396200 |
| H | -3.40286200 | -1.01056200 | -0.52778900 |
| H | -3.37355800 | 0.82024300 | 1.57619500 |

b) TS2
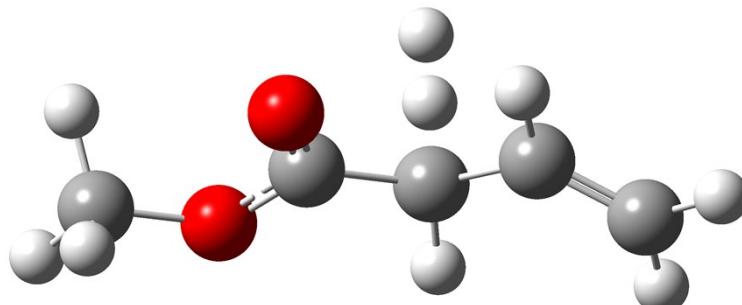


Coordinates

| C | -0.79351800 | -0.54462800 | 0.20959700 |
| C | -1.98847600 | 0.30511200 | 0.06727600 |
| H | -0.73772300 | -0.93412900 | 1.37555800 |
| H | -0.82488600 | -1.48238600 | -0.33996700 |
| C | -3.14663100 | -0.13326500 | -0.41203900 |
| H | -1.87802700 | 1.33302500 | 0.39364700 |
| H | -4.00613600 | 0.51882900 | -0.48733400 |
| H | -3.27027600 | -1.15607000 | -0.74892800 |
| C | 0.51716800 | 0.16015200 | 0.06411600 |
| O | 0.68005400 | 1.34500700 | 0.17292300 |
| O | 1.51296400 | -0.70766800 | -0.15638700 |
| C | 2.81458300 | -0.13026500 | -0.24559700 |

| | | | |
|---|---|---|---|
| H | 3.06354300 | 0.38462600 | 0.68109200 |
| H | 2.85601900 | 0.58171300 | -1.06843200 |
| H | 3.49545100 | -0.95748800 | -0.41970000 |
| H | -0.66086300 | -1.32946600 | 2.38164900 |

c) TS3
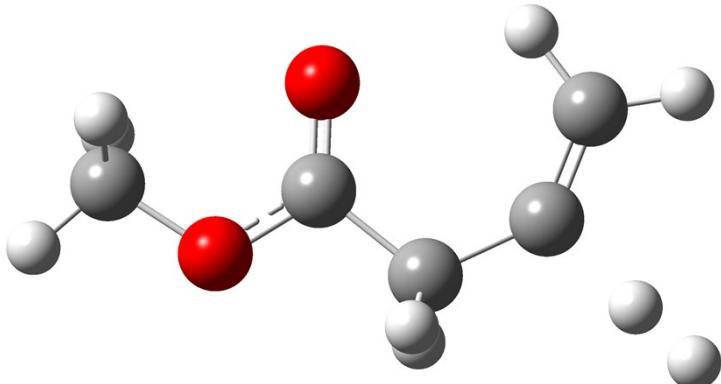


Coordinates

| | | | |
|---|---|---|---|
| C | -0.70565200 | -0.94271300 | -0.00026000 |
| C | -2.05407300 | -0.33170800 | 0.00005000 |
| H | -0.58717300 | -1.59870700 | 0.86721900 |
| H | -0.58737800 | -1.59822600 | -0.86813900 |
| C | -2.54575200 | 0.88367200 | 0.00033300 |
| H | -3.03010700 | -1.32262400 | 0.00005200 |
| H | -3.61874200 | 1.04078800 | 0.00054900 |
| H | -1.90044600 | 1.75575500 | 0.00034300 |
| C | 0.46787100 | 0.01476300 | -0.00017200 |
| O | 0.41879000 | 1.21162200 | -0.00045000 |
| O | 1.61771800 | -0.67428100 | 0.00021400 |
| C | 2.80463300 | 0.11820100 | 0.00023200 |
| H | 2.83689600 | 0.74993800 | 0.88655500 |
| H | 2.83718700 | 0.74954700 | -0.88636000 |
| H | 3.63135000 | -0.58514900 | 0.00052700 |
| H | -3.67582200 | -1.94334000 | 0.00005600 |

