

A High-Temperature Shock Tube Kinetic Study for the Branching Ratios of Isobutene + OH Reaction

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Isobutene ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$) is the smallest branched alkene which appears as an important intermediate specie during the combustion of larger-chain branched alkanes. Isobutene is also produced in large concentration during the pyrolysis and oxidation of methyl-tert-butyl-ether (MTBE) and ethyl-tert-butyl-ether (ETBE). Both of these ethers are widely used for gasoline reformulation to boost the octane number. The chemistry of isobutene is an essential component of the chemical kinetic mechanisms of large hydrocarbons and oxygenated fuels. Therefore, it is crucial to understand the oxidation pathways of isobutene for the hierarchical development of detailed chemical kinetic models.

In this work, we measured the rate coefficients for the reaction of OH radicals with isobutene behind reflected shock waves over the temperature range of 830 – 1289 K and pressures near 1.5 atm. We followed the reaction progress by measuring mole fraction of OH radicals near 306.7 nm using UV laser absorption technique. In a similar way, we measured the rate coefficient of the reaction of OH radicals with three deuterated isotopes of isobutene, namely isobutene-1-d2 ($\text{D}_2\text{C}=\text{C}(\text{CH}_3)_2$), isobutene-3-d6 ($\text{H}_2\text{C}=\text{C}(\text{CD}_3)_2$) and isobutene-d8 ($\text{D}_2\text{C}=\text{C}(\text{CD}_3)_2$). Using these measured rate constants, we deduced branching ratios of the allylic and vinylic H-abstraction channels from isobutene by OH radicals. Our results revealed that H-abstraction from the allylic site is the dominant reaction pathway, and that it constitutes about 80% of the total rate in the entire temperature range of this work. Our experimentally determined branching ratios are in good agreement with the recent theoretical work of Zhou et al. (1).

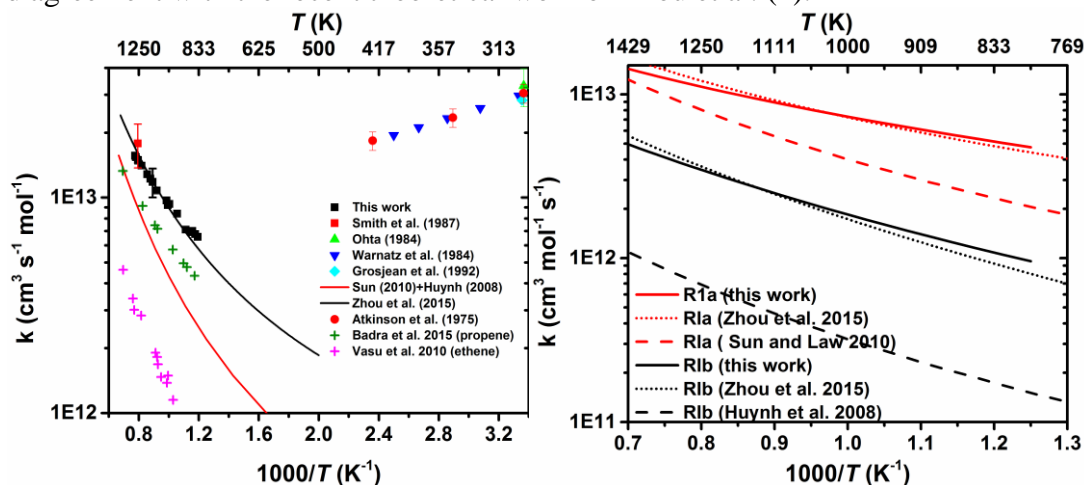


Figure: Left: Rate coefficients for isobutene + OH; data for propene + OH and ethane + OH are also shown. Right: Rate coefficients for the allylic (R1a) and the vinylic (R1b) H-abstraction channels of isobutene + OH.

References:

- (1) Zhou, C.-W... Curran, H. J., A comprehensive experimental and modeling study of isobutene oxidation. **2016**. In press, Combust. Flame.