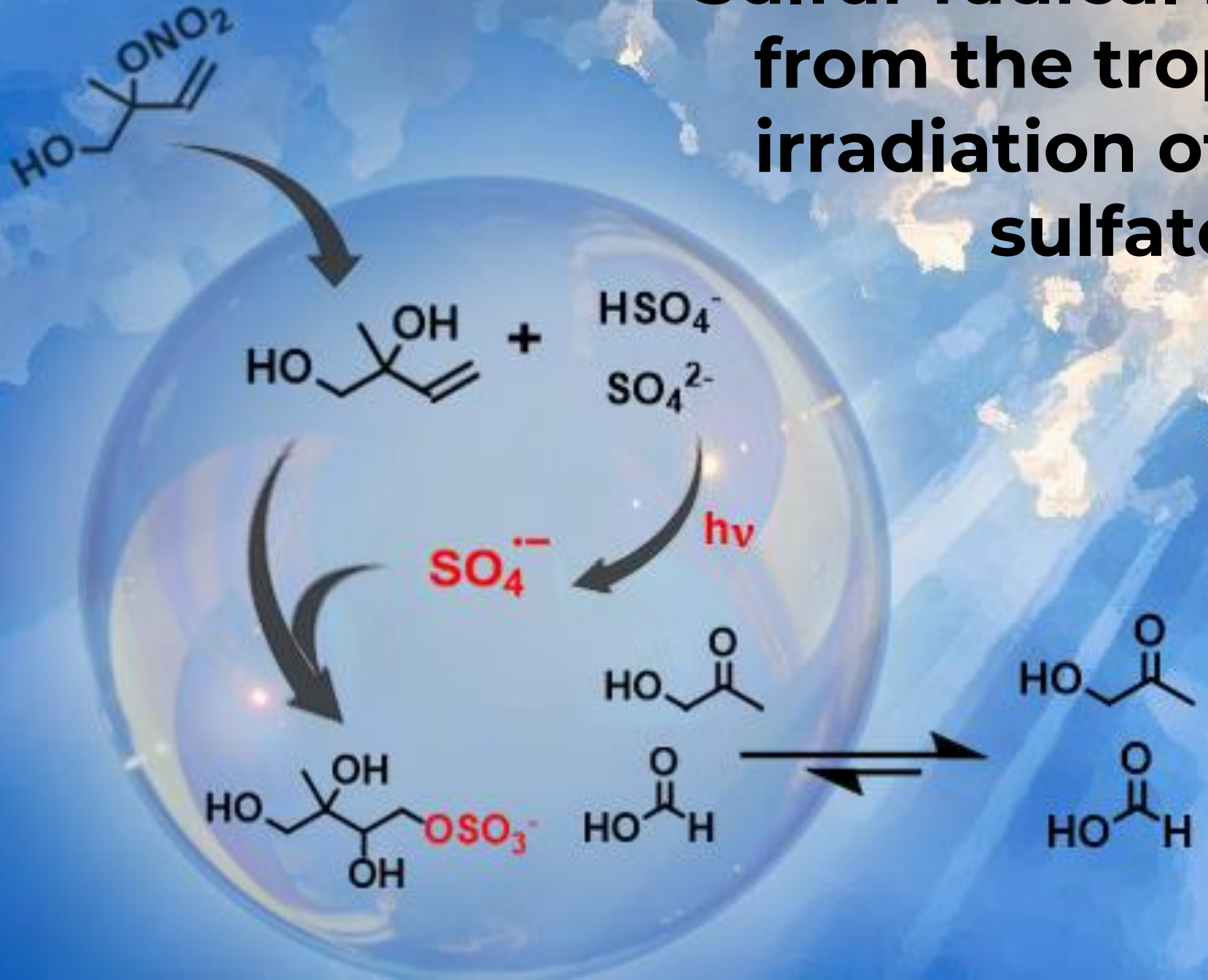
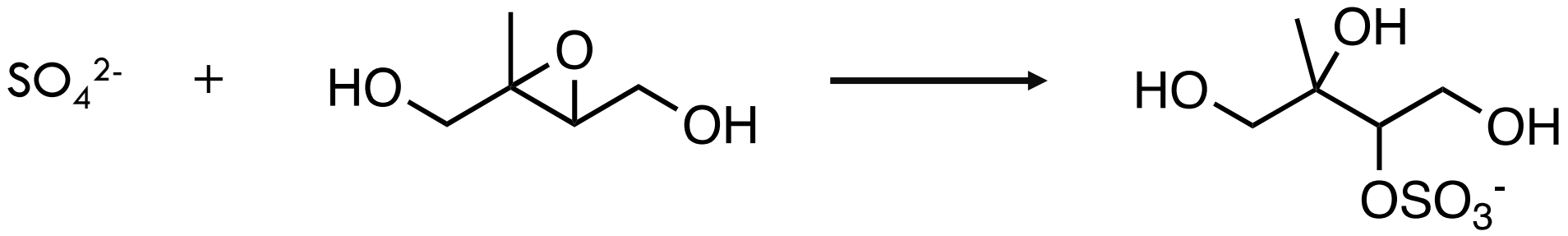
Sulfur radical formation from the tropospheric irradiation of aqueous sulfate aerosols

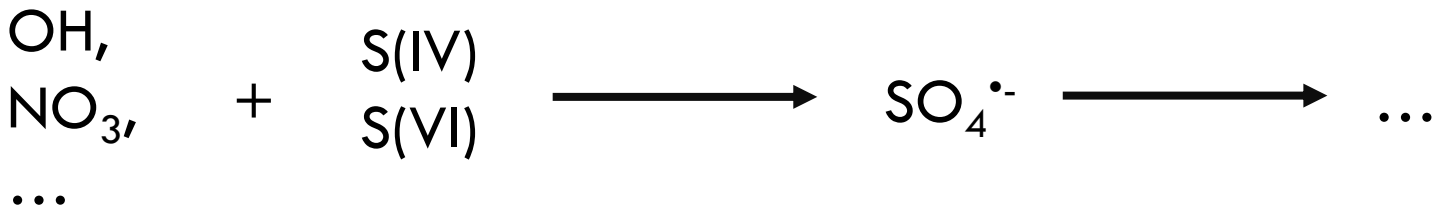
Kelvin Bates
James Cope
Lillian Tran
& Tran Nguyen

UC Davis



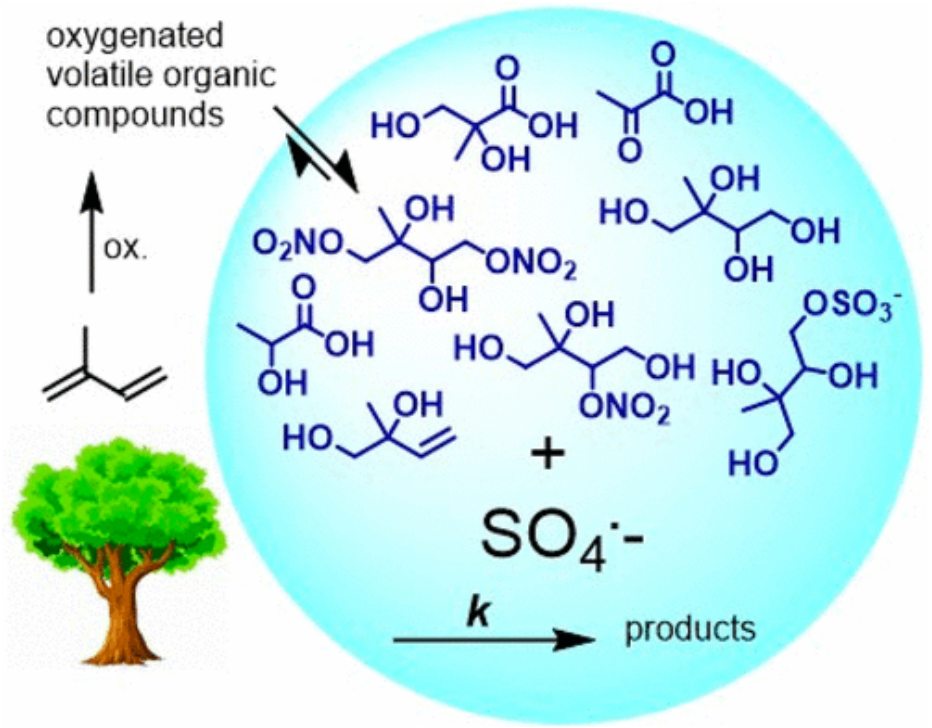
Atmospheric sulfur chemistry doesn't end at sulfate!

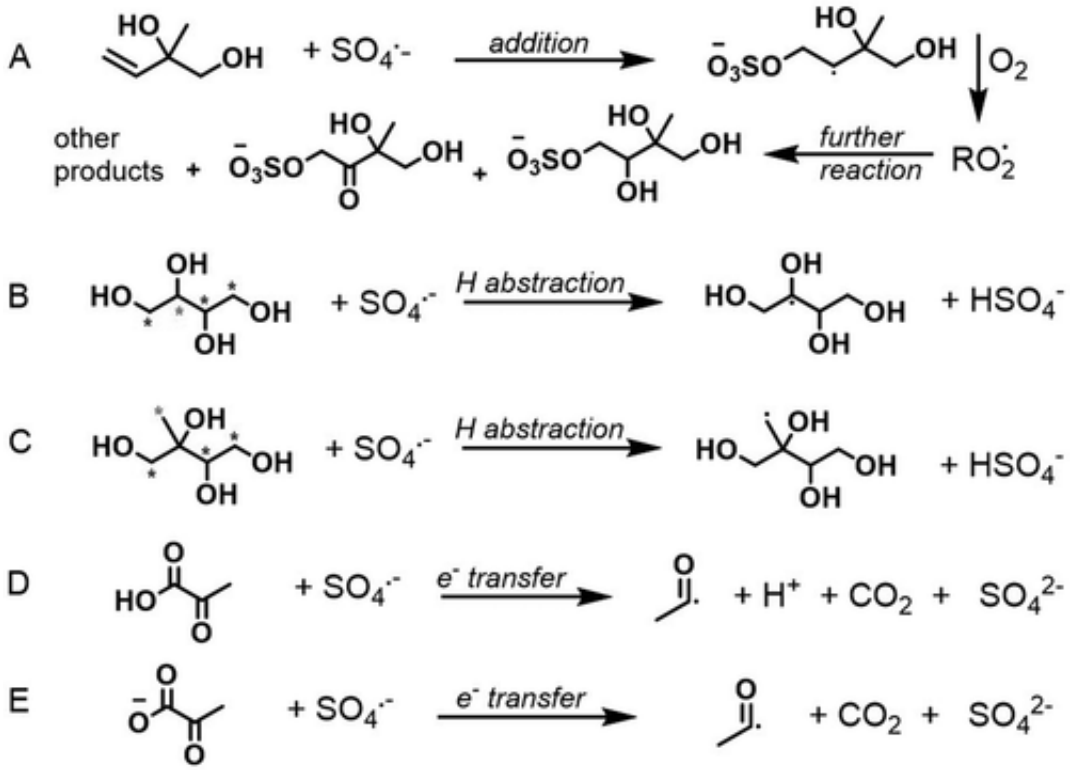




… but the sulfate anion radical ($SO_4^{\bullet-}$) is considered scarce, and only thought to be formed by more reactive radicals (e.g. OH, NO_3)

Atmospheric sulfur chemistry doesn't end at sulfate!