d) TS4
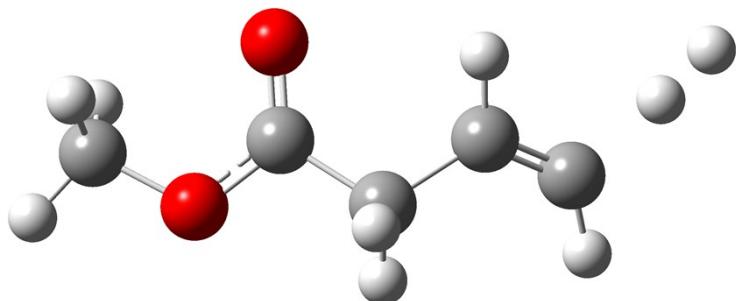


Coordinates

| | | | |
|---|---|---|---|
| C | 0.67047400 | -0.66650800 | 0.45348900 |
| C | 1.92012500 | 0.13824500 | 0.22978700 |
| H | 0.67149000 | -1.59253000 | -0.11954600 |
| H | 0.59034800 | -0.94803800 | 1.50927400 |
| C | 2.97503100 | -0.31071700 | -0.40618700 |
| H | 1.91121300 | 1.14807100 | 0.63046500 |
| H | 4.06631300 | 0.61577400 | -0.49951200 |
| H | 3.16622700 | -1.26500800 | -0.88084600 |
| C | -0.57990400 | 0.12090100 | 0.13644700 |

| O | -0.65093500 | 1.31628900 | 0.07774900 |
|---|---|---|---|
| O | -1.62892600 | -0.69159300 | -0.04262200 |
| C | -2.87075200 | -0.03633100 | -0.29884000 |
| H | -2.80052500 | 0.56378200 | -1.20461600 |
| H | -3.13527100 | 0.61165400 | 0.53541100 |
| H | -3.60497300 | -0.82681300 | -0.41833000 |
| H | 4.68421600 | 1.22199200 | -0.52149600 |

e) TS5
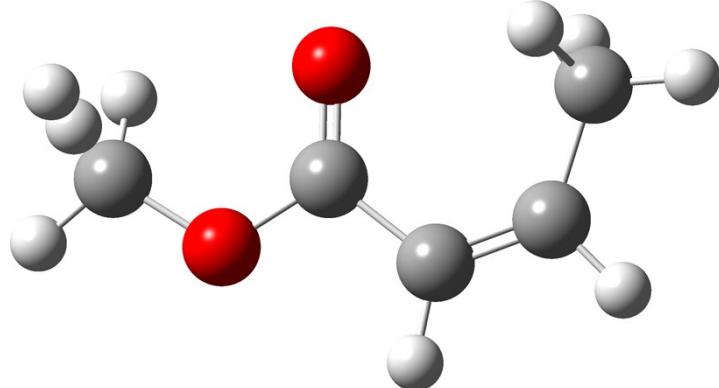


Coordinates

| C | -2.04704300 | 0.67550900 | 0.08049900 |
|---|---|---|---|
| C | -0.76323500 | 1.03204200 | 0.04390900 |
| H | -0.47274900 | 2.07193500 | 0.09873800 |
| C | 0.33241800 | 0.05652300 | -0.06761600 |
| O | 0.23081200 | -1.13710700 | -0.16069900 |
| O | 1.53577200 | 0.68622400 | -0.06021400 |
| C | 2.65685100 | -0.12762000 | -0.13924400 |
| H | 3.53537800 | 0.48843700 | -0.29101600 |
| H | 2.54230500 | -0.97270600 | -0.81175800 |
| H | 2.82264400 | -0.69196100 | 1.04998900 |
| H | -2.76943300 | 1.48135400 | 0.16290200 |
| C | -2.59515100 | -0.71549900 | 0.02023700 |
| H | -3.67729400 | -0.70962700 | 0.12827500 |
| H | -2.15724500 | -1.34072600 | 0.79835500 |
| H | -2.33489200 | -1.19153600 | -0.92628300 |
| H | 2.87557100 | -1.05383800 | 1.93138600 |

