Supporting Information

How Phenol and α-Tocopherol React with Ambient Ozone at Gas/Liquid Interfaces

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Appendix SA

The pH values used in the text are defined as the pH values in methanol referenced to water as standard state solvent.[1] The pH so defined, ${}^{s}_{w}\mathrm{pH}$, is correlated with pH values in methanol referenced to methanol itself, ${}^{s}_{s}\mathrm{pH}$, according to equation (I).[1]

$$ {}^{s}_{w}\mathrm{pH} = {}^{s}_{s}\mathrm{pH} - \log({}^{s}_{w}\gamma^{0}_{H}) \qquad \text{(I)} $$

where ${}^{s}_{w}\gamma^{0}_{H}$ is the single-ion activity coefficients of the hydrogen ion listed in Table 1 of Rosés & Bosch's review.[1] The $-\log({}^{s}_{w}\gamma^{0}_{H})$ value in 100% methanol is -2.00.

The p*K*a value of α-TOH in methanol solution in the ${}^{s}_{w}\mathrm{pH}$ scale, ${}^{s}_{w}p\mathit{K}a$, is obtained from the p*K*a in the ${}^{s}_{s}\mathrm{pH}$ scale, ${}^{s}_{s}p\mathit{K}a$, as follows:

$$ {}^{s}_{w}p\mathit{K}a = {}^{s}_{s}p\mathit{K}a - \log({}^{s}_{w}\gamma^{0}_{H}) \qquad \text{(II)} $$

where ${}^{s}_{s}p\mathit{K}a$ is evaluated from the equation (III):

$$ {}^{s}_{s}p\mathit{K}a = a_s \, {}^{w}_{w}p\mathit{K}a + b_s \qquad \text{(III)} $$

In equation (III), ${}^{w}_{w}p\mathit{K}a$ is the p*K*a value of α-TOH in water, reported to be 13.1,[2] a_s and b_s are the empirical parameters calculated from Table 6 in Rosés & Bosch's review by assuming similar values for phenol and α-TOH.[1] From the equations above and the values listed in the Tables, we get: ${}^{s}_{s}p\mathit{K}a = 17.7$ and ${}^{s}_{w}p\mathit{K}a = 15.7$ at 298 K.

[1] Roses, M.; Bosch, E., *J. Chromatogr. A* **2002**, *982*, 1-30.
[2] Mukai K. et al. *J. Phys. Chem. B* **2007**, *111*, 652-662.