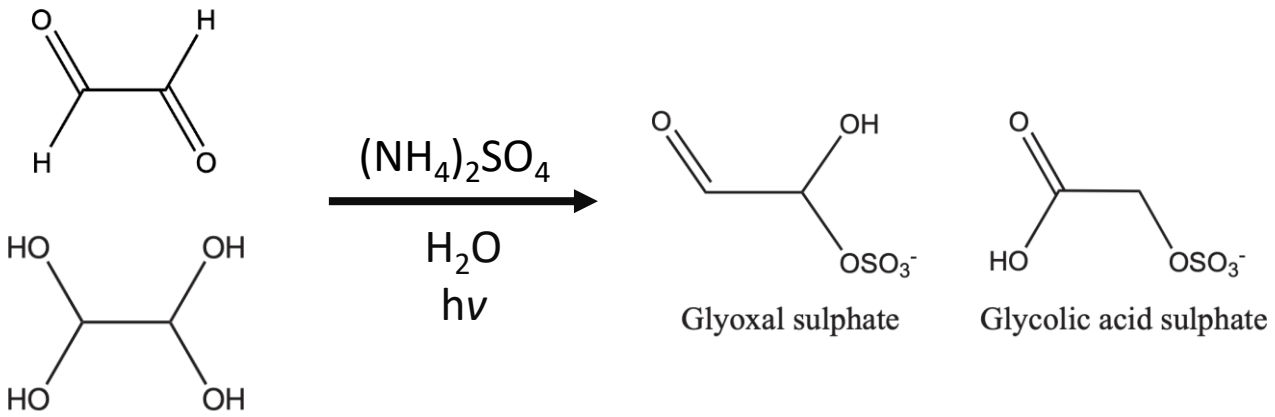


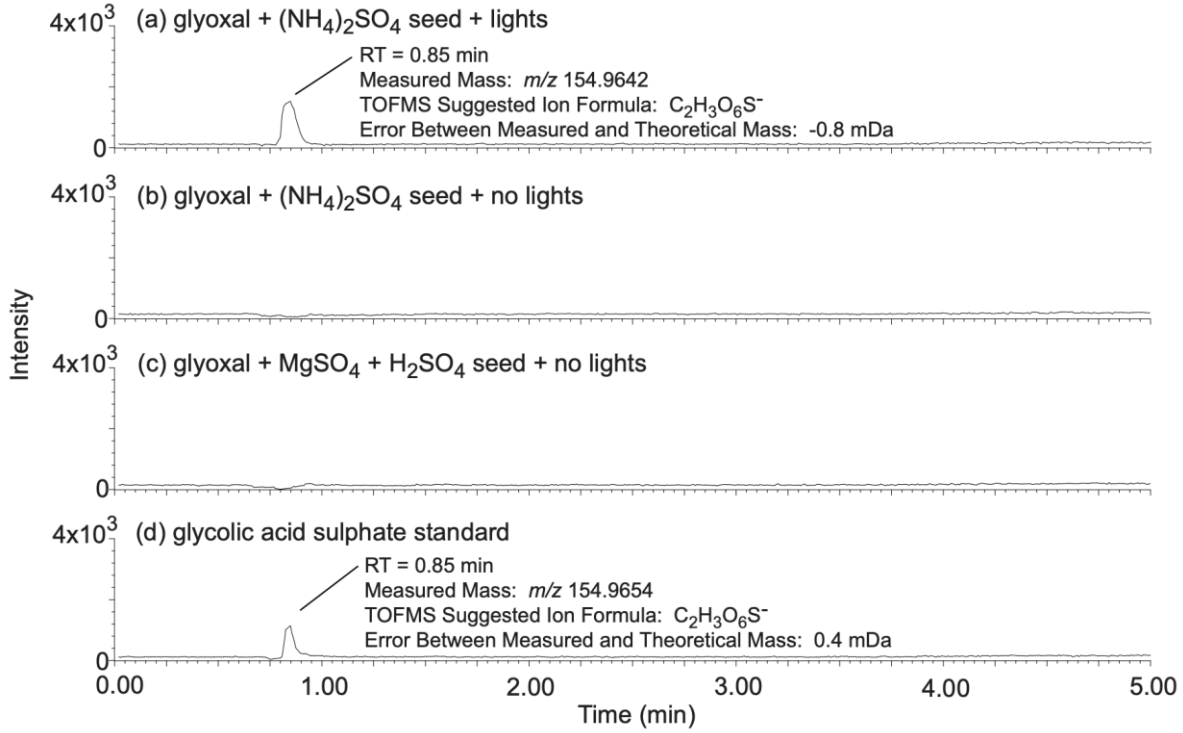


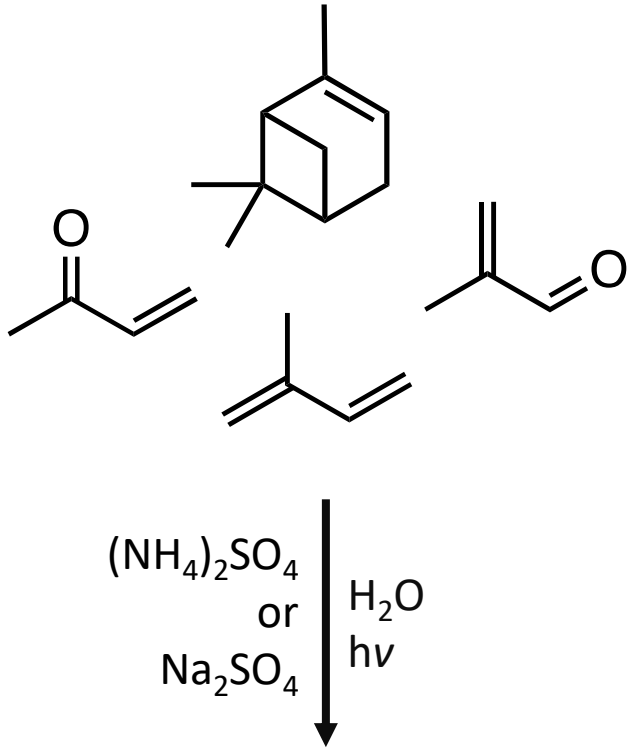
… but the sulfate anion radical ($SO_4^{\bullet-}$) is considered scarce, and only thought to be formed by more reactive radicals (e.g. OH, NO_3)

Tran *et al.*, JPCA, 2022

Previous findings cast doubt on the need for another radical source



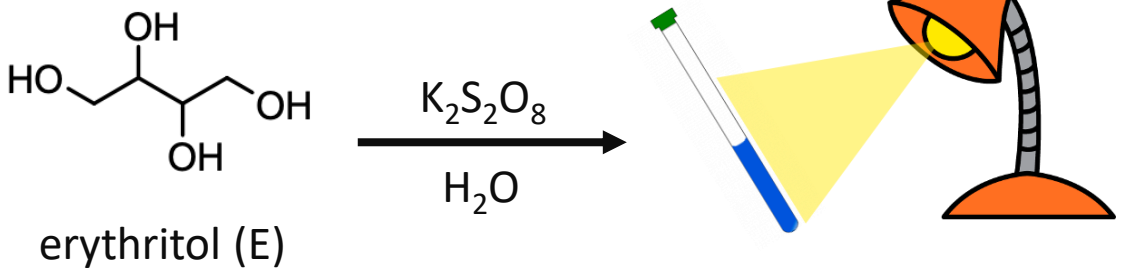




organosulfates

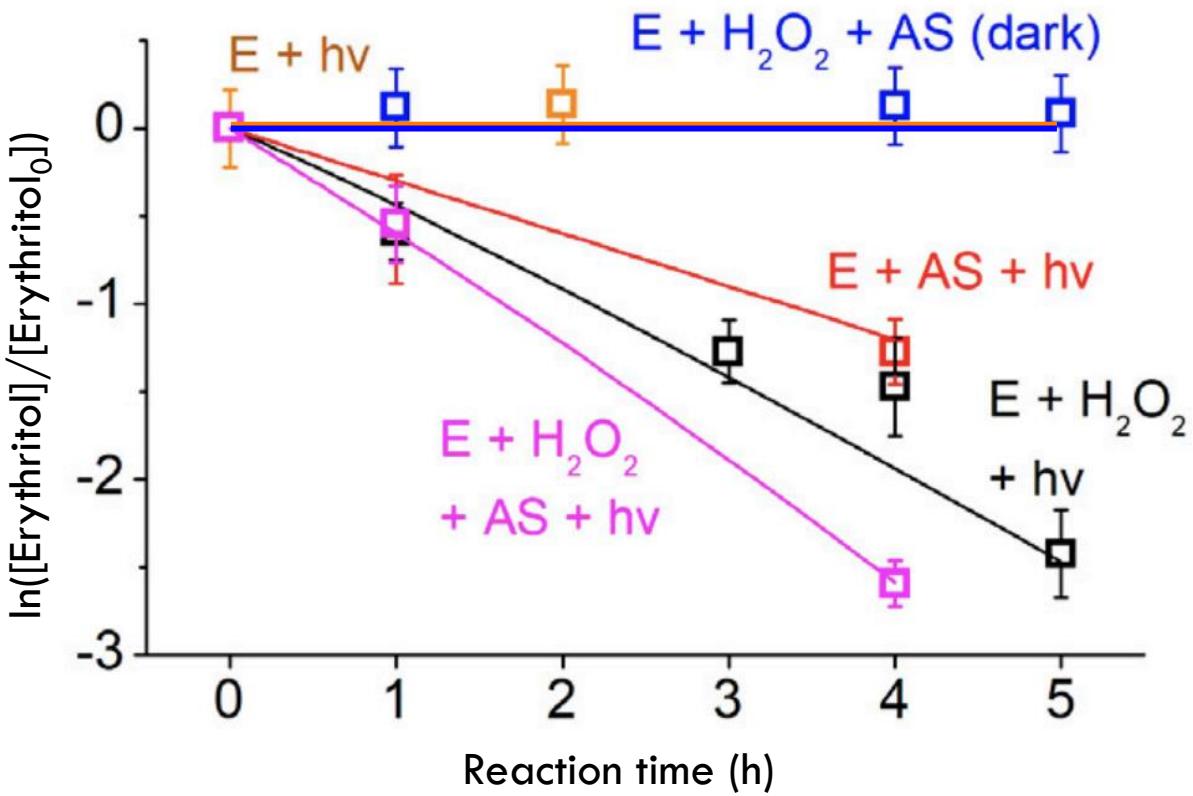
Galloway *et al.*, ACP, 2009
Nozière *et al.*, GRL, 2010

