Supporting Information

Kinetic Solvent Effects on Peroxyl Radical Reactions

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General

Materials and methods. α-Tocopherol (α-TOH) was purified by flash chromatography (5% ethyl acetate/hexanes, silica gel) and dried overnight under high vacuum (protected from light). Other H-atom donors, *trans*-styrylacetic acid, and the decomposition products of the peroxyester clock were purchased from commercial sources. GC analysis was carried out with an Agilent Technologies 6890 equipped with a DB-5 column (30 m × 0.32 mm × 0.25 mm). The non-conjugated, conjugated and epoxy alcohols were separated using the temperature program: 95 °C for 2 min; 95-100 °C @ 0.5 °C/min; 100-150 °C @ 5 °C /min; 150-280 °C @ 40 °C/min; 280 °C for 2.8 min. The response factors for non-conjugated, conjugated and epoxy alcohols relative to benzyl alcohol are 1.40, 1.30 and 1.31, respectively.

Synthesis of *t*-butyl-4-phenylperbut-3-enoate (9)[1,2]: A solution of *trans*-styrylacetic acid (3.1 mmol, 500 mg) in anhydrous benzene (10 mL) was treated with $SOCl_2$ (6.2 mmol, 461 µL) and the mixture was stirred at room temperature for 6 hours. Benzene and excess $SOCl_2$ were removed under reduced pressure. The residue obtained was dissolved in diethyl ether (20 mL), cooled to -20 °C and *t*-butyl hydroperoxide (8.0 mmol) was added. Pyridine (11.1 mmol, 543 µL) dissolved in diethyl ether (5 mL) was then added slowly to the reaction mixture. The mixture was stirred at -20 °C for an additional 30 minutes and then poured on ice and washed with cold 10% sulfuric acid followed by 10% sodium carbonate and water. The ether extract was dried over $MgSO_4$ and concentrated. The residue obtained was subjected to flash column chromatography (95 % hexane-ethyl acetate, silica gel) to give *t*-butyl-4-phenylperbut-3-enoate (**9,** 516 mg) in 72 % yield which was stored in the freezer. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.34 (m, 5 H), 6.57 (d, *J* = 14 Hz, 1 H), 6.28 (dt, *J* = 14, 7 Hz, 1 H), 3.29 (d, *J* = 7 Hz, 2H), 1.36 (s, 9 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 169.5, 137.2, 135.0, 129.2, 128.4, 127.0, 120.9, 84.3, 36.2, 26.8. HRMS: *m/z* measured 234. 1261 (234.1256 calculated for $C_{14}H_{18}O_3$. EIMS: *m/z* (relative abundance) 234 (M^+, 22), 117 (100), 91 (23).

General procedure for clock calibration (thermal conditions). Stock solutions of α-TOH (1.0 and 2.0 M) and *t*-butyl-4-phenylperbut-3-enoate (**9**, 0.1 M) were freshly prepared in benzene (without additional aeration) before use. α-TOH (0.01-1.0 M) and perester (**9**, 0.01 M, 10 µL of 0.1 M) were mixed and diluted up to 100 µL with benzene in 2.0 mL HPLC vials. The vials were capped and incubated at 37 °C for 4 h. After the incubation reaction mixtures were quenched with PPh_3 (50 µL of 1.0 M in benzene) and diluted up to 1.8 mL with hexanes. Decomposition products were determined by GC. The ratio of non-conjugated (**7a**) to conjugated (**8a**) alcohols was plotted versus the α-TOH concentration. A non-linear curve fit to the following equation was performed using Microcal Origin 6.0 to obtain the values of k_β and α.

$$\frac{[7\mathrm{a}]}{[8\mathrm{a}]} = \frac{k_H[\alpha\text{-TOH}]}{k_\beta + k_H[\alpha\text{-TOH}]} \bullet \left(\frac{1-\alpha}{\alpha}\right)$$

