Long-Distance Proton Transfer in Protonated Aminocinnamic Acid Studied by Collision-Induced Dissociation and Ion Mobility-Mass Spectrometry

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Intramolecular proton transfer reactions proceed in protonated *p*-aminobenzoic acid (PABA·H^+) between two isomers: N-protomer, where the proton is added to the amino group's nitrogen, and O-protomer, where the proton is added to the carboxyl group's oxygen. By ion mobility-mass spectrometry (IM-MS), ions can be separated based on their collision cross sections (CCSs) with buffer gas. We recently demonstrated that a proton was transported from N-protomer to O-protomer in PABA·H^+ by a collision with ammonia using IM-MS[1]. The proton transfer was examined in this study for the protonated aminocinnamic acid (ACA·H^+), which has a longer distance between the amino and carboxyl groups compared to PABA·H^+ (**Fig. 1(a)**). As a result, similar proton transfer was also observed for ACA·H^+, however, unlike PABA·H^+, not only the O-protomer but also the C-protomer could be formed as the current reaction products. It was not possible to separate the O- and C-protomers in IM-MS due to their close CCSs (**Fig. 1(b)**). Therefore, collision-induced dissociation (CID) with argon gas was employed after ion mobility analysis to assign the reaction products based on their fragmentation patterns. CID results indicated the release of H_2O at relatively low collision energies, with subsequent CO loss observed at higher energies (**Fig. 1(c)**). Quantum chemical calculations revealed that the transition state barrier for H_2O loss from the O-protomer is lower than from the C-protomer, and only the O-protomer leads to subsequent CO loss. These suggest the predominant formation of O-protomer in the proton transfer reactions within ACA·H^+.

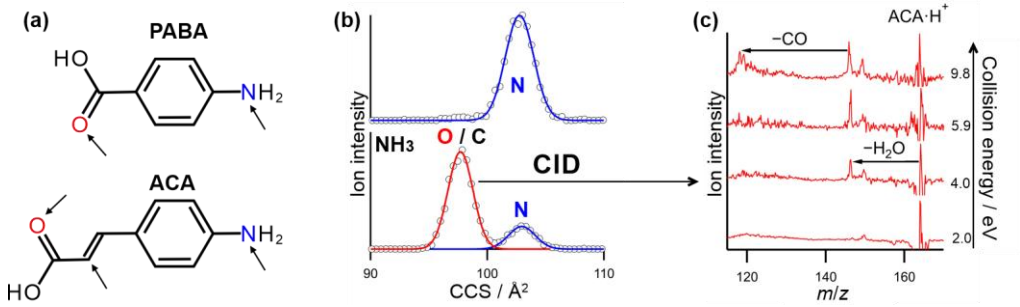

Fig. 1. (a) Structures of PABA and ACA, with arrows indicating the positions where protons are added. (b) Experimental results for ACA·H^+: (top) without reaction gas, (bottom) with NH_3 as the reaction gas. (c) Product ion spectra observed in CID experiments of reaction products of ACA·H^+ + NH_3.

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