To Jump or Not Jump? C_α Hydrogen Atom Transfer in Post-Cleavage Radical-Cation Complexes

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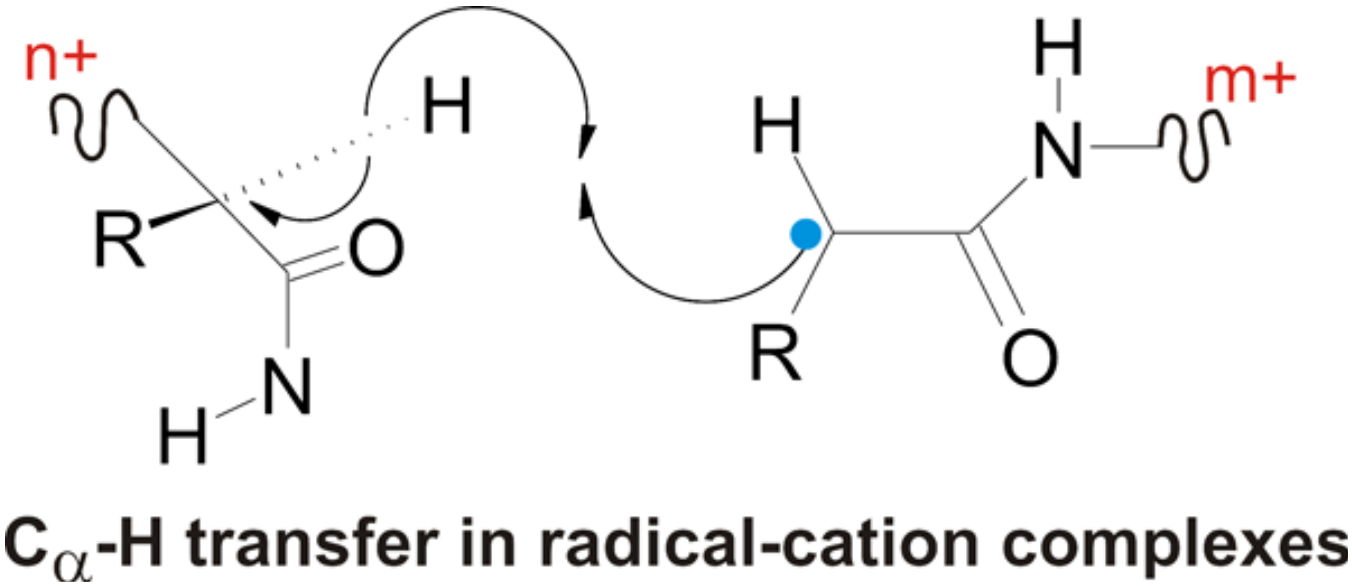
Results and Discussion

Conventionally, electron capture or transfer to a polyprotonated peptide ion produces an initial radical-cation intermediate which dissociates "directly" to generate complementary c_n' and z_m• sequence ions (or ions and neutrals). Alternatively, or in addition, the initial radical-cation intermediate can undergo H· migration to produce c_n· (or c_n − H·) and z_m' (or z_m· + H·) species prior to complex separation ("nondirect"). This reaction significantly complicates spectral interpretation, creates ambiguity in peak assignment, impairs effective algorithmic processing (reduction of the spectrum to solely ^{12}C m/z values), and reduces sequence ion signal-to-noise. Experimental evidence indicates that the products of hydrogen atom transfer reactions are substantially less prevalent for higher charge state precursors. This effect is generally rationalized on the basis of decreased complex lifetime. Here, we present a theoretical study of these reactions in post N−Cα bond cleavage radical-cation complexes as a function of size and precursor charge state. This approach provides a computational estimate of the barriers associated with these processes for highly charged peptides with little charge solvation. The data indicate that the H· migration is an exothermic process and that the barrier governing this reaction rises steeply with precursor ion charge state. There is also some evidence for immediate product separation following N−Cα bond cleavage at higher charge state.



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References

[1] Bythell, B.J., J. Phys. Chem. A, **117**, 1189-1196 (2013)