

Obtaining the phenomenological rate constants to describe the decomposition kinetics of corannulene oxyradical at very high-temperatures

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Unimolecular reactions play an important role in combustion kinetics. It is one of the principal tasks to obtain the phenomenological rate constants for unimolecular reactions based on a master equation approach¹. In most cases, the eigenvalues of the transition matrix describing internal energy relaxation are much larger than and well separated from the chemical significant eigenvalues, so that phenomenological rate constants may be derived for incorporation in combustion mechanisms. However, when dealing with unimolecular reactions for large molecules, especially at high temperatures, the large densities of states of the reactant tend to cause the majority of population distributions to lie at very high energies level where the microcanonical reaction rates are so large that chemical reaction competes with the collisional relaxation, the relaxation and chemical eigenvalues overlap and well defined rate constants cannot be determined. This work attempts to analyze the effect of overlapping eigenvalues on the high-temperature kinetics of a large oxyradical, based on microcanonical reaction rates and population distributions as well as the eigenvalue spectrum of the transition matrix from the master equation, and provide a pragmatic method for obtaining the most effective rate constants for competing elimination, dissociation and bimolecular reactions for incorporation in combustion mechanisms. Our approach is demonstrated with a representative example, thermal decomposition of corannulene oxyradical².

References

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- (2) You, X.Q., Wang, H.M., Zhang, H.-B., Pilling, M.J, *Phys. Chem. Chem. Phys.*, **2016**, DOI: 10.1039/C6CP00917D