Can we initiate sulfate radical chemistry from only tropospheric radiation?



erythritol (E)

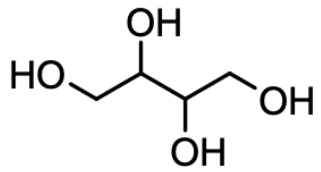
photolysis only:	X
with $(NH_4)_2SO_4$, dark:	X
with $h\nu + H_2O_2$:	✓
with $h\nu$ + 4M $(NH_4)_2SO_4$:	✓
with $h\nu + H_2O_2 + (NH_4)_2SO_4$:	✓ ✓



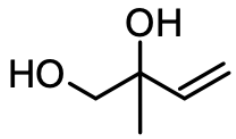
Lines: kinetic model with $SO_4^{2-} + h\nu \rightarrow e^- + SO_4^{\bullet-}$

So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

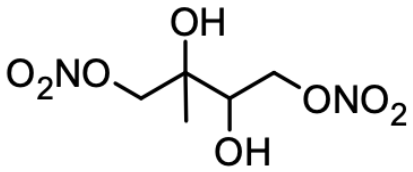
it's just erythritol?



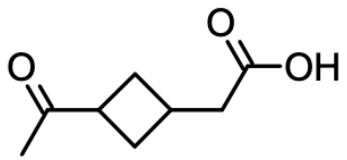
erythritol



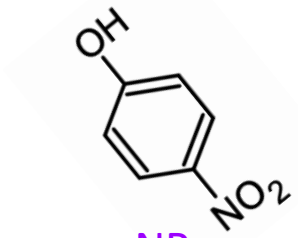
1,2-DHI
(dihydroxy-isoprene)



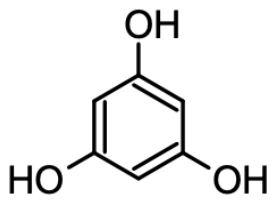
DHDN (dihydroxy-dinitrooxy-isoprene)



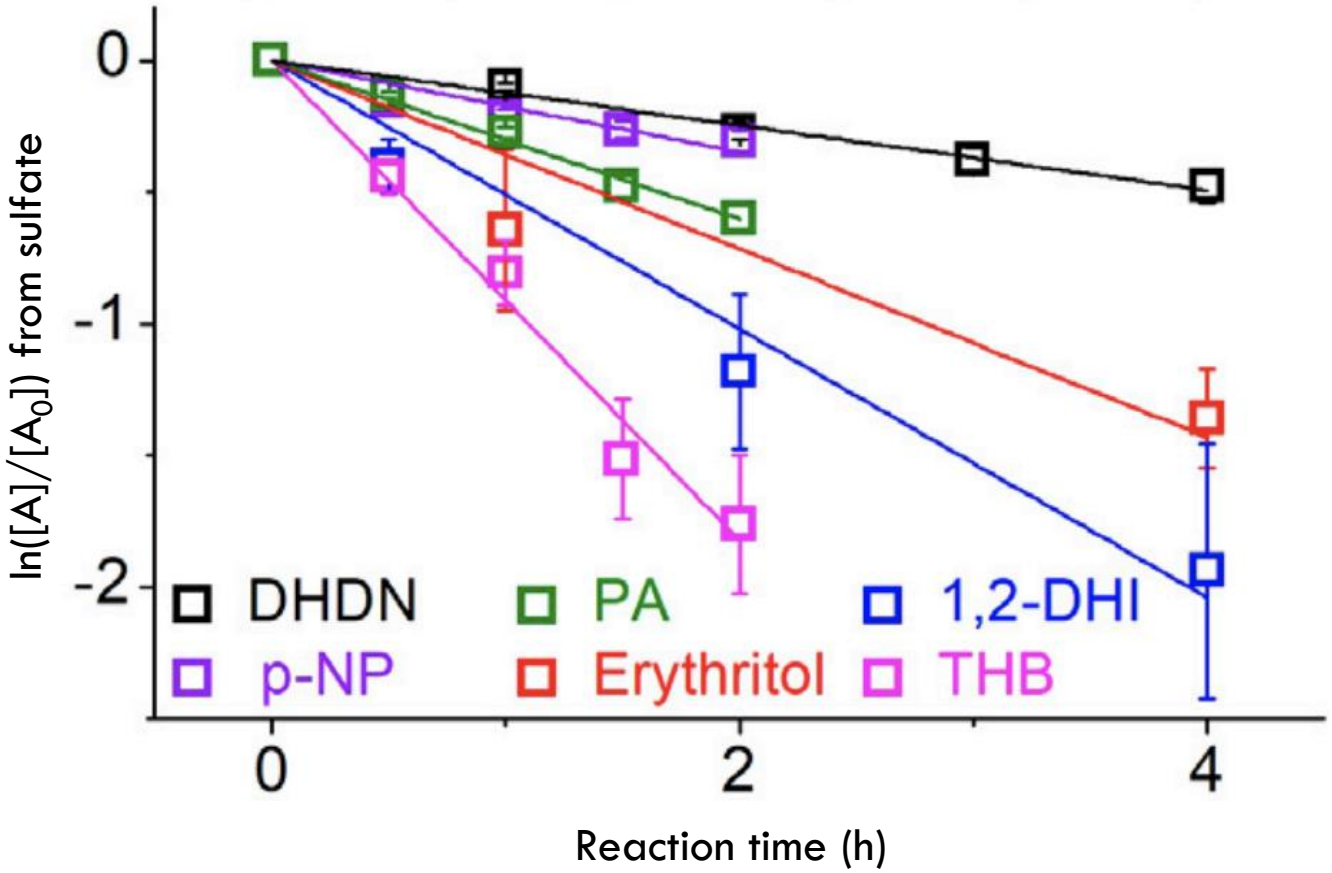
PA
(pinonic acid)



p-NP
(*para*-nitrophenol)



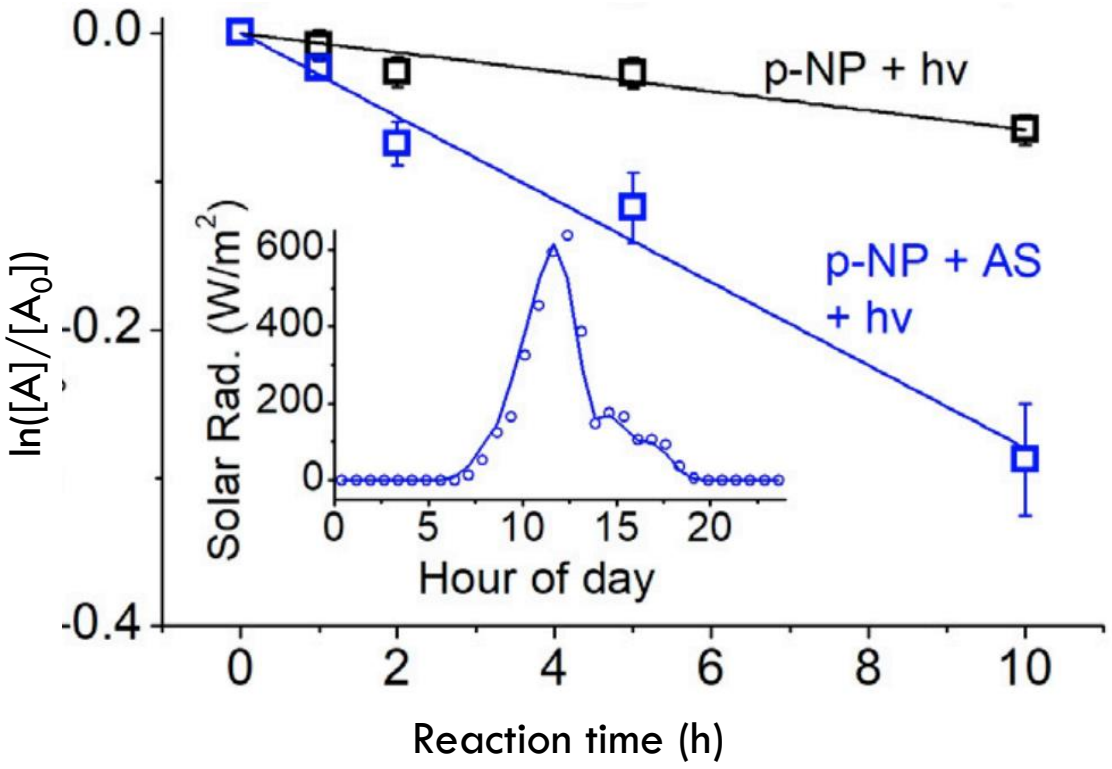
THB
(trihydroxy benzene)

