Formation, Isomerization, and Dissociation of ε- and α-Carbon–Centered Tyrosylglycylglycine Radical Cations

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The fragmentations of the ε-carbon–centered radical cations $[\mathbf{Y}^{\varepsilon\bullet}(L/I)G]^+$ and $[\mathbf{Y}^{\varepsilon\bullet}G(L/I)]^+$ are substantially different from those of their π-centered isomeric analogues $[\mathbf{Y}^{\pi\bullet}(L/I)G]^+$ and $[\mathbf{Y}^{\pi\bullet}G(L/I)]^+$, but are similar to those of $[Y(L/I)\mathbf{G}^{\alpha\bullet}]^+$ yet different from those of $[Y\mathbf{G}^{\alpha\bullet}(L/I)]^+$ (their α–carbon-centered isomeric analogues); this behavior is affected by the proximity of the σ_ε and σ_α radical centers. We have used density functional theory calculations and Rice–Ramsperger–Kassel–Marcus modeling to perform systematic mechanistic investigations of selected isomerization and fragmentation reactions of ε-carbon–, α-carbon–, and π–centered radical cations of tyrosylglycylglycine. Direct interconversion from the ε-carbon–centered radical of the tyrosine residue to the α-carbon–centered radical of the terminal glycine residue is both energetically and kinetically favorable, leading to identical product ion spectra. Our preliminary results suggest that the close proximity of the α-C–H atom of the C-terminal glycine residue with the ε-carbon–centered radical in the tyrosine residue leads to ready direct interconversion and facile radical migrations.