f) TS6
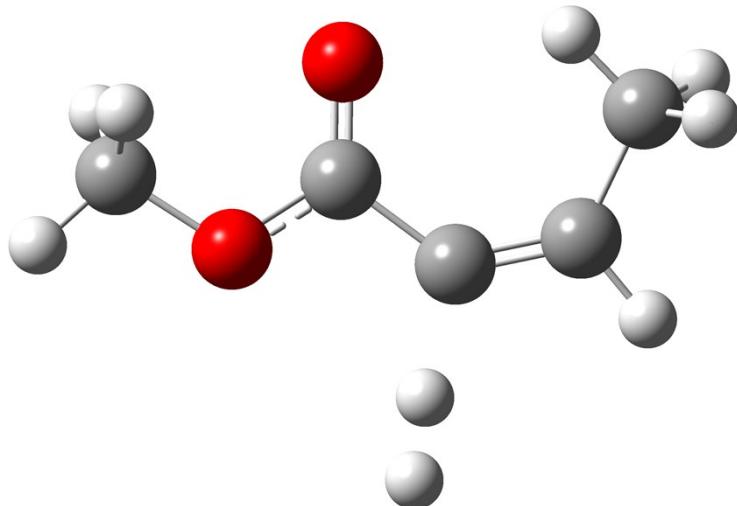


Coordinates

| C | -2.00189500 | 0.61823400 | 0.00469600 |
| C | -0.70873400 | 0.85452400 | -0.09349200 |
| H | -0.36625900 | 2.23454400 | -0.19326200 |
| C | 0.44082900 | -0.06273800 | -0.09119400 |
| O | 0.37915600 | -1.25357300 | -0.26055500 |
| O | 1.58820300 | 0.59261700 | 0.11363900 |
| C | 2.75895300 | -0.22079300 | 0.12657100 |
| H | 3.58915900 | 0.45733900 | 0.29679400 |
| H | 2.87158200 | -0.73607600 | -0.82625600 |
| H | 2.69699900 | -0.96060100 | 0.92340600 |
| H | -2.66451700 | 1.48177900 | -0.02664100 |
| C | -2.66674200 | -0.71535000 | 0.16310100 |
| H | -3.30872900 | -0.70178600 | 1.04607500 |
| H | -1.94317800 | -1.52027200 | 0.24325800 |
| H | -3.31260500 | -0.90258900 | -0.69779600 |
| H | -0.23578800 | 3.09204800 | -0.24834100 |

g) TS7
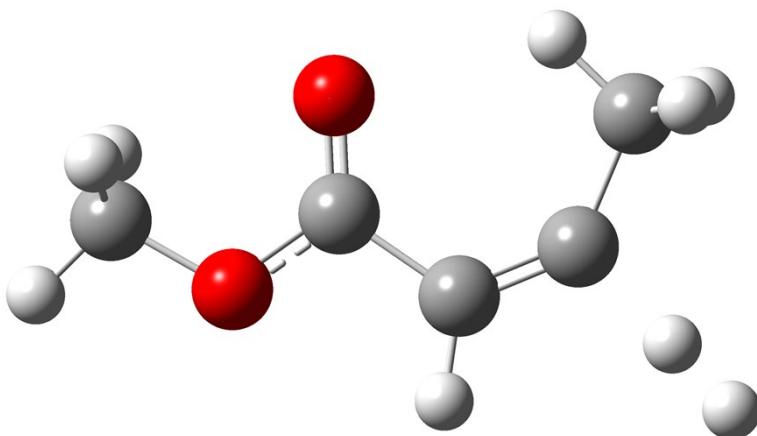


Coordinates

| C | 1.92201200 | 0.49477300 | 0.00000000 |
| C | 0.66983800 | 0.91023900 | -0.00000400 |
| H | 0.43538500 | 1.96820100 | -0.00000700 |
| C | -0.49309600 | -0.01256700 | -0.00000300 |
| O | -0.45443800 | -1.21504700 | -0.00000600 |
| O | -1.64158100 | 0.68110900 | 0.00000200 |
| C | -2.82816700 | -0.10828900 | 0.00000400 |
| H | -3.65418000 | 0.59602200 | 0.00000600 |
| H | -2.86185500 | -0.74059000 | 0.88605300 |
| H | -2.86185800 | -0.74058800 | -0.88604600 |
| H | 2.80875200 | 1.55130600 | 0.00000100 |
| C | 2.59548900 | -0.81630300 | 0.00000500 |
| H | 3.23790500 | -0.90389200 | 0.87869000 |
| H | 3.23786600 | -0.90391600 | -0.87870800 |
| H | 1.86644800 | -1.62618100 | 0.00003000 |
| H | 3.36324300 | 2.26402400 | 0.00000200 |