Table S1. MS/MS of α-TO^- and its ozonolysis products

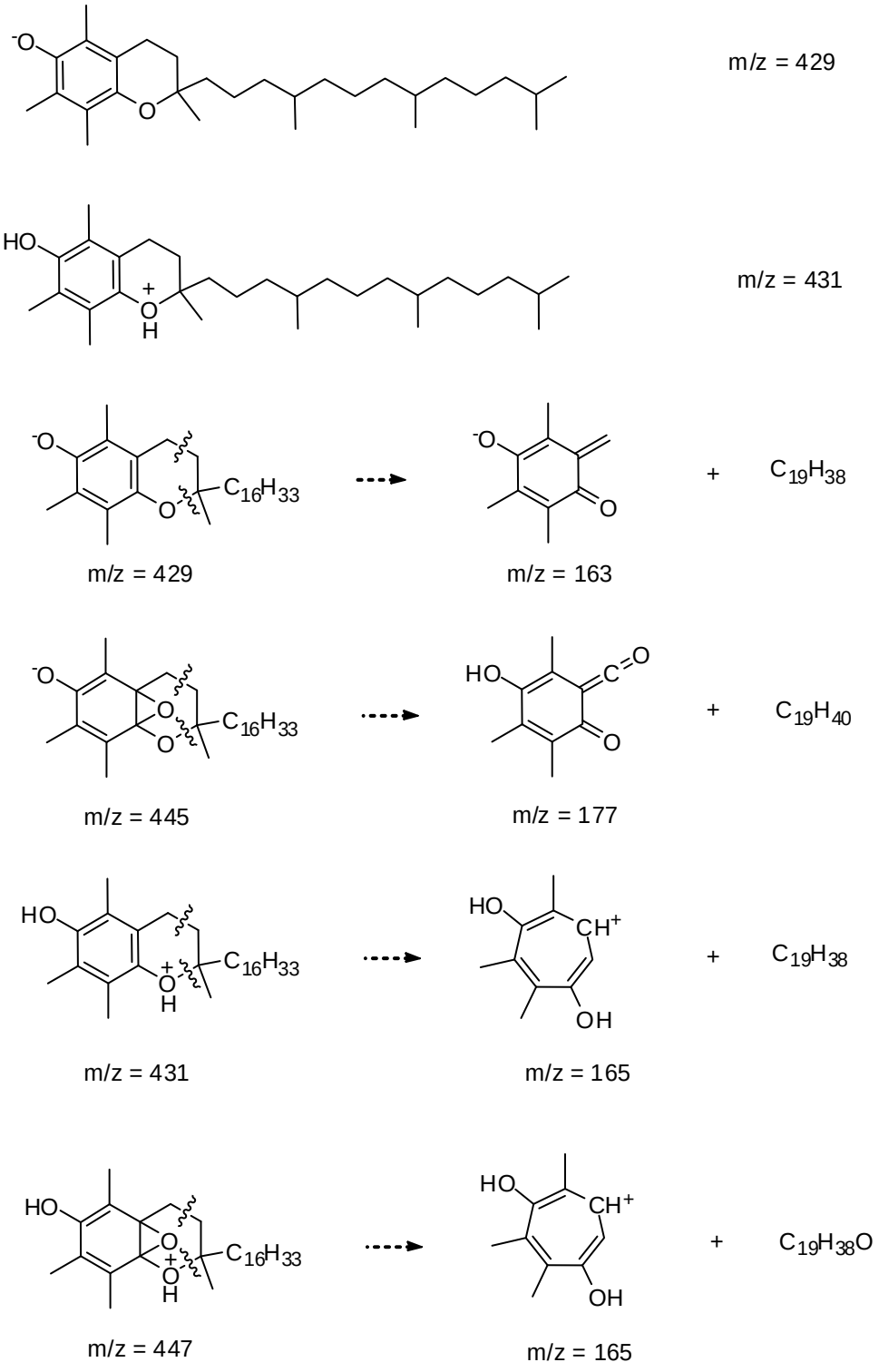
Parent anion Da	Threshold voltage V *	Fragment Anion Da	Neutral loss Da
429 (α-TO)$^-$	0.45 ± 0.05	163	266 ($C_{19}H_{38}$)
445 (α-TO-O)$^-$	0.47 ± 0.05	177	268 ($C_{19}H_{40}$)
461 (α-TO-O_2)$^-$	0.40 ± 0.05	419/417	42 (C_2H_2O)/44 (CO_2)
477 (α-TO-O_3)$^-$	0.52 ± 0.05	433/407	44 (CO_2)/70 (?)
493 (α-TO-O_4)$^-$	0.48 ± 0.05	447/449	46 (CH_2O_2)/44 (CO_2)
509 (α-TO-O_5)$^-$	0.40 ± 0.05	463/419	46 (CH_2O_2)/90 (?)

*Parent ion decreases by > 90% at threshold voltage.

Table S2. MS/MS of α-TOH_2^+ and its ozonolysis products

Parent cation Da	Threshold voltage V *	Fragment cation Da	Neutral loss Da
431 $(\alpha\text{-}TOH_2)^+$	0.40 $\pm$ 0.05	165	266 ($C_{19}H_{38}$)
447 $(\alpha\text{-}TOH_2\text{-}O)^+$	0.35 $\pm$ 0.05	429/165	18 (H_2O)/282 ($C_{19}H_{38}O$)
461 [**5**(+H)]$^+$ **	0.35 $\pm$ 0.05	443/335	18 (H_2O)/126 ($C_6H_6O_3$)
463 $(\alpha\text{-}TOH_2\text{-}O_2)^+$	0.35 $\pm$ 0.05	445	18 (H_2O)

*Parent ion decreases by > 90% at threshold voltage. ** See Scheme 1.



