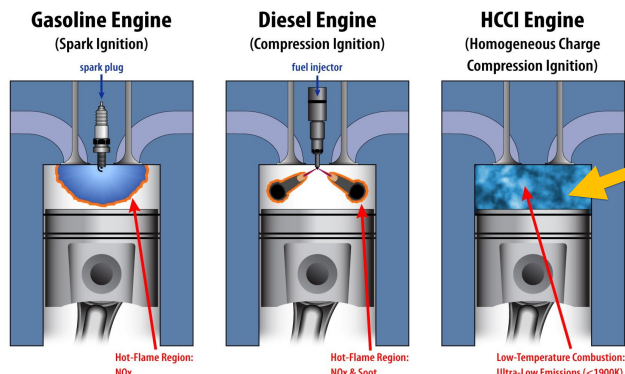


# Direct Observation and Kinetics of a Hydroperoxyalkyl Radical (QOOH)

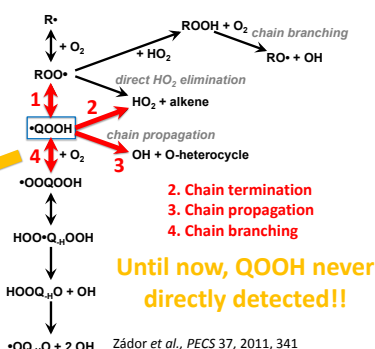
John D. Savee, Ewa Papajak, Brandon Rotavera, Haifeng Huang, Arkke J. Eskola, Oliver Welz, Leonid Sheps, Craig A. Taatjes, Judit Zádor, David L. Osborn

Four decades of research show that the QOOH intermediate plays an important role in autoignition

New clean efficient engine strategies depend on controlling autoignition chemistry

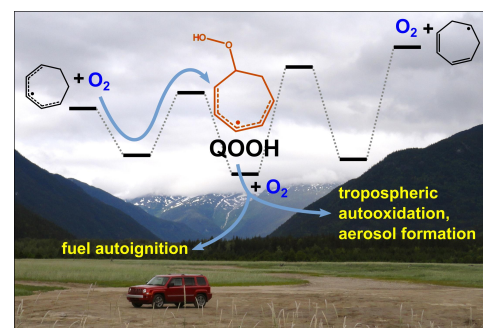


Manley et al., *Physics Today*, November 2008, 47–52

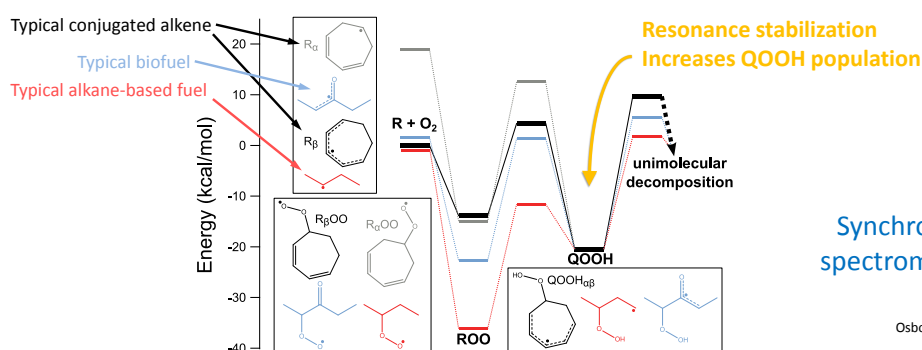


Zádor et al., *PECS* 37, 2011, 341

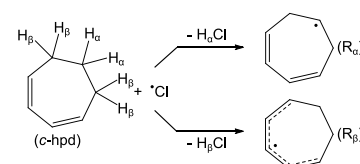
Autoignition and tropospheric oxidation driven by similar chemistry



Energy landscape illustrates why QOOH is hard to detect:



1,3-cycloheptadiene allows exploration of a system with varying influence from resonance stabilization



Synchrotron photoionization mass spectrometry allows isomer-resolved probe of reaction

Osborn et al., *Rev. Sci. Instrum.* 79, 2008, 104103

Direct Kinetics of  $R + O_2$  and  $QOOH + O_2$

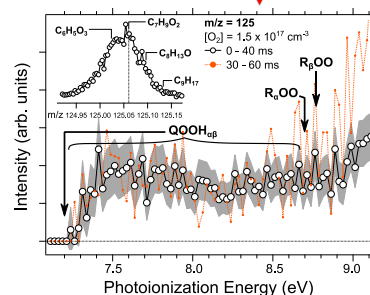
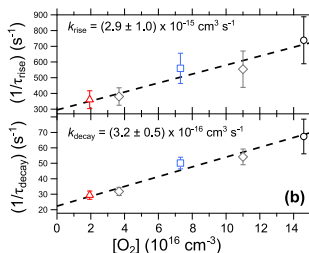
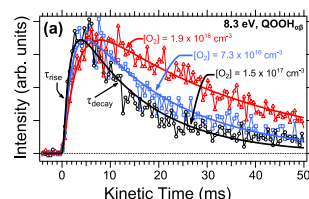
Savee et al., *Science* 347, 2015, 643

Product Identification

Direct observation of time-dependence of QOOH yields its reactivity with  $O_2$

Very long QOOH lifetime due to resonance stabilization

$QOOH + O_2$  is 10 times faster than  $R + O_2$  – will influence modeling



ROO and QOOH have the same chemical formula ( $C_7H_9O_2$ )

Photoionization spectrum, exact mass, and quantum chemical calculations allow unambiguous assignment as QOOH

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Exceptional service in the national interest

