New Efficient Methods for Predicting Kinetics of Combustion

Scientific Achievement

- ✧ **Multi-structural method with torsional anharmonicity (MS-T) for thermochemistry**
- ✧ **Multi-structural and multi-path Variational Transition State theory with multidimensional tunneling (MS-VTST/MT and MP-VTST/MT)**

Significance and Impact

The newly developed MS-T and MP(MS)-VTST/MT methods make it possible to study thermodynamics and kinetics of complex combustion reactions more efficiently and accurately.

Advantages of the New Methods

- The MS-T method is capable of treating cases with multiple torsions that are coupled to each other and to other modes.
- Assigning a torsion to a specific normal mode is not necessary in the MS-T method.
- The MS-T method uses conformational information about stable structures obtained by a search form all local-minimum structures, and no potential energy surface scan for barriers is needed.
- The MS-VTST and MP-VTST methods include multidimensional tunneling and account for multiple conformational structures of reactants, transition state, and products.
- The MP-VTST/MT methods provides a way of including variational effects and tunneling contributions for a reaction with multiple reaction paths.

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- T. Yu, J. Zheng, and D. G. Truhlar, Chem. Sci. **2**, 2199 (2011).
- T. Yu, J. Zheng, and D. G. Truhlar, J. Phys. Chem. A **116**, 297(2012).
- J. Zheng and D. G. Truhlar, Faraday Discuss., **157**, in press (2012)

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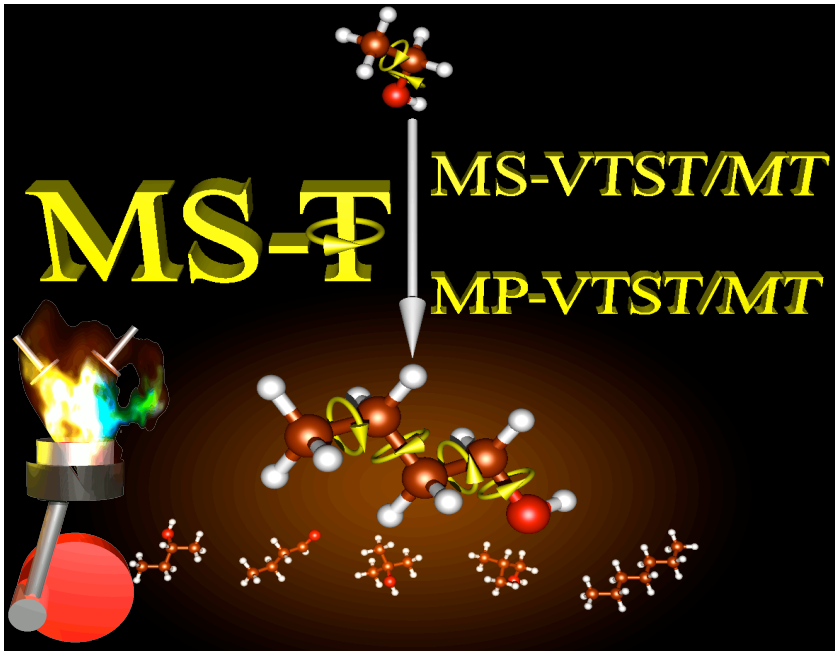
Goals and Applications

- Our goal is to develop and validate theoretical strategies for obtaining quantitatively accurate rate constants for elementary reactions of biofuels that are used in computational fluid dynamics to optimize engine designs and fuel performances.

- We work synergistically with the other groups in the CEFRC to provide data that is difficult to be obtained under experimental conditions.

- Hydrogen abstraction from fuel molecules by OH, HO_2 and CH_3 radicals is a major driver of combustion reactions at low and intermediate temperatures.

- We have thus computed validated thermodynamic properties and rate coefficients for hydrogen abstraction reactions involving methanol, ethanol, *n*-butanol, isobutanol and butanal using the MS-T and MS(MP)-VTST methods.



As of August 13, 2012, our methods and applications supported by the CEFRC have been published in 17 journal articles in 2011 and 2012.

