Uncovering Fundamental Autoignition Chemistry: – Synchrotron PIMS Measurements of Product Formation in Low-Temperature Isobutane Oxidation

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Introduction

- Autoignition chemistry plays crucial role in the development of modern, high-efficiency, low-emission HCCI engine technologies

- Isooctane is both important reference fuel and a constituent of gasoline. Its decomposition leads to t-butyl (t-C_4H_9) and i-butyl (i-C_4H_9) radicals; their oxidation chemistry in temperature range 575 K – 700 K is subject of the current work

- Whereas t-C_4H_9 + O_2 reaction leads in practice exclusively to i-butene + HO_2, other product channels are open for i-C_4H_9 + O_2 reaction, of which especially interesting for autoignition chemistry are those leading to OH + cyclic ethers via QOOH intermediate
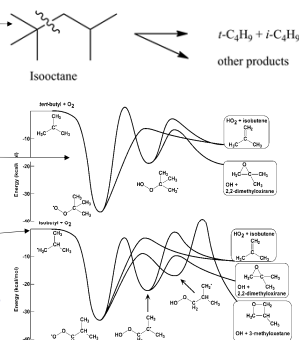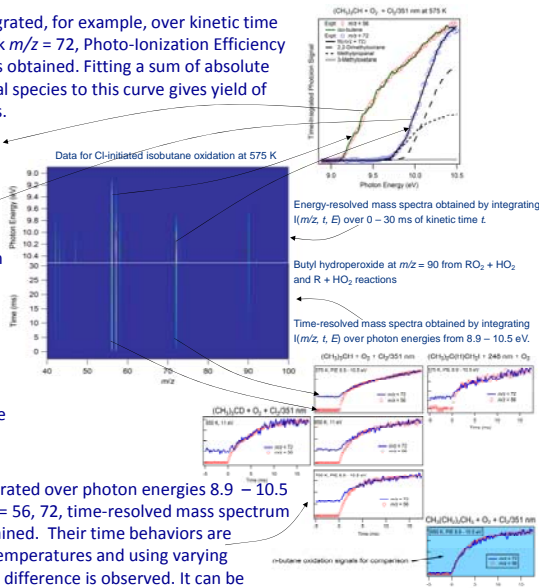
Experimental

- Radical chemistry is initiated by eximer laser photolysis of a photolytic reactant along a reactor tube; reactant-mixture is sampled *via* small hole on the wall of the tube and a beam formed into a vacuum is intersected by ionizing VUV synchrotron light; ions formed are mass-separated using orthogonal-acceleration time-of-flight mass spectrometer

- Whole mass-range is mass-separated at 50 kHz, providing simultaneous detection of all masses with high sensitivity due to single-ion counting

- Isomer-resolved detection (here we are especially interested in identities of species at m/z = 72) is accomplished by performing single-energy measurements, I(m/z, t), as a function of VUV-photon energy employing ALS-synchrotron, producing I(m/z, t, E). I(m/z, t, E) can then be integrated in several ways.
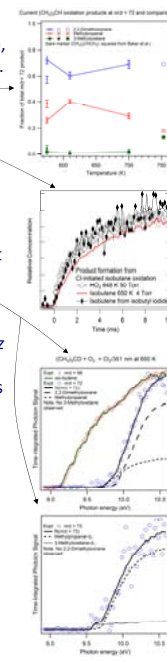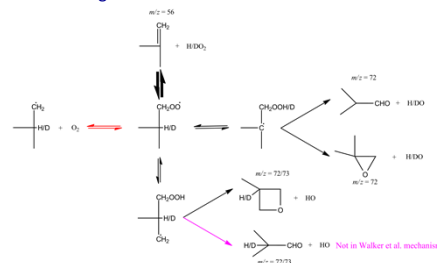
Results

- When I(m/z, t, E) is integrated, for example, over kinetic time 0 – 30 ms and mass peak m/z = 72, Photo-Ionization Efficiency (PIE) curve of m/z = 72 is obtained. Fitting a sum of absolute PIE spectrum of potential species to this curve gives yield of each isomer at this mass.

- The strong signal at m/z = 56 corresponds solely to isobutene, i-C_4H_8.

- However, at m/z = 72 several compounds containing oxygen atom are observed. Product of highest yield is 2,2-dimethyloxirane, methylpropanal also giving significant contribution, whereas yield of 3-methyloxetane is small.

- When I(m/z, t, E) is integrated over photon energies 8.9 – 10.5 eV and mass peaks m/z = 56, 72, time-resolved mass spectrum at these masses are obtained. Their time behaviors are compared at different temperatures and using varying photolytic sources. Clear difference is observed. It can be explained using a methodology of "prompt" vs. thermal product formation. Contribution of "prompt" vs. thermal product formation is more significant at m/z = 56 than at m/z = 72. Note a clear difference between i-butane and n-butane.

Data for CI-initiated isobutane oxidation at 575 K

Energy-resolved mass spectra obtained by integrating I(m/z, t, E) over 0 – 30 ms of kinetic time t.

Butyl hydroperoxide at m/z = 90 from RO_2 + HO_2 and R + HO_2 reactions

Time-resolved mass spectra obtained by integrating I(m/z, t, E) over photon energies from 8.9 – 10.5 eV.

n-butane oxidation signals for comparison.

Discussion and Comparison

- Current results are in good agreement with those from the work of Walker et al. (J. Chem. Soc. Faraday Trans. 1, 74 (1978), 2229), as can be seen for the isomeric composition at m/z = 72.

- Similarly, current i-butene formation kinetics are in good agreement with previous results from this lab for the companion product, HO_2.

- Mechanism proposed by Walker et al. (see below) seems to explain fairly well current results. However, a few measurement was performed using $(CH_3)_3CD$ precursor and results obtained for methylpropanal formation do not agree with Walker et al. mechanism. Note that methylpropanal is not observed as a direct QOOH decomposition product in *ab initio* calculations. Current measurements observe methylpropanal formation both at m/z = 72 and 73, while according to Walker et al. mechanism, methylpropanal should not be formed at m/z = 73 at all. Probably reaction barrier for 4-centre hydrogen abstraction mechanism, as proposed below, is smaller than has been thought before.