Aqueous Ozone For Photoresist Stripping

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Aqueous Ozone as an Alternative to H_2SO_4/H_2O_2 mixture for Resist Stripping

- Environmental Gain
  - Eliminates H_2SO_4 use and waste.
  - Eliminates extensive rinsing required after H_2SO_4/H_2O_2.
- Safety
  - Eliminates exposure to hot H_2SO_4/H_2O_2.
  - However, must learn how to handle O_3 safely.
- CoO; expected reduction compared to H_2SO_4/H_2O_2.

Chemistry of Ozone Decomposition

- Direct O_3 consumption

$$O_3 + C_6H_5OH \rightarrow O_2 + C_6H_4(OH)_2$$

- OH• generation reaction

$$3O_3 + H_2O \rightarrow 2OH\bullet + 4O_2$$

$$H_2O_2 + 2O_3 \rightarrow 2OH\bullet + 3O_2$$

Rate-limiting initiation step (pH sensitive)

$$O_3 + OH^- \rightarrow HO_2\bullet + O_2\bullet^-$$

$$O_3 + HO_2\bullet^- \rightarrow OH\bullet + O_2\bullet^- + O_2$$

- OH• catalyzed O_3 decomposition

$$OH\bullet + 2O_3 \rightarrow OH\bullet + 3O_2$$

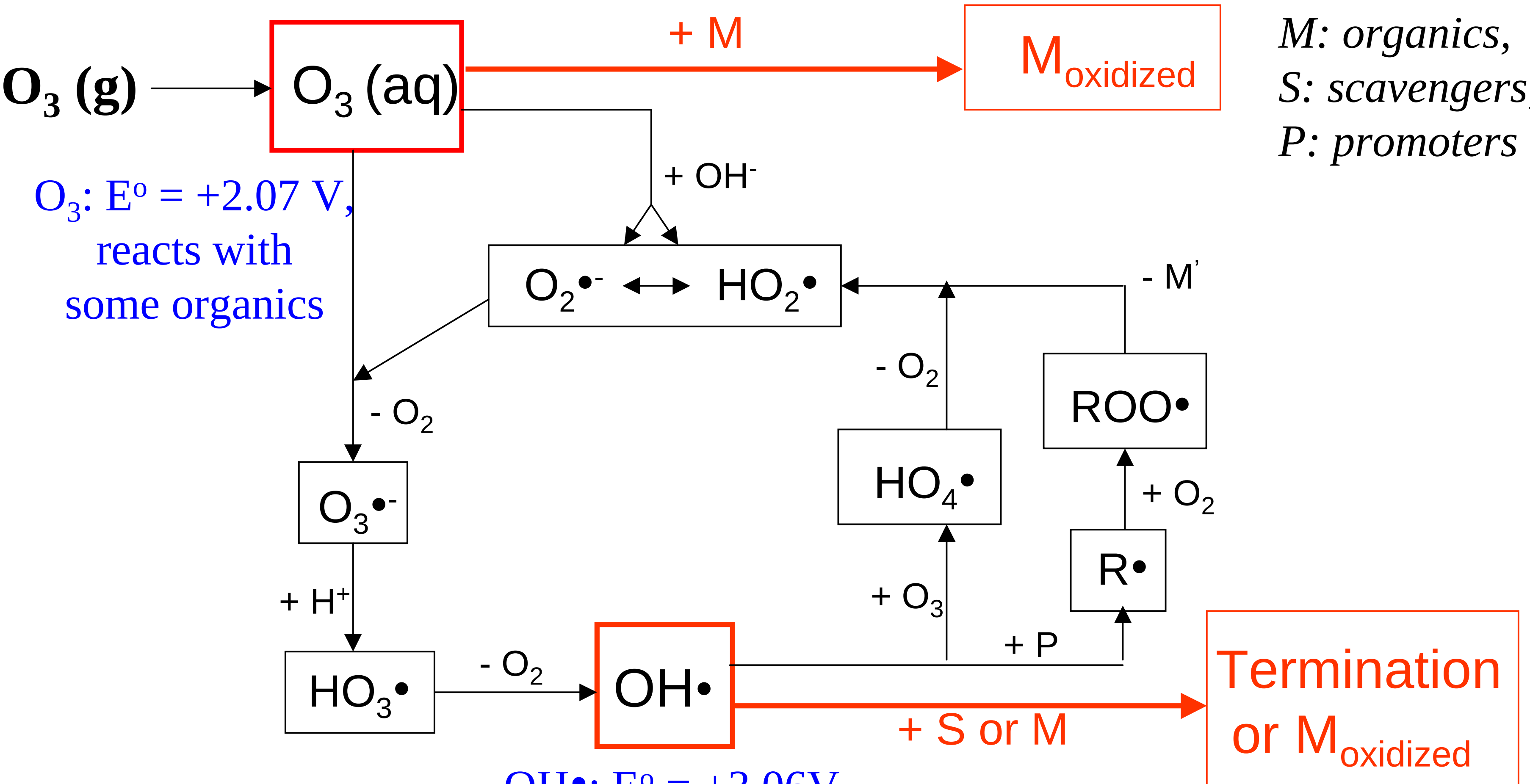
- OH• scavenging

$$OH\bullet + (CH_3)_3COH \rightarrow H_2O + (CH_3)_2COHCH_2\bullet \xrightarrow{O_2} (CH_3)_2COHCH_2OO\bullet$$

- $O_2\bullet^-$ promotion (speedup O_3 consumption)

$$OH\bullet + CH_3OH \rightarrow H_2O + H_2\dot{C}OH \xrightarrow{O_2} H_2CO\dot{O}\,OH \xrightarrow[-BH]{+B^-} O_2\bullet^- + H_2CO$$

O_3 Decomposition Model



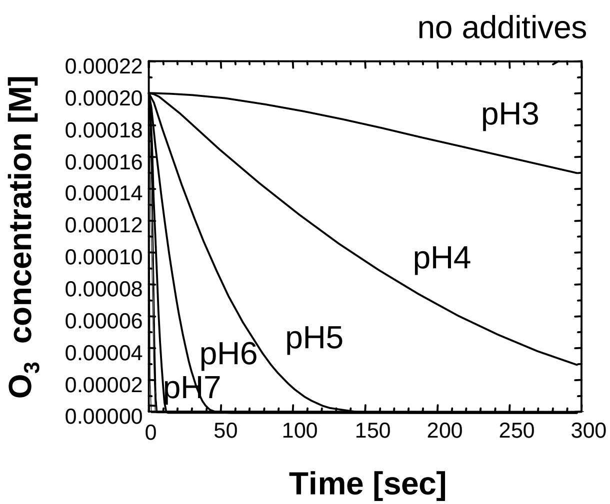
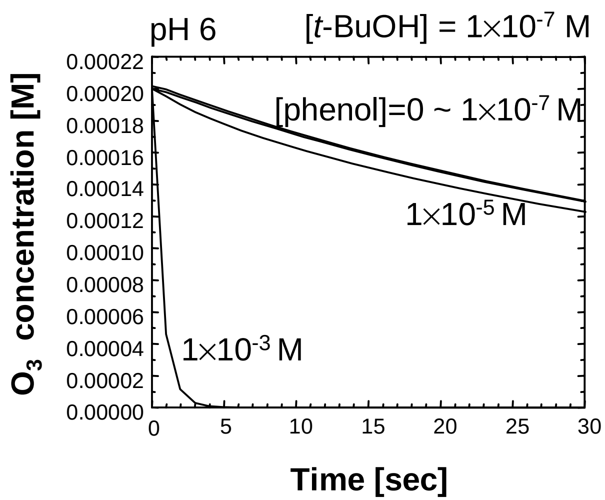
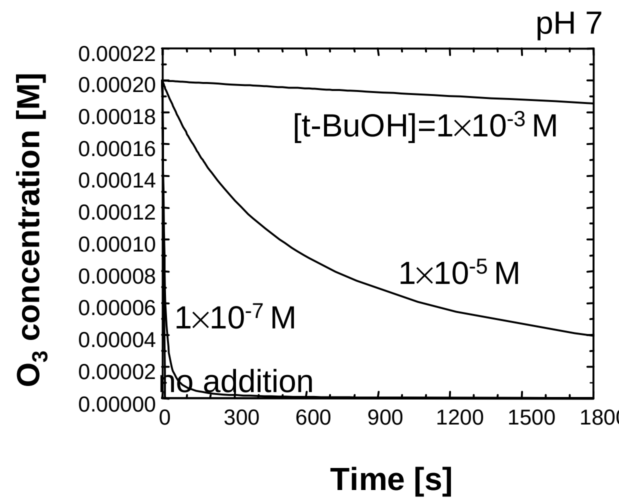
OH•: E° = +3.06V

