Tracking the reaction networks of acetaldehyde oxide and glyoxal oxide Criegee intermediates in the ozone-assisted oxidation reaction of crotonaldehyde

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Tracking the Reaction Network of Acetaldehyde Oxide and Glyoxal Oxide Criegee Intermediates in the Ozone-Assisted Oxidation of Crotonaldehyde

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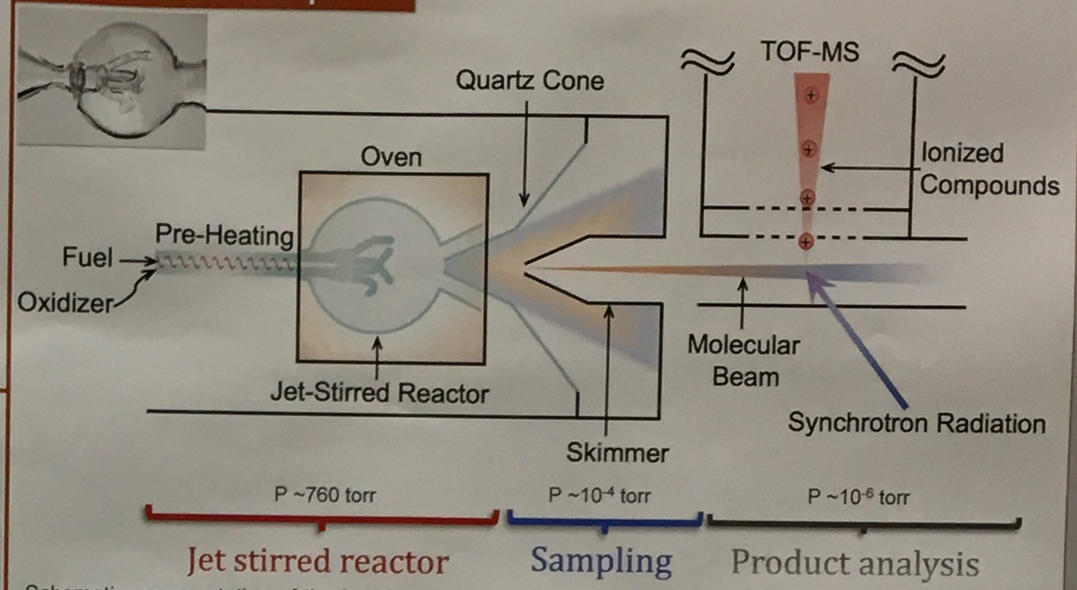
Abstract

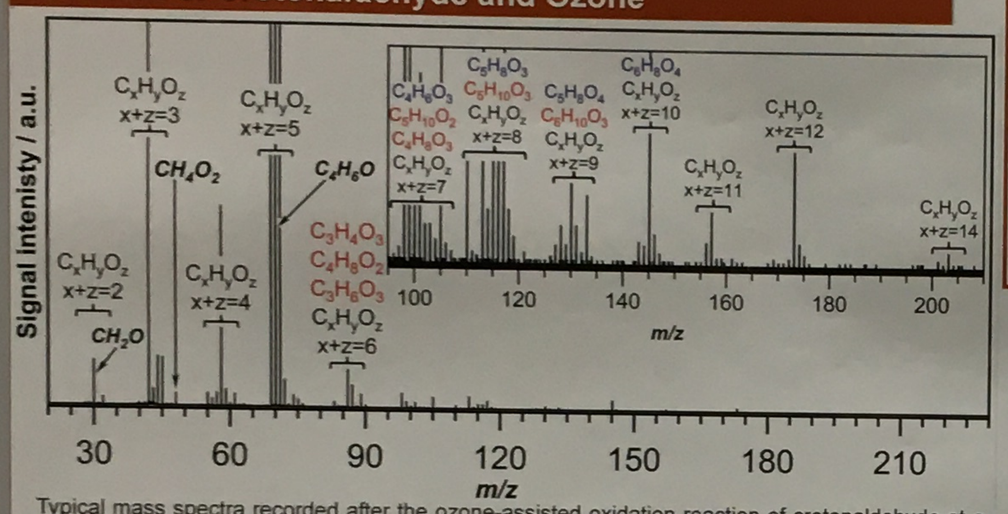
The reaction of unsaturated compounds with ozone is recognized to lead to the formation of Criegee intermediates (CIs), which play a key role in controlling the atmospheric budget of hydroxyl radicals and secondary organic aerosols. The reaction network of two CIs (CH_3CHOO and CHOCHOO) formed in the ozone-assisted oxidation reaction of crotanaldehyde (CA), is investigated over a temperature range between 390 K and 800 K in an atmospheric pressure jet stirred reactor (JSR). Molecular beam in conjunction with single photon tunable synchrotron VUV radiation is used to identify elusive intermediates and separate structural isomers. Addition of ozone (1000 ppm) is observed to trigger the oxidation of CA already at 390 K, below the temperature where the oxidation reaction of CA in the absence of ozone was observed. The observed CA + O_3 product, $C_4H_6O_4$, is found to be linked to the ketohydroperoxide resulting from the isomerization of the primary ozonide. A network of CI reactions identified in the temperature region below 600 K is characterized by CIs addition to species like alkenes and aldehydes. The results of these studies provide new mechanistic insights into ozone-assisted oxidation reactions of aldehydes, which is critical for the development of improved kinetics models.