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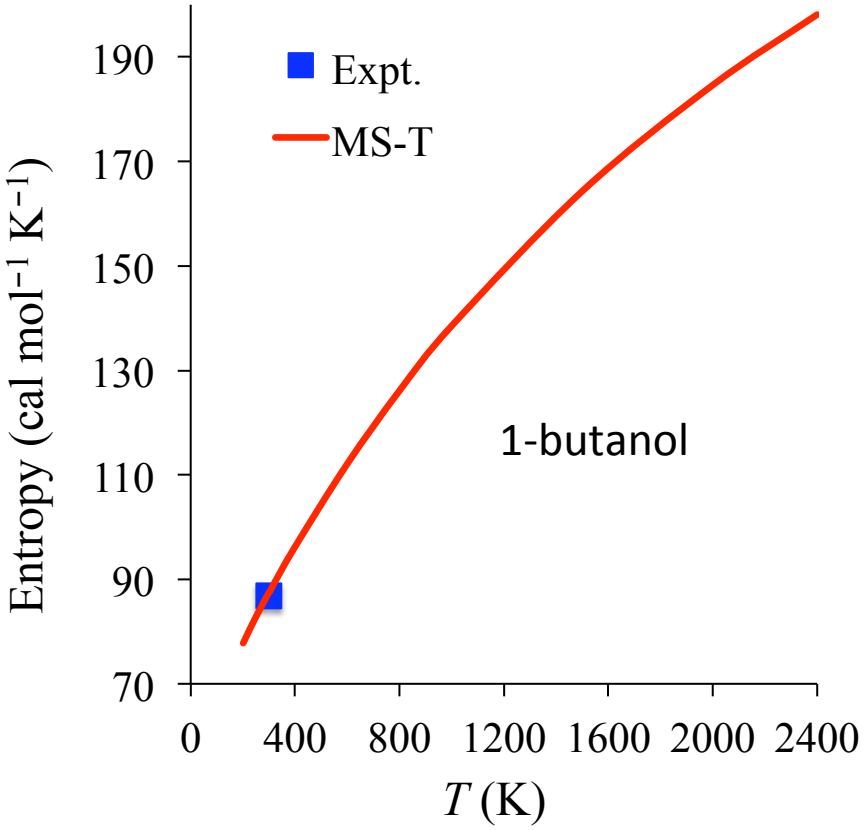
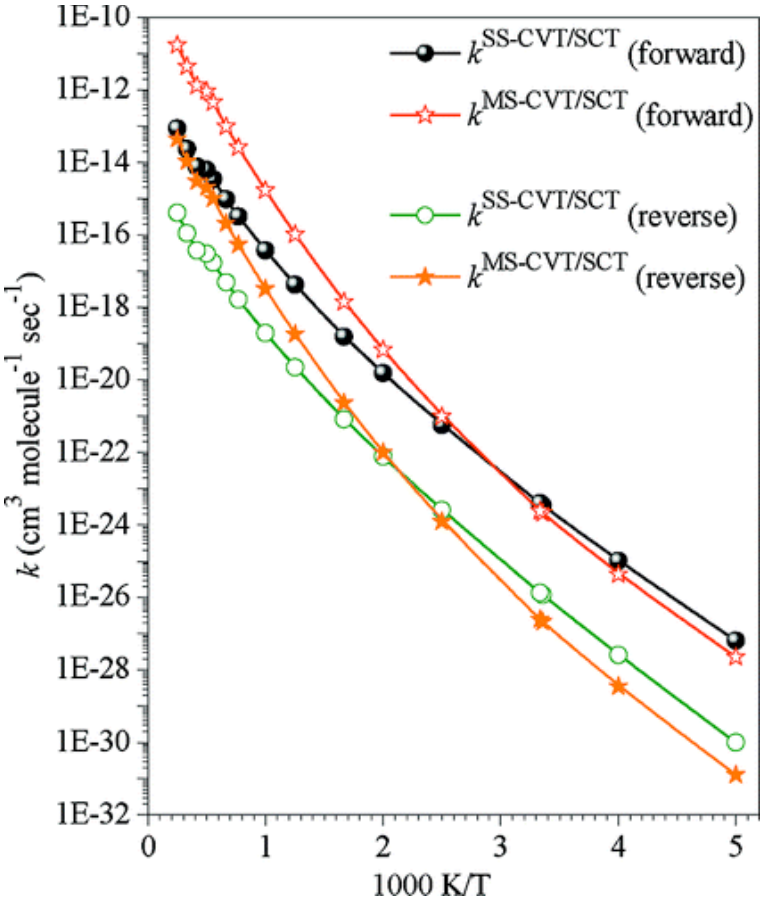
Example: $CH_3CH_2CH_2CH_2OH + HO_2 \rightarrow CH_3C{\bullet}HCH_2CH_2OH + H_2O_2$





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