more reactive and less selective than O_3

Staehelin, et al., *Environ. Sci. Technol.* **1985**, *19*, 1206

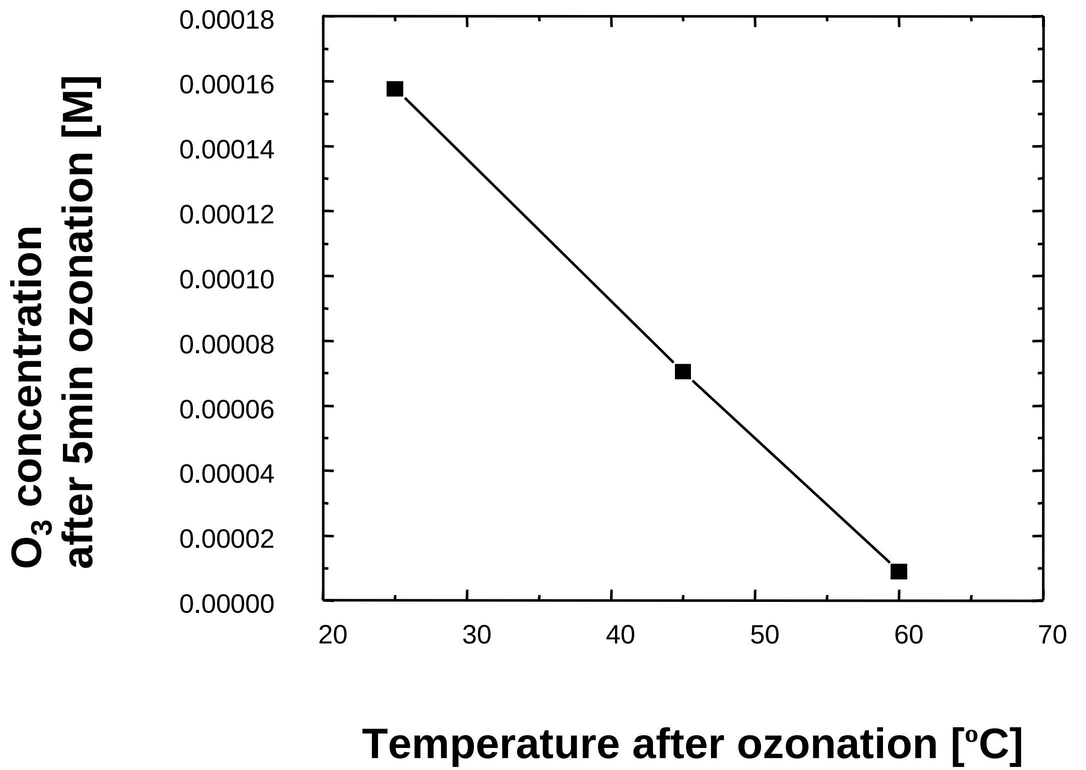
Parameters of Ozone Chemistry

Simulation

pH effect	Effect of direct consumer (phenol)	Effect of radical scavenger (t- butyl alcohol)
		

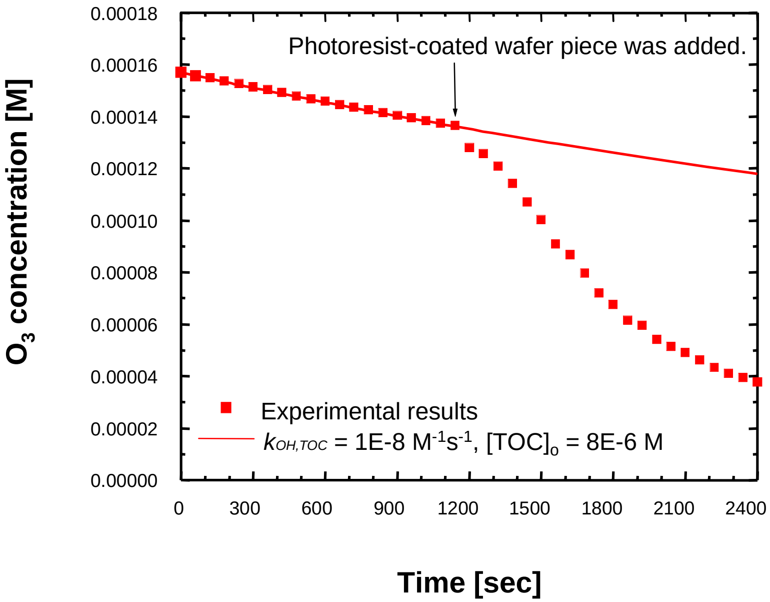
pH ↑ :	[consumer] ↑ :	[scavenger] ↑ :
O_3 decomposition ↑	O_3 consumption ↑	O_3 decomposition ↓