General procedure for clock calibration (photolytic conditions). Stock solutions of α-TOH (1.0 and 2.0 M) and *t*-butyl-4-phenylperbut-3-enoate (**9**, 0.1 M) were freshly prepared in the solvent of choice (without additional aeration) before use. α-TOH (0.01-1.0 M) and perester (**9**, 0.01 M, 10 µL of 0.1 M) were mixed and diluted up to 100 µL with the solvent in 2.0 mL HPLC vials (Type 1 borosilicate glass). The vials were capped and were irradiated using UVB lamps (centered at 300 nm) in a Luzchem photoreactor (LZC-ORG) for 30 min at 25 °C. After the irradiation reaction mixtures were quenched with PPh_3 (50 µL of 1.0 M in benzene) and diluted up to 1.8 mL with hexanes. Decomposition products were determined by GC. The ratio of non-conjugated (7**a**) to conjugated (**8a**) alcohols (corrected for epoxide **10** formation, see text) was plotted versus the α-TOH concentration. A non-linear curve fit to following equation was performed using Microcal Origin 6.0 to obtain the values of k_β and α.

$$\frac{[7\mathrm{a}]}{[8\mathrm{a}+10]} = \frac{k_H[\alpha\text{-TOH}]}{k_\beta + k_H[\alpha\text{-TOH}]} \bullet \left(\frac{1-\alpha}{\alpha}\right)$$

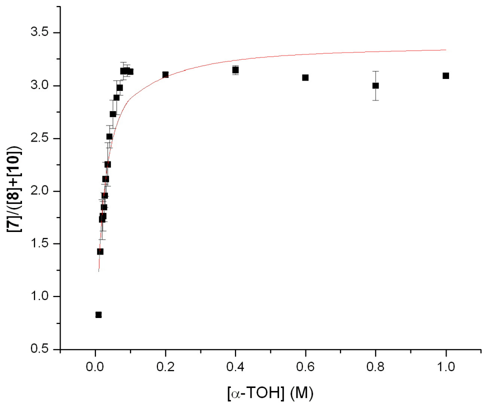

Figure SI-1. Ratio of **7** to (**8** + **10**) formed from the decomposition of **9** as a function of [α-TOH] following 30 min irradiation (300 nm) at 25 °C in hexane.

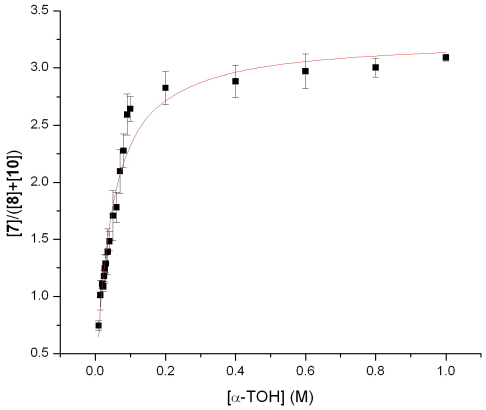

Figure SI-2. Ratio of **7** to (**8** + **10**) formed from the decomposition of **9** as a function of [α-TOH] following 30 min irradiation (300 nm) at 25 °C in benzene.

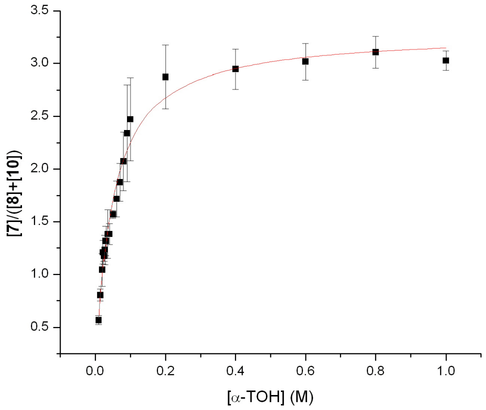

Figure SI-3. Ratio of **7** to (**8** + **10**) formed from the decomposition of **9** as a function of [α-TOH] following 30 min irradiation (300 nm) at 25 °C in anisole.

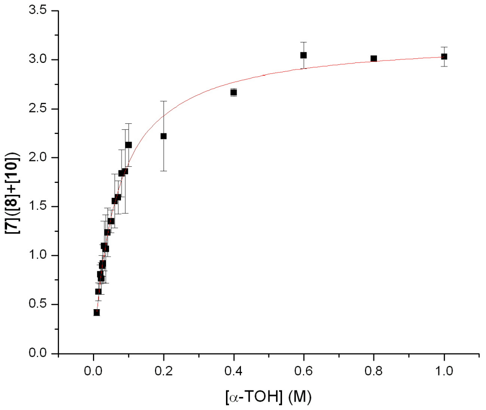

Figure SI-4. Ratio of **7** to (**8** + **10**) formed from the decomposition of **9** as a function of [α-TOH] following 30 min irradiation (300 nm) at 25 °C in *t*-amyl alcohol.

