

## Uncovering Fundamental Autoignition Chemistry: Synchrotron Photoionization Mass Spectrometry Measurements of Product Formation in Low-Temperature Isobutane Oxidation

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Product formation in laser-photolytic Cl-initiated low-temperature (550 K – 700 K) oxidation of isobutane was investigated by tunable synchrotron photoionization time-of-flight mass spectrometry in a slow-flow reactor at low pressure (4 Torr). These experiments probe the time-resolved formation of products following laser-photolytic initiation of the oxidation, and identify isomeric species by their photoionization spectra. The main oxidation products were observed at  $m/z = 56$  ( $C_4H_8$ ) and  $72$  ( $C_4H_8O$ ), whose accompanying products are  $HO_2$  and  $OH$ , respectively. Isobutene was the sole  $C_4H_8$  isomer observed, whereas several isomers contribute to the  $C_4H_8O$  product spectrum. The relative yields of these oxygenated product isomers (2,2-dimethyloxirane, methylpropanal, and 3-methyloxetane) are in reasonable concord with measurements from Walker and coworkers (1) at higher temperature. Oxidation of isotopically labeled isobutane,  $(CH_3)_3CD$ , suggests that methylpropanal formation can proceed from both  $(CH_3)_2CCH_2OOH$  and  $CH_3CH(CH_2)CH_2OOH$  hydroperoxyalkyl (QOOH) isomers. Bimodal time behavior is observed for the formation of both isobutene and the  $C_4H_8O$  products; the initial prompt formation reflects “formally direct” channels, principally chemical activation, and the longer-timescale “delayed” component arises from dissociation of thermalized peroxy (ROO) and QOOH radicals. The proportion of prompt to delayed signal is smaller for the oxygenated products than for the isobutene product. This channel-specific behavior can be qualitatively understood by considering the different energetic distributions of ROO and QOOH in formally direct vs. thermal channels and the fact that higher-entropy transition states involved in the formation of oxygenated products are “tighter” than that for isobutene formation.

### References

(1) Baker, R.R.; Baldwin, R.R.; Walker, R.W. *J. Chem. Soc. Faraday Trans. 1*, **1978**, 74, 2229-2251.

### Acknowledgements

This work was supported as part of the Saudi Aramco “Kinetics Cluster of Excellence” under a cooperative research and development agreement (CRADA) between Sandia National Laboratories and Aramco Services Company, a U.S.-based subsidiary of Saudi Aramco, the state-owned national oil company of Saudi Arabia (CRADA SC10/01773.00, ASC Contract No. 6500007287). Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.