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Temperature and pressure dependence of cyclohexyl radical reaction with O_2: How relevant are chemical activation pathways at high pressure?

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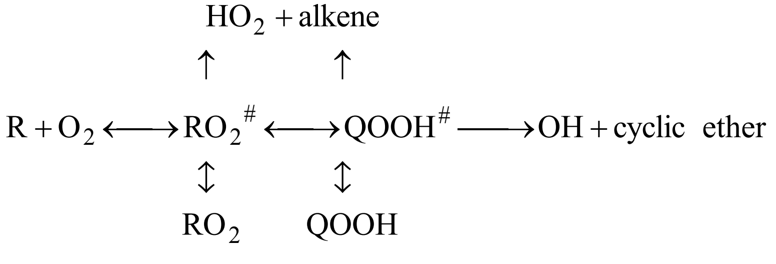
Reactions of alkyl and substituted alkyl radicals with oxygen are key processes in hydrocarbon oxidation, particularly for autoignition. These processes cannot be described by a single rate coefficient because the reactions involve competing steps of stabilization, dissociation and elimination, resulting in a complex kinetic behavior as a function of temperature and pressure. Understanding the complicated chemistry of ignition requires detailed characterization of these critical initial reactions over wide ranges of temperature and pressure. In particular, rate equation modeling of these reactions at low pressure has been shown to require "formally direct" reactions to account for chemically activation. Here the cyclohexyl + O_2 reaction is used as an example to determine the extent to which such chemical activation steps remain important at elevated pressure. Time resolved formation of OH from the cyclohexyl + O_2 reaction was studied in pulsed-photolytic Cl-initiated oxidation of cyclohexane at pressures up to 40 bar and temperatures near 500 K in a heatable high-pressure flow reactor. The amount of OH formation and its subsequent decay was modeled with a detailed reaction mechanism assuming homogenous and isothermal conditions. An extension of recently-developed theoretical models suggests that chemical activation remains a significant part of the mechanism even up to the highest pressures investigated, but the models are unable to reproduce the transient-OH observations.

1. Introduction

The reactions of alkyl radicals with O_2 are key to atmospheric oxidation of hydrocarbons and are a central component in hydrocarbon ignition chemistry. The interest in the chemistry of autoignition has recently increased because of the emergence of advanced engine technologies that rely on compression ignition of a fuel-air mixture. [1] The reactions of alkyl radicals (R) with molecular oxygen proceed via formation of an alkylperoxy radical (ROO), which can undergo isomerization to form hydroperoxyalkyl (QOOH) radicals and dissociate into various bimolecular products:



$$\begin{array}{ccccccc} & & \mathrm{HO_2} & + & \mathrm{alkene} & & \\ & & \uparrow & & \uparrow & & \\ \mathrm{R} + \mathrm{O_2} & \longleftrightarrow & \mathrm{RO_2}^{\#} & \longleftrightarrow & \mathrm{QOOH}^{\#} & \longrightarrow & \mathrm{OH} + \text{cyclic ether} \\ & & \updownarrow & & \updownarrow & & \\ & & \mathrm{RO_2} & & \mathrm{QOOH} & & \end{array} \qquad (1)$$

where # designates a chemically activated species. The QOOH species are particularly important in autoignition, because subsequent reactions with a second O_2 molecule lead to chain branching.[2,3]

Ab initio computation of stationary point energies and frequencies, coupled with master equation evaluation of pressure-dependent kinetics, has been applied to a series of alkyl + O_2 reactions.[4] These studies for alkanes and cycloalkanes at low pressure have shown that treatment of chemical activation processes by "formally direct" reactions is required to describe the results with a rate equation model. The chemically activated nature of reaction 1 compels the use of a rate equation, for example, having R + O_2 proceeding directly to OH + cyclic ether. Despite the fact that this process passes through configurations corresponding to the RO_2 and QOOH intermediate species, some fraction of the R + O_2 will yield the final OH + cyclic ether products without collisional stabilization of any intermediate. However, detailed chemical mechanisms for ignition generally do not employ these formally-direct steps. The contributions of these chemically activated reactions decrease as the pressure increases and collisional stabilization into the intermediate wells becomes more dominant. The present study investigates the importance of these processes at tens of bar.