SCHEME S1

PROPOSED FRAGMENTATION PATTERNS

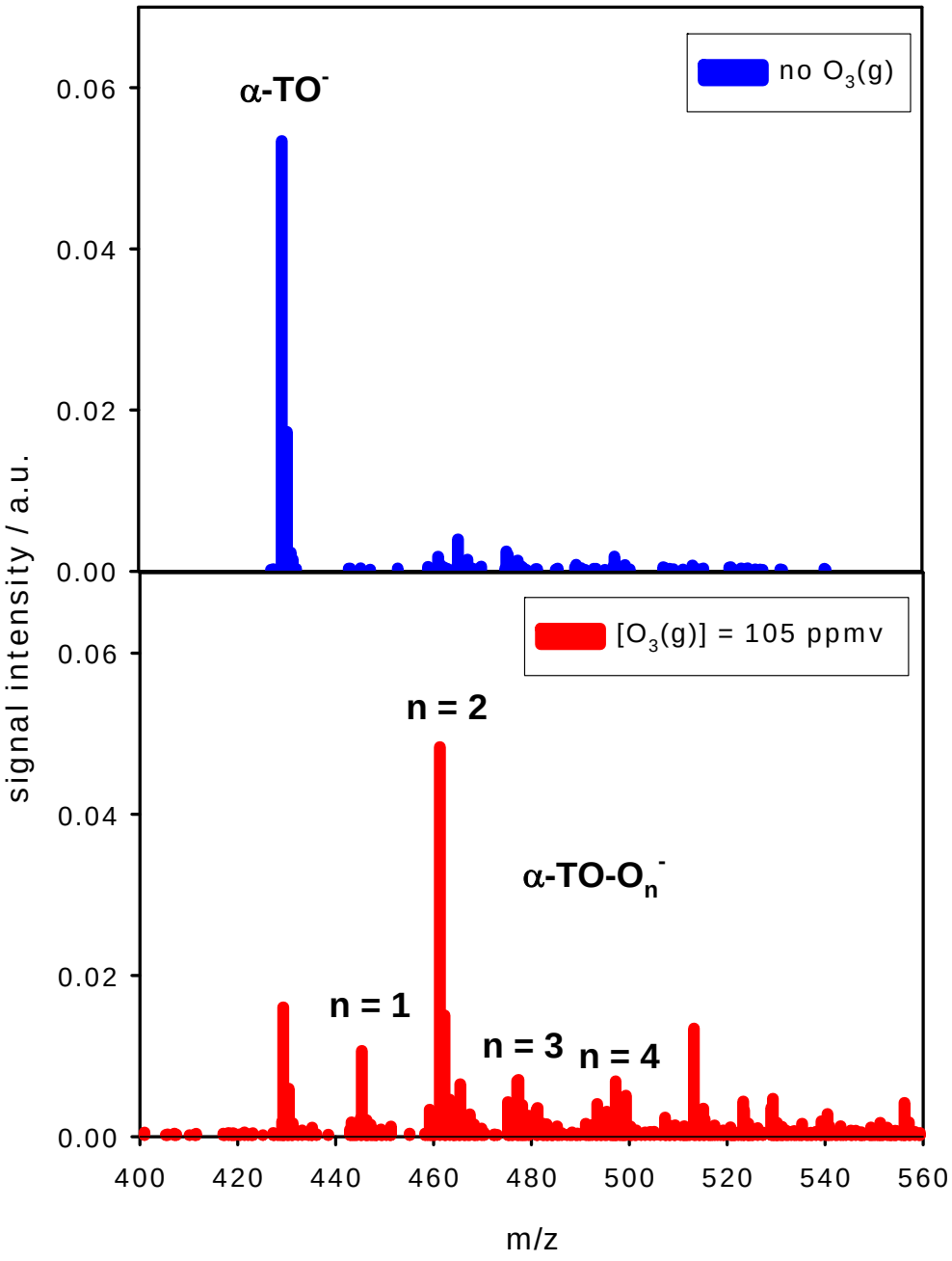


Figure S1. Negative ion mass spectra of 3 mM α-TOH/acetonitrile at pH 10.4 in the absence (upper panel) or presence of 105 ppmv O_3(g) (lower panel). Note that the same α-TO-O_n^- (n = 1 - 4) products as methanol solution are observed.

