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Elucidating reactivity regimes in cyclopentane oxidation: Jet stirred reactor experiments, computational chemistry, and kinetic modeling

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Abstract

This study is concerned with the identification and quantification of species generated during the combustion of cyclopentane in a jet stirred reactor (JSR). Experiments were carried out for temperatures between 740 and 1250 K, equivalence ratios from 0.5 to 3.0, and at an operating pressure of 10 atm. The fuel concentration was kept at 0.1% and the residence time of the fuel/O_2/N_2 mixture was maintained at 0.7 s. The reactant, product, and intermediate species concentration profiles were measured using gas chromatography and Fourier transform infrared spectroscopy. The concentration profiles of cyclopentane indicate inhibition of reactivity between 850–1000 K for $\varphi = 2.0$ and $\varphi = 3.0$. This behavior is interesting, as it has not been observed previously for other fuel molecules, cyclic or non-cyclic. A kinetic model including both low- and high-temperature reaction pathways was developed and used to simulate the JSR experiments. The pressure-dependent rate coefficients of all relevant reactions lying on the PES of cyclopentyl + O_2, as well as the C–C and C–H scission reactions of the cyclopentyl radical were calculated at the UCCSD(T)-F12b/cc-pVTZ-F12//M06-2X/6-311++G(d,p) level of theory. The simulations reproduced the unique reactivity trend of cyclopentane and the measured concentration profiles of intermediate and product species. Sensitivity and reaction path analyses indicate that this reactivity trend may be attributed to differences in the reactivity of

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allyl radical at different conditions, and it is highly sensitive to the C–C/C–H scission branching ratio of the cyclopentyl radical decomposition.

Keywords: Cyclopentane; Jet stirred rector; Species profiles; Modeling

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1. Introduction

Cycloalkanes are significant constituents of fuels, particularly those derived from oil sands and shale. They have greater propensity for soot formation than their non-cyclic counterparts due to dehydrogenation reactions [1]. Cycloalkanes and *n*-alkanes have similar chemistry except for some reactions whose rate coefficients are affected by the ring structure [2]. Studies have shown that cycloalkanes are less reactive, as evidenced by their longer ignition delay times [3] and higher octane numbers [4]. Moreover, methyl substitution, which is known to reduce reactivity of normal alkanes, has the opposite effect on cycloalkanes [5] since the addition of a methyl group promotes alkylperoxy isomerizations resulting in low-temperature chain branching [6]. Data currently available is not enough to explain the differences in ignition properties and reactivity trends of these compounds. This emphasizes the need for comprehensive and well validated cycloalkane kinetic models.

Among the different cycloalkane species, cyclopentane and cyclohexane are of particular importance because they are often used to represent naphthenes in surrogate fuels. These components, especially cyclopentane, significantly influence the fuel combustion and ignition characteristics of a gasoline surrogate, as demonstrated recently by Sarathy et al. [7]. However, most of the cycloalkane combustion research has been focused on cyclohexane [8–10]. Only a few studies provide kinetic models for cyclopentane combustion. These include high-temperature oxidation mechanisms developed by Tian et al. [5] based on the JetSurF2.0 mechanism and by Sirjean et al. [11] using EXGAS software. These mechanisms have been validated against shocktube ignition data measured under relatively dilute conditions (0.5% and 1% fuel/oxidant mixtures) in Argon for the temperature range of 1100–1800 K, at pressures up to 8.4 atm, and equivalence ratios between 0.5 and 2.0 [5,11]. Daley et al. [12] provided high-temperature ignition data for cyclopentane and cyclohexane fuel/air mixtures at lean/stoichiometric conditions and relatively high pressures (13 and 45 atm). One experimental study measured the flame speeds of cyclopentane using the counterflow configuration at atmospheric pressure [13]. Finally, Simon et al. [14] measured species profiles of cyclopentane/O_2 mixtures in a jet stirred reactor at 873 K and 0.5 atm.

Here we develop a detailed kinetic model comprising low- and high-temperature reaction pathways capable of predicting the combustion characteristics of cyclopentane. We also calculated pressure-dependent rate coefficients for the cyclopentyl + O_2 reaction [17] for which no good estimates were available. Computations of the C–C and C–H cyclopentyl scission kinetics were also conducted to reconcile discrepancies in the literature. The mechanism is validated against species profiles measured in a jet stirred reactor. A unique reactivity trend is observed for experimental and simulated profiles at rich conditions. To the best of our knowledge, this study is the first to fully develop a detailed mechanism of cyclopentane combustion and to provide experimental concentration profiles.

2. Experimental

The experimental setup used has been described previously [15]. Briefly, it consists of a fused silica jet stirred reactor (JSR) placed inside an electrical resistance oven which in turn is placed inside a pressure resistant jacket. 98% pure liquid cyclopentane (2% *n*-pentane), supplied by Aldrich, was pumped, vaporized and atomized at 100 °C using an HPLC pump and a flow of nitrogen. The preheated flow of fuel/N_2 was blended with a flow of oxygen diluted in nitrogen at the entrance of the injectors. Flow rates of all gases were controlled using mass-flow controllers, and the temperature measured by a Pt/Pt-Rh 10% thermocouple placed along the vertical axis of the reactor to check thermal uniformity. Experiments were performed at temperatures between 740 and 1250 K at a pressure of 10 atm. The fuel concentration was kept at 0.1%; however, the concentration of O_2 was varied from one experiment to the other such that the equivalence ratios were 0.5, 1.0, 1.5, 2.0 and 3.0. The measurements were conducted under steady state conditions at a constant mean residence time of 0.7 s.

The reaction mixtures were collected at low pressures in 1 l Pyrex bulbs using a sonic sampling probe. The collected samples were analyzed by a gas chromatograph (GC). Flame ionization detection was used to identify and quantify hydrocarbon and oxygenated species whereas thermal conductivity detection was used for the analysis of H_2 and O_2.