

Reaction profiles for radical-radical hydrogen abstraction via multireference coupled cluster theory

Chia-Hua Wu¹, Brandon D. Magers¹, Lawrence Harding², Stephen J. Klippenstein² and Wesley D. Allen¹

¹Center for Computational Chemistry and Department of Chemistry, University of Georgia, Athens, GA 30602;

²Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439

We applied the multireference coupled cluster theory (Mk-MRCCSD, Mk-MRCCSD(T) and the companion Mk-MRPT2 theory) as well as several different popular multireference methods (MRCISD, MRCISD+Q, CASPT2) to study the hydrogen abstraction processes in different radical-radical reactions. One-dimensional reaction paths were constructed by CASPT2 constrained geometry optimizations using the hydrogen abstraction coordinate. The energies of all multireference methods were computed based on the CAS(2e,2o) reference wavefunction. Several prototypes of hydrogen abstraction reactions were selected to investigate, as shown below:



The performances of the dynamic correlations in different multireference methods were compared. Full configuration interaction (Full CI) computations with small basis sets were carried out as the benchmark for different approaches. We also analyzed the difference in Mk-MRCC performance when localized or delocalized orbitals were used as the reference wavefunction. In order to facilitate studies of reaction kinetics, the reported energies for reactions (3), (4) and (5) were computed with correlation-consistent basis sets (cc-pVXZ, $X = \text{T}, \text{Q}, 5$) and extrapolated to the complete basis set (CBS) limit.