Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Detection of the Tetrahedral Reaction Intermediate of the Reaction of Acetyl Chloride with Ethanol in Microdroplets via Laser Desorption/Ionization Mass Spectrometry

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Reagent Information

Acetyl chloride (99%) was purchased from Oakwood Chemicals, and 200 proof ethanol (≥ 99.5%), ethyl acetate (≥ 99.5%), and acetaldehyde diethyl acetal (≥ 99%) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

Fast Reagent-Mixing Apparatus

Two independent 500 µL syringes, secured by individual syringe pumps, were each connected to a stainless-steel tubing with 0.5588 mm inner diameter (1.5875 mm outer diameter). Approximately 3 µL of each reactant was injected into separate stainless-steel tubing to generate a droplet at the tip. The bottom tubing was held stationary while the top tubing was coupled to a high-speed linear actuator (Ultra Motion, Cutchogue, NY) with an actuation speed of 355.6 mm s^{-1} and spatial resolution of 1 µm. The linear actuator was used to bring reactant droplets together during the experiment which was triggered using an automated triggering program (LabVIEW, National Instruments, TX). After the droplets combine, the linear actuator rapidly returns the top tubing to its starting position.

LDI Mass Spectrometry Parameters

Ionization was achieved using the fourth harmonic of a Nd:YAG laser (266 nm, 6 ns, 10 Hz; Q-smart 850 2W4W, Lumibird, Bozeman, MT). A single laser pulse, fired at a power of 100 mJ (6 ns) was allowed through a beam shutter and focused (750.0 mm lens, UV Fused Silica Plano-Convex Lens, AR Coating: 245-400 nm, Thor labs) between the mass spectrometer, heated extended capillary, and reactant tubes. Low-resolution positive ion mode mass measurements were performed using a Thermo Scientific LTQ XL (linear ion trap) mass spectrometer. The temperature of the extended ion transfer capillary was set at 275 °C.

APCI Mass Spectrometry Sample Preparation

Approximately 1 M ethyl acetate solution in ethanol, 1 M acetaldehyde diethyl acetal solution in ethanol, and pure ethanol samples were prepared for structural verification experiments.

APCI Mass Spectrometry Parameters

All (+) APCI low- and high-resolution tandem mass spectrometry experiments were performed using a Thermo Scientific LTQ Orbitrap XL mass spectrometer. The solutions were injected at a flow rate of 10 µL min^{-1} into the APCI source using the following conditions: 20 (arbitrary units) flow rate of sheath gas (N2), 10 (arbitrary units) flow rate of auxiliary gas (N2), 100 °C vaporizer temperature, and 275 °C capillary temperature.

