Atmospheric chemistry of maleic anhydride (MA): reaction with OH radicals

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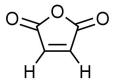
Introduction



Maleic anhydride (MA)
Furan-2,5-dione

Atmospheric sources & sinks of MA

Sources: Biomass burning [1]
Chemical industry
Sinks: Reaction with OH, Cl, NO_3, O_3
Photodissociation
Heterogeneous chemistry
Dry/wet deposition

Motivation

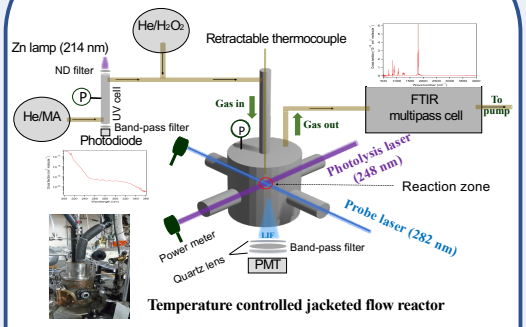
Reaction with OH radical is most likely the major degradation pathway of MA in the atmosphere. The atmospheric degradation of MA has potential impacts on tropospheric ozone (O_3) and secondary organic aerosol (SOA) formation. Prior to this work, there was a single room temperature relative rate (RR) study of the OH + MA reaction rate coefficient.[2] The present work used an absolute kinetic method to measure the reaction rate coefficient and its temperature dependence. In addition, we have evaluated the atmospheric degradation reaction mechanism for MA. The findings of the present study have been recently published.[3]

Experimental Details

A pulsed laser photolysis – laser-induced fluorescence (PLP-LIF) method was employed for measuring the OH + MA rate coefficients.
OH source: 248 nm photolysis of H_2O_2 vapor.
Pseudo 1st order condition in OH i.e. [MA] >> OH is maintained.
Following are the typical experimental parameters.

- Temperature: 283 - 374 K
- [MA] = (0.6 - 25.1) x 10^{14} molecule cm^{-3}
- Pressure: 50 - 200 Torr; Bath gas (He/N_2)
- Addition of O_2 (0.8 - 2.6 Torr)
- OH precursor (H_2O_2) concentration = (5 - 16) x 10^{13} molecule cm^{-3}
- Photolysis Laser fluence: (2 – 4) mJ cm^{-2} $pulse^{-1}$
- $[OH]_0$ = (2.6 - 14.6) x 10^{10} cm^{-3}
- Linear flow velocity: (6 - 12 cm s^{-1})

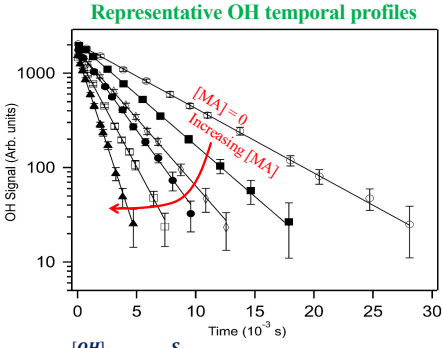
A schematic of pulsed laser photolysis – laser-induced fluorescence (PLP-LIF) apparatus



Temperature controlled jacketed flow reactor

Results

Representative OH temporal profiles

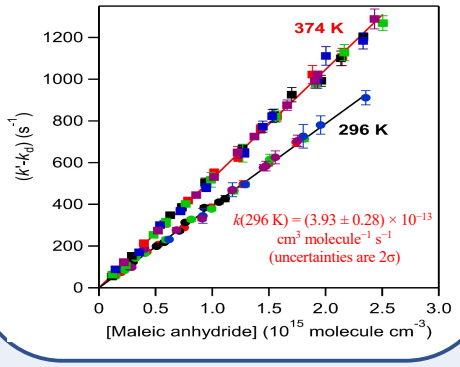


$$\ln\left(\frac{[OH]_t}{[OH]_0}\right) = \ln\left(\frac{S_t}{S_0}\right) = -(k_d + k\,[MA])t = -k' t$$

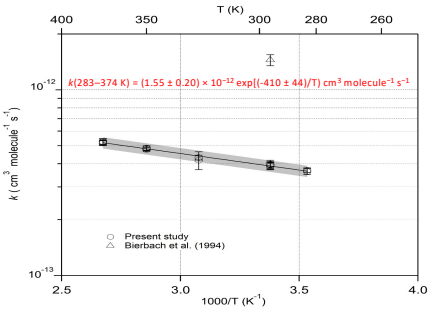
$$k' = k_d + k\,[MA]$$

k = bimolecular rate coefficient
k' = pseudo first-order rate coefficient
k_d = 1st order rate coefficient for OH loss in absence of MA

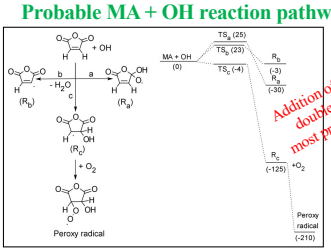
2nd Order Plots



Arrhenius plot

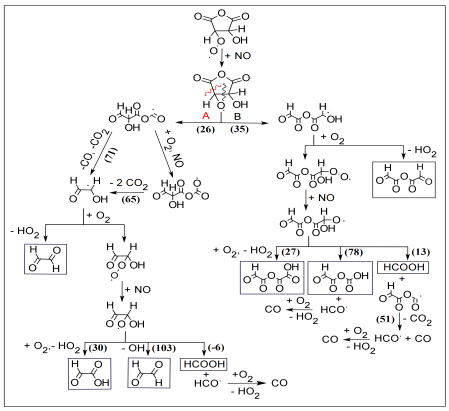


Probable MA + OH reaction pathways



Values in parentheses are barrier heights (in kJ mol^{-1}) calculated using CBS-QB3 method

Atmospheric degradation mechanism of MA



Conclusion

- Week positive temperature dependence of k_{OH}
- Measured k_{OH} at room temperature is about 4 times lower than that reported by Bierbach et al.[2]
- Atmospheric lifetime of MA with respect to OH reaction is ~ 15 days

References

[1] Coggon et al., *Atmos. Chem. Phys.* **19**, 14875-14899 (2019)
[2] Bierbach et al., *Environ. Sci. Technol.* **28**, 715-729 (1994)
[3] Chattopadhyay et al., *Int. J. Chem. Kinet.* (doi:10.1002/kin.21387) (2020)