Naphthenes (cyclic alkanes) are prominent components of real fuels, particularly those derived from heavier hydrocarbon sources, such as tar sands, that are gaining significance in the fuel stream.2,3 The ignition chemistry of napthenes remains poorly characterized relative to the autoignition of straight-chain hydrocarbon fuels, but a detailed cyclohexane oxidation mechanism has recently been developed and validated against a number of experiments. [5] Pulsed-photolytic Cl-initiated oxidation of cyclohexane has also been used to compare to kinetic models based on high-level quantum chemistry and master-equation calculations of cyclohexyl + O_2 reactions. [6] Cyclohexane oxidation at relatively low temperatures was hence chosen as a test for the persistence of "formally direct" pathways to higher pressures.

2. Experiment

The cyclohexyl + O_2 reaction is investigated in the context of pulsed-photolytic Cl-initiated cyclohexane oxidation. Oxalyl chloride, $(ClCO)_2$, is photolyzed at 193 nm in the presence of cyclohexane and oxygen in a helium buffer. The reactants are premixed and are flowed slowly through a heated reactor. The photolyte and cyclohexane are present in mole fractions of approximately 10^{-6} and O_2 at a mole fraction of 1.4×10^{-4}. The production of OH is monitored by laser-induced fluorescence (LIF) pumped in the $1 \leftarrow 0$ vibrational band of the $A \leftarrow X$ transition and detected by $1 \rightarrow 1$ (and vibrationally relaxed $0 \rightarrow 0$) emission near 308 nm. The delay time between the photolysis laser and the LIF pump laser is varied to map the time dependence of the OH concentration.

3. Model

The detailed oxidation mechanism of Silke et al.[5] and the master-equation calculations of Knepp et al.[6] formed the two starting points for the modeling of the pulsed-photolytic Cl-initiated oxidation of cyclohexane. The reaction was modeled as an isobaric and isothermal reaction, and the rate equations were integrated using CHEMKIN 4.1. The initiation of the reaction was modeled by assuming the instantaneous formation of cyclohexyl radicals at a mole fraction of 10^{-7}, and the reactions of the oxalyl chloride were ignored in the simulation. Oxalyl chloride photolysis results in the production of 2 Cl atoms and 2 CO molecules (at the temperatures of the present studies ClCO is not stable) and the reaction of Cl with cyclohexane is rapid. The Silke et al. mechanism was used as published or was adjusted by replacing their representations of the cyclohexyl + O_2 reactions with those calculated from master equation solutions at the pressures of the experiment, using the stationary point energies and configurations determined in Knepp et al. [6] The time-dependent multiple-well master equation was solved using the Variflex code. [7] For comparison, the limited model reported by Knepp et al., with rate constants for cyclohexyl + O_2 determined by the master equation calculations, was directly integrated.

