Direct Measurement of OH and HO$_2$ Formation in R + O$_2$ Reactions of Cyclohexane and Tetrahydropyran: Influence of Oxygenation in Cyclic Hydrocarbons

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Hydroxyl radical (OH) and hydroperoxyl radical (HO$_2$) formation during Cl-initiated oxidation of tetrahydropyran and cyclohexane are measured with time-resolved IR absorption in a temperature-controlled Herriott multipass cell in the temperature range of 500-750 K at 20 Torr. These experiments, which directly probe OH and HO$_2$ radicals formed from R + O$_2$ reactions, show two distinct timescales for HO$_2$ formation in the oxidation of both fuels. These timescales can be attributed to the underlying rate coefficients, which ultimately depend on the features of the potential energy surface (PES) of the R + O$_2$ reaction, but the presence of several possible reaction pathways complicates the correlation of these timescales to specific elementary kinetic steps in the formation of HO$_2$. In order to mitigate this complexity, analysis of the weighted eigenvalues of a system of kinetic equations for the key pathways is used to interpret the experimental timescales of HO$_2$ formation.

In our timescale analysis for cyclohexane oxidation, the faster timescale is strongly related to the "well-skipping" (R + O$_2$ → alkene + HO$_2$) mechanism and is expected to have, at most, a weak temperature dependence. Experimentally, we also found that the fast HO$_2$ formation timescale is nearly temperature independent below 700 K for tetrahydropyran-yl + O$_2$. However, the OH yield in the same temperature region is significantly higher for tetrahydropyran-yl + O$_2$ than for cyclohexyl + O$_2$. The higher probability of chain-propagating pathways in tetrahydropyran-yl + O$_2$ may increase competition with the HO$_2$ formation channels. The slower HO$_2$ formation timescale in cyclohexane oxidation is shown to be linked to the sequential R + O$_2$ → ROO → alkene + HO$_2$ pathway, and displays a strong temperature dependence mainly from the final step (with energy barrier ~32.5 kcal/mol). Both timescales of HO$_2$ formation are consistent with the master equation model for cyclohexane oxidation. In contrast, we found that the slower HO$_2$ formation timescale in tetrahydropyran oxidation is surprisingly temperature insensitive across all measured temperatures. This significant difference of HO$_2$ formation kinetics for the tetrahydropyran can arise from a more substantial contribution of lower activation energy pathway of tetrahydropyran-yl + O$_2$.

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