ELECTRON CAPTURE DISSOCIATION OF PEPTIDES AND PROTEINS DOES NOT REQUIRE A HYDROGEN ATOM MECHANISM

ROBERT R. HUDGINS, KRISTINA HAKANSSON, CHRIS L. HENDRICKSON, ALAN G. MARSHALL,
FT-ICR, National High Magnetic Field Laboratory, Tallahassee, FL 32310.

Electron capture dissociation (ECD) allows for extensive fragmentation of gas-phase peptides and proteins. A proposed mechanism involves formation of hydrogen atoms that cause cleavage at sites of high H-atom affinity.[1] Here, we examine ECD of natural and synthetic peptides designed to test this hypothesis. ECD experiments are performed on peptides designed to be helical in the gas phase (to keep hydrogen atoms generated at protonated sites at a distance from the sites of cleavage), peptides charged with alkali cations instead of protons [e.g (LHRH + 2Na)2+], peptides with fixed charges [(Ac-Kbt-Gly5-Kbt-NH2)2+, Kbt=derivative of lysine], and peptides devoid of labile hydrogens [(Ac-Sar15-Ome + 2Na)2+]. The appearance of the expected c/z ions in these peptides indicates that a hydrogen atom is not needed for ECD fragmentation. The present results are compared to previous electron transmission spectroscopy/dissociative electron attachment experiments on small neutrals. A more general mechanism involving direct dissociative electron attachment is suggested.

1. R.A. Zubarev, N.A. Kruger, E.K. Fridriksson, M.A. Lewis, D.M. Horn, B.K. Carpenter, F.W. McLafferty, J. Am. Chem. Soc. 1999, 121, p. 2857.