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Cyclopentane combustion chemistry. Part I: Mechanism development and computational kinetics

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ABSTRACT

Cycloalkanes are significant constituents of conventional fossil fuels, in which they are one of the main contributors to soot formation, but also significantly influence the ignition characteristics below ~900 K. This paper discusses the development of a detailed high- and low-temperature oxidation mechanism for cyclopentane, which is an important archetypical cycloalkane. The differences between cyclic and non-cyclic alkane chemistry, and thus the inapplicability of acyclic alkane analogies, required the detailed theoretical investigation of the kinetics of important cyclopentane oxidation reactions as part of the mechanism development. The cyclopentyl + O_2 reaction was investigated at the UCCSD(T)-F12a/cc-pVTZ-F12//M06-2X/6-311++G(d,p) level of theory in a time-dependent master equation framework. Comparisons with analogous cyclohexane or non-cyclic alkane reactions are presented. Our study suggests that beyond accurate quantum chemistry the inclusion of pressure dependence and especially that of formally direct kinetics is crucial even at pressures relevant for practical application.

1. Introduction

Cycloalkanes are important constituents of petroleum-derived liquid fuels. They make up ~40 wt% of diesel [1,2], ~20 wt% of kerosene [3,4], and ~10–15 wt% of gasoline [5]. Some studies have shown that at high temperatures, cycloalkanes may contribute to the production of soot by means of de-hydrogenation reactions [6]. Generally, cycloalkanes exhibit less low-temperature reactivity than their non-cyclic counterparts due to the conformational inhibition of the alkylperoxy↔hydroperoxyalkyl isomerization, an important low-temperature chain branching pathway. Yang et al. [7,8] have shown that in the case of cyclohexane, the suppression of low-temperature isomerization renders the HO_2-elimination pathway more important. This leads to higher concentrations of olefins, which reduces reactivity, delays ignition and also promotes soot formation [7]. The ring strain energy changes the oxidation kinetics, particularly for the ring-opening reactions, which also involve significant change in entropy [8]. Furthermore, unlike in *n*-alkanes, methyl substitution in cycloalkanes increases low-temperature reactivity [9] for reasons that are not well known on the molecular level. Therefore, more detailed kinetic research is needed to better explain the observed trends, and to enable accurate predictive modeling of cycloalkane-containing fuels.

Due to their simplicity and abundance, particularly in shale- and oil sand-derived fuels [10], cyclohexane and cyclopentane are often used to represent the naphthenic fraction in surrogate fuels. While models for cyclohexane [11-14] cover a wide temperature range, the cyclopentane models currently available in the literature are limited to high-temperature [15,16]. The rate coefficients of elementary reactions in these mechanisms are mostly based on analogies with cyclohexane due to the lack of cyclopentane-relevant kinetic data.

Kinetic determinations pertaining to cyclopentane reactivity are mostly concerned with high-temperature pathways such as unimolecular decomposition [17], H-abstraction by OH [18-20], and the β-scission of C–C and C–H bonds in cyclopentyl radicals [21-24]. Only Sirjean et al. [25] provide kinetic data of low-temperature cyclopentane reactivity. Specifically, they report high-pressure limit rate constants of cyclopentylperoxy (ROO) reactions, including alkylperoxy↔hydroperoxyalkyl isomerization (ROO↔QOOH) and cyclic ether formation, calculated at the CBS-QB3 level of theory. However, considering the importance of formally direct (aka well-skipping) pathways even at high pressures,

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as demonstrated by Fernandes et al. [11] for cyclohexane, pressure-dependent rate coefficients are needed for accurate predictions of reactivity under a wide range of conditions. Rate constants of the hydroperoxycyclopentyl (QOOH), HO_2-elimination, and β-scission pathways are also needed.

This study is concerned with the development of a detailed cyclopentane combustion mechanism comprising high- and low-temperature reaction pathways. The pressure-dependent kinetics of the low-temperature oxidation reactions lying on the potential energy surface (PES) of cyclopentyl + O_2 is determined using *ab-initio* methods and Master Equation (ME) analysis. The calculated rate constants are compared to those available in the literature for cyclopentane, as well as to those of analogous cyclohexane or non-cyclic alkane reactions. To the best of our knowledge, this work provides the first reported comprehensive chemical kinetic model for cyclopentane. The model developed herein allows for the prediction of the ignition properties of cyclopentane-containing fuels, and gives further insight into the differences between *n*-alkane and cycloalkane reactivity trends.

2. Mechanism development and computational methods

Our detailed mechanism of low- and high-temperature cyclopentane oxidation was developed based on the reaction scheme proposed by Sarathy et al. for 2-methyl alkanes [26]. The updated C_0–C_4 chemistry from NUI Galway's AramcoMech 1.4 was used as base chemistry in the model [27]. The cyclohexane and methylcyclohexane sub-mechanisms from [14] and [13], respectively, were included in the model for the purpose of elucidating the effect of ring size and ring substitution on reactivity. Overall, the cyclopentane sub-mechanism consists of 148 reactions and 33 species, while the complete mechanism consists of 6816 reactions and 1598 species. The dictionary of species names and molecular structures is available in the Supplementary Material along with the mechanism and thermodynamic data files.