Collision Activated Dissociation (CAD) Mass Spectra

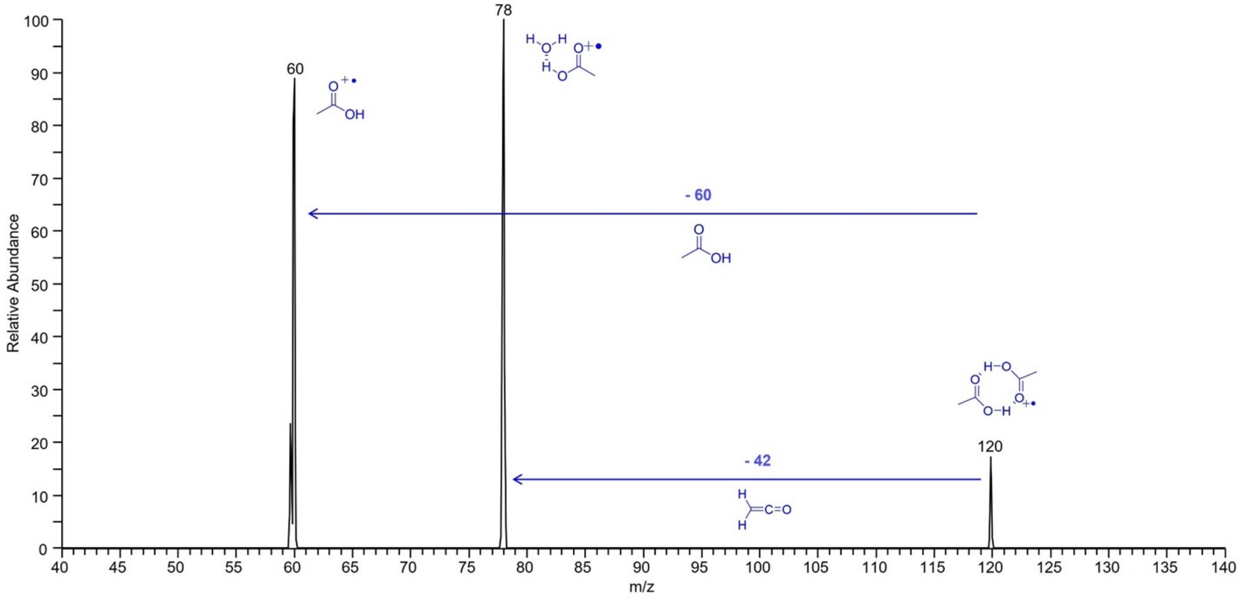

Figure S1. The low-resolution (+) LDI CAD mass spectrum of the unknown ions of *m/z* 120 measured at a nominal collision energy of 17.

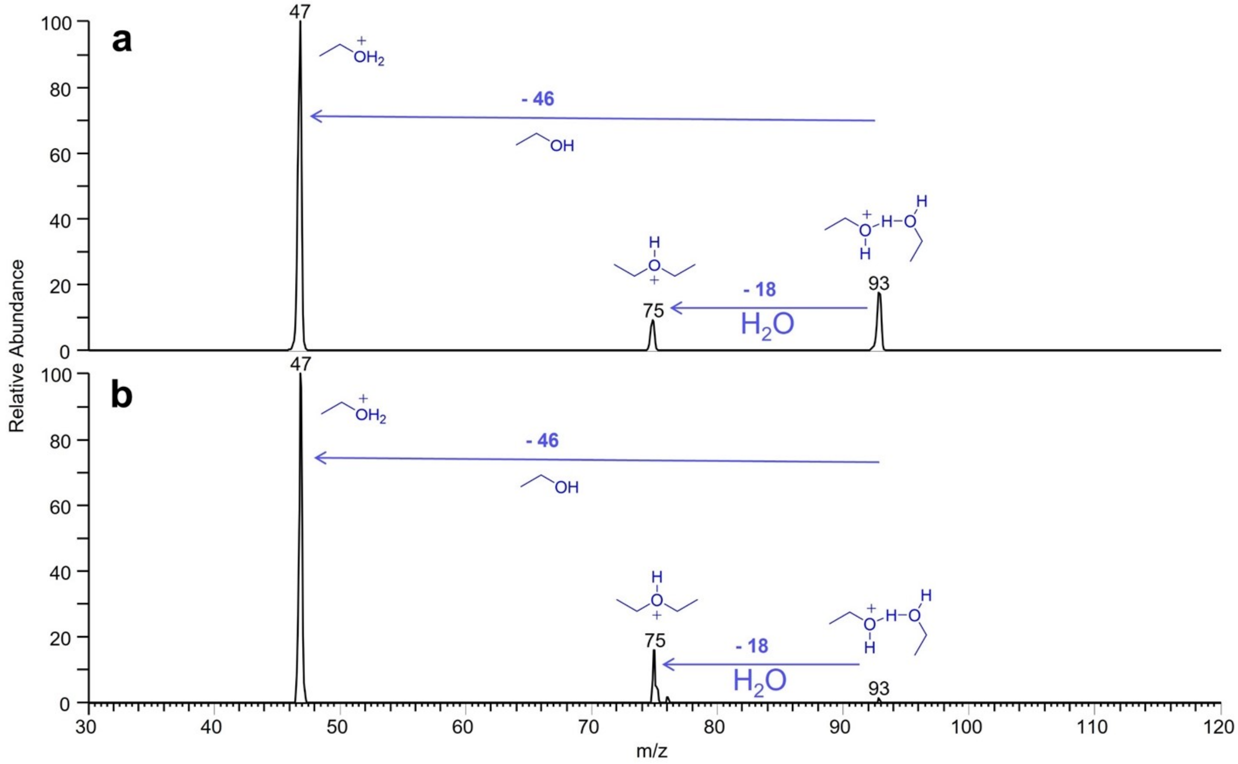

Figure S2. (a) The low-resolution (+) APCI CAD mass spectrum of authentic protonated ethanol dimer of *m/z* 93 measured at a nominal collision energy of 19 and (b) the low-resolution (+) LDI CAD mass spectrum of unknown ions of *m/z* 93 measured at a nominal collision energy of 25.

