

Supporting Information for:

Kinetics of the Methyl-Vinyl Radical + O₂ Reactions Associated with
Propene Oxidation

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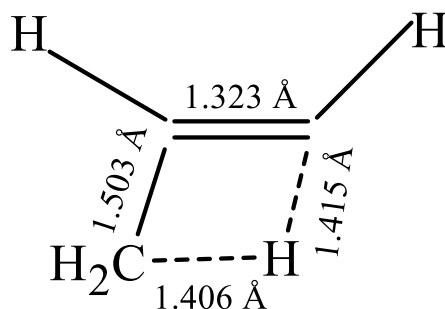


Figure S1. Bond distances for the H-atom shift in the transition state associated with *cis*-CH₃CHCH ↔ CH₂CHCH₂ isomerization.

Methods used in the electronic structure calculations

Molecular geometries and vibrational frequencies have been determined - after preliminary M052X/cc-pVTZ optimization – at the CCSD/cc-pVDZ level. This step was followed by an additional CCSD/cc-pVTZ geometry optimization and energy calculation at the CCSD(T)/cc-pVTZ level. No further refinement was found to be necessary because the differences of the relative energies obtained at the CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ levels do not exceed 2 kJ/mol. Notably, the M052X/cc-pVTZ energies are not further than 3 kJ/mol from our highest-level energy and enthalpy differences, except for the resonance-stabilized isomer, which is too stable by about 11 kJ/mol according to the density-functional theory calculations. Each of the transition structures is characterized by a single imaginary frequency mode, which corresponds to motion of the H atom between the expected structures.

All electronic structure calculations were performed using the Gaussian 09 suite of programs.^{S1}

References

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