

QOOH-MEDIATED REACTIONS IN CYCLOHEXENE OXIDATION

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Multiplexed photoionization mass spectrometry (MPIMS) is utilized to examine reaction mechanisms of QOOH radicals derived from cyclohexene, a primary intermediate in low-temperature oxidation of cyclohexane, in order to assess the influence of a single C=C bond in a cyclic hydrocarbon on reactions relevant to chain-branching. The experiments were conducted using Cl-initiated oxidation at 10 Torr and from 500 to 700 K; [O₂] remained fixed at 3 · 10¹⁶ cm⁻³. To complement the experiments, *ab initio* calculations of saddle point energies on the potential energy surfaces (PES) of cyclohex-1-en-3-peroxy and cyclohex-1-en-4-peroxy were conducted at the CBS-QB3 level of theory. In total, saddle point energies for 32 pathways were calculated across four surfaces, accounting for axial/equatorial conformers of ROO. The main results from the experiments and calculations include:

- i. Ketohydroperoxide formation is identified by exact mass measurements (m/z 128.047, C₆H₈O₃). Notably, the measured photoionization spectra are nearly identical to those of analogous species formed in *n*-butane and cyclohexane oxidation. Saddle point energy calculations reveal that, relative to the equivalent pathway in cyclohexane oxidation, resonance-stabilization in the γ -QOOH radical cyclohex-1-en-3-yl-5-hydroperoxy lowers the barrier for ROO → QOOH isomerization by 8.3 kcal/mol, yet increases the barrier for QOOH unimolecular decomposition by a similar amount. The net effect is facilitation of QOOH + O₂ reactions and subsequent ketohydroperoxide formation, evident by the observation of C₆H₈O₃ despite [O₂] of only ~10¹⁶ cm⁻³, approximately 10² lower than in prior measurements of ketohydroperoxide formation in *n*-butane and cyclohexane oxidation. The same effect also occurs for resonance-stabilized β -QOOH.
- ii. Isomeric ratios of 1,3-cyclohexadiene and 1,4-cyclohexadiene were quantified. At 500 K, most chain-inhibiting HOO formation via R + O₂ arises from the alkylic radical of cyclohexene (cyclohex-1-en-4-yl) forming 1,4-cyclohexadiene. However, at 600 K, pathways leading to 1,3-cyclohexadiene become favored and at 700 K the latter becomes the only isomer formed.
- iii. Co-products from chain-propagating OH-formation via QOOH decomposition were measured directly, including 3,4-epoxycyclohex-1-ene and 4,5-epoxycyclohex-1-ene. Evidence for QOOH ring-opening to hexa-3,5-dienal is also observed experimentally and supported by adiabatic ionization energy calculations. Other products from ring-opening reactions were identified, including ethene, formaldehyde, 1,3-butadiene, acrolein, and 3-butenal, and potential reaction mechanisms are postulated.

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