h) TS8
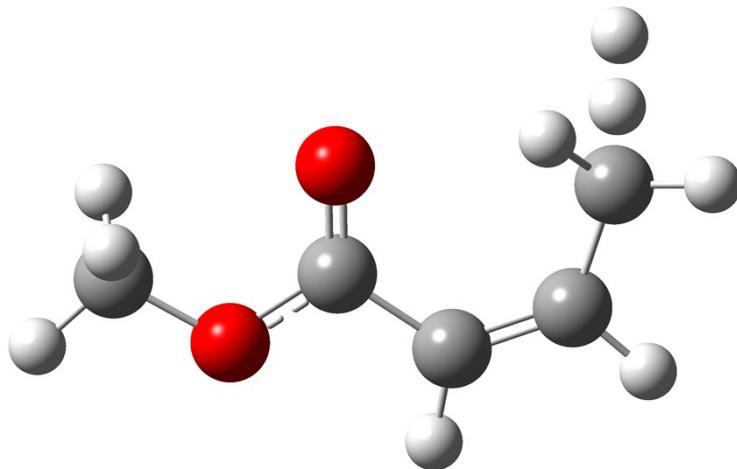
Coordinates

| | | | |
|---|---|---|---|
| C | 1.92308300 | 0.76651400 | -0.04616600 |
| C | 0.61897000 | 1.05088600 | 0.06595300 |
| H | 0.29472900 | 2.07222600 | 0.20958800 |
| C | -0.45438900 | 0.04259900 | -0.00111600 |
| O | -0.31550200 | -1.15194000 | -0.08279100 |
| O | -1.66207800 | 0.63049100 | 0.04766800 |
| C | -2.77273900 | -0.25935300 | -0.00197600 |
| H | -3.65856700 | 0.36574900 | 0.05445900 |
| H | -2.73909100 | -0.95484500 | 0.83563600 |
| H | -2.76272400 | -0.82754700 | -0.93121300 |
| H | 2.60908200 | 1.60307300 | 0.04298800 |
| C | 2.53443000 | -0.54988600 | -0.23379100 |
| H | 1.90783900 | -1.29414400 | -0.71097300 |
| H | 2.69288400 | -1.04744900 | 0.89668500 |
| H | 3.54758600 | -0.51474500 | -0.62353000 |
| H | 2.83277500 | -1.53528300 | 1.80993400 |

- Products
a) Product of R1
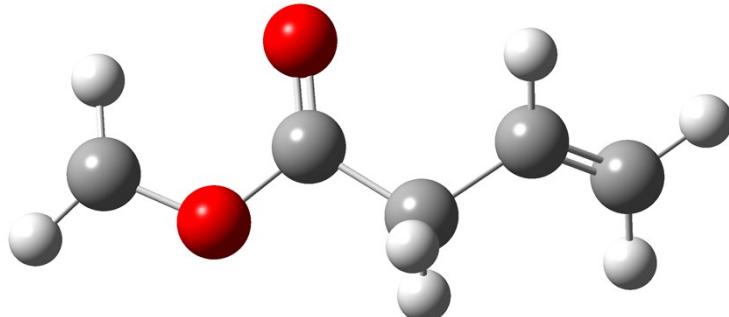


Coordinates

| | | | |
|---|---|---|---|
| C | 0.72340400 | -0.61105800 | 0.40207500 |
| C | 1.95763400 | 0.21836200 | 0.23881900 |
| H | 0.75043600 | -1.50720000 | -0.21851900 |
| H | 0.62298700 | -0.95549900 | 1.43793200 |
| C | 3.02294700 | -0.17722300 | -0.43823800 |
| H | 1.94176000 | 1.19231500 | 0.71499500 |
| H | 3.90123600 | 0.44863800 | -0.52189700 |
| H | 3.05396700 | -1.14073800 | -0.93429000 |
| C | -0.53559300 | 0.15962400 | 0.09877400 |
| O | -0.63244000 | 1.34450200 | -0.01730900 |

