Energetics and Dynamics of Electron Transfer and Proton Transfer in Dissociation of Metal^{III}(salen)-Peptide Complexes in the Gas Phase

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Peptides and proteins control nearly all of the chemical reactions in biological systems. This work studies the fundamental energetics and dynamics of model peptides in order to deepen the understanding of these biologically important molecules.

Electron transfer and proton transfer are the most fundamental processes in chemistry and biology. Electron transfer is particularly important in enzyme catalysis, photosynthesis, and respiration. Gas-phase decomposition of ternary complexes of transition metal ions with organic and peptide ligands provides a unique opportunity to explore the competition between these processes using relatively simple model systems. It can also be used for the formation of different types of odd-electron peptide ions for analytical applications focused on identification of peptides and proteins using mass spectrometry.

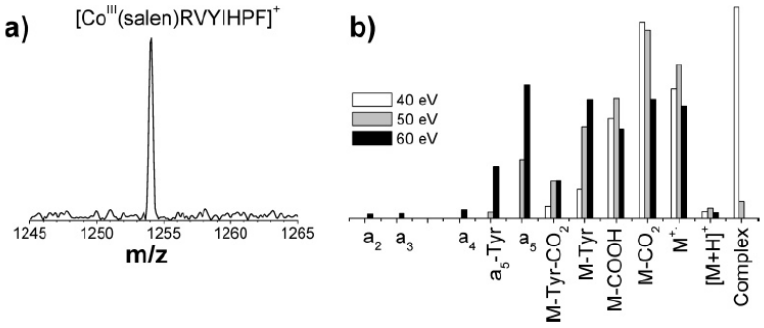

Figure 1. *(a) Mass selected Co^{III}(salen)RVYIHPF precursor ion and (b) fragment distribution for SID of Co^{III}(salen)RVYIHPF complex on the HSAM surface at three collision energies.*

Here we present the first detailed study of the energetics and dynamics of dissociation of positively charged metal^{III}(salen)-peptide complexes in the gas phase using time and collision-energy-resolved surface-induced dissociation (SID) experiments combined with RRKM modeling. Several fragmentation pathways are commonly observed during collision-induced dissociation of the positively charged metal-salen complexes. These include proton transfer to the peptide molecule or to the ligand, reduction of the metal center followed by electron transfer from the peptide molecule and formation of the radical cation, dissociation of the complex into the [metal^{III}(salen)]$^+$ ion and neutral peptide molecule (D), and dissociative electron transfer resulting in formation of fragment ions of the corresponding peptide radical cation. We examine factors that affect the competition between proton-transfer and electron-transfer processes in gas-phase fragmentation of these model systems.

Figure 1 shows a mass-selected [Co^{III}(salen)RVYIHPF]$^+$ precursor ion and its SID fragment distributions obtained at three collision energies. The four primary dissociation pathways are observed. Losses of CO_2 and COOH• are characteristic dissociation pathways of peptide radical

cations that have been previously observed for dissociation of both doubly-charged and singly-charged ternary complexes of transition metals with peptides. Formation of these ions requires electron transfer from the peptide to the metal core of the complex. In addition, electron transfer results in formation of the peptide radical cation, $M^{+}\bullet$, while the [M + H]+ ion is formed by proton transfer from the organic ligand to the peptide.

Time-resolved survival curves (SCs) were obtained by plotting the relative abundance of the intact precursor ion as a function of collision energy at different reaction delays. The SCs obtained at reaction delays of 1 ms and 1 s are shown for cobalt-salen complexes with three different peptides are displayed in Figure 2. The relative position of the SCs reflects the relative stability of different complexes toward fragmentation. The experimental SCs for $[Co^{III}(salen)DRVYIHPF]^{+}$ are slightly shifted toward higher collision energies for both 1 ms and 1 s reaction delays, while SCs obtained for cobalt-salen complexes of RVYIHPF and RVYIHDF show an almost perfect overlap. It should be noted that this trend follows the trend in the number of vibrational degrees of freedom (DOF) of the complexes (540 for DRVYIHPF, 501 for RVYIHPF, and 498 for RVYIHDF). The DOF effect can be eliminated by plotting the relative abundance of the precursor ion as a function of collision energy scaled by the number of DOF of the precursor ion. Perfect overlap between the SCs plotted versus the scaled collision energy clearly demonstrates that the observed shift in the position of the SCs shown results only from the DOF effect and suggests that both the energetics and dynamics of dissociation of all three cobalt-salen-peptide complexes are very similar.

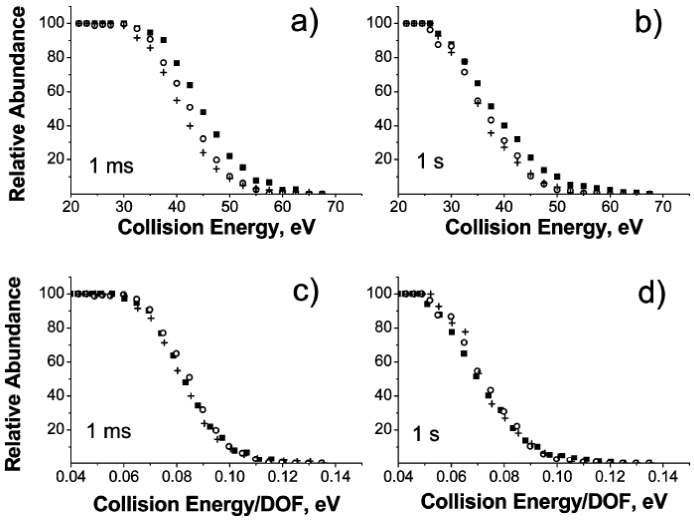

Figure 2. *SCs (Panels a and b) and SCs plotted as a function of collision energy scaled by the number of the vibrational degrees of freedom of the precursor ion (Panels c and d) for Co^{III}(salen)DRVYIHPF (square), Co^{III}(salen)RVYIHPF (O), and Co^{III}(salen)RVYIHDF (+), 1 ms (left panels) and 1 s (right panels).*

This work represents the first detailed study of the factors that affect gas-phase fragmentation of ternary complexes of angiotensin analogues with trivalent metal-salen systems. Time- and collision-energy-resolved SID provide interesting insight on the competition between proton transfer, electron transfer, and loss of the neutral peptide ligand in these model systems. We found that both the fragmentation behavior and the stability of the complexes are similar for different peptide ligands examined in this study. In contrast, the observed fragmentation pathways, the mode of binding, and the energetics and dynamics of dissociation of these systems strongly depend on the electronic properties of the metal center. Interestingly, a very different kinetics of formation of the $M^{+}\bullet$ fragment ion from the cobalt-salen and iron-salen complexes was observed experimentally. We concluded that the electron-transfer process in the dissociation of the $[Fe^{III}(salen)RVYIHPF]^{+}$ ion requires substantial rearrangement of the complex. Details of this exciting research were recently published in the *Journal of the American Chemical Society*.

Citation:

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