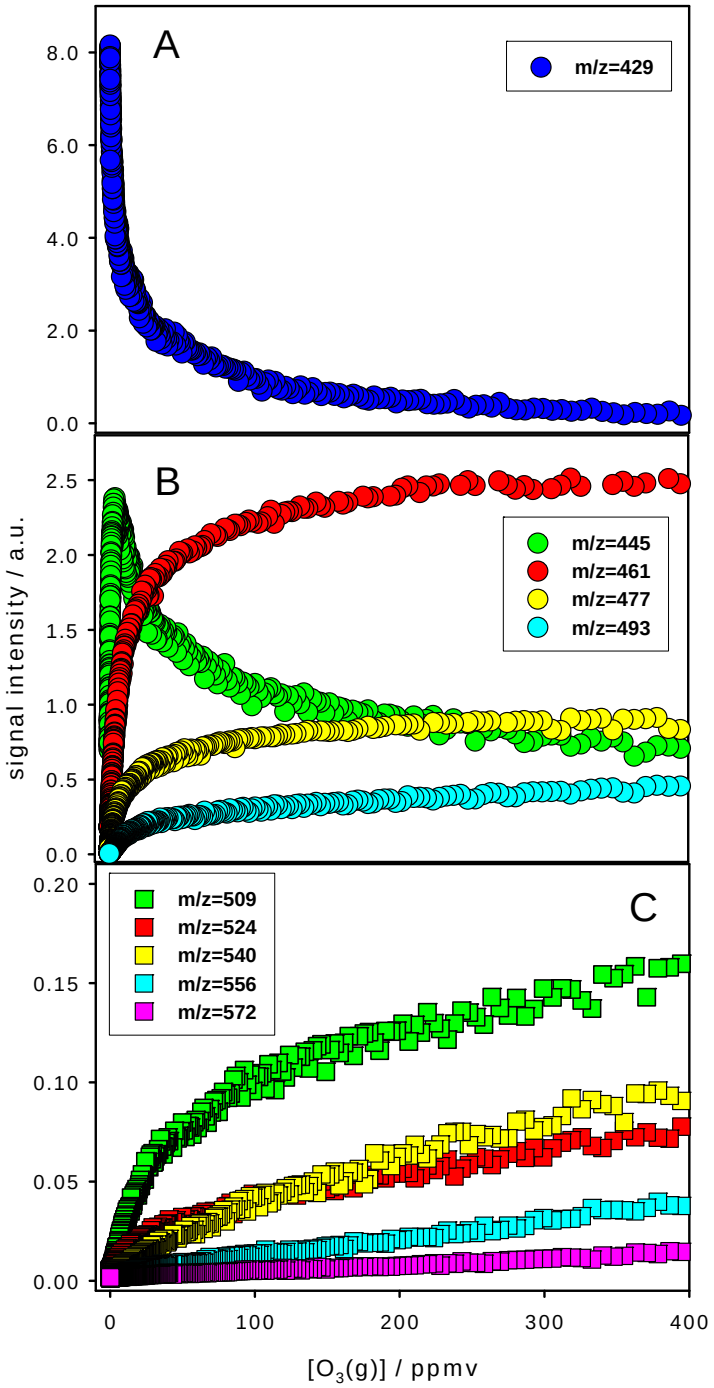


Figure S2. Reactant and anion products (signal intensities/a.u.) of the ozonolysis of 1.0 mM α-TOH:methanol at the air/liquid interface as a function of $[O_3(g)]$ in the range of 0 – 400 ppmv at bulk pH 11.3. A: reactant m/z = 429 (α-TO^-). B: reaction products m/z = 445 (α-TO-O)$^-$, m/z = 461 (α-TO-O_2)$^-$, m/z = 477 (α-TO-O_3)$^-$, and m/z = 493 (α-TO-O_4)$^-$. C: other reaction products m/z = 509, m/z = 524, m/z = 540, m/z = 556, and m/z = 572.