Experimental setup

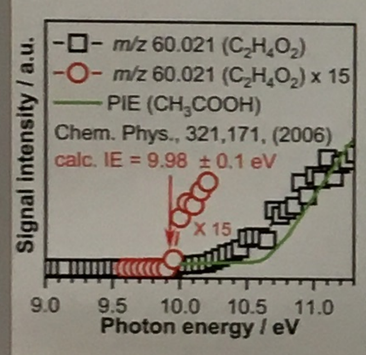


Schematic representation of the jet-stirred reactor (JSR) used in conjunction with a high-resolution time-of-flight mass spectrometer coupled to tunable synchrotron-generated radiation. This setup was used to detect and identify key products and intermediates formed during the ozone-assisted low-temperature oxidation of crotonaldehyde.

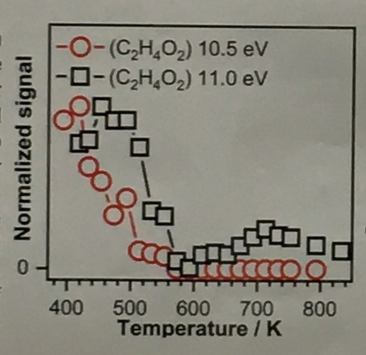
Reaction of Crotonaldehyde and Ozone

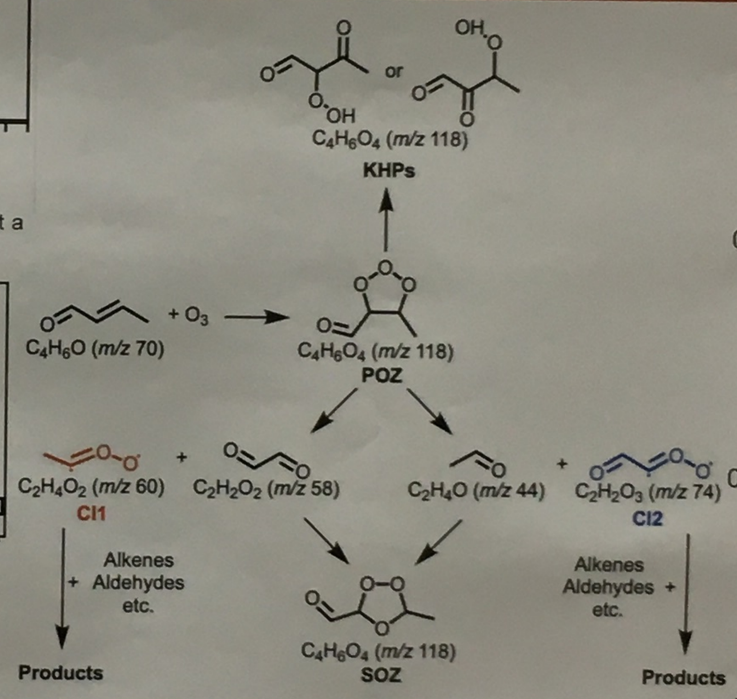


Typical mass spectra recorded after the ozone-assisted oxidation reaction of crotonaldehyde at a temperature of 390 K and ionization energy of 11.0 eV.

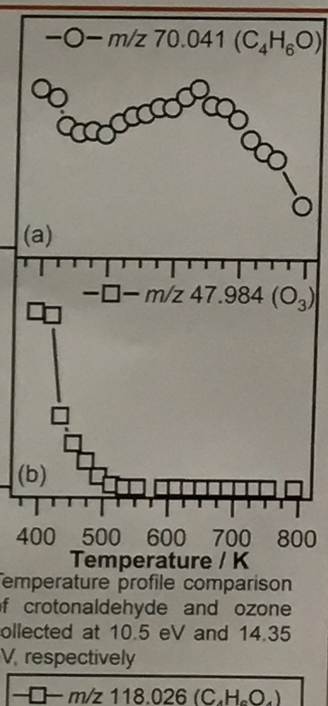


(Left) Photo-ionization efficiency curve of the signal recorded at *m/z* 60.021. The recorded signal is attributed to glycolaldehyde an isomer of CI1 and acetic acid. (Right) Temperature profile of the signal recorded at *m/z* 60.021 and ionization energy of 10.5 eV and 11.0 eV, respectively.



