I. Oxidation of isolated Met in the gas phase, using guided-ion-beam scattering methods

\[ \text{Met}^+ + { }^1\text{O}_2 \]

No oxidation products were observed

II. Using hydrated protonated/deprotonated Met to capture intermediates & mimic solution-phase behaviors

\[ \text{Met}^+(\text{H}_2\text{O})_n + { }^1\text{O}_2 \]

\[ \text{Met} - \text{H}^- + { }^1\text{O}_2 \]

Potential energy surface for the reaction of MetH^+(H2O) with ^1O2.

-b) Path A: forming MetOOH+, followed by water elimination

-c) Path B: elimination H2O2 and then water

Changes of PE and various CM distances during the trajectory B

Products and kinetics in basic solution

1. [Met - H^-] (m/z 148) + ^1O2
2. [Met - H^-] + ^1O2 (m/z 180), rate-limiting step, k_2 = 2.1 \times 10^9 M^{-1} s^{-1}
3. [Met - H^-] + ^1O2 (m/z 164), and k_3 = 0

(a) Time profiles and (b, c) kinetics analysis of [Met - H^-] -O and [Met - H^-] -OH Met.

Reaction intermediate [Met - H^-] -O was observed in solution, and can be treated with pseudo-steady-state approximation.

Products and kinetics in acidic solution

1. MetH^+(m/z 150) + ^1O2
2. MetH^+ + ^1O2, rate-limiting step, k_4 = 1.9 \times 10^9 M^{-1} s^{-1}

(a) Time profiles and (b, c) kinetics analysis of MetH^+ and MetH^-O

Reaction intermediate MetH^-O is more reactive than its negative counterpart, and we were not able to detect it in solution.

III. Oxidation of Met in solution: Fates of peroxides in solution

On-line spectroscopy and MS monitoring of solution-phase ^1O2 reactions

- Oxidation of Met is mediated by a hydroperoxide.
- The hydroperoxide dissociates in the gas phase by H2O2 elimination.
- However, the hydroperoxide can be stabilized in gas-phase hydrated clusters by water evaporation.
- In aqueous solution, hydroperoxides further react with another molecule of Met, leading to ultimate products MetO.
- Oxidation of Met in all different media present similar pH dependence, with the protonated form being more reactive than the deprotonated ones.
- Gas-phase hydrated clusters provide a promising platform to elucidate reaction intermediates, and bridge the gas-phase and solution chemistry.

Conclusions

Acknowledgements

NSF CAREER (CHE-0954507)
PSC-CUNY Research Awards
QC Research Enhancement Funds
Al Viggiano (AFRL)
Bill Hase (Texas Tech)