Reliable Kinetic Predictions for Key Butanol Combustion Reaction

Scientific Achievement

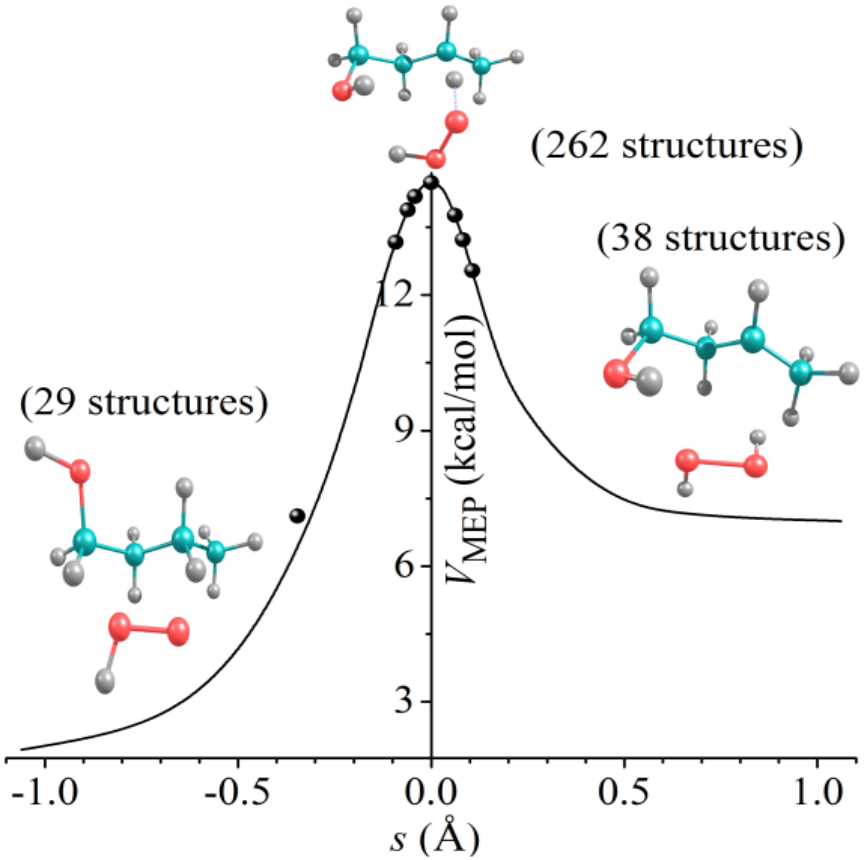
Calculated rate constants for the hydrogen abstraction from carbon-3 of 1-butanol by hydroperoxyl radical with multi-structural variational transition-state theory.

Significance and Impact

Reaction with HO_2 provides dominant uncertainty in ignition delay times for 1-butanol at high pressures and intermediate temperatures

Research Details

- multi-configurational Shepard interpolation used to obtain the portion of the potential energy surface needed for single-structure variational transition state theory rate constants including multidimensional tunneling
- M08-HX/MG3S electronic model chemistry was used to calculate multi-structural torsional anharmonicity factors
- neglect of multi-structural anharmonicity would lead to errors of factors of 0.3, 46, and 171 at 200, 1000, and 2400 K for this reaction



Schematic of potential energy surface for HO_2 + $CH_3CH_2CH_2CH_2OH$ = H_2O_2 + $CH_3CHCH_2CH_2OH$:

Prasenjit Seal, Ewa Papjak and Donald G. Truhlar, *J. Phys. Chem. Lett.* 3,264-271 (2012).

Work was performed at the University of Minnesota.