Gas-Phase Kinetic Fragmentation of Norpinonic Acid: Energetic Insights into the Reaction Mechanism via DFT and Advanced Mass Spectrometry Techniques.

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Norpinonic acid has been known as an important α-pinene atmospheric secondary organic aerosol (SOA) component. It is formed in the reaction of α-pinene, β-pinene or verbenone with atmospheric oxidizing reagents.

In the presented study, modidied tandem mass spectrometry techniques were used to determine the exact norpinonic carboxylate fragmentation pathway in the gas phase. The precursor anion – deprotonated norpinonic acid (169), generated in an electrospray (ESI) source – was introduced into the collision cell of the mass spectrometer and fragmented using the energy-resolved collision-induced dissociation (ER-CID) technique.

The experimental energy values of degradation processes were determined via analysis of the breakdown curves. Quantum chemical calculations of the reaction models were also constructed, including calculation of all transition states. Comparison between the experimental and the theoretical threshold energies calculated at a ωB97XD/6-311+G(2d,p) theoretical level has shown a good correlation. Two main pathways of the fragmentation of the precuror anion $[M-H]^-$ (169) were observed. First, leads to the decarboxylation product (125) and secondly to the loss of a neutral molecule (C_4H_6O), together with the formation of the anion 99. On the other hand, the breakdown of the anion 125 gives rise to the 69, 57 and 55 ions. To confirm structures formed during ER-CID experiments, the gas-phase proton transfer reactions were examined of all norpinonic acid anionic fragments with a series of neutral reagents, characterized by proton affinity (PA) values. Based on PA difference analysis, the most possible chemical structures were proposed for the observed fragment anions.