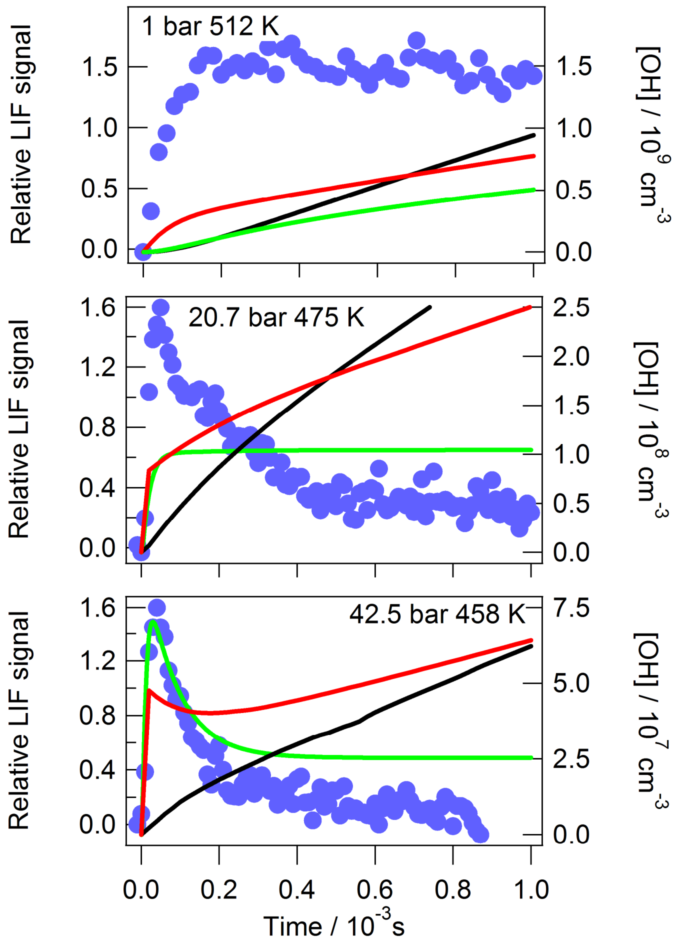


Figure 2: Measured (left axis) and modeled (right axis) OH profiles from Cl-initiated cyclohexane oxidation for three different pressure and temperature conditions. The solid black lines are predictions using the mechanism of Silke et al.[5]; the red lines are computed after modifying the cyclohexyl + O_2 reactions in the Silke et al. mechanism; the green lines are the limited mechanism of Knepp et al., with master equation calculations of the cyclohexyl + O_2 reactions for the given pressure and temperature.

4. Results and Discussion

Measured OH LIF profiles for three different pressure and temperature conditions are shown in Figure 1. The mole fractions are the same in all experiments, hence the absolute concentrations of the reactants increases with increasing pressure. The experiments show a relatively rapid production of OH after the photolysis pulse, followed by a gradual decrease, similar to that observed in the low pressure experiments of Knepp et al. [6] The decay of the OH tends to be faster at higher pressures. As in the low pressure experiments, the removal of OH is expected to be dominated by reaction with cyclohexane, which regenerates a cyclohexyl radical. The overall branching to OH product channels in the cyclohexyl + O_2 reaction was hence proposed to strongly influence the rate of decay of the OH concentration.[6] At the temperatures of the present study, the cyclohexylperoxy radical is relatively stable, and increasing collisional stabilization would be expected to reduce the production of OH in the cyclohexyl + O_2 reaction. This may provide a qualitative rationalization for the apparent pressure dependence in the OH decay.

However, detailed modeling of the experimental traces fails to fully reproduce the observations. The predictions of the mechanism of Silke et al., which do not include “formally direct” representations for chemically activated reactions, are depicted as the solid black lines in Figure 1. The predictions show a rise in OH concentration much slower than that observed experimentally. It should be noted that the present experiments are particularly sensitive to rapid production of OH, as would occur from chemically activated pathways. The photolytic initiation and the relatively quick removal of OH by cyclohexane focus the experiments on short timescales. However, although the experiment focuses on the formally direct pathways, they are inherent to the chemistry and do not depend on the method of reaction initiation.

The master equation modeling predicts a contribution from chemically activated, formally direct pathways that decreases monotonically with pressure. This decrease is less pronounced at higher temperatures, where collisional stabilization is less efficient. The master-equation-predicted rate constants at 512 K for several formally direct channels in cyclohexyl + O_2 are shown in Figure 2. The rate constants are much smaller than the rate constants for collisional stabilization, which may suggest a *prima facie* conclusion that they are insignificant in describing the initial kinetic behavior of cyclohexane oxidation. However, at least for the transient experiments reported here, the model predicts non-negligible contributions from these channels to the initial OH production. Replacing the cyclohexyl + O_2 reaction in the Silke et al. mechanism by the set of rate equations given by the master equation solution yields the predicted OH concentration shown as the solid red lines in Figure 1. At all pressures the formally direct channels give prompt OH formation, visible as a “bump” at early time, which in fact becomes more prominent at higher pressure (partly because the increasing absolute concentration of cyclohexane increases the reactive removal rate of OH).

