

Development of a Computational Chemical Kinetic Model for Cyclopentanone Combustion: H-atom Abstraction and Radical Decomposition

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Abstract

Cyclopentanone is a ketone that can be bio-derived because this chemical class is formed when fungi break down cellulose, a major component of biomass.^{1,2} Moreover, cyclopentanone is a component in mixtures formed from the pyrolysis of biomass, for example, during the fast pyrolysis of aspen wood chips.³ It has the lowest autoignition reactivity of a number of biofuels.⁴ These properties make cyclopentanone especially attractive as a blending component for use in boosted spark-ignition engines because of its resistance to autoignition. Downsized, boosted spark-ignition engines are an attractive technology that allows higher efficiencies than most current spark-ignition engines in the light-duty ground transportation market.⁵ This means cyclopentanone is not only attractive because it can be bio-derived, but also because its properties allow gains in engine efficiency; both of these characteristics yield potential reductions in greenhouse gas emissions.

Engine simulations can be used to assess the potential of cyclopentanone as a blending agent in gasoline, but these require a chemical kinetic model to simulate its ignition properties; such a mechanism is not currently available. H-atom abstraction from cyclopentanone by $\dot{\text{O}}\text{H}$, $\text{H}\dot{\text{O}}_2$ and $\dot{\text{C}}\text{H}_3$ radicals and $\dot{\text{H}}$ and $\dot{\text{O}}$ atoms are very important reaction classes in cyclopentanone combustion chemistry and also cyclopentanone radical decompositions. All of these reaction rate constants have been calculated in this work. These key rate constants and their associated product channels will help towards the development of a detailed chemical kinetic mechanism to describe cyclopentanone oxidation.

Computational methodology

The geometries of the reactants, transition states, products and complexes were optimized at the M062X/6-311++G(d,p) level of theory.⁶ Single point energies were carried out with the G4 composite⁷ model chemistry. Rate constants were calculated using conventional transition theory in the temperature range of 500–2000 K. The low frequency torsional modes were treated as hindered rotors except for those transition states involving abstraction by a methyl radical where a free rotor approximation was used due to the very low rotational barrier.

Primary results

Rate constants for all the channels mentioned above will be calculated. Rate constants comparison of the OH-abstraction reaction channels for the formation of CPO-2 and CPO-3 radicals are shown in Figure 1 (a) together with the potential for OH-group internal rotation in α_{eq} and β_{ax} , Figure 1 (b).

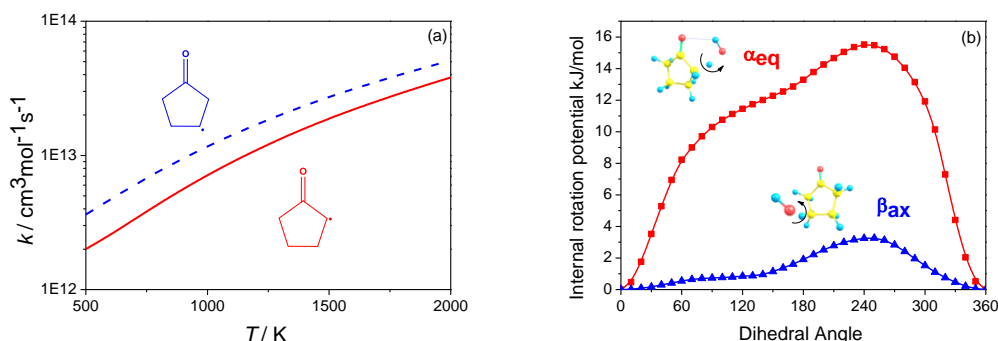


Figure 1. (a) Total rate constants comparison of OH-abstraction channels for the formation of CPO-2 and CPO-3 radicals. (b) OH group internal rotation potential comparison in the transition states of α_{eq} and β_{ax} .

References

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