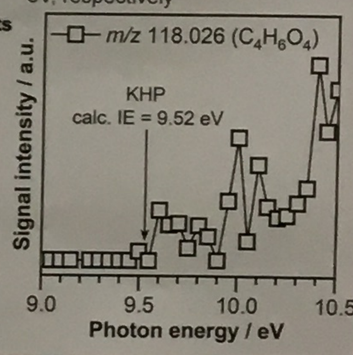


(Top) Primary unimolecular processes and bimolecular reactions involved in the ozone-assisted oxidation of crotonaldehyde. The numbers in parentheses correspond to the nominal mass of the respective structure.

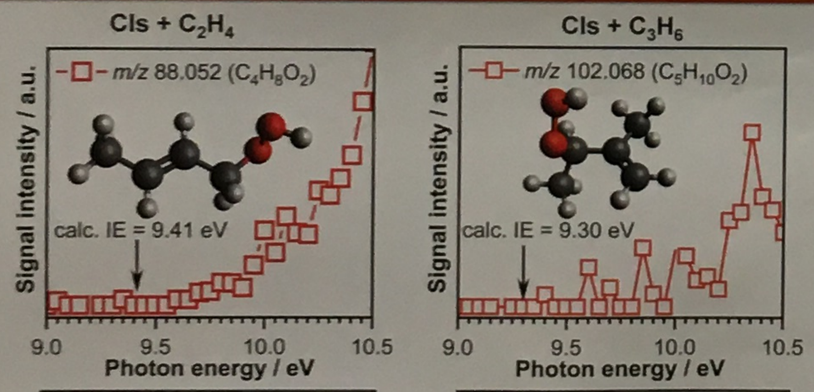


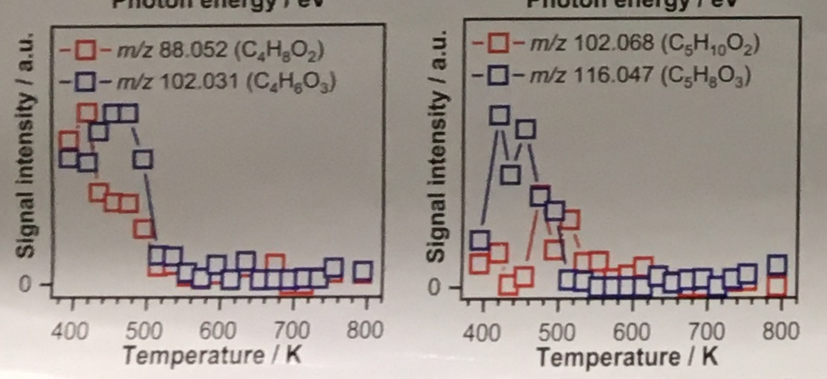
Temperature profile comparison of crotonaldehyde and ozone collected at 10.5 eV and 14.35 eV, respectively

(Right) Photo-ionization efficiency curve of the signal recorded at *m/z* 118.026 corresponding to mass of either POZ, SOZ, or KHP. The signal is attributed in part to the KHP based on the calculated ionization energy that matches the signal onset.



Reactions of Criegee intermediates

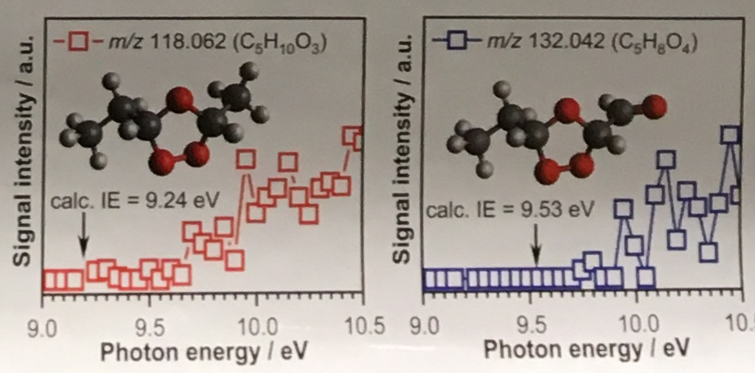




(Top row) Photo-ionization efficiency curves for m/z 88 and m/z 102.06 corresponding to mass of CI1 + C_2H_4 and C_3H_6, respectively (Middle row) Photo-ionization efficiency curve for m/z 102.03 and m/z 116 corresponding to mass of CI2 + C_2H_4 and C_3H_6, respectively. (Bottom row) Temperature profiles of both CIs with C_2H_4 and C_3H_6, respectively

CIs + aldehydes

(Left) Photo-ionization efficiency curve for *m/z* 130 and (middle) 144 corresponding to the mass of CI1 + CA and CI2 + CA, respectively. (Right) temperature profiles for both CIs with CA.



(Left) Photo-ionization efficiency curve for *m/z* 118 and (right) 132 corresponding to the mass of CI1 + propionaldehyde and CI2 + propionaldehyde, respectively.

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