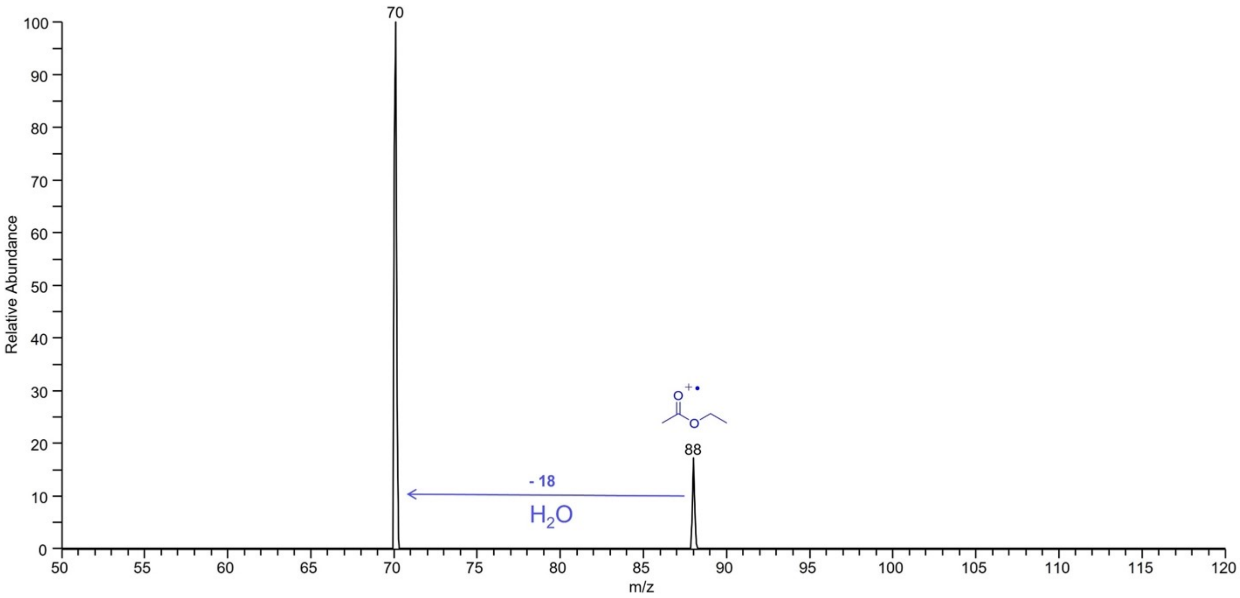

Figure S3. The low-resolution (+) LDI CAD mass spectrum of the unknown ions of *m/z* 88 measured at a nominal collision energy of 24. Based on this fragmentation reaction, the ions are assigned to be the radical cations of ethyl acetate.

