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Computational Chemistry of Cyclopentane Low Temperature Oxidation

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Abstract

Cycloalkanes are significant constituents of conventional fossil fuels, but little is known concerning their combustion chemistry and kinetics, particularly at low temperatures. This study investigates the pressure dependent kinetics of several reactions occurring during low-temperature cyclopentane combustion using theoretical chemical kinetics. The reaction pathways of the cyclopentyl + O₂ adduct is traced to alkylhydroperoxide, cyclic ether, β -scission and HO₂ elimination products. The calculations are carried out at the UCCSD(T)-F12b/cc-pVTZ-F12//M06-2X/6-311++G(d,p) level of theory. The barrierless entrance channel is treated using variable-reaction-coordinate transition state theory (VRC-TST) at the CASPT2(7e,6o) level of theory, including basis set, geometry relaxation and ZPE corrections. 1-D time-dependent multiwell master equation analysis is used to determine pressure- and temperature-dependent rate parameters of all investigated reactions. Tunneling corrections are included using Eckart barriers. Comparison with cyclohexane is used to elucidate the effect of ring size on the low temperature reactivity of naphthenes. The rate coefficients reported herein are suitable for use in cyclopentane and methylcyclopentane combustion models, even below ~900 K, where ignition is particularly sensitive to these pressure-dependent values.

Introduction

Cycloalkanes are significant constituents of transportation fuels, particularly of those derived from oil sands and shale [1]. They also have a greater propensity for soot formation via dehydrogenation than their non-cyclic counterparts [2]. Therefore, adequate knowledge of cycloalkane chemistry and kinetics is needed in order to improve fuel combustion efficiencies and reduce emission profiles. Generally speaking, cycloalkane chemistry is similar to that of *n*-alkanes; however, the ring structure and the ring strain has an effect on the rate coefficients of some reactions. For example, cyclohexane is significantly less reactive than *n*-hexane, as evidenced by its longer ignition delay times in rapid compression machines [3], as well as its higher octane number [4]. This is due to the fact that the ring structure in cycloalkanes suppresses some low temperature chain branching pathways, particularly peroxyalkyl/alkylhydroperoxide isomerizations. When these pathways are suppressed, alternative pathways, namely HO₂ elimination, become more important, resulting in higher concentrations of olefins compared to non-cyclic hydrocarbons [5]. The cyclic olefins produced from naphthenes slow ignition and may contribute to soot formation in the high-temperature (i.e. post-ignition) regime.

A more profound understanding of cycloalkane oxidation chemistry requires knowledge concerning the reactivity and degradation kinetics of these

compounds. Sirjean et al. [6] provide theoretical rate parameters of several important low temperature combustion reactions of cyclopentane, including peroxyalkyl/alkylhydroperoxy isomerization, and cyclic ether formation, using CBS-QB3 computations. However, they did not consider HO₂ elimination and alternative isomerization pathways; nor did they consider pressure dependence of the kinetic rate constants. The purpose of this study is to determine pressure-dependent kinetic rate constants of the low temperature cyclopentane combustion reactions lying on the cyclopentyl + O₂ potential energy surface, using computational methods. The implicated methods allow for the evaluation of the contribution of formally direct pathways, which has been shown to be significant at low pressures [7].

Computational kinetics

The reaction pathways of the fuel radical + O₂ adduct are traced to alkylhydroperoxide, cyclic ether, β -scission and HO₂ elimination products. The geometries and frequencies of stable chemical species and transition states are calculated at the M06-2X/6-311++G(d,p) level of theory; whereas accurate energies are determined using UCCSD(T)-F12b/cc-pVTZ-F12. Conformational analyses, geometry and frequency calculations are accomplished using the Gaussian 09 suite of programs [8], and the MOLPRO software [9] was used for the CCSD(T) calculations. The barrierless

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O₂ addition step is treated using variable-reaction-coordinate transition state theory (VRC-TST) at the CASPT2(7e,6o) level of theory [10, 11]. 1-D hindered rotor treatment was applied to the torsional modes. The pressure-dependent rate parameters of all investigated reactions are determined by solving the time-dependent multiwell master equation for the temperature range 300-2500 K, at pressures 0.001, 0.01, 0.1, 1, 10 and 100 bar. The rate coefficients of the formally direct pathways obtained directly from the solution of the multi-well master equation. Tunneling corrections are included using Eckart barriers. The master equation was solved using the empirical $\langle \Delta E_{\text{down}} \rangle = 200 \times (T/300)^{0.85} \text{ cm}^{-1}$ exponential-down energy transfer parameterization. Implemented by the PAPER (Predictive Automated Phenomenological Elementary Rates) code [12].