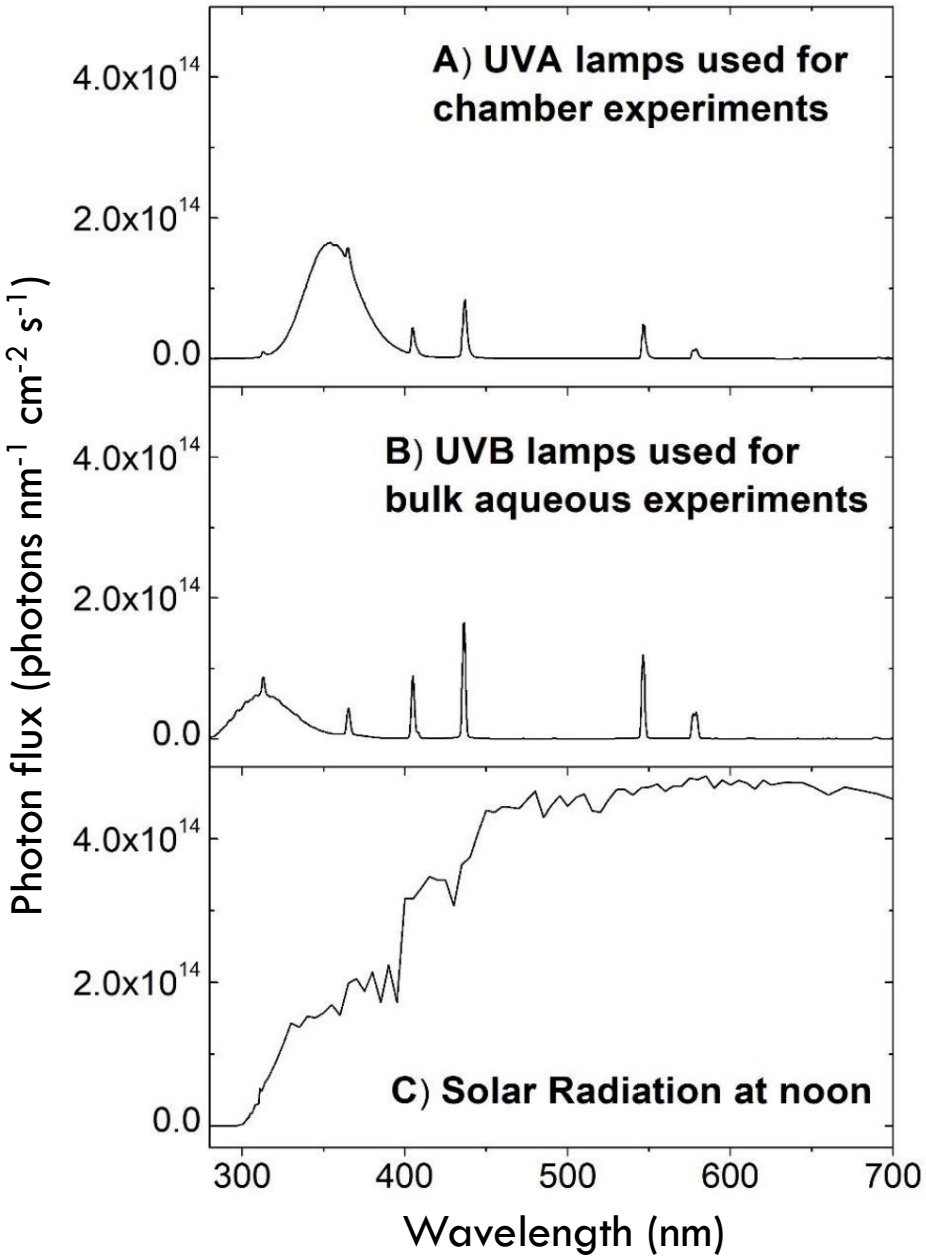


So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

~~it's just erythritol?~~

it's just our lamp?





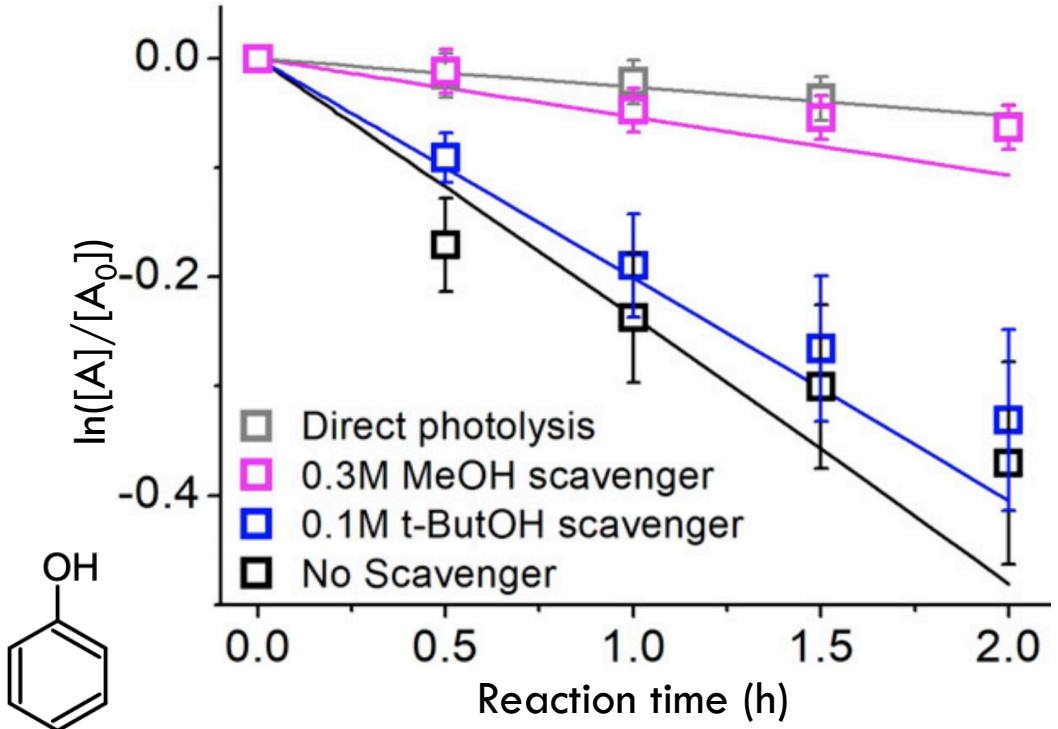
So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

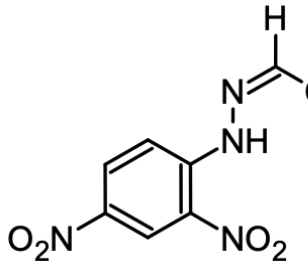
~~it's just erythritol?~~

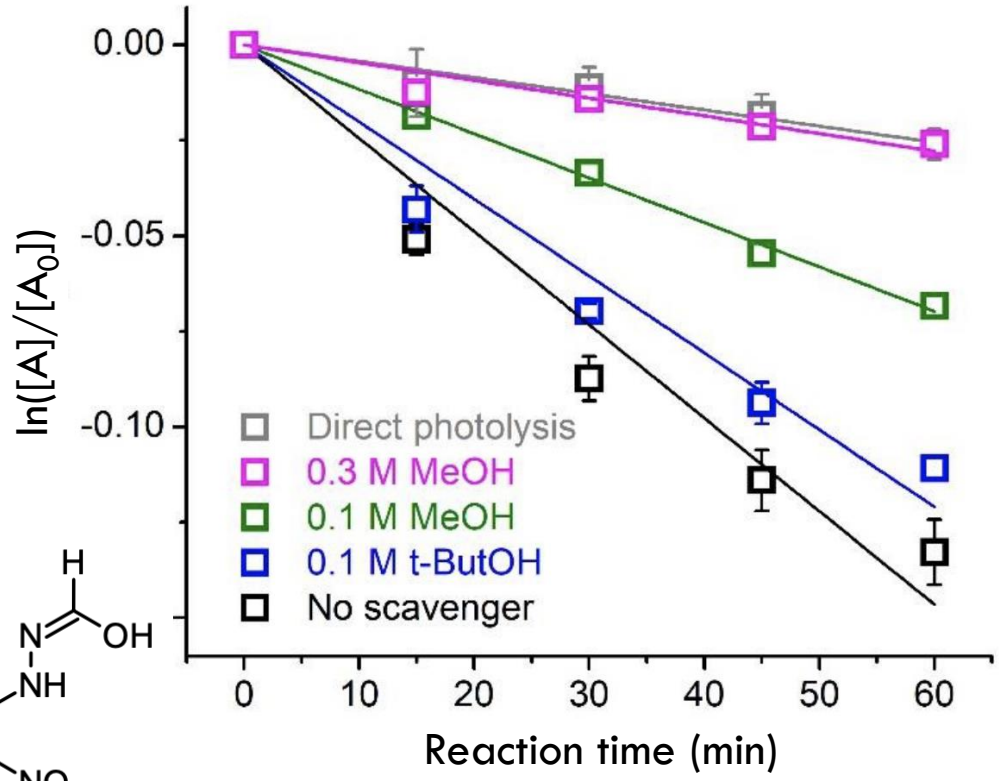
~~it's just our lamp?~~

it's actually OH?

	k(OH)	$k(SO_4^{\bullet-})$
tert-butanol	fast	slow
methanol	fast	fast







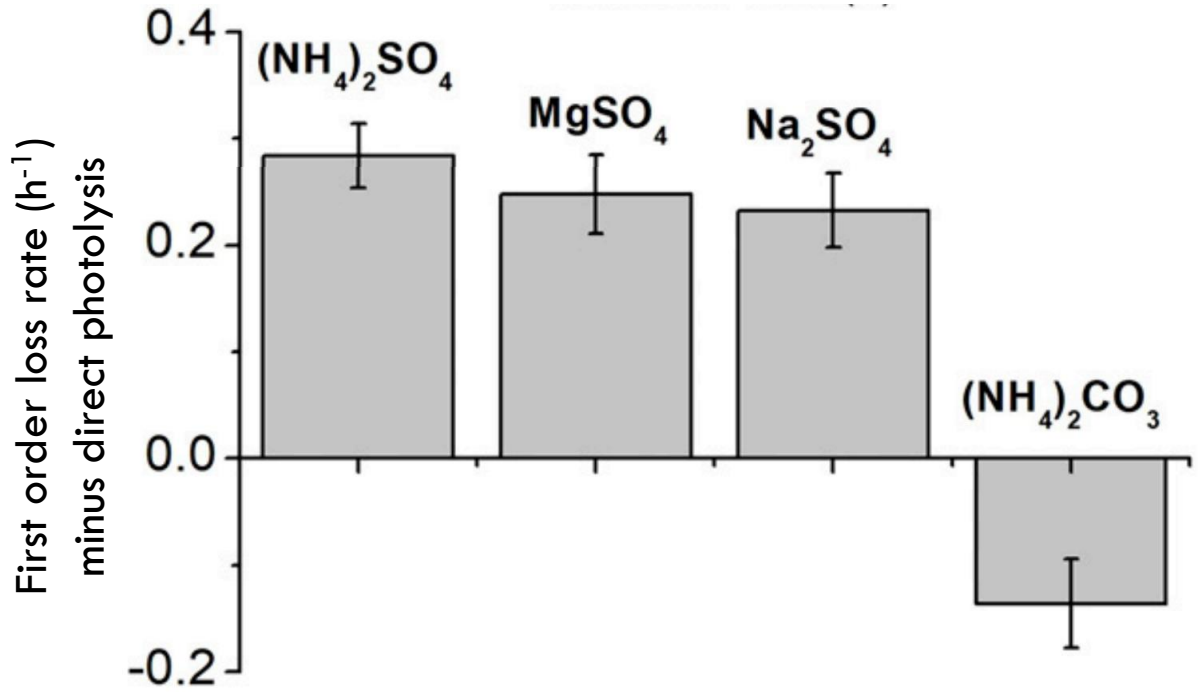
So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

~~it's just erythritol?~~

~~it's just our lamp?~~

~~it's actually OH?~~

it's the ammonium?