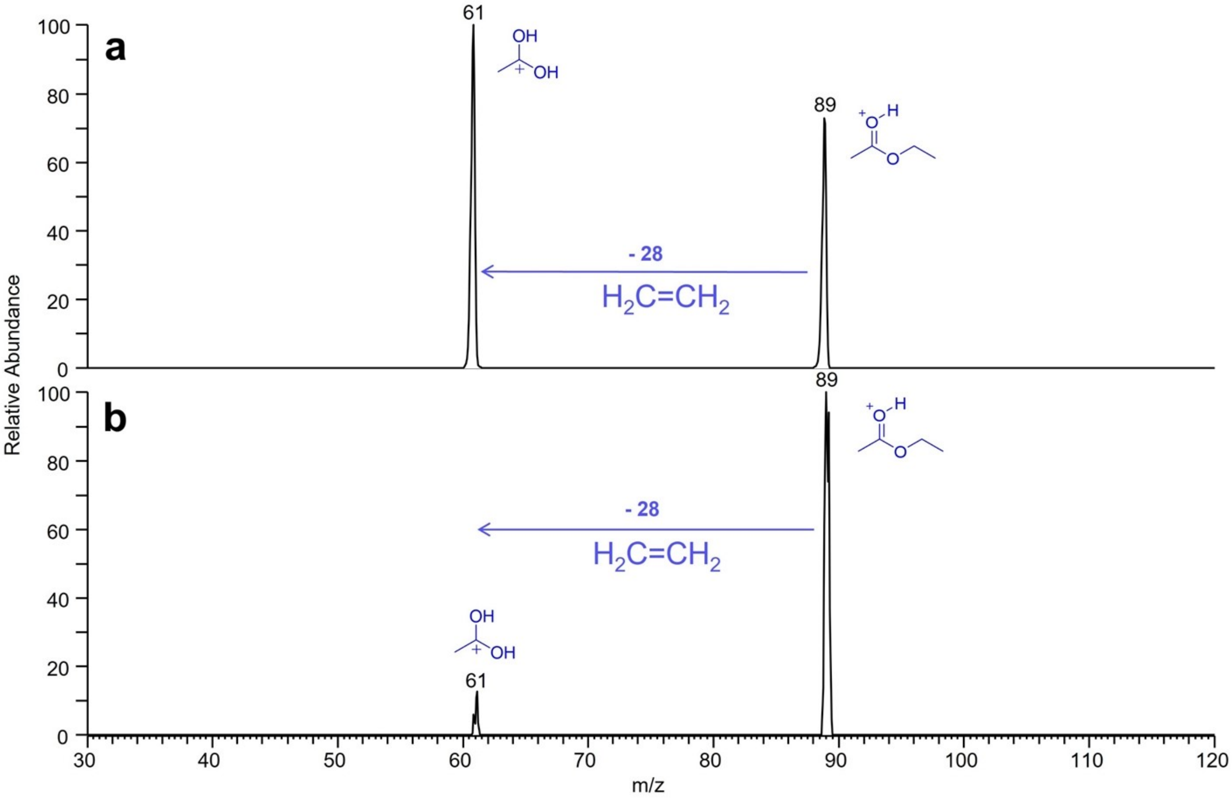

Figure S4. The low-resolution (+) APCI CAD mass spectrum of protonated ethyl acetate, *m/z* 89, (a) measured at a nominal collision energy of 20, and the low-resolution (+) LDI CAD mass spectrum of unknown ions of *m/z* 89 (b) measured at a nominal collision energy of 10.

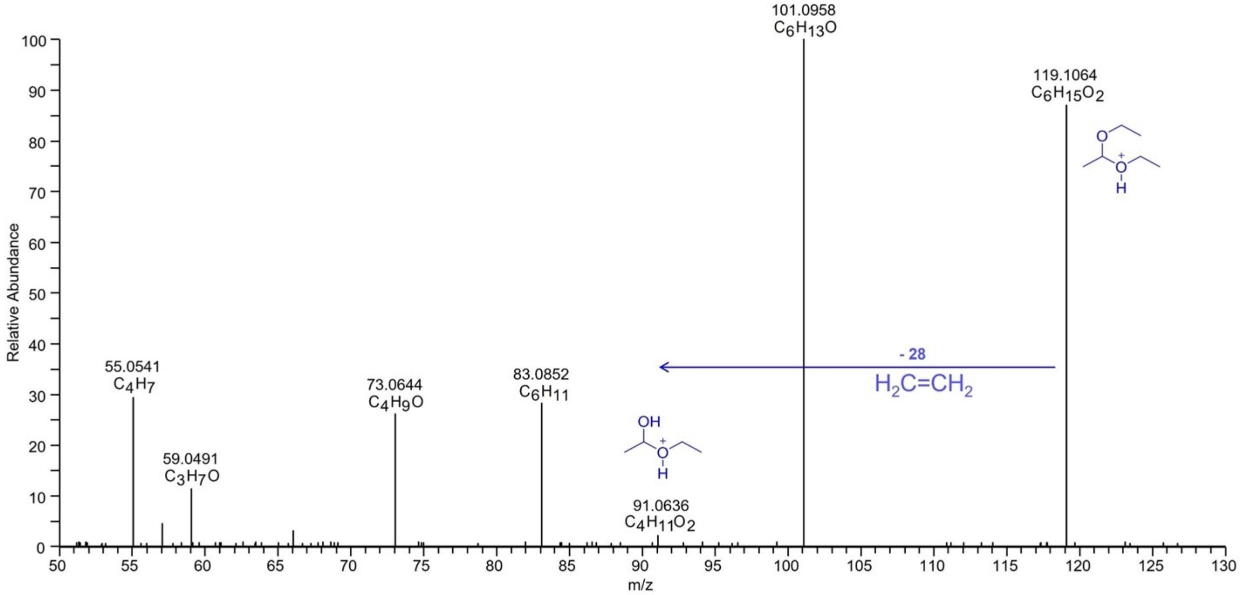

Figure S5. The high-resolution (+) APCI CAD mass spectrum of protonated acetaldehyde diethyl acetal, *m/z* 119, measured at a nominal collision energy of 20. The high-resolution mass spectrum was measured to verify the elemental composition of ions of *m/z* 91. The fragment ions of *m/z* 101 are formed via elimination of water.