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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 $[\mathbf{Y}^{\epsilon\bullet}(\text{L/I})\mathbf{G}]^+$ and $[\mathbf{Y}^{\epsilon\bullet}\mathbf{G}(\text{L/I})]^+$ are substantially different from those of their π -centered isomeric analogues $[\mathbf{Y}^{\pi\bullet}(\text{L/I})\mathbf{G}]^+$ and $[\mathbf{Y}^{\pi\bullet}\mathbf{G}(\text{L/I})]^+$, but are similar to those of $[\mathbf{Y}(\text{L/I})\mathbf{G}^{\alpha\bullet}]^+$ yet different from those of $[\mathbf{Y}\mathbf{G}^{\alpha\bullet}(\text{L/I})]^+$ (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.