Results and discussion

Figure 1 depicts the potential energy surface of the cyclopentyl + O₂ reaction, calculated at the UCCSD(T)-F12b/cc-pVTZ-F12 level of theory. The

energy values are reported relative to that of cyclopentyl + O₂. As shown in Figure 1, the 3- and 4-membered ring transition states involved in the inter-conversion between the QOOH species have energies that are much higher than the entrance channel (17 and 24 kcal mol⁻¹, respectively). The contribution of these channels, including the formally direct pathways that involve skipping through the neighboring wells will be negligible. Thus these two barriers were not included in the ME analysis. The cyclopentyl + O₂ oxidation kinetics on this surface is characterized by 132 irreversible reactions, 24 of which connect adjacent reactants, wells or bimolecular products. The temperature and pressure dependent rate constants of these reactions are fitted to the modified Arrhenius equation using the method of least squares in order to determine the rate parameters *A*, *n* and *E_a* (pre-exponential factor, temperature coefficient and activation energy, respectively) at each pressure.

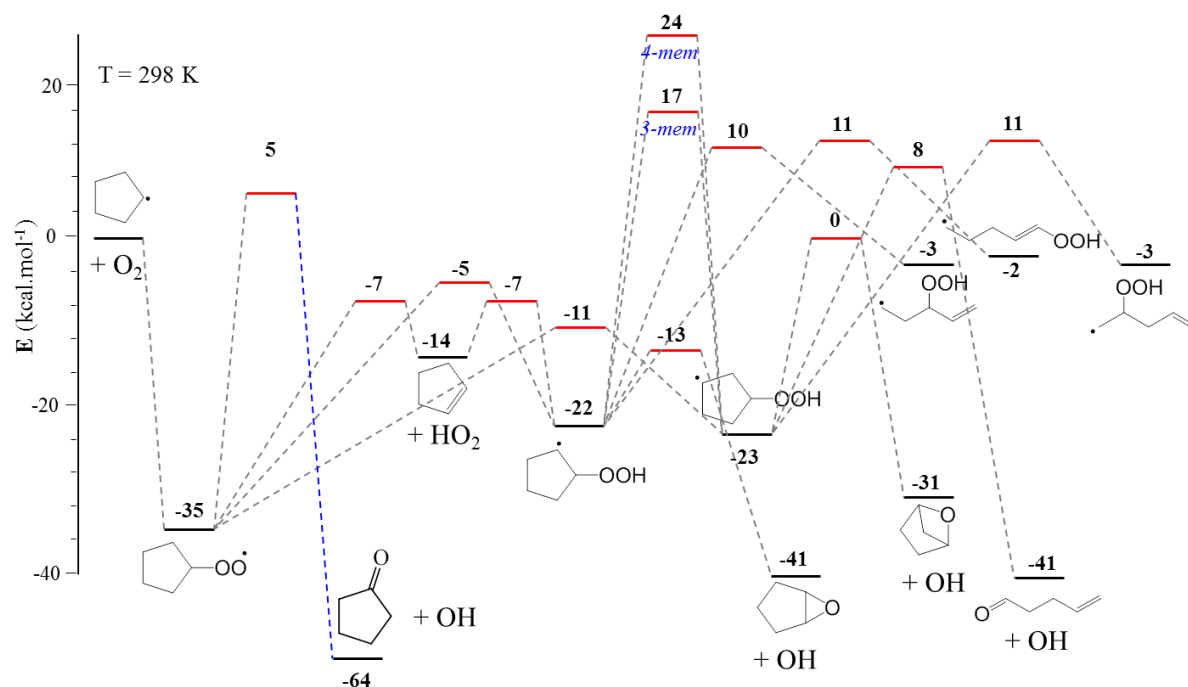


Figure 1. Cyclopentyl + O₂ potential energy surface. Energy values in kcal mol⁻¹ calculated at the UCCSD(T)-F12b/cc-pVTZ-F12 level of theory and reported relative to the cyclopentyl+ O₂ energy.

The fitted rate constants of the cyclopentyl + O₂, peroxyalkyl/alkylhydroperoxy and cyclic ether formation reactions are plotted in Figure 2 at different pressures. The plots depict the expected falloff at lower pressures and higher temperatures. The high pressure limit rate constants of the isomerization and cyclic ether formation reactions are

compared to those calculated by Sirjean et al. [6] at the CBS-QB3 level of theory (Figure 2) The CBS-QB3 rate constants at the high pressure limit are in reasonable agreement with the values calculated herein (less than a factor of 10 difference), except for the cyclic ether formation reaction whose CBS-QB3 rate constants are up to 23 times greater than those

calculated using ab initio methods and ME analysis. Meanwhile, the rate coefficients for O₂ addition and HO₂ elimination are compared to the cyclohexane analogs, which are calculated using ab initio methods [7, 13]. The comparison shows that the calculated

rates of both compounds are relatively similar, with those of cyclohexane being up to 4 times slower in the case of O₂ addition and up to 24 times faster in the case of HO₂ elimination.