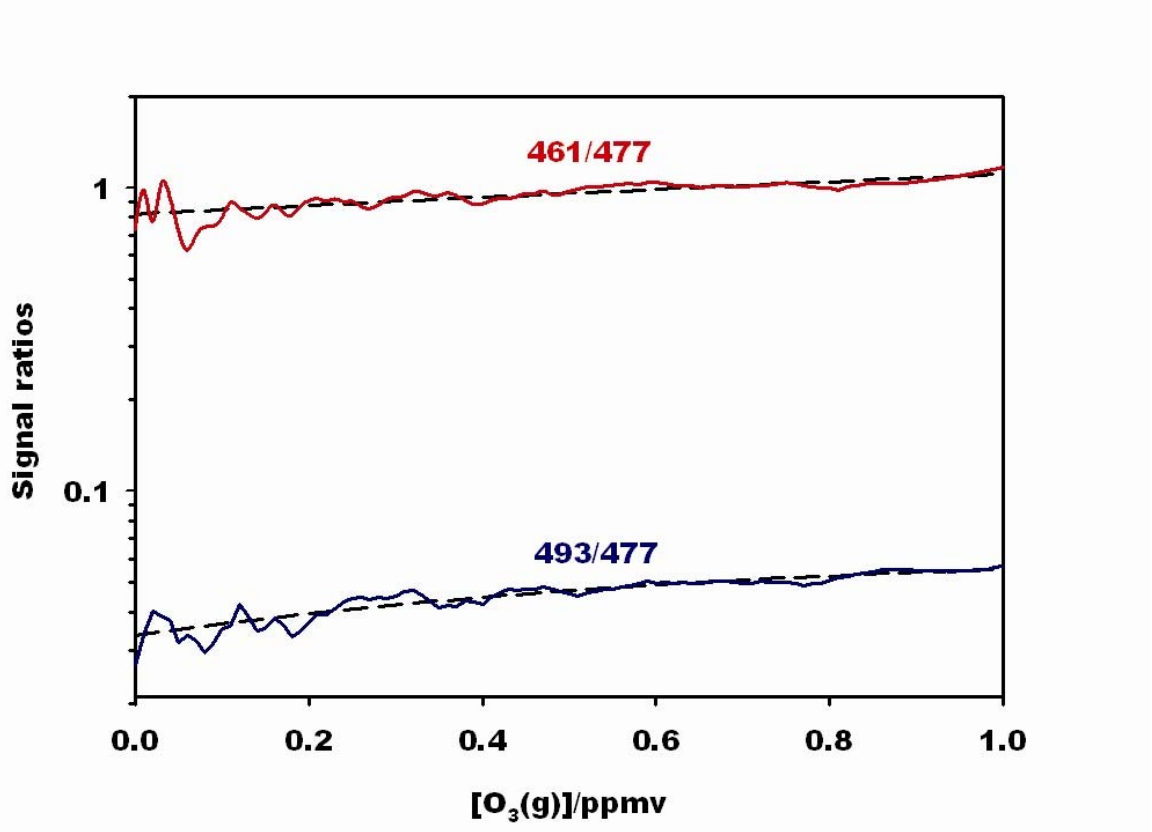


Figure S3. The ratios of $(\alpha\text{-TOH-O}_2)^-/(\alpha\text{-TOH-O}_3)^-$ (red) and $(\alpha\text{-TOH-O}_4)^-/(\alpha\text{-TOH-O}_3)^-$ (blue) in the ozonolysis of 1.0 mM α-TOH:methanol at the air/liquid interface as a function of $[O_3(g)]$ in the range of 0 – 1.0 ppmv at bulk pH 11.3.