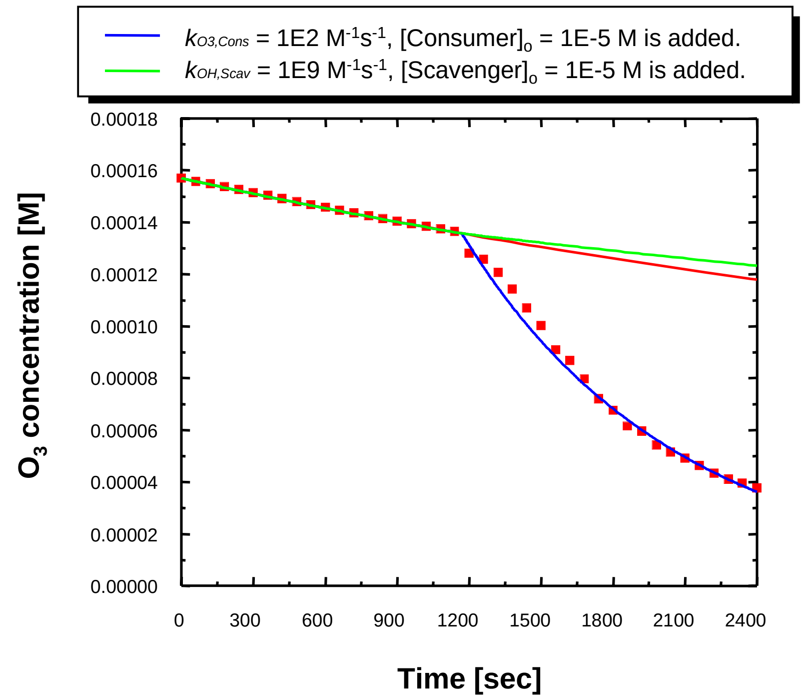
Ozone Concentration vs. Temperature



- Solubility of ozone depends on the temperature.
- Process temperature and ozone chemistry should be optimized.

Which is Main Reactive Species?





- Experimental and simulation results imply that the main reactive species is aqueous ozone.

Strategy

I. In order to get a higher concentration of O_3?

radical scavenger addition: long lifetime of O_3 and high $[O_3]$

(*e.g.* CO_2 addition)

$OH\bullet + HCO_3^- \text{ (or } CO_3^{2-}) \longrightarrow HCO_3\bullet \text{ (or } CO_3\bullet^-)$

II. For the removal of highly ion-implanted photoresist?

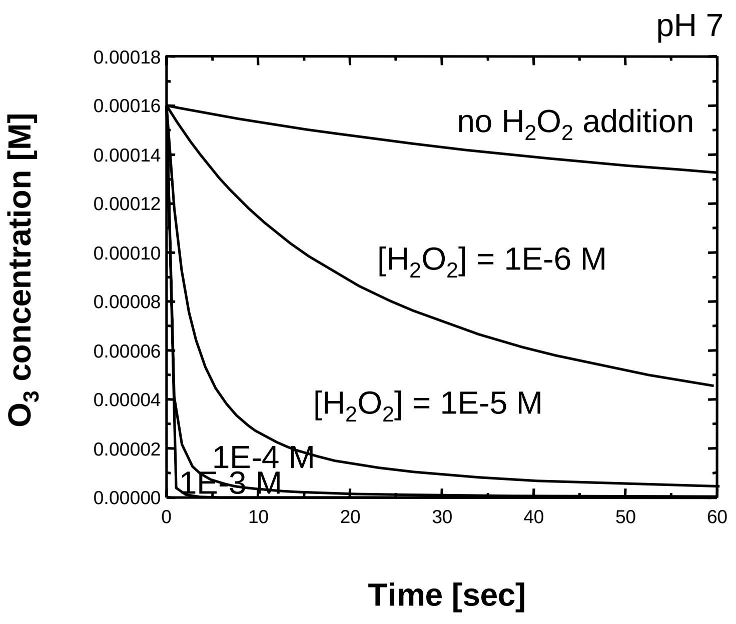
Try initiator addition: short lifetime of O_3, but high $[OH\bullet]$

