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Probing the low-temperature chain-branching mechanism of *n*-butane autoignition chemistry *via* time-resolved measurements of ketohydroperoxide formation in photolytically initiated *n*-C₄H₁₀ oxidation

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Abstract

Ketohydroperoxide formation in Cl-atom initiated low-temperature (550–700 K) oxidation of *n*-butane was investigated using a time-of-flight mass spectrometer and either tunable synchrotron radiation or a H₂ discharge for photoionization. Experiments were performed at 1–2 atm pressure using a new high-pressure reactor and also at ~5 Torr pressure for comparison. Direct kinetic observations of ketohydroperoxide formation qualitatively agree with previous atmospheric pressure jet-stirred reactor studies of Battin-Leclerc et al. (*Angew. Chem. Int. Ed.*, 49 (2010) 3169–3172) where the maximum ketohydroperoxide signal was observed near 600 K. Oxidation of partially deuterated *n*-butanes provided additional information on the QOOH radical intermediates that proceed to form ketohydroperoxides. The photoionization spectrum of the observed ketohydroperoxide is independent of pressure and is the same when using different deuterium substituted *n*-butanes, suggesting that one ketohydroperoxide isomer dominates in *n*-butane oxidation. We conclude that 4-hydroperoxy-2-butyl + O₂ is the main reaction leading to ketohydroperoxide and 3-hydroperoxybutanal is the sole ketohydroperoxide that is observed.

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1. Introduction

The development of high-efficiency and low-emission engine technologies such as homogeneous charge compression ignition (HCCI) relies heavily on understanding the autoignition chemistry of a premixed fuel–air charge. Combustion phasing and heat release rates in HCCI engines

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are largely determined by the fuel-specific chemical kinetics of autoignition [1]. For the reliable modeling of autoignition it is essential to describe the kinetics and mechanisms of alkyl radical + O₂ reactions, requiring extensive theoretical and experimental effort [2]. Time-resolved measurements of pulsed laser-photolytically initiated fuel radical + O₂ reactions can distinguish between well-skipping (e.g., chemical activation) and sequential pathways. The recent construction of a multiplexed photoionization mass spectrometer (MPIMS) [3] extends the range of products that can be monitored in time-resolved experiments. When combined with tunable synchrotron radiation for ionization, this method can also reveal the isomeric structures of reaction products.

A recent milestone in the field of autoignition chemistry has been the observation of ketohydroperoxides by Battin-Leclerc et al. [4,5] in jet-stirred reactor (JSR) measurements of low-temperature (~600 K) *n*-butane oxidation using time-of-flight mass spectrometry and tunable synchrotron radiation. Because ketohydroperoxides are intermediates in low-temperature chain branching, knowledge of their formation and decomposition chemistry is essential for accurate ignition modeling [6]. In this article we present direct time-resolved measurements of ketohydroperoxide formation in high-pressure ($p_{\max} \sim 2$ atm) pulsed-photolytic Cl-initiated *n*-butane oxidation experiments, performed using the MPIMS with a new high-pressure reactor.

Abstraction of a hydrogen atom from *n*-butane by Cl atoms forms both 1-butyl and 2-butyl radicals. For the subsequent 1-butyl + O₂ and 2-butyl + O₂ reactions several channels are open in the 550–700 K range investigated in the current work (see Fig. S1). In this temperature range the butylperoxy radicals, RO₂, become thermally unstable and can either decompose back to the reactants, isomerize to form a QOOH radical *via* internal H-abstraction, or decompose to bimolecular products [7]. In *n*-butane oxidation the highest-yield decomposition channel leads to 1- or 2-butene + HO₂, which is effectively a chain-terminating channel below ~900 K. Chain-propagating channels lead to OH + cyclic ether *via* unimolecular decomposition of QOOH radicals (QOOH(1)–QOOH(6) in Fig. S1). In competition with this decomposition, carbon-centered QOOH radicals can react with a *second* oxygen molecule, and, after internal H-abstraction and dissociation, form OH and a labile ketohydroperoxide (KHP), QOOH + O₂ → KHP + OH (e.g., Scheme 1). KHPs are relatively stable at lower temperatures, but due to their weak O–O peroxide bond, start to decompose at moderate temperatures, forming OH and an oxy radical. The overall chain-branching process, QOOH + O₂ → KHP + OH → 2 OH + oxy radical, is critical in the first stage of autoignition [6].

2. Experimental

Both low-pressure ($p \sim 5$ Torr) and high-pressure ($p \sim 1$ –2 atm) reactors (abbreviated as LPR and HPR), interfaced with the MPIMS, were employed in this study. The oxidation was initiated by pulsed-photolytic production of Cl atoms (351-nm dissociation of Cl₂ in the LPR or 193-nm dissociation of CFCl₃ in the HPR), which then react with *n*-butane in the presence of O₂ with He as the bath gas. The LPR has been described before [3]; briefly, it consists of a 60 cm-long uncoated quartz tube of 1.05 cm inner diameter with the photolysis laser propagating along its axis and a ~650 μm sampling pinhole located in the sidewall. The HPR is an Inconel flow cell (inner diameter: 0.5 cm, length: 4 cm), suitable for pressures up to 100 atm at temperatures up to 1000 K. A fused silica window at the front wall of the reactor provides optical access for the photolysis laser, and an interchangeable sampling orifice is positioned in the center of the opposite end wall. The pinhole size is selected based on the experimental pressure in order to maintain appropriate sample flow into the mass spectrometer; the experiments described here used a 100 μm-diameter orifice. Diffusion is rather slow at the elevated pressures used in the HPR; therefore, we take care to uniformly illuminate the entire sample volume with the photolysis laser. The reactor geometry is designed to achieve laminar plug flow along the reactor length, and the sample volume is refreshed completely between successive laser shots. In several experiments we protected the metal inner surfaces of the reactor with a quartz insert to provide a more chemically inert surface around the reaction mixture.

The sampled molecular beam from the reactors is skimmed and intersected by ionizing vacuum ultraviolet (VUV) radiation from the Advanced Light Source (ALS) synchrotron. Some experiments were also performed using radiation from a H₂-discharge lamp, which although nominally at 10.2 eV, contains a broad range of photon energies. Ionized species were mass-separated using an orthogonal-acceleration time-of-flight mass spectrometer, and full mass spectra were taken at 20 μs intervals, providing near-simultaneous (i.e., multiplexed) detection of all masses up to $m/z = 156$. In order to obtain more information on the isomeric nature of reaction products, photoionization spectra were measured by scanning the energy of the ionizing synchrotron radiation. Procedures described previously [7] were used to obtain product branching ratios. In order to identify specific pathways, experiments were also performed using partially deuterated *n*-butanes, CH₃CD₂CD₂CH₃ and CD₃CH₂CH₂CD₃.

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