

THERMAL DECOMPOSITION OF BENZYL RADICAL VIA MULTIPLE ACTIVE PATHWAYS

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The thermal decomposition of benzyl radical ($C_6H_5CH_2$) has been investigated using a combination infrared absorption spectroscopy in a neon matrix and 118.2 (10.487 eV) photoionization mass spectrometry. Both techniques are coupled with a heated tubular reactor to allow temperature control over the decomposition to indicate relative barrier heights of fragmentation pathways. Three possible chemical mechanisms have been considered. 1) Ring expansion to cycloheptatrienyl radical (C_7H_7) with subsequent breakdown to HCCH and C_5H_5 , 2) isomerization to the substituted five-membered ring fulvenallene ($C_5H_4=C=CH_2$), which is of interest to kinetic theorists and finally 3) hydrogen shift to form methyl-substituted phenyl radical, which can then form ortho-benzyne, diacetylene and other fragments. Benzyl radical is generated from two precursors, $C_6H_5CH_2CH_3$ and $C_6H_5CH_2Br$, and both lead to the appearance of HCCH and C_5H_5 . At slightly hotter temperatures peaks are observed at m/z 90, presumed to be $C_5H_4=C=CH_2$, and 89, potentially the substituted propargyl $C_5H_4=C=CH$. Additionally, decomposition of isotopically substituted parent molecules $C_6H_5CD_2CD_3$ and $C_6D_5CH_2CH_3$ indicates C_7H_7 as an intermediate due to H/D ratios in fragment molecules.