So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

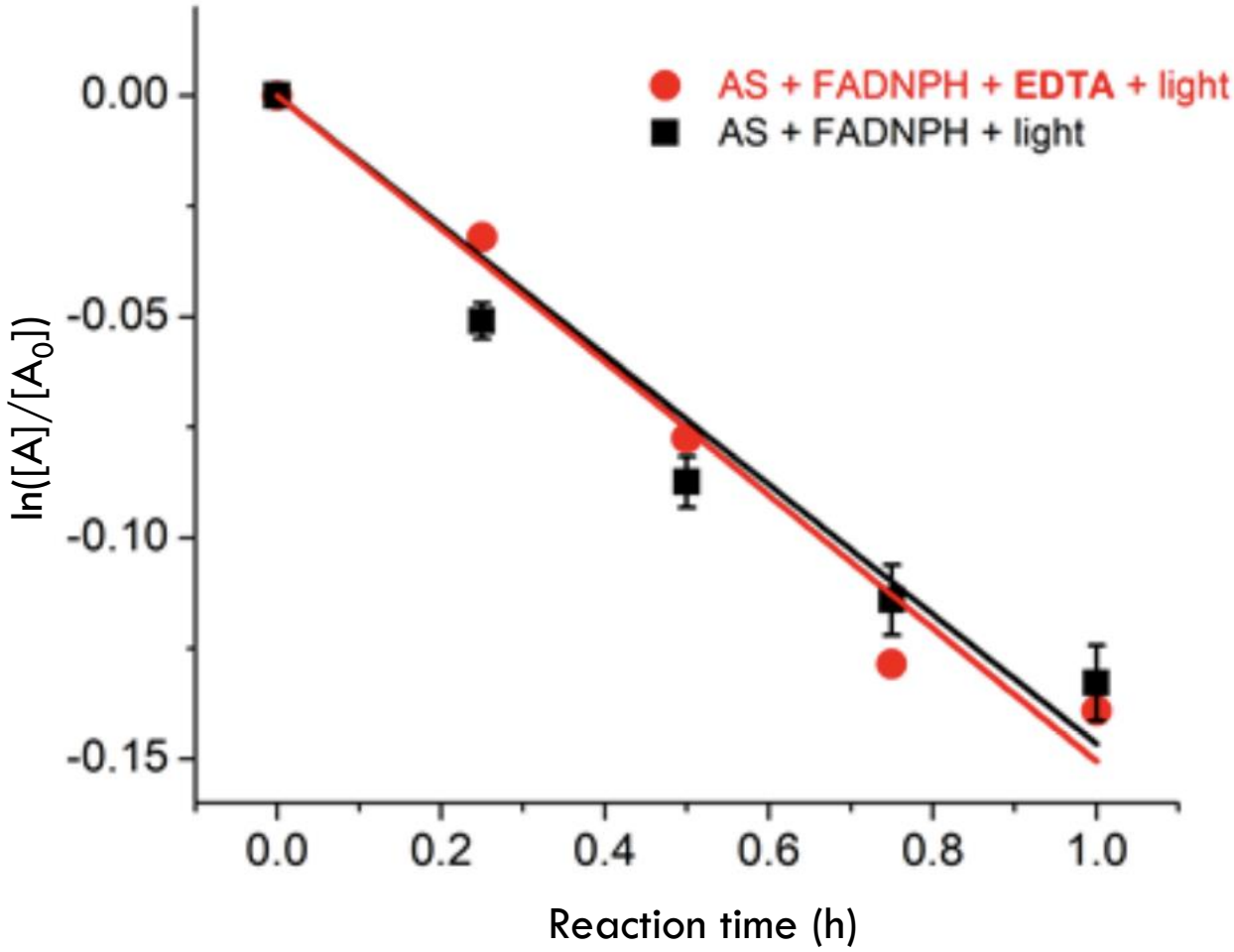
~~it's just erythritol?~~

~~it's just our lamp?~~

~~it's actually OH?~~

~~it's the ammonium?~~

it's a metal impurity?



So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

~~it's just erythritol?~~

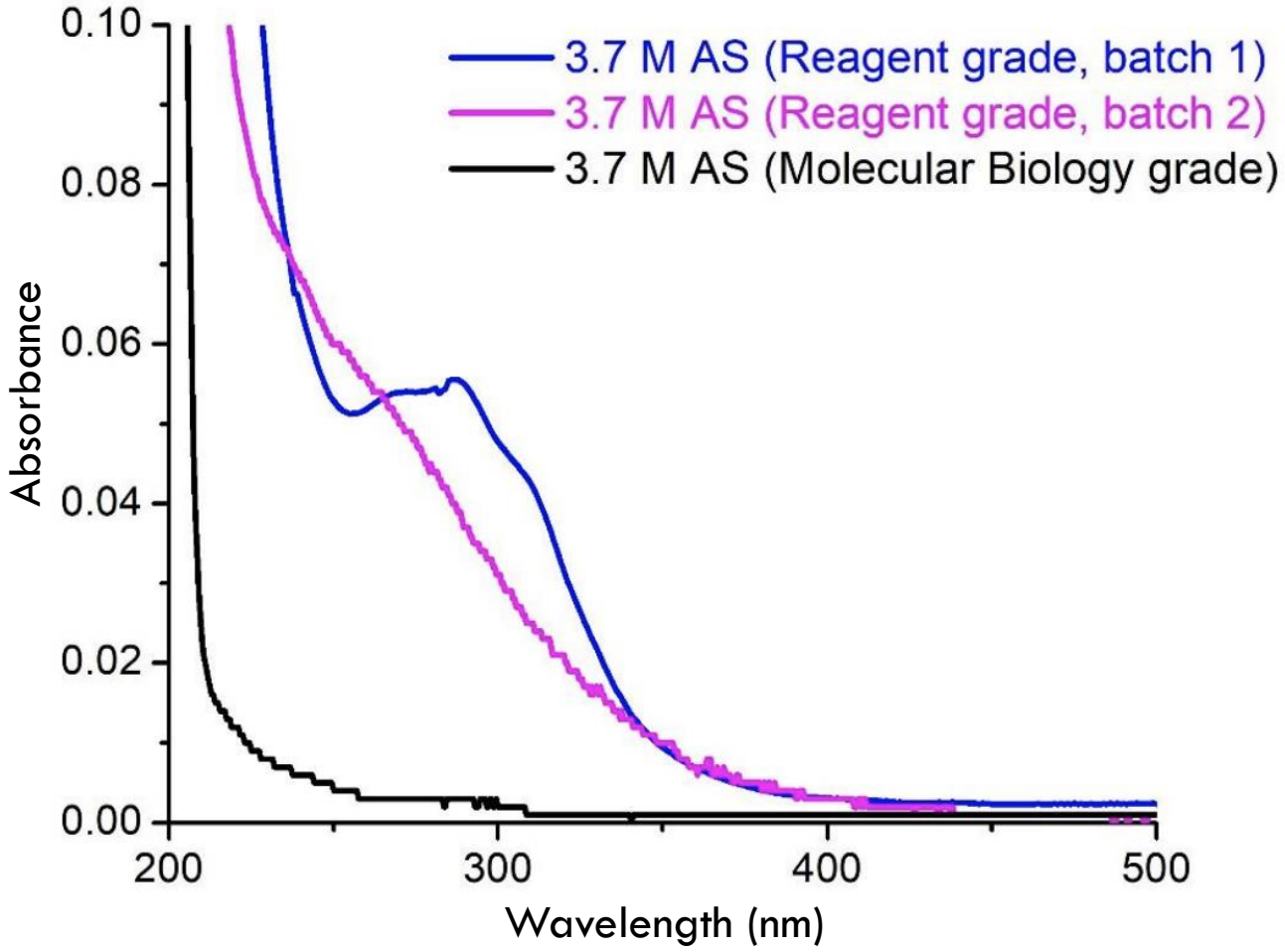
~~it's just our lamp?~~

~~it's actually OH?~~

~~it's the ammonium?~~

~~it's a metal impurity?~~

it's an absorbing impurity?



