

## Rate coefficient measurements of the OH + *n*-, *i*-, *s*-, and *t*-butanol gas-phase reactions between 220–380 K: non-Arrhenius behavior and competitive reaction mechanisms

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Butanols are poised to become a major alternative to fossil fuel gasoline formulations with widespread usage. As a result, the emission of butanol into the atmosphere is likely to increase with time and it may impact the oxidative capacity of the troposphere and ozone production. The reaction of butanol with the OH radical is expected to be its dominant loss process in the atmosphere. In this work, reaction rate coefficients for the *n*-, *i*-, *s*-, and *t*-butanol isomers with the OH radical were measured under *pseudo*-first-order conditions in OH using pulsed laser photolysis to produce OH radicals and laser induced fluorescence to monitor its temporal profile. Rate coefficients were measured over the temperature range 220 to 381 K at total pressures between 50 and 200 Torr (He). Each of the butanol isomers exhibited a non-Arrhenius temperature dependence and no dependence on pressure.

The observed non-Arrhenius temperature dependence was interpreted as the result of a competition between reactive sites possessing different activation energies and pre-exponential factors. The results from this work were combined with available literature data from high temperature shock tube studies (~1200–1800 K) and room temperature reaction product yield studies and guided by structure-activity relationships to derive a self-consistent set of site specific temperature dependent reactivities between 220 to 1800 K. The strengths and weaknesses of this semi-empirical approach as well as possible explanations for the observed enhanced reactivity at temperatures relevant to the chemistry of the upper troposphere lower stratosphere will be discussed.