

PRF Grant Number: 56901

Project Title: Spectroscopy and Kinetics of the Combustion Radical Intermediate QOOH

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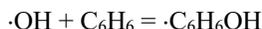
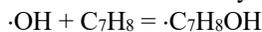
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NARRATIVE

In the combustion of hydrocarbon and related oxygenated fuels, peroxy radicals are ubiquitous. In addition to the bimolecular reactions they may undergo, they can also isomerize via hydrogen transfer to form ‘QOOH’ intermediates – hydroperoxy-alkyl radicals. These short-lived species can subsequently react with O₂ to form ·OOQOOH or further isomerize and are key intermediates in hydrocarbon oxidation. Despite extensive experimental and theoretical studies on this chemistry, there has been only one experimental detection of a QOOH species, and our knowledge of ·QOOH and ·OOQOOH remains poor. Our goal is to detect ·QOOH radicals by mid-IR Cavity Ringdown Spectroscopy (CRDS) and photodissociation-mediated action spectroscopy. Our multipronged approach will provide definitive detection of these species and open the door to a fuller mechanistic understanding of hydrocarbon oxidation.

During the past year, we have successfully formed and detected the related hydroxylated radicals, highly reactive resonance-stabilized ·ROH radicals. Specifically, we have detected the radical adducts ·ROH formed from the association reactions of ·OH with toluene and benzene by mid-IR CRDS. These species serve as prototypes for QOOH and have allowed us to demonstrate the sensitivity and feasibility of our approach.

The oxidation of toluene and benzene are also important reactions in fuel combustion chemistry, since these aromatics are significant constituents of gasoline. Initial oxidation by OH at high pressures form the radical adducts ·ROH:



Like QOOH, these adducts have unique signatures in both the mid-IR (hydroxyl stretch) and are predicted to absorb in the visible/UV as well. At high O₂ concentrations, they will further associate to form ·OOQOOH peroxy radicals. **This work is the first spectroscopic detection of these long-predicted hydroxy-aromatic adducts and represent an important step in our understanding of combustion chemistry.**

We formed the ·ROH adducts in a flow cell from the reactions between the hydroxyl radical (OH) and the relevant aromatic species in buffer gas. OH was formed by the 248 nm pulsed photodissociation of trace of O₃, which formed O(¹D), and the subsequent reaction of O(¹D) with H₂. We then detected the OH stretch vibration by CRDS aligned along the reactor axis, within the first few ms of reaction.

The IR spectra of the hydroxy-methyl-cyclohexadienyl radical, formed from the addition of the hydroxyl radical to the aromatic ring of toluene, can be seen in Figure 1. The analogous hydroxy-cyclohexadienyl radical formed from addition of OH to benzene is shown in Figure 2. From modeling of the chemistry, we infer that no other hydroxyl-bearing products are formed in the timescale of our detection.

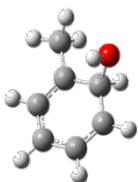
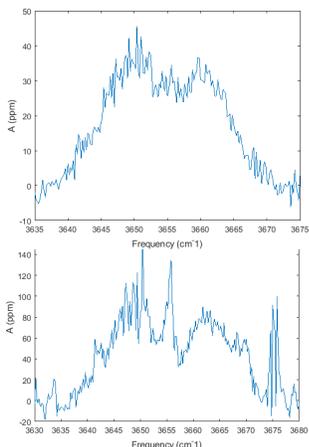


Figure 1: Preliminary spectrum of the OH stretch band of the OH=toluene radical adduct.



Figure 2. Preliminary spectrum of the OH stretch band of the OH-benzene radical adduct.

As can be seen, partially resolved rotational sub-bands can be observed. To further confirm our observations, we performed ab initio calculations coupled with spectral simulations to predict the band contours. Our predictions are in good agreement in the case of benzene adduct. However, for toluene, we expect multiple isomers depending on the location of OH attack (meta, ortho, para and ipso – H-abstraction to form benzyl radical is low in yield and will not lead to hydroxylated radical formation).

Like QOOH, these are resonance-stabilized hydrocarbon radicals that are predicted to have strong transitions in the visible or near-UV. We have performed ab initio calculations to predict the location of the vertical optical transitions, and will use high reflectivity mirrors in the visible/UV to detect these spectra by dye-laser CRDS. These measurements will provide additional confirmation of our detection of these radicals.

We have also upgraded the temperature control cell for this instrument. These upgrades have raised the maximum temperature of the flow cell from 80 °C to over 130 °C, where QOOH formation is enhanced. This temperature cell will be used to obtain the first temperature dependent rate constants of QOOH formation and its subsequent chemistry.

We continued reassembling our IR-action spectrometer. In this apparatus, as described in the proposal, we detect QOOH using vibrationally-mediated photodissociation spectroscopy by detecting OH products from the photodissociation of the QO-OH bond. This technique has previously been used by our group to observe the first overtone of the –OH stretch of HOONO [4]. We have recently acquired high repetition rate lasers ideal for detecting kinetics with LIF. Graduate student Ai leen Hui has also developed a mid-IR laser system for detecting OH radicals using wavelength modulation spectroscopy, which provides an alternate means for detecting OH. Graduate student Elizabeth Lunny has been exploring the feasibility of using photoacoustic spectroscopy.

FUTURE WORK

•ROH Spectroscopy. We are in the process of improving our signal-to-noise on the IR spectra of these species. We will then switch to detect the predicted visible transitions. Finally, addition of O₂ will allow us to detect the subsequent formation of the -OOROH peroxy radicals through their unique near-IR transitions. A manuscript will then be prepared for submission.

QOOH spectroscopy. We will then search for spectra of the resonance-stabilized QOOH species. We will begin by forming QOOH from the photolysis and subsequent oxidation of 5-iodo-1,3-cycloheptadiene. We will then use the approaches used for the ROH spectroscopy to search for visible and IR (OO-H stretch) spectra of QOOH, as well as implementing the action spectroscopy. We will also explore forming QOOH through the reaction of OH or atomic chlorine with stable alkyl hydroperoxides. In particular, we will look at the reaction between Cl and tert-butyl hydroperoxide, where 20% of the reaction leads to the formation of QOOH [4]. This system has previously been attempted, but they were unable to directly detect the QOOH compound by photoionization, because the parent ion isomerize, resulting in poor Franck-Condon factors. Instead, in this work, we will target the -CH₂ stretch in the MIR, as well as the visible transition, as unique signatures of this QOOH.

IMPACT

The work to date has introduced our group to the chemistry of free radicals in combustion. We have discovered new intermediates in the initial steps of aromatic oxidation, important in fuel chemistry, and have demonstrated the feasibility of our approach for our next step, the search for QOOH intermediates. We plan to use results as proof of principle experiments for upcoming proposals to NSF and DOE, to be submitted in the next six months. The team of graduate and undergraduate students have developed expertise in free radical chemistry, high sensitivity spectroscopy, quantum chemical calculations of highly fluxional radicals, and chemical modeling. Two undergraduate students have been exposed to experimental methods in physical chemistry.