So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

~~it's just erythritol?~~

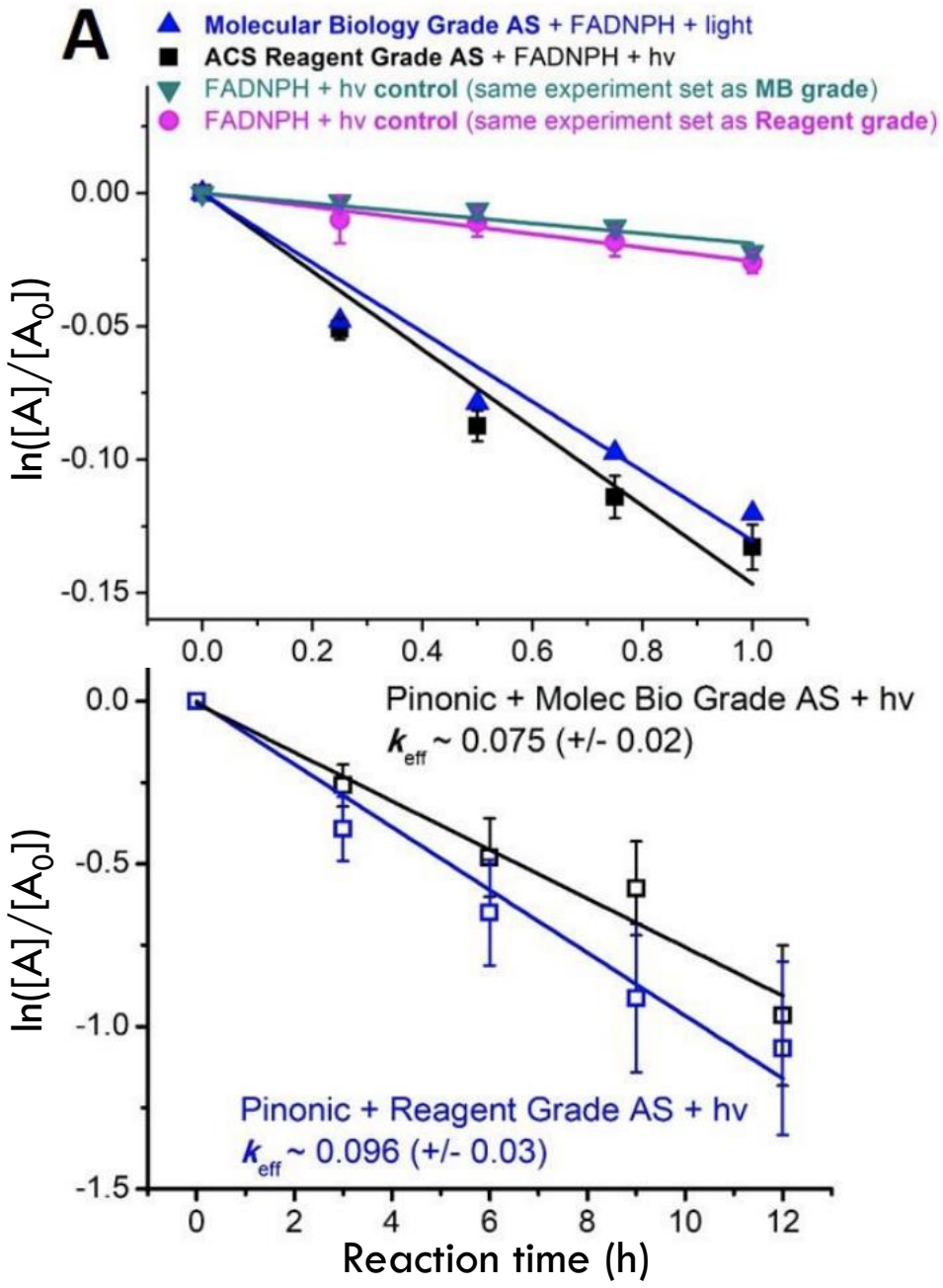
~~it's just our lamp?~~

~~it's actually OH?~~

~~it's the ammonium?~~

~~it's a metal impurity?~~

it's an absorbing impurity?



So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

~~it's just erythritol?~~

~~it's just our lamp?~~

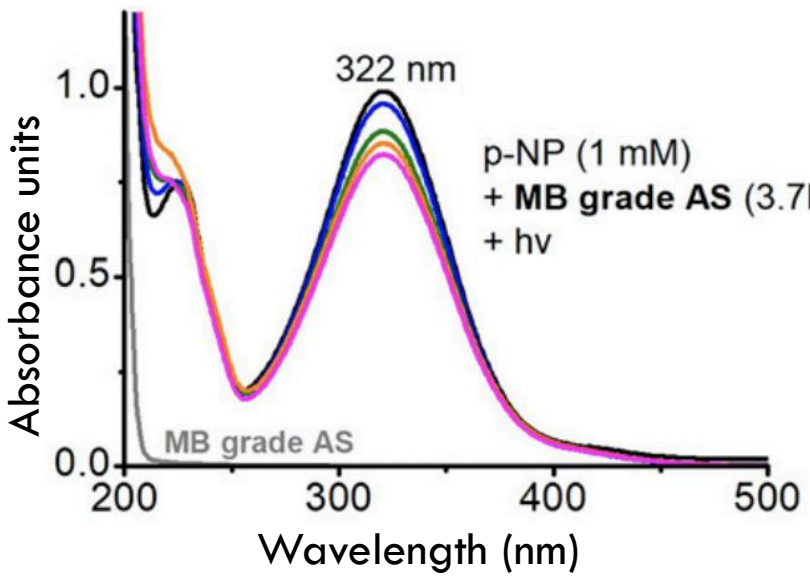
~~it's actually OH?~~

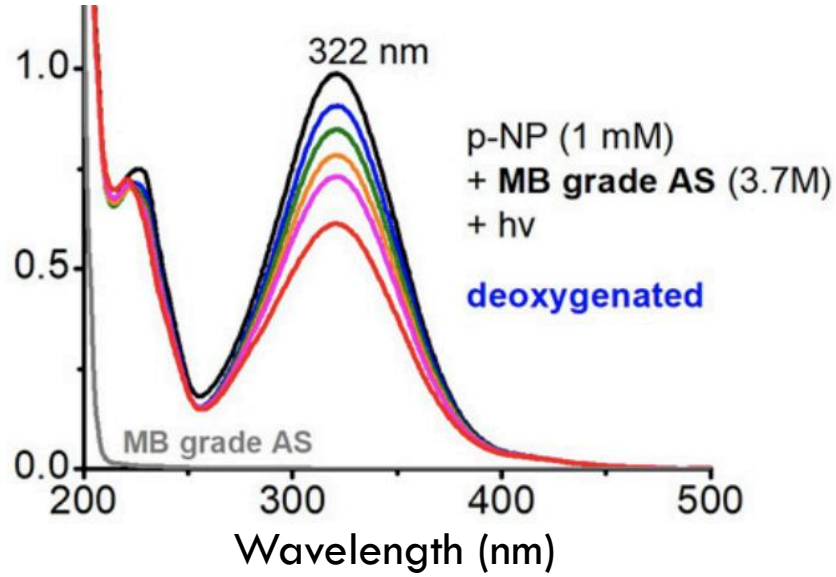
~~it's the ammonium?~~

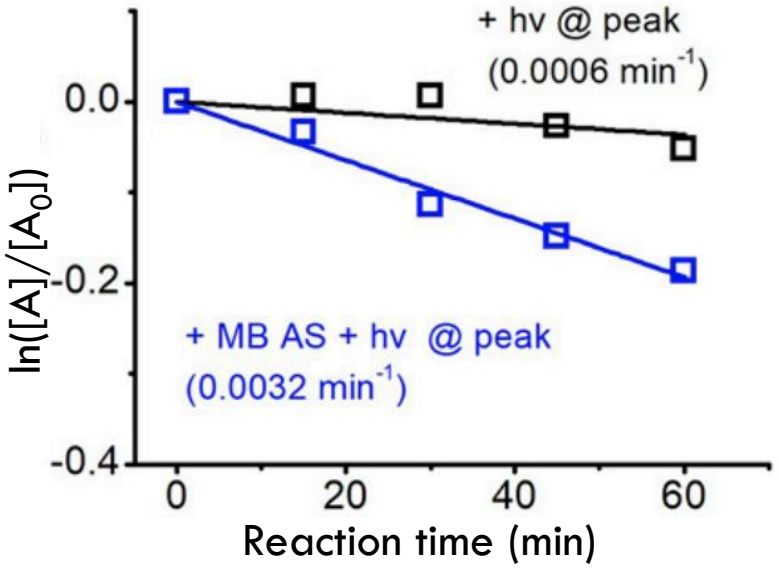
~~it's a metal impurity?~~

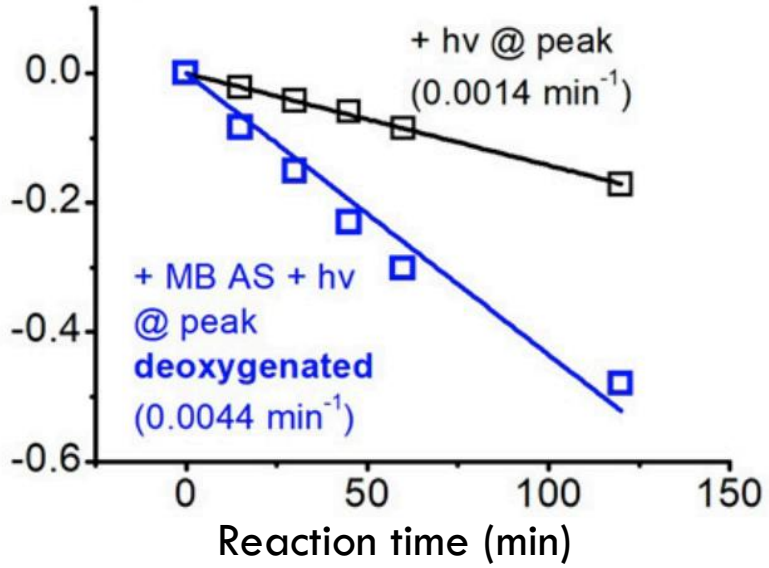
~~it's another impurity?~~

it's oxygen?









So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

~~it's just erythritol?~~

~~it's just our lamp?~~

~~it's actually OH?~~

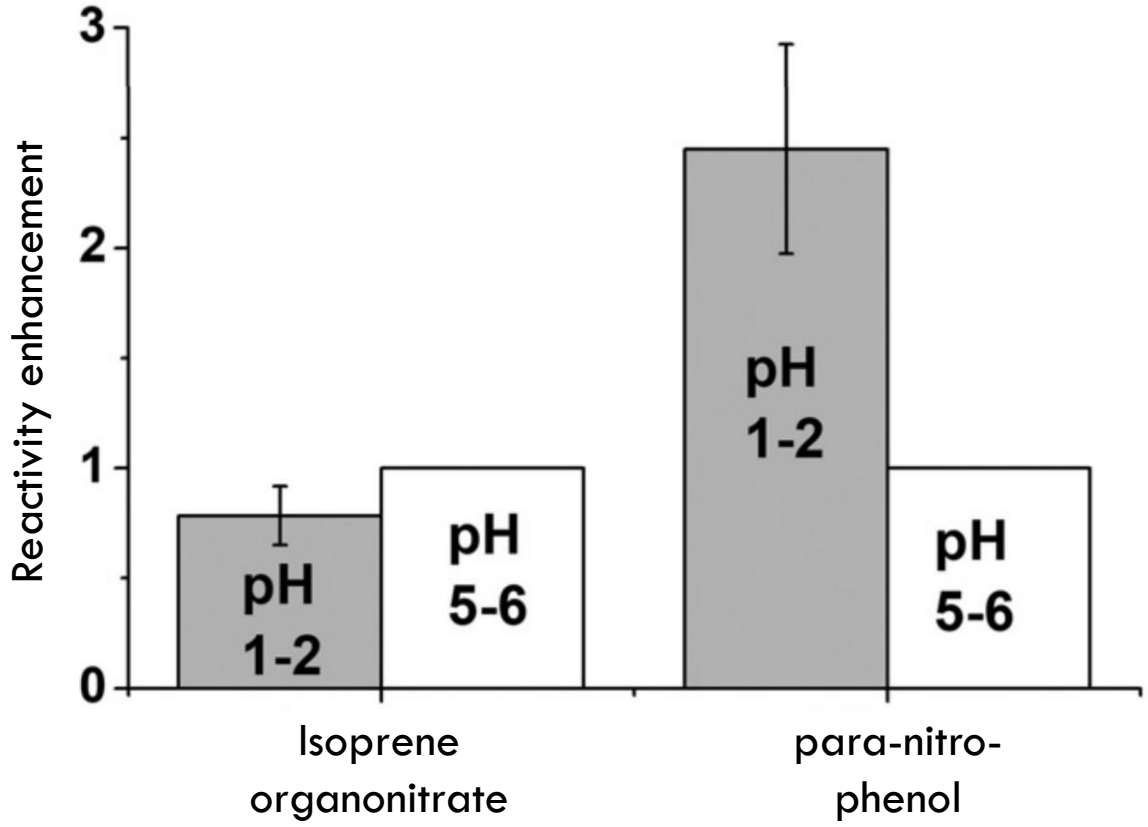
~~it's the ammonium?~~

~~it's a metal impurity?~~

~~it's another impurity?~~

~~it's oxygen?~~

it's pH dependent?