However, the modified mechanism still fails to reproduce the experimental traces satisfactorily. It is unclear at present what the source of the discrepancy is. For comparison, the predictions of the limited mechanism used by Knepp et al.[6] are shown as the green lines in Figure 1. This mechanism accounts for only the first steps in the oxidation, but includes some chlorine chemistry absent in the detailed mechanisms. The agreement with experiment is perhaps marginally improved with this limited mechanism. Furthermore, the experimental traces are arbitrarily scaled; the predicted transient OH concentration drops more dramatically with increasing pressure than the experiments indicate. Experimental measurements under more conditions and refinement of the models will be necessary to adequately describe the system.

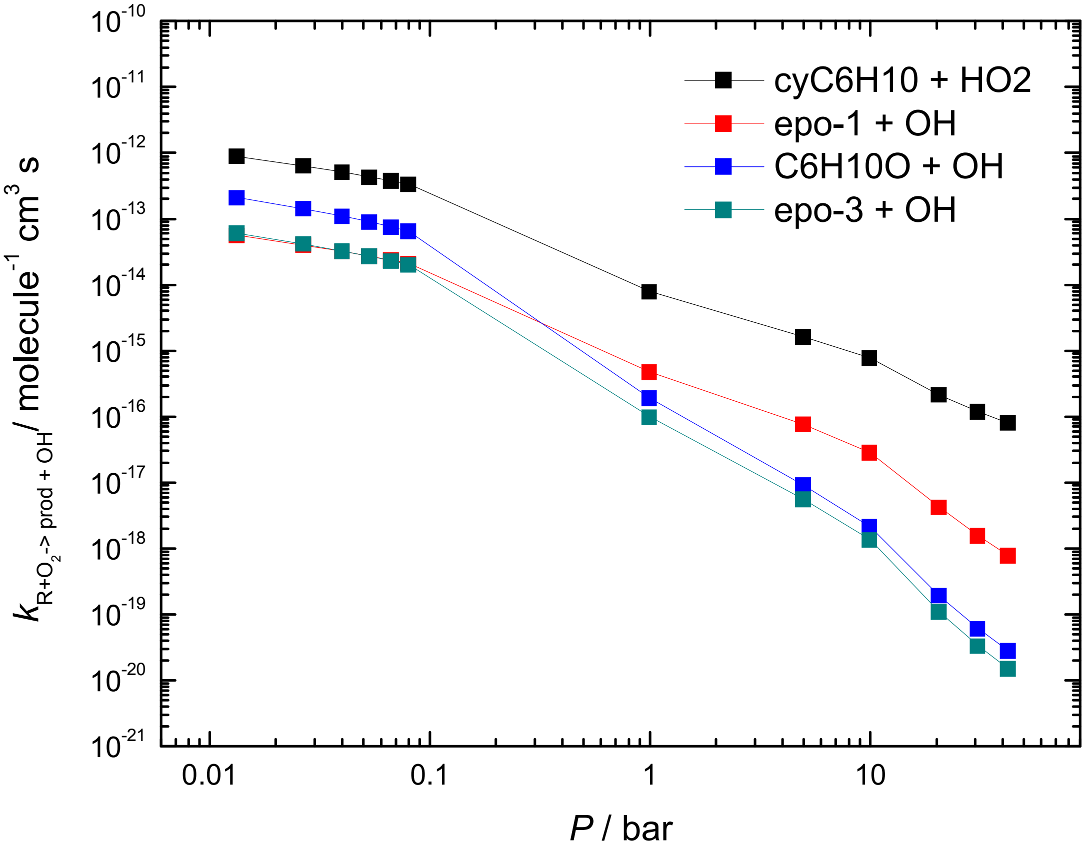


Figure 2: Pressure dependence at 500 K of formally direct product channels in the cyclohexyl + O_2 reaction, from master equation calculations. The designation cyC6H10 refers to cyclohexene, epo-1 to 1,2-epoxycyclohexane, epo-3 to 1,4-epoxycyclohexane, and C6H10O to 5-hexenal

5. Concluding Remarks

The OH production in the Cl-initiated oxidation of cyclohexane has been investigated near 500 K at pressures up to 42.5 bar. Modeling of the experiments suggests that OH formation from chemically activated species continues to play a prominent role at high pressure, but the model does not satisfactorily predict the OH profiles over the pressure range observed. Higher temperature experiments are expected to show a larger influence from chemical activation.

Acknowledgments

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