Pressure Dependence of the Decomposition of *n*-Pentyl Radicals near 1000 K

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Alkyl radicals are important intermediates in the combustion of hydrocarbon fuels and an understanding of their behavior is needed over a wide range of pressures and temperatures. The decomposition and intramolecular H-transfer isomerization reactions of the 1-pentyl radical have been studied over an extended pressure range in joint shock tube studies carried out at the National Institute of Standards and Technology (NIST) and the University of Illinois. Experiments were performed in an argon bath gas at temperatures between 850 K and 1070 K and pressures of 80 kPa to 680 kPa (NIST) and 2300 kPa to 5000 kPa (University of Illinois). 1-pentyl radicals are generated by shock heating dilute mixtures of 1-iodopentane and the stable olefin products of its decomposition observed by post-shock gas chromatographic analysis. Ethene and propene are the main olefin products and account for > 97% of the carbon balance from the 1-pentyl radical. The ethene/propene ratio can be can be related to the concentrations of 1-pentyl and 2-pentyl radicals in the system and the relative rates of 5-center intramolecular H-transfer reactions and beta C-C bond scissions. 3-pentyl radicals, formed via four-center intramolecular H transfers, lead to 1-butene and play only a very minor role in the system. Beta C-H bond scissions in the radical intermediates are likewise of minor importance. Ethene/propene product ratios are temperature and pressure dependent and vary from about 3 to 7 over the experimental conditions. The ratio appears to approach high pressure limiting values at the highest pressures studied. A consistent kinetics model that reproduces the observed branching ratios and pressure effects has been developed on the basis of the present experiments, a Rice Ramsberger Kassel Marcus/Master Equation (RRKM/ME) analysis, computational chemistry results, and relevant experimental literature data from lower temperatures. If an exponential-down model is employed for energy transfer, the results require a value of $<\Delta E_{down}(1000 \text{ K})> = (675 \pm 100) \text{ cm}^{-1}$ for the average energy transferred in deactivating collisions in an argon bath gas. The present model can be used to extrapolate the results over a wide range of conditions of interest.