| O | -1.59627600 | -0.68556200 | -0.00204000 |
|---|---|---|---|
| C | -2.82804200 | -0.14545300 | -0.21153700 |
| H | -2.89176200 | 0.90173200 | -0.45250700 |
| H | -3.59100000 | -0.87628300 | -0.41028000 |

b) Product of R2
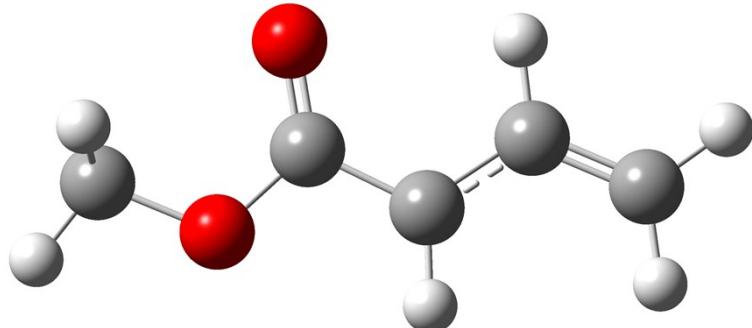


Coordinates

| C | 0.82319500 | -0.49032100 | 0.00014300 |
|---|---|---|---|
| C | 1.98080500 | 0.27450600 | -0.00009300 |
| H | 0.85972900 | -1.57124500 | 0.00031000 |
| C | 3.23933300 | -0.26013100 | -0.00006500 |
| H | 1.85279600 | 1.35139300 | -0.00027700 |
| H | 4.11799100 | 0.36765600 | -0.00024800 |
| H | 3.38944700 | -1.33181900 | 0.00012500 |
| C | -0.49037700 | 0.15022700 | 0.00017700 |
| O | -0.68684200 | 1.34138400 | -0.00019400 |
| O | -1.48352600 | -0.75713500 | 0.00015400 |
| C | -2.79845000 | -0.21273900 | -0.00004600 |
| H | -2.95513900 | 0.40162000 | -0.88571000 |
| H | -2.95529800 | 0.40188000 | 0.88540800 |
| H | -3.47361700 | -1.06273700 | 0.00001600 |

c) Product of R3
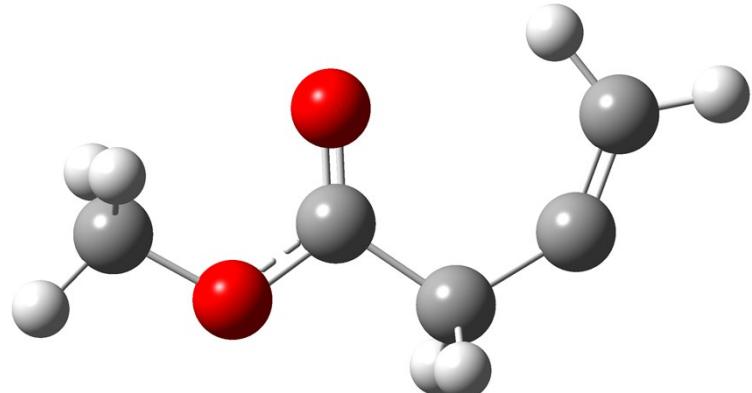


Coordinates

| C | 0.74807900 | 1.06788700 | 0.00002700 |
|---|---|---|---|
| C | 2.11674600 | 0.53744100 | 0.00002800 |
| H | 0.58220000 | 1.70981700 | 0.86977200 |
| H | 0.58222200 | 1.70981100 | -0.86972800 |
| C | 2.76954500 | -0.59034200 | -0.00005500 |
| H | 3.85440900 | -0.61271900 | -0.00007900 |
| H | 2.24355900 | -1.54329900 | -0.00009100 |
| C | -0.35253700 | 0.02005900 | 0.00002100 |
| O | -0.20371500 | -1.16787900 | 0.00006600 |
| O | -1.55298500 | 0.61546900 | -0.00004000 |

| C | -2.67291500 | -0.26949400 | -0.00002400 |
| H | -2.65445000 | -0.90153400 | 0.88647100 |
| H | -2.65451600 | -0.90148300 | -0.88655900 |
| H | -3.55332800 | 0.36538200 | 0.00002400 |

