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High-pressure, low-temperature combustion chemistry: a combined experimental, theoretical, and modeling study of propane oxidation.

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High-pressure combustion chemistry is an important, yet relatively underexplored area of research. Of particular interest is the pressure dependence of reaction rate coefficients and product yields that underpins the chemical reactivity of fuels and combustion intermediates in modern internal combustion engines. A key step that governs the low-temperature ($T < 800$ K) autoignition chemistry of alkanes is the reaction of alkyl radicals (R) with O_2, leading to the isomerization of the peroxy radical (RO_2) ↔ hydroperoxyalkyl radical (QOOH). The subsequent fate of QOOH depends on the competition between unimolecular decomposition and the addition of a second O_2 molecule to form OOQOOH. Whereas the unimolecular decomposition pathways are chain propagating or chain terminating, the second O_2 addition can lead to chain branching and an increased radical yield. Because QOOH needs to be stabilized by collisions for the O_2 addition to become important, this competition is pressure-dependent. Yet, much of our understanding of chemical reactivity hinges solely on low-pressure experimental data.

We will present a coupled experimental and computational study of propane oxidation over a range of conditions relevant to internal combustion engines, i.e. pressures up to 50 bar and temperatures below 800 K. 1-propyl radicals (one of the initial species formed in propane combustion) are the smallest alkyl radicals that react in significant proportion via pathways involving QOOH and the second O_2 addition. Owing to its relatively small size, the propyl + O_2 system is well-suited to accurate theoretical treatment and therefore serves as a benchmark for understanding low-T autoignition reactions. On the experimental side, we form the 1- and 2-propyl radicals by photolytically-generated Cl atom attack on propane and probe the subsequent OH radical production in an excess of O_2 by time-resolved laser-induced fluorescence. The observed OH time profiles show a complex temperature- and pressure-dependent competition of prompt (i.e., well-skipping) and slower, sequential OH formation pathways. We interpret the experimental results with the help of high-level quantum chemical calculations and RRKM-based master equation methods. The predicted rate coefficients for the individual reaction steps are incorporated into a chemical mechanism that includes the O_2 + QOOH addition and the OOQOOH decomposition pathways as well as secondary chemistry.

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