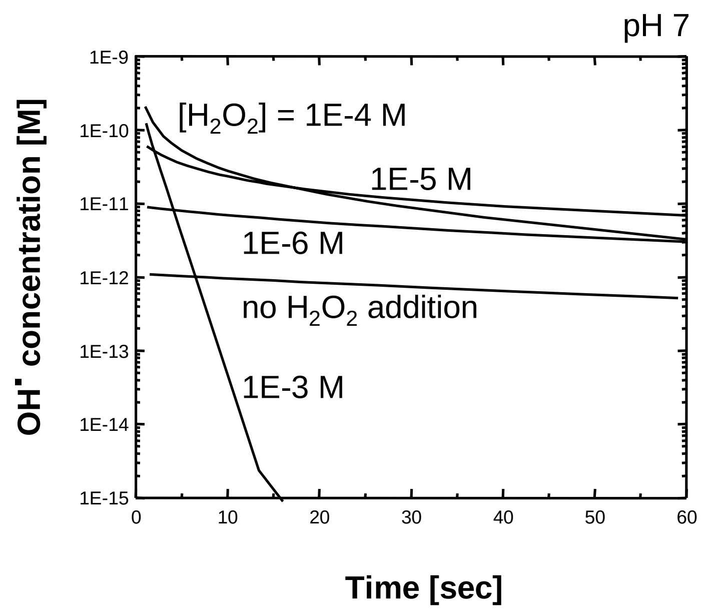
(*e.g.* H_2O_2 addition)