d) Product of R4
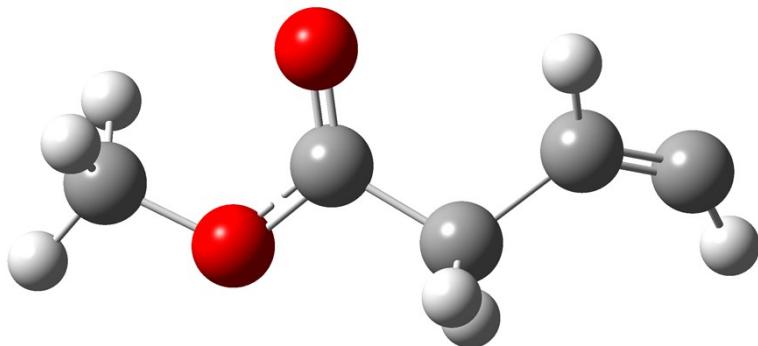


Coordinates

| C | 0.87353300 | -0.56570300 | 0.45230200 |
| C | 2.07884800 | 0.28432700 | 0.14178900 |
| H | 0.90620900 | -1.52485400 | -0.06193700 |
| H | 0.83428600 | -0.78229800 | 1.52533900 |
| C | 3.13326900 | -0.14892500 | -0.49093500 |
| H | 2.02575200 | 1.31655400 | 0.47883400 |
| H | 3.45405800 | -1.07651700 | -0.93977200 |
| C | -0.42035800 | 0.14069800 | 0.12067400 |
| O | -0.55173900 | 1.32578300 | -0.00476900 |
| O | -1.43197600 | -0.73022100 | 0.01443300 |
| C | -2.70979800 | -0.15119400 | -0.24767800 |
| H | -2.68917100 | 0.39846300 | -1.18736900 |
| H | -2.98768800 | 0.53044100 | 0.55484300 |
| H | -3.40670200 | -0.98150500 | -0.30415900 |

e) Product of R5
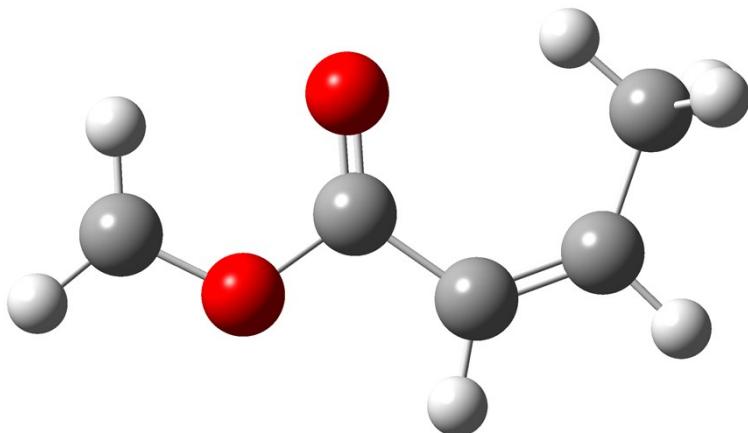


Coordinates

| C | -1.92078600 | -0.70939900 | -0.00001300 |
| C | -0.61486100 | -0.97758000 | -0.00018900 |
| H | -0.27330000 | -2.00365600 | -0.00031300 |
| C | 0.45646300 | 0.03246000 | -0.00018700 |
| O | 0.35967300 | 1.22853000 | -0.00029600 |
| O | 1.67071300 | -0.59492100 | 0.00010200 |
| C | 2.78451100 | 0.17295600 | 0.00026200 |
| H | 3.70478600 | -0.38079900 | 0.00031800 |
| H | 2.68179400 | 1.24333600 | -0.00008400 |

| | | | |
|---|---|---|---|
| H | -2.58396200 | -1.57024100 | -0.00002900 |
| C | -2.60033300 | 0.61746500 | 0.00024300 |
| H | -3.25123000 | 0.69101300 | -0.87446200 |
| H | -1.90037700 | 1.44516500 | 0.00011100 |
| H | -3.25076100 | 0.69089800 | 0.87531000 |