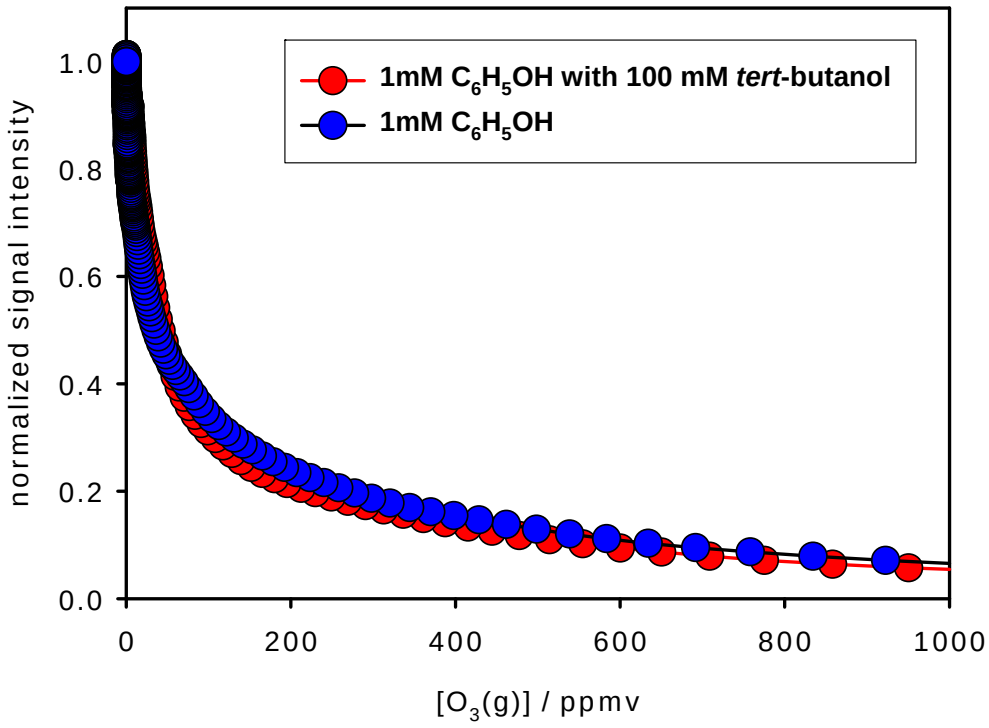


Figure S4. $C_6H_5O^-$ decay in the ozonolysis of aqueous 1 mM C_6H_5OH microdroplets as a function of $[O_3(g)]$ in the absence (blue)/presence (red) of 100 mM *tert*-butanol at pH 10.0.

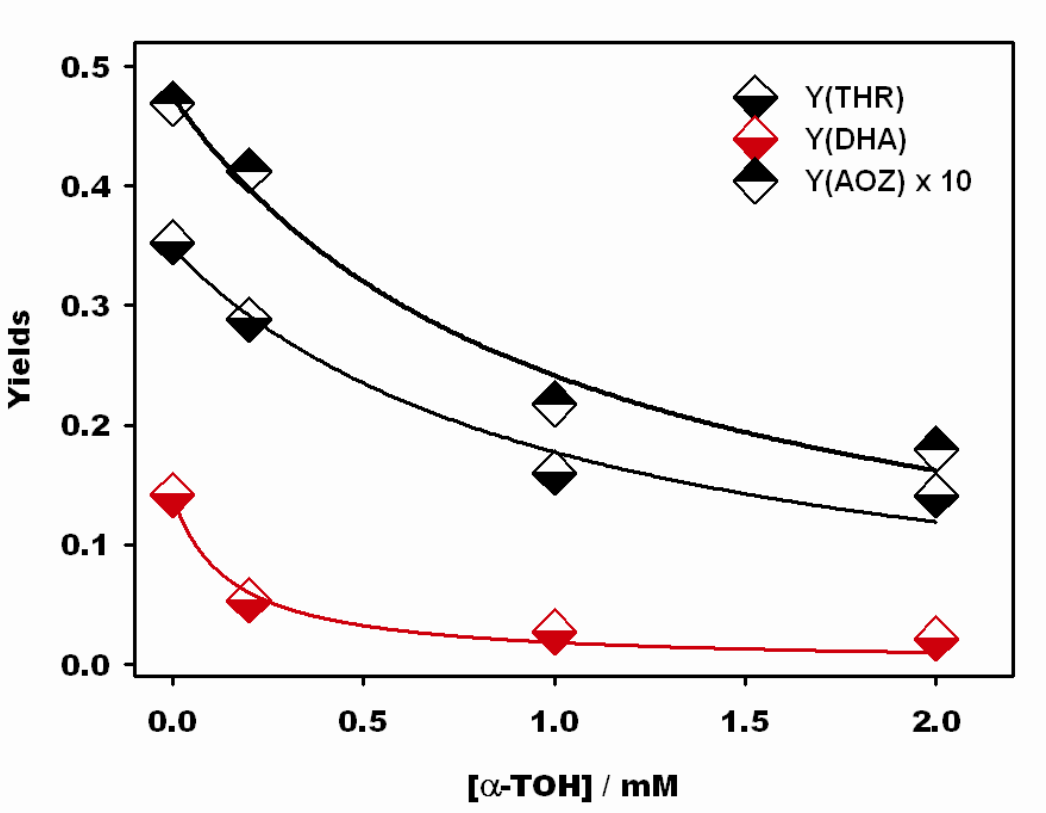


Figure S5. THR^-, DHA^- and AOZ^- yields based on interfacial AH^- loss versus [α-TOH] in the mixture of 1mM AH_2 + X mM α-TOH in methanol solutions at pH 7.2 in 500 ppmv O_3(g). See text for details.