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Isomerization versus dissociation of phenylalanyl glycyl tryptophan radical cations

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Herein we report the propensity of radical migration and hence isomerization, or there lack of, in four tripeptide structures (FGW) that differ only in their initial radical locations: the π-system of Trp, the indole nitrogen, the α-carbon of Gly, and C-4 of the Phe ring. These radicals were generated by well-defined means and examined using tandem mass spectrometry. The π- and the N-radical centered on Trp interconvert after collisional activation; by contrast, the α-radical and the ζ-radical (on Phe) retain their distinctness even after collisional activation. Density functional calculations reveal a relatively low (31.1 kcal mol-1) barrier against interconversion between the π- and the N-radical, while interconversion between the α-radical and the ζ-radical exhibits much higher barriers, and these radicals will dissociate before they can interconvert. This study illustrates the intricate balance between radical migration and dissociation as exhibited by the four isomeric tripeptide radicals.

Biography

Ivan K Chu is a Faculty member in Department of Chemistry at University of Hong Kong since 2002. He is an Editorial Board Member of *Journal of the American Society for Mass Spectrometry and Journal of Mass Spectrometry*. His group has been innovative in advancing the understanding of radical-mediated protein oxidation. Their pioneering studies of the molecular mechanisms of pathological processes under oxidative stress have extended to biophysical, bio-analytical, and biomedical applications and drug discovery. They have made many inroads implementing and applying new multidimensional liquid chromatography/mass spectrometric hardware for novel research purposes

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