f) Product of R6
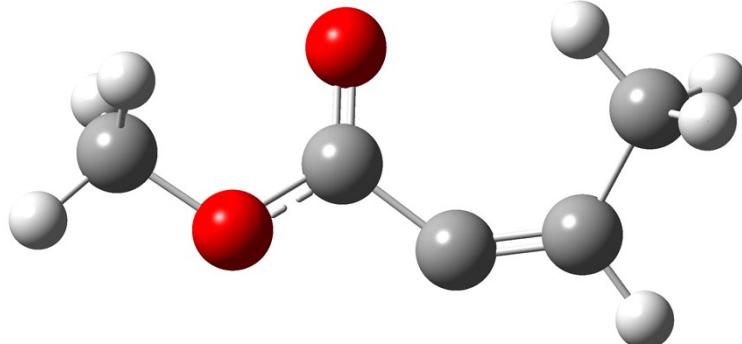


Coordinates

| | | | |
|---|---|---|---|
| C | 2.01366300 | -0.73406700 | -0.07147100 |
| C | 0.72243800 | -0.89172100 | -0.22323300 |
| C | -0.44162500 | -0.01058700 | -0.15177200 |
| O | -0.40405000 | 1.18168600 | -0.32069700 |
| O | -1.56276000 | -0.68686200 | 0.11245300 |
| C | -2.74513400 | 0.10666000 | 0.19451000 |
| H | -3.55282000 | -0.58705700 | 0.40517100 |
| H | -2.91834400 | 0.62500100 | -0.74749800 |
| H | -2.65280000 | 0.84276000 | 0.99185300 |
| H | 2.65225000 | -1.60621700 | -0.20115100 |
| C | 2.70469000 | 0.55522400 | 0.27603200 |
| H | 3.29342900 | 0.42595300 | 1.18600600 |
| H | 1.99073800 | 1.36291400 | 0.41036600 |
| H | 3.39784100 | 0.82499200 | -0.52319400 |

g) Product of R7
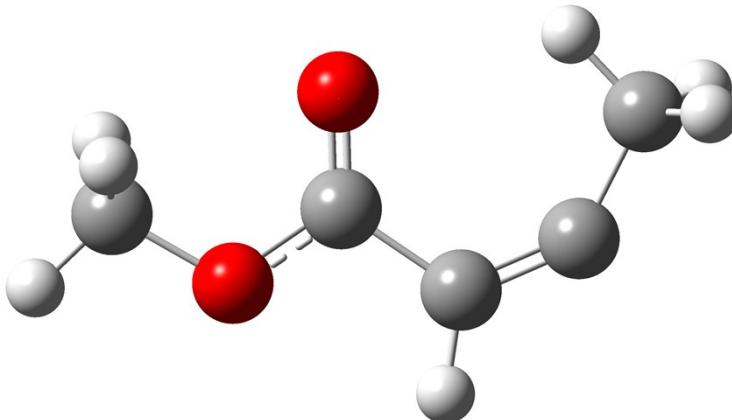


Coordinates

| | | | |
|---|---|---|---|
| C | 1.96614100 | 0.69194300 | 0.00001900 |
| C | 0.70163400 | 1.04040400 | 0.00000800 |
| H | 0.39362500 | 2.07983800 | 0.00000000 |
| C | -0.38938500 | 0.03092200 | -0.00000200 |
| O | -0.25171300 | -1.16440500 | 0.00001700 |
| O | -1.59011200 | 0.62976300 | -0.00003300 |
| C | -2.70887400 | -0.25311300 | -0.00004200 |

| | | | |
|---|---|---|---|
| H | -3.58931000 | 0.38203300 | -0.00005100 |
| H | -2.69155500 | -0.88606700 | 0.88607000 |
| H | -2.69153900 | -0.88606800 | -0.88615400 |
| C | 2.80363700 | -0.50586500 | 0.00003800 |
| H | 3.44830200 | -0.51752100 | -0.88072700 |
| H | 2.17802600 | -1.40322800 | -0.00005500 |
| H | 3.44813400 | -0.51759900 | 0.88092700 |