So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

~~it's just erythritol?~~

~~it's just our lamp?~~

~~it's actually OH?~~

~~it's the ammonium?~~

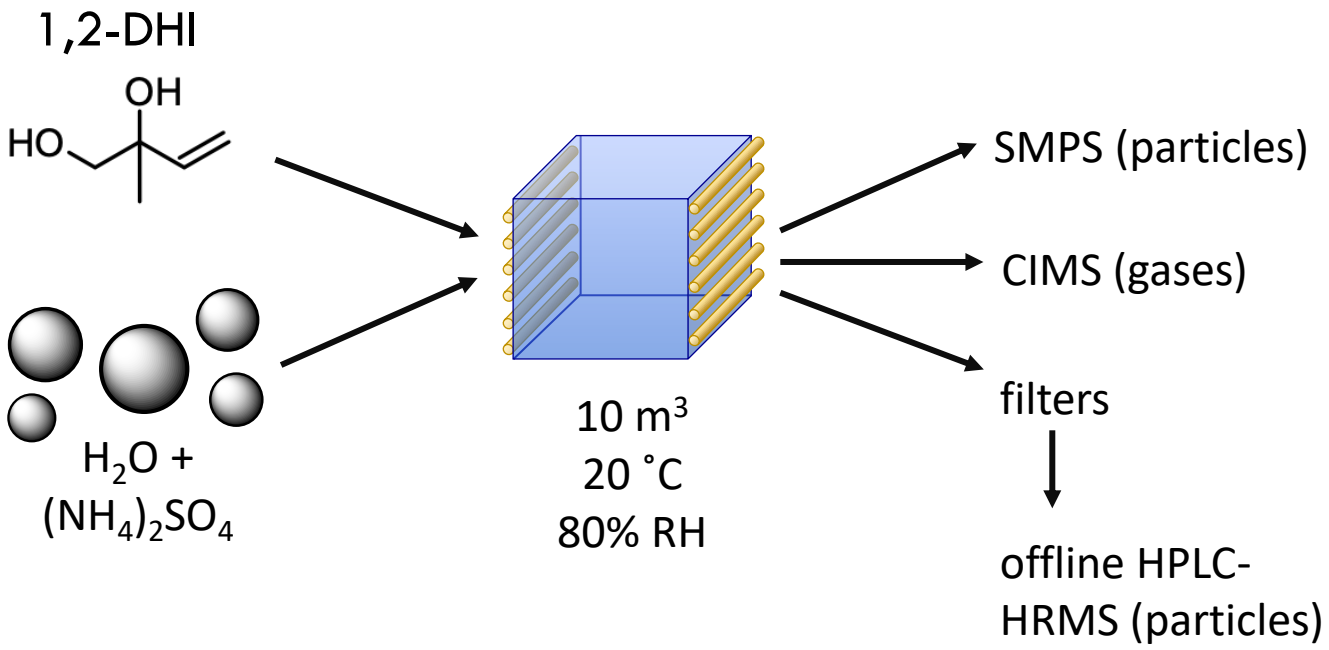
~~it's a metal impurity?~~

~~it's another impurity?~~

~~it's oxygen?~~

~~it's pH dependent?~~ (…?)

it's only in bulk solution?



So, ***yes***, we can photochemically generate $SO_4^{\bullet-}$, but what if…

~~it's just erythritol?~~

~~it's just our lamp?~~

~~it's actually OH?~~

~~it's the ammonium?~~

~~it's a metal impurity?~~

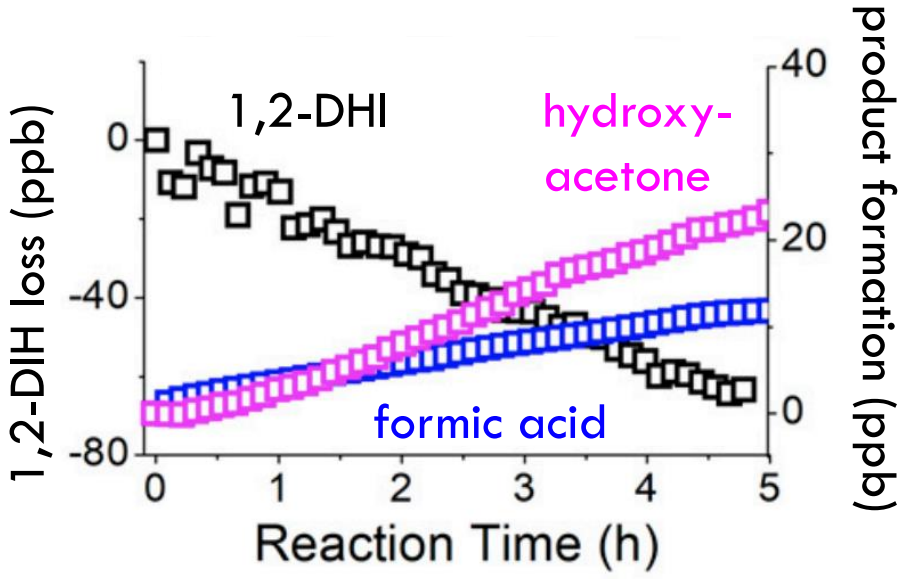
~~it's another impurity?~~

~~it's oxygen?~~

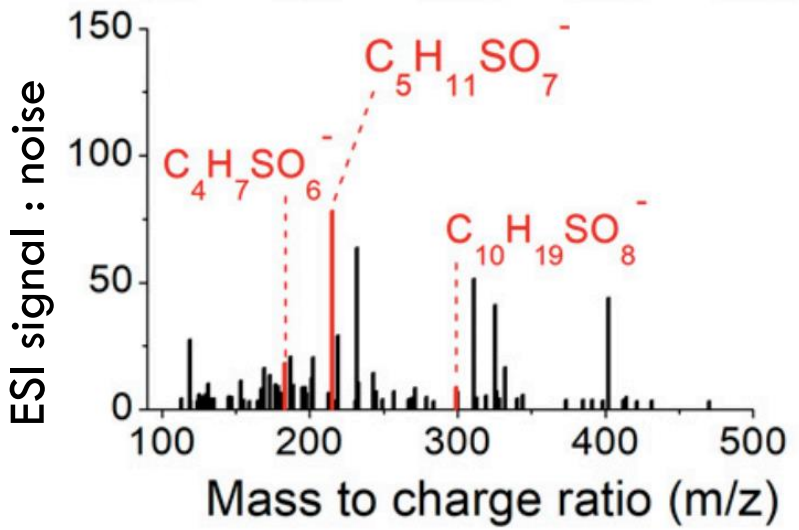
~~it's pH dependent?~~

it's only in bulk?

<u>gas phase:</u>
fragmentation products



<u>particle phase:</u>
organo-sulfates



Limitations & implications

What's the mechanism? (direct e^- ejection?)

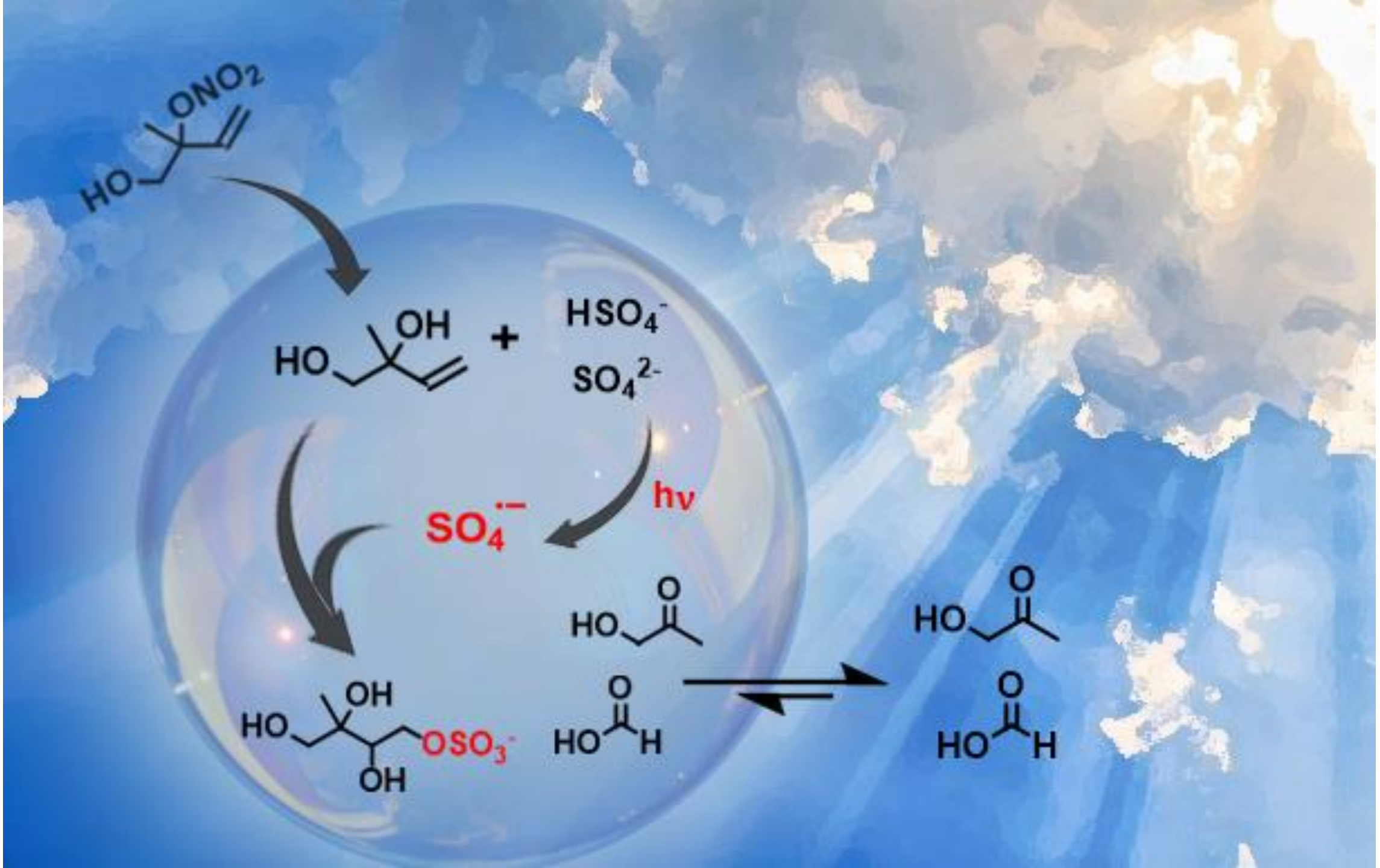
Estimated aerosol $[SO_4^{\bullet-}]_{ss}$ of 10^{-14}=10^{-12} M, potentially exceeding OH

