

Oxidation of five-member rings in combustion

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Ab initio calculations of potential energy surfaces in conjunction with the RRKM-Master Equation theoretical approach have been employed to evaluate temperature- and pressure-dependent total and product specific rate constants and product branching ratios for unimolecular thermal decomposition of 2,4-cyclopentadienone C_5H_4O and for the $C_5H_4O + H$ and $C_5H_5 + O$ reactions. The formation of the cyclobutadiene + CO products via a ring contraction/CO elimination mechanism is shown to be the prevailing channel for the unimolecular decomposition of C_5H_4O . The unimolecular reaction is found to be relatively slow, but decomposition of cyclopentadienone can be greatly facilitated through bimolecular encounters with H atoms. The $C_5H_4O + H$ reaction is predicted to be fast, with rate constants ranging from 4.6×10^{-12} to 1.8×10^{-10} cm^3 molecule⁻¹ s⁻¹ at $T = 500$ - 2500 K and finite pressures. Cyclic C_5H_5O intermediates formed after the initial H addition undergo ring openings by β -scissions and then decompose to either butadienyl $C_4H_5 + CO$ or 1-oxoprop-2-enyl $H_2CCHCO + C_2H_2$, which are respectively predicted as the major and the minor reaction products. The calculations predict that thermal decomposition of the *ortho* and *meta* C_5H_5O radicals as well as pyranyl nearly exclusively forms the $C_4H_5 + CO$ products, whereas decomposition of hydroxycyclopentadienyl C_5H_4OH predominantly produces cyclopentadienone + H. The $C_5H_5 + O$ reaction is shown to proceed by barrierless oxygen addition to the ring followed by fast H migration, ring opening, and dissociation to $C_4H_5 + CO$. The $C_5H_5 + O$ rate constant is calculated to be close to 1×10^{-10} cm^3 molecule⁻¹ s⁻¹ and to be pressure-independent and nearly independent of temperature. Modified Arrhenius expressions for rate constants for all considered reactions at the high-pressure limit and at finite pressures are generated for kinetic modeling.