h) Product of R8
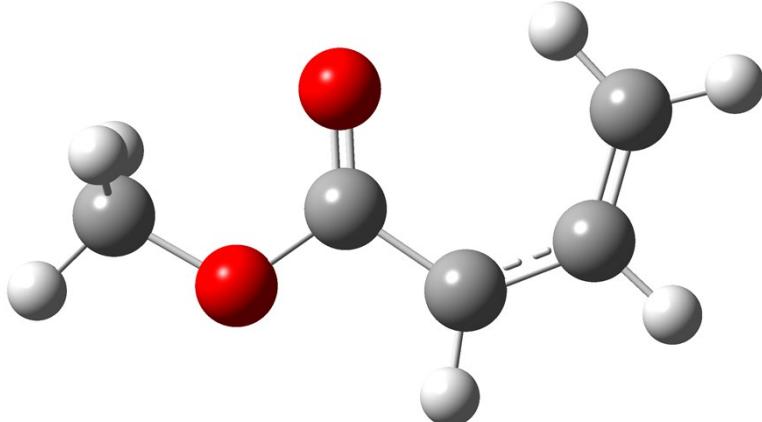


Coordinates

| | | | |
|---|---|---|---|
| C | -2.10117000 | -0.59665000 | 0.00006700 |
| C | -0.75815700 | -0.95533900 | -0.00014200 |
| H | -0.48585200 | -2.00098900 | -0.00022300 |
| C | 0.35741500 | -0.01020700 | -0.00026600 |
| O | 0.28498100 | 1.19537700 | 0.00003300 |
| O | 1.53593500 | -0.66413700 | -0.00010000 |
| C | 2.68925200 | 0.16969000 | 0.00009200 |
| H | 3.54285300 | -0.50134200 | 0.00006100 |
| H | 2.69995800 | 0.80375200 | 0.88589700 |
| H | 2.70007500 | 0.80399600 | -0.88553500 |
| H | -2.80723200 | -1.42039000 | 0.00012700 |
| C | -2.61416100 | 0.67585600 | 0.00020000 |
| H | -3.68478600 | 0.82285800 | 0.00036400 |
| H | -1.97141200 | 1.54208600 | 0.00014100 |
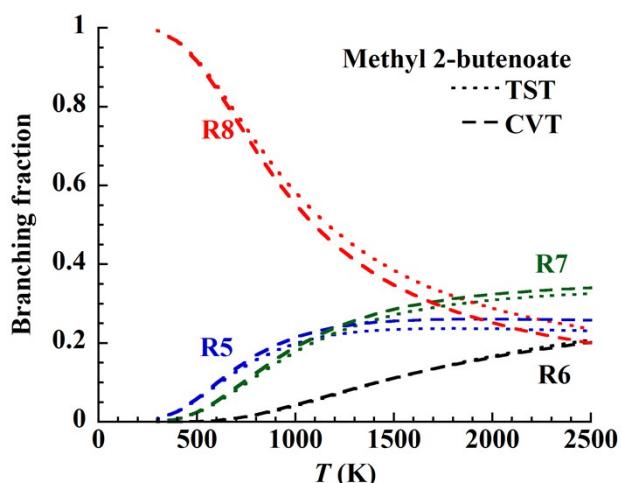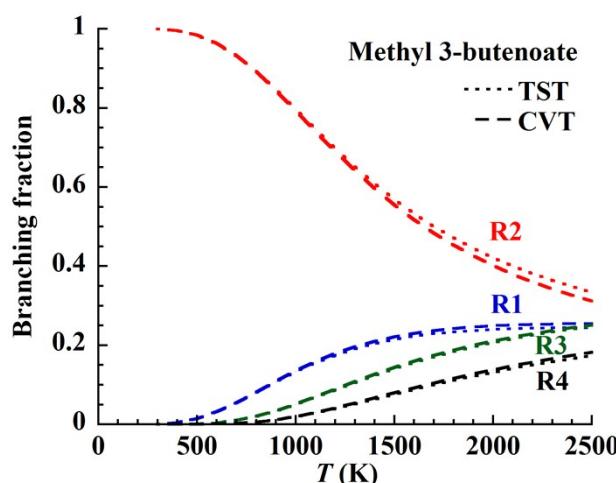


**Figure S2.** The branching fraction of the hydrogen abstraction from all sites of methyl 3-butenoate and methyl 2-butenoate by H atom by TST and CVT. Dotted lines: TST; dashed lines: CVT.

The details of direct dynamic calculations:

In this work, we used M06-2X/ma-TZVP for calculating reaction path. We used the Euler steepest-descents integrator to follow the reaction path, and used a quadratic fit to obtain the derivative of the gradient with respect to the reaction coordinate for computing the reaction path curvation components, The reaction path was calculated from $s=-1.6$ bohr to $s=1.6$ bohr, and the step size is 0.002 bohr.