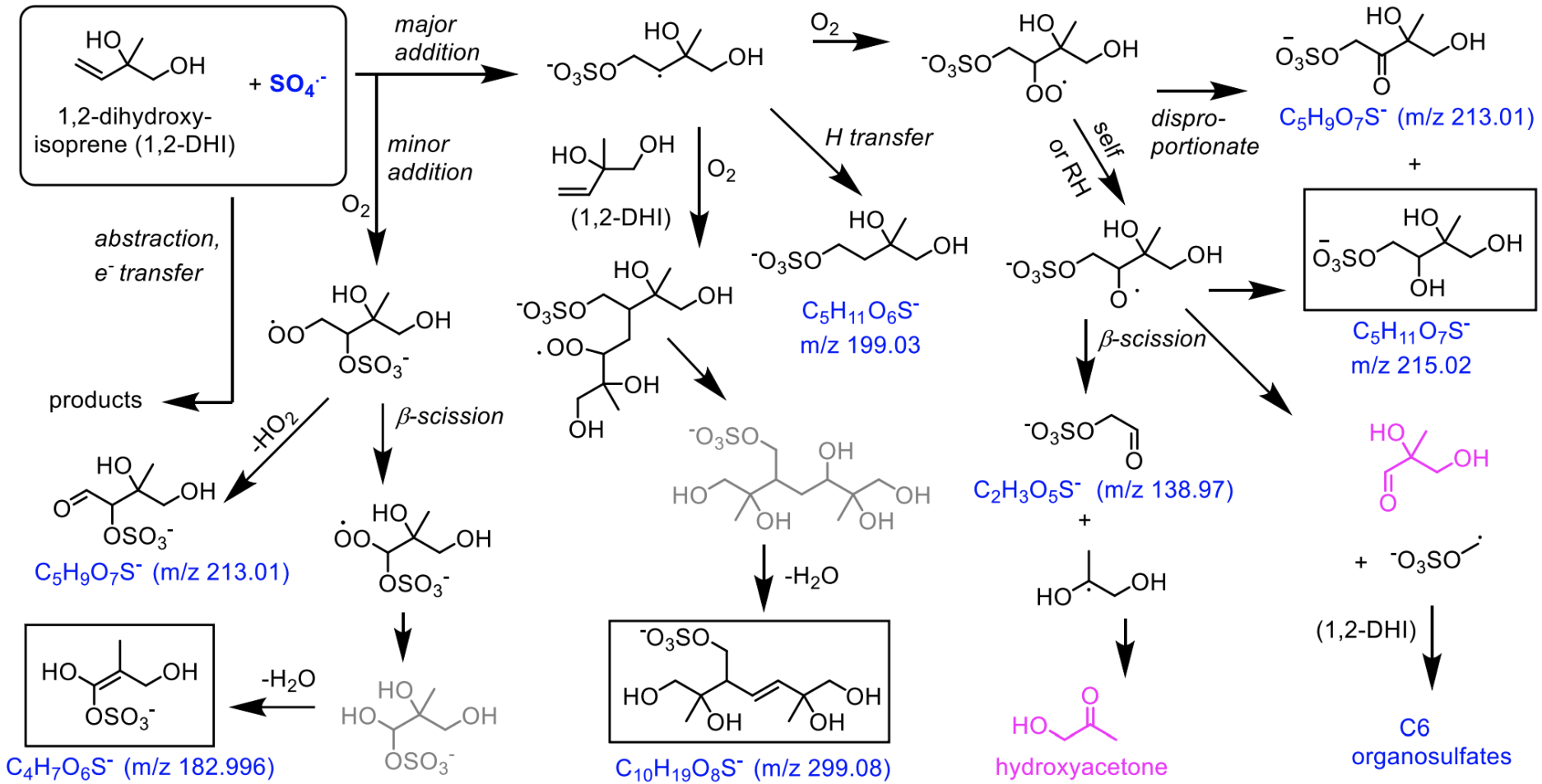
$SO_4^{\bullet-}$ oxidation of S(IV) could catalyze more sulfate formation

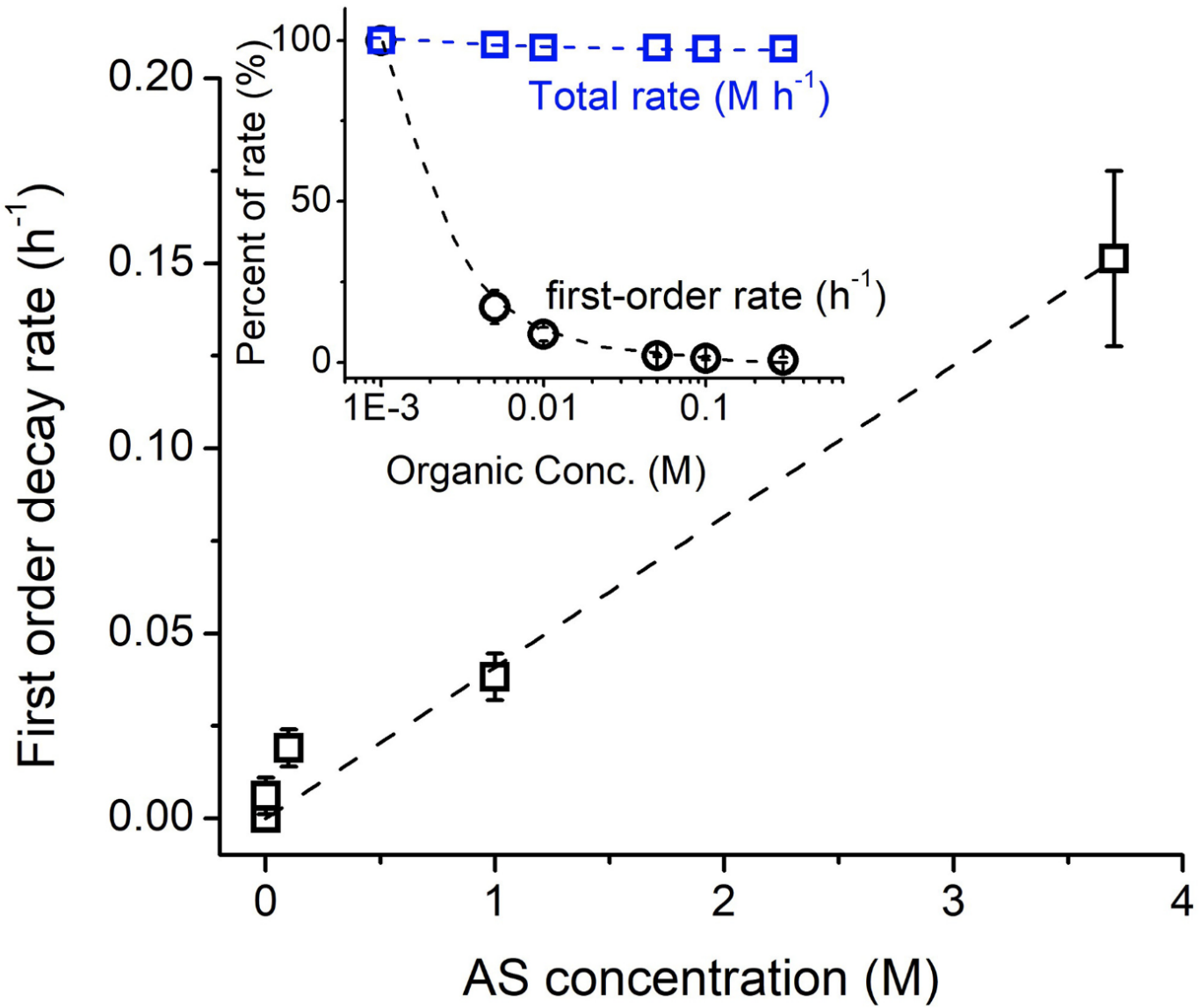
Fragmentation of organics by $SO_4^{\bullet-}$ could lead to particle mass loss and production of gas-phase acids & oxygenates

Functionalization of organics by $SO_4^{\bullet-}$ could lead to particle mass gain and changes in surface properties

Chamber experimental results may be complicated (and to some extent explained) by $SO_4^{\bullet-}$ chemistry


ONO2
HO
OH
HO
+
HSO4-
SO4 2-
hν
SO4 •−
HO
O
HO
OH
HO
OSO3-
OH
O
HO
H
O
HO
O
HO
H


1,2-dihydroxy-isoprene (1,2-DHI)
+ SO4•-
major addition
minor addition
O2
abstraction, e- transfer
products
-HO2
β-scission
C5H9O7S- (m/z 213.01)
-H2O
C4H7O6S- (m/z 182.996)
(1,2-DHI)
H transfer
C5H11O6S-
m/z 199.03
-H2O
C10H19O8S- (m/z 299.08)
self or RH
dispro-portionate
C5H9O7S- (m/z 213.01)
+
C5H11O7S-
m/z 215.02
β-scission
C2H3O5S- (m/z 138.97)
+
hydroxyacetone
+
(1,2-DHI)
C6 organosulfates


First order decay rate (h-1)
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
AS concentration (M)
Percent of rate (%)
100
50
0
Total rate (M h-1)
first-order rate (h-1)
1E-3
0.01
0.1
Organic Conc. (M)