

Crossed Molecular Beam Studies of Phenyl Radical Reactions with Propene and 2-Butene

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Abstract

The reaction of phenyl radicals with propene has been studied at collision energies of 84 and 108 kJ/mol using the crossed molecular beams technique. The branching ratios between methyl radical elimination forming C_8H_8 , and H-atom elimination forming C_9H_{10} , were found to be 10:1 at 84 kJ/mol and 3:1 at 108 kJ/mol. By using “soft” vacuum ultraviolet photoionization at 9.9 eV for product detection, we were able to observe both product channels with negligible fragmentation of C_9H_{10} to $C_8H_8^+$. In agreement with a recent study, we find that the contribution of C_8H_8 decreases as the collision energy increases. However, we find at both collision energies that the formation of C_8H_8 is more significant than the results of a previous study and its RRKM predictions. In the case of phenyl radical reaction with propene, addition to the C=C bond can occur at either the 1- or 2- positions, leading to different products. However, a low-energy isomerization pathway can interconvert the two intermediates. For comparison, we have also studied the reaction of phenyl radicals with trans-2-butene at a collision energy of 97 kJ/mol. In this case, the symmetry of trans-2-butene allows for only one addition site, which is similar to the beta addition intermediate in phenyl radical reactions with propene. We only observe methyl elimination in the reaction with 2-butene, implying that in the propene reaction all of the H-atom elimination products are generated from decomposition of the alpha addition intermediate.