In our mechanism, the rate coefficients of most elementary reactions were taken from the literature, if available, or estimated based on analogies. However, in light of the above-mentioned differences between cyclic and non-cyclic alkane low-temperature kinetics [7,8], reliable estimates of the kinetic parameters could not be made for cyclopentyl + O_2 with analogies. Therefore, the kinetics of important low-temperature oxidation pathways that affect the autoignition quality of a fuel [11] and that lie on the PES of cyclopentyl + O_2 were determined computationally in this current paper. The rate coefficients of cyclopentyl scission reactions were also determined computationally, because although several studies available in the literature are concerned with the estimation or computation of these reaction rates, the reported values are not in good agreement with each other [15,21,23,24]. Considering that the C–C/C–H scission branching ratio and kinetics have a great influence on the fuel concentration profile [28], and thus, on reactivity, it was necessary to recalculate the rate coefficients of these reactions at a higher level of theory than the earlier studies. Further details regarding the computed parameters for scissions and how they compare to the literature values may be found in Ref. [28].

Simplified schemes of the high- and low-temperature cyclopentane oxidation mechanisms are depicted in Figs. 1 and 2, respectively. A detailed account of the kinetics used for the reaction classes appearing in these schemes is given below.

2.1. Unimolecular decomposition

In our detailed mechanism, the unimolecular decomposition pathways of cyclopentane include fission reactions to form 1-pentene, ethene + propene, and cyclopentyl radical + H. Similar to the high-temperature cyclopentane mechanisms of Tian et al. [16] and Sirjean et al. [15], the rate coefficients of these reactions are taken from the shocktube experiments of Tsang [17]. The same rate coefficients were used for the unimolecular decomposition reaction of cyclopentene to 1,4-pentadiene as for cyclopentane, except, the activation energies were corrected to account for the difference in bond dissociation energies (BDE) between vinylic-secondary (cyclopentene) and secondary-secondary (cyclopentane) bonds, as well as for the difference between cyclopentene and cyclopentane ring strain: 0.8 kcal mol^{-1}, calculated at the CBS-QB3 level of theory [29]. These ring strain values were extracted by Ritter [30] from thermodynamic evaluations of cyclic species by Dorofeeva et al. [31]. The BDE correction was estimated as 12.8 kcal mol^{-1} by analogy with ΔBDE of $n\text{-}C_4H_{10} \rightarrow C_2H_5 + C_2H_5$ and $1\text{-}C_4H_8 \rightarrow C_2H_3 + C_2H_5$. The pathway cyclopentene → 1,3-pentadiene, where 1,3-pentadiene is a lumped species (1,3-pentadiene and vinylcyclopropane) has also been included. This reaction involves the generation of a resonantly stabilized allylic di-radical, and its activation energy was estimated by analogy with 1-pentene = ethyl + allyl. A correction factor of −5.1 kcal corresponding to the destabilizing ring strain energy in cyclopentene was applied. The thermal decomposition of the C–H bond in cyclopentane was written in the exothermic recombination direction, and the recommended rate constants of Allara and Shaw [32] were used. Finally, rate coefficients from Lewis et al. [33] were used for H_2 elimination from cyclopentene (included in the mechanism, but not shown in Fig. 1).

2.2. H-abstraction

The H-abstracting species that were taken into consideration are H, O, OH, O_2, HO_2, CH_3, CH_3O_2, CH_3O and C_2H_5 (referred to as X in Figs. 1 and 2). The rate coefficients of the abstraction reactions were assigned based on Sarathy et al.'s [26] rate rules for H-abstraction from secondary sites, except in the case of H-abstraction by OH. Although several experimental and theoretical studies of H-abstraction by OH from cyclopentane exist in the literature [18,20,34-40], most of them are limited to a narrow temperature range (<500 K) [18,36,37,39,40] or even just to a single temperature [34,35,38]. In this work we used rate coefficients for the cyclopentane + OH reaction based on the work of Sivaramakrishnan and Michael, who investigated this reaction using shocktube experiments between 813 and 1341 K [20]. The measured rate constants were combined with lower-temperature experimental data available in the literature, and then fitted to a modified Arrhenius equation. They also used high level electronic structure calculations to extrapolate the rate constants over an even wider range of temperatures (250–2000 K). The two expressions resulting from experimental data and computations yield rate constants that differ by only up to 15% in the 813–1341 K temperature range for which rate constants are directly measured in the shocktube [20]. Below 813 K they are within 7% of each other. The calculated rate constant values from Ref. [20] are also in good agreement with those obtained using our rate rule [26] (<50% different between 250 and 2000 K), as well as with those reported by Handford-Styring and Walker [19] (<10% different between 250 and 2000 K). The experimentally-derived rate coefficient values from Ref. [20] were used in the mechanism.

Unlike cyclopentane, cyclopentene has three different abstraction sites: vinylic, allylic and secondary. The abstraction rate coefficients from the secondary and allylic sites were equated on a per-H-atom-basis by those from cyclopentane and 1-hexene [41], respectively, while abstraction from the vinylic sites was neglected because of the high barrier.