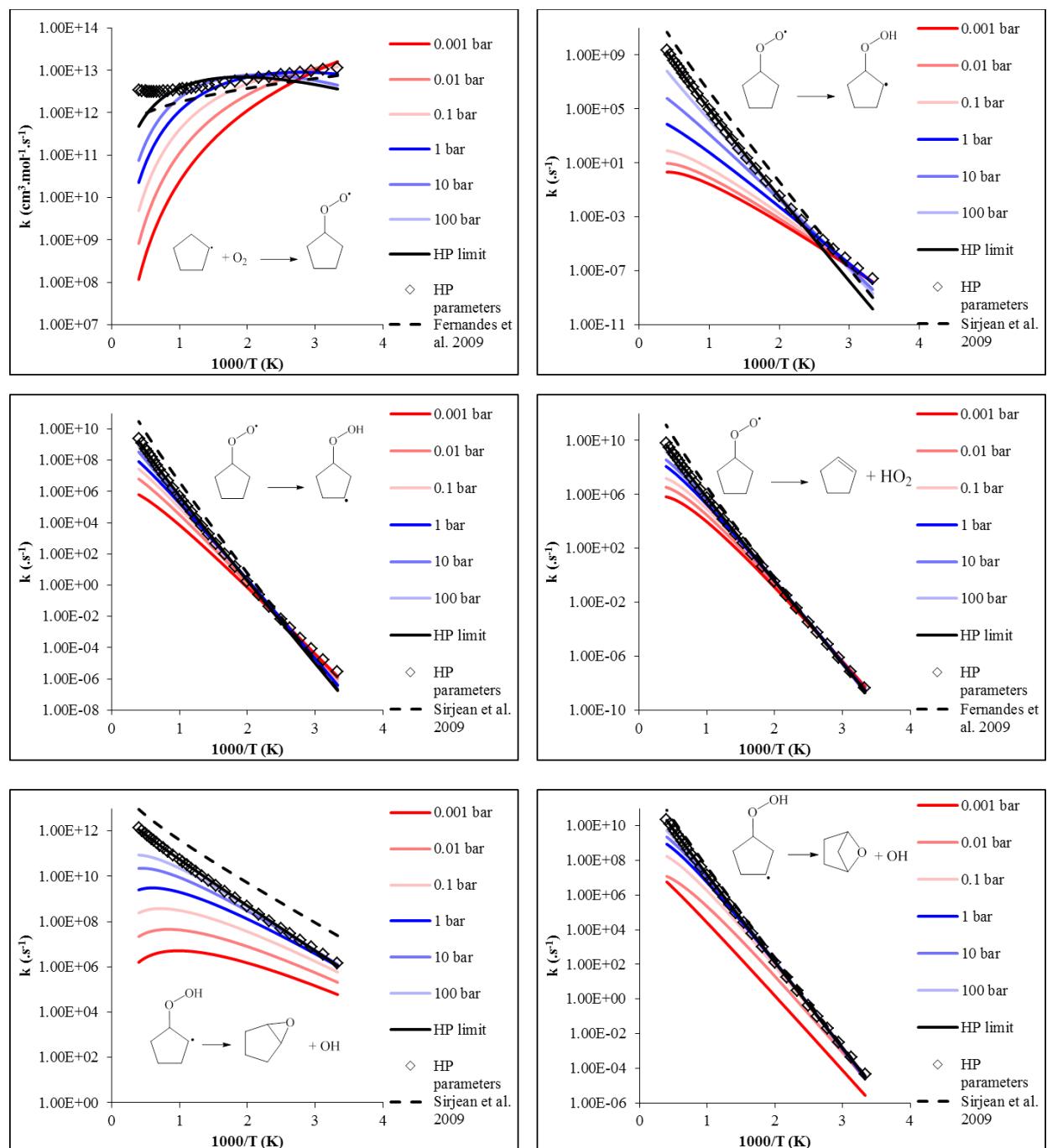


Figure 2. Pressure-dependent fitted rate constants for O₂-addition, isomerization and concerted HO₂ elimination reactions. The fitted high pressure (HP) limit rate constants are compared to the values generated by the ME analysis (HP parameters) as well as to those calculated by Sirjean et al. [6] at the CBS-QB3 level of theory and those of analogous cyclohexane reactions calculated by Fernandes et al. [7, 13].

Conclusions and perspectives

The kinetics of the cyclopentyl + O₂ reaction pathways has been investigated theoretically using ab initio methods and master equation analysis over a wide range of temperatures and pressures relevant to combustion modeling. These reaction pathways have a strong influence on low temperature chain branching and thus, accurate rate parameters are required for predictive modeling.

The potential energy surface comprises some low-lying barrier, which shows that the contribution of formally direct pathways to the reactivity of the system is significant, particularly at lower pressures and higher temperatures where collisional stabilization of the chemically activated adduct is minimal.

The calculated rate parameters may be used to simulate the combustion of cyclopentane under a wide range of conditions. The calculated energies may also be used to evaluate the thermodynamic properties of the chemical species involved.

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