Kinetics of thermal oxidations between allyl and propargyl radicals with molecular oxygen

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Reactions of allyl and propargyl radicals with molecular oxygen were investigated using electronic structure theory, transition state theory, and the RRKM - Master Equation approach. Thermochemical properties of $C_3H_3^{\bullet}$ (propargyl) and $C_3H_5^{\bullet}$ (allyl) oxidation were obtained from potential energy surfaces constructed using CCSD(T)-F12/cc-pVTZ-f12//ωB97XD/6-311G** + ZPE(ωB97XD/6-311G**) composite quantum chemistries. Temperature- and pressure-dependent rate coefficients of thermal oxidations were calculated from ab initio results to evaluate the kinetics of various reaction paths. Quantum chemistry calculations indicate that oxidations of allyl and propargyl radicals are initiated by reversible O_2 addition to form energized peroxy adducts, R-OO$^{\bullet}$, which then proceed along cyclization and isomerization reaction channels. Subsequent hydrogen migrations in cyclization paths of propargyl form the stable adduct (CH2CCH-OO$^{\bullet}$) observed by Douberly[1] and coworkers. Major products identified in thermal oxidations of propargyl, ketene, and the formyl radical, are consistent with experimental results reported by Slagle and Gutman[2]. The thermal oxidation of allyl is also dominated by hydrogen migrations, which undergo beta scission, forming ketene and formaldehyde as stable hydrocarbon combustion products.

References

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