$2O_3 + H_2O_2 \longrightarrow 2OH\bullet + 3O_2$

Effect of H_2O_2 Addition

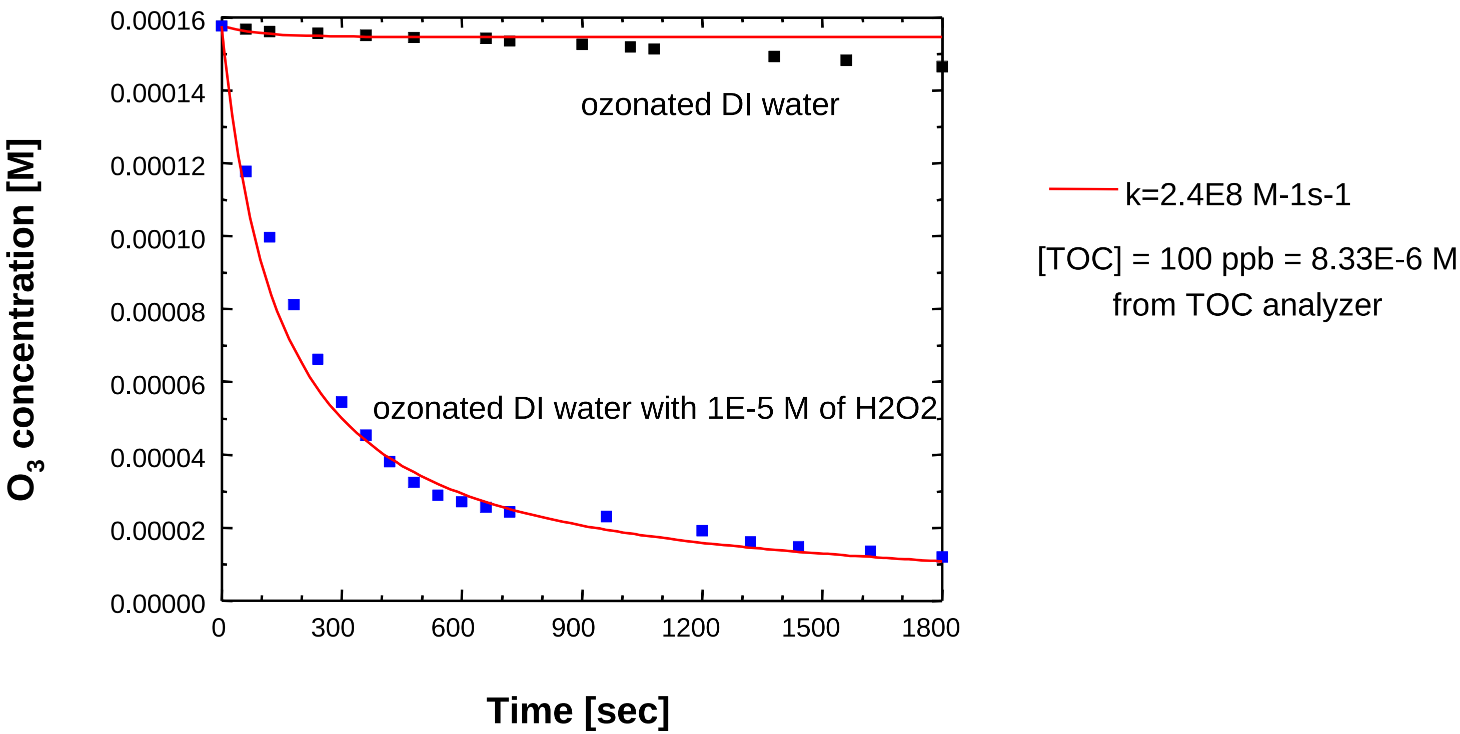
Simulation





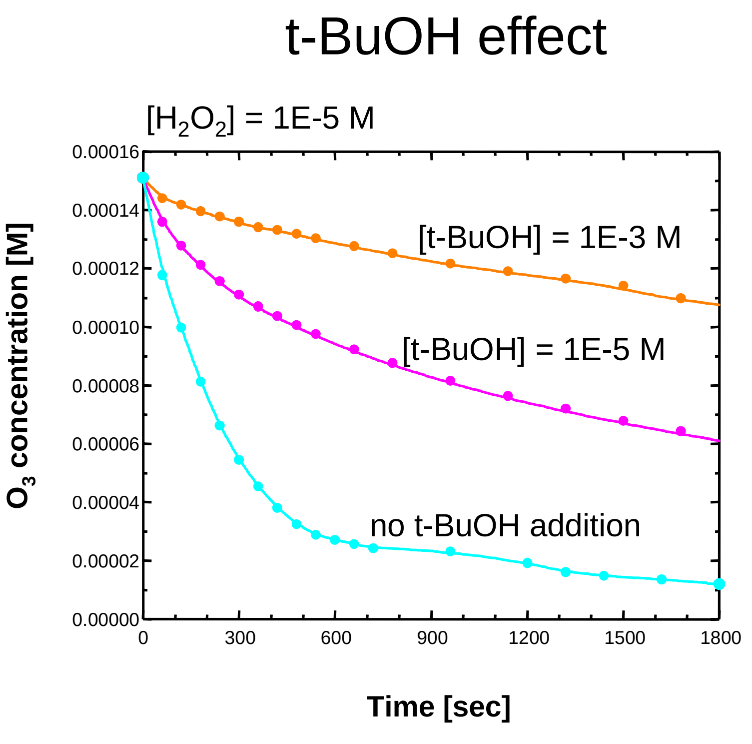
- H_2O_2 addition reduces the lifetime of ozone, but increases the formation of OH•.

