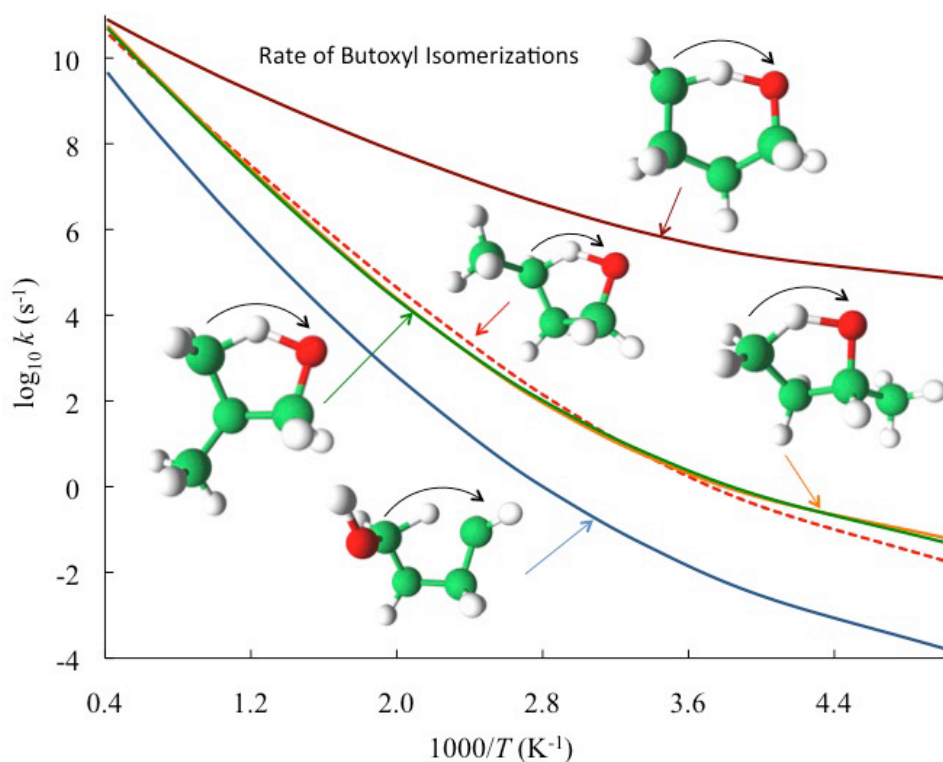


“Kinetics of Hydrogen-Transfer Isomerizations of Butoxyl Radicals,”
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Five isomerization reactions involving intramolecular hydrogen-transfer in butoxyl radicals have been studied using variational transition state theory with small curvature tunneling. A set of best estimates of barrier heights and reaction energies for these five reactions was obtained by using coupled cluster theory including single and double excitations with a quasiperturbative treatment of connected triple excitations and a basis set extrapolated to the complete basis set limit plus core-valence correlation contributions and scalar relativistic corrections. This work predicts high-pressure limiting rate constants of these five reactions over the temperature range 200 – 2500 K and clarifies the available experimental data from indirect measurements. This study shows the importance of performing rate calculations with proper accounting for tunneling and torsional anharmonicity. We also proposed two new non-Arrhenius expressions for use in fitting rate constants over wide ranges of temperature.

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