

Products distribution in the reaction of atomic carbon with pyridine: theory and experiment

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We investigated the reaction of atomic carbon ($C; {}^3P_j$) with pyridine ($C_5H_5N; X^1A_1$) at a collision energy of $34 \pm 4 \text{ kJ mol}^{-1}$ utilizing the crossed molecular beams technique. Forward-convolution fitting of the data was combined with high-level electronic structure calculations and statistical (RRKM) calculations on the triplet C_6H_5N potential energy surface (PES). These investigations reveal that the reaction dynamics are indirect and dominated by large range reactive impact parameters leading via barrier-less addition to the nitrogen atom and to two chemically non-equivalent 'aromatic' carbon-carbon bonds forming three distinct collision complexes. At least two reaction pathways through atomic hydrogen loss were identified on the triplet surface. These channels involve multiple isomerization steps of the initial collision complexes via *ring-opening* and *ring expansion* forming an acyclic 1-ethynyl-3-isocyanoallyl radical (**P1**; ${}^2A''$) and a hitherto unreported seven-membered 1-aza-2-dehydrocyclohepta-2,4,6-trien-4-yl radical isomer (**P3**; 2A), respectively. Based on the computations, the molecular fragmentation channel eliminating acetylene (C_2H_2) plus 3-cyano-2-propen-1-ylidene (**P6**; ${}^3A''$) plays also an important role the reaction of atomic carbon with pyridine proposing a probable destruction pathway of interstellar pyridine. These results are also discussed in light of the isoelectronic carbon – benzene ($C_6H_6; X^1A_1$) system with important implications to the rapid degradation of nitrogen-bearing polycyclic aromatic hydrocarbons (NPAHs) in the interstellar medium compared to mass growth processes of PAH counterparts through ring expansion.