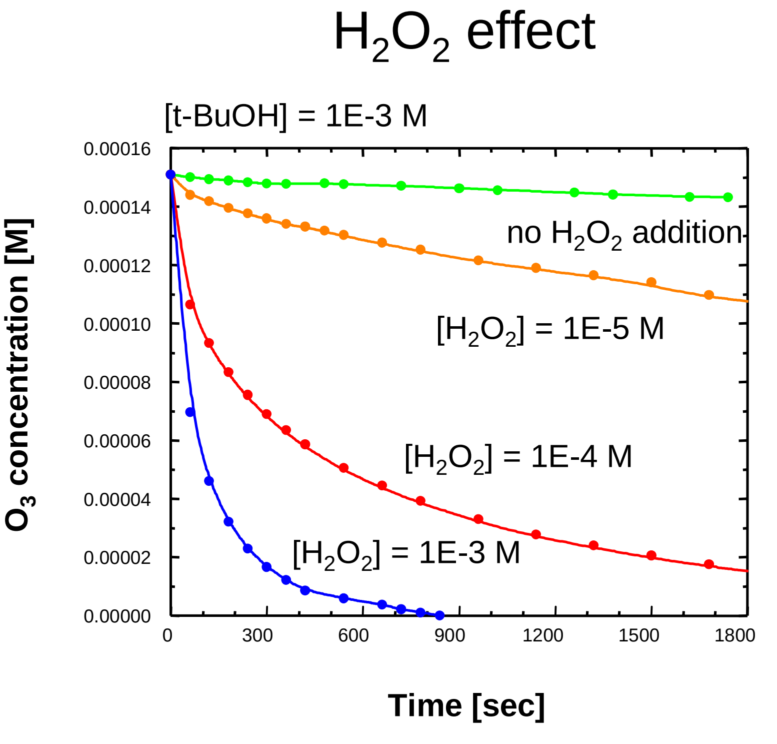
Effect of H_2O_2 Addition



- Decrease in lifetime of ozone is observed when H_2O_2 is added, which might be due to the acceleration of OH• formation.

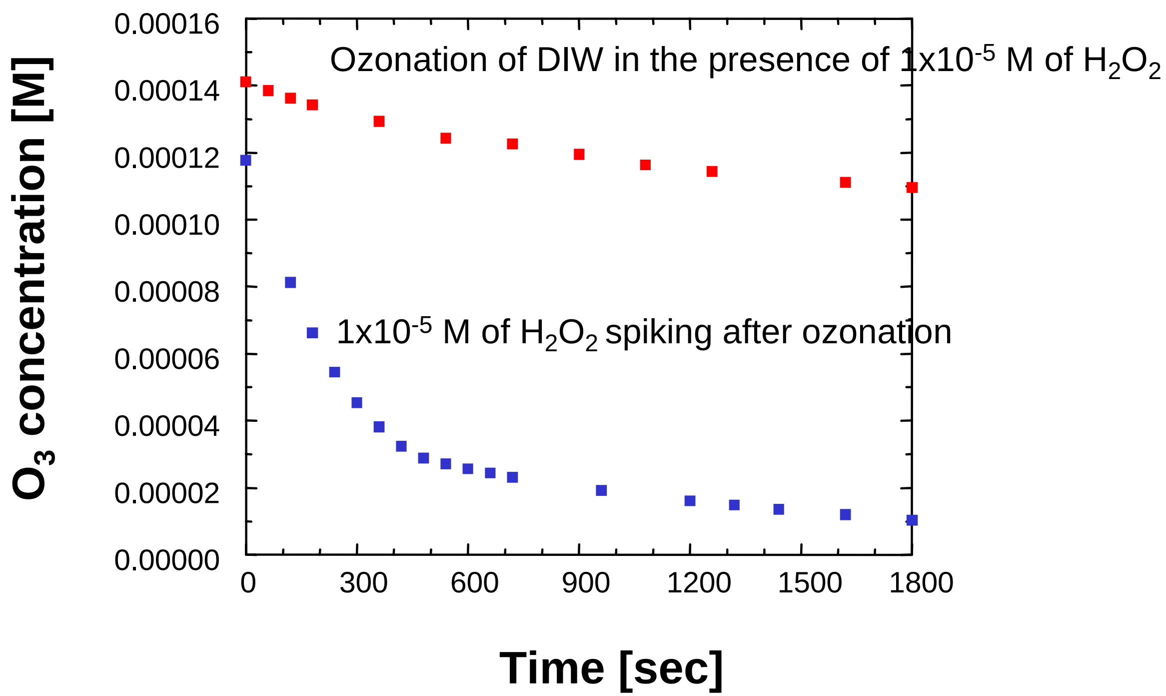
H_2O_2 and t-BuOH Addition





- In the presence of H_2O_2, *t*-BuOH addition increases the lifetime of ozone, which implies that the removal of organic species is accelerated by OH• formation due to H_2O_2 addition.

Optimization of the Process



- H_2O_2 is removed by an unknown reaction.
- Process sequence is important to enhance the photoresist stripping rate.

Summary

- If ozone is the required species in photoresist stripping, remove OH• by adding radical scavenger.

- If OH• is the required species, accelerate the formation of OH• by adding initiator. However, there is yet no evidence that sufficient concentrations of OH• can be obtained.

- Ozone chemistry, process temperature and process sequence are all expected to be important for maximization of photoresist strip rates.

Future Work

- Investigate role of swelling agents in increasing permeation of ozone into photoresist film.
  - hot water and other solvent vapors
  - aqueous base
  - reactive gases
- What are the products of stripping reaction?
  - hplc-ms of aqueous strip solutions
  - Complete oxidation to CO_2?