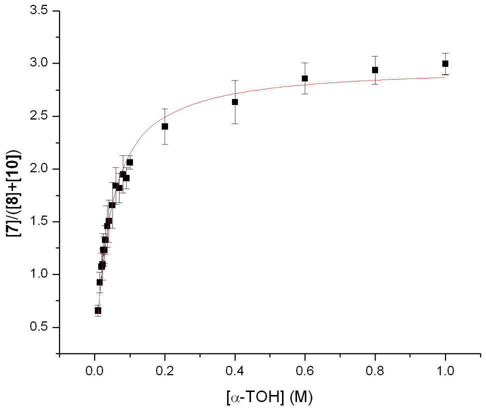

Figure SI-5. Ratio of **7** to (**8** + **10**) formed from the decomposition of **9** as a function of [α-TOH] following 30 min irradiation (300 nm) at 25 °C in acetic acid.

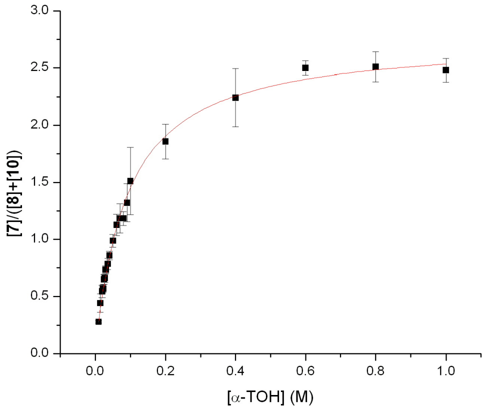

Figure SI-6. Ratio of **7** to (**8** + **10**) formed from the decomposition of **9** as a function of [α-TOH] following 30 min irradiation (300 nm) at 25 °C in ethyl acetate.

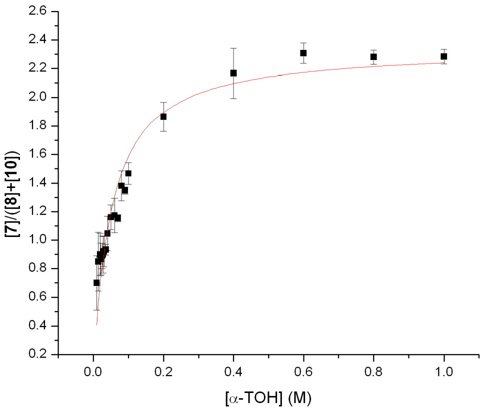

Figure SI-7. Ratio of **7** to (**8** + **10**) formed from the decomposition of **9** as a function of [α-TOH] following 30 min irradiation (300 nm) at 25 °C in propionitrile.

General procedure for clocking experiments (photolytic conditions). The experiments were performed in various solvents as described above except substituting α-TOH with new H-atom donors **11**, **12**, **13** and **14**. Double reciprocal plots were used to avoid the need to perform a prohibitive number of experiments. A linear curve fit to the following equation was performed using Microcal Origin 6.0 to obtain the values of k_{H} for new H-atom donors.

$$\frac{[8+10]}{[7]} = \frac{k_{\beta}}{k_{H}[H-donor]}\left(\frac{1-\alpha}{\alpha}\right) + \frac{1-\alpha}{\alpha}$$

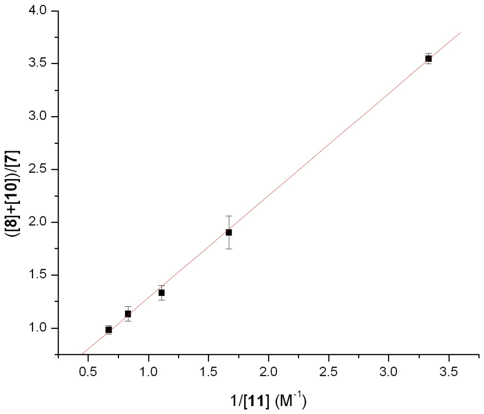

Figure SI-8. Ratio of (**8** + **10**) to **7** formed from the decomposition of **9** as a function of 1/[**11**] following 30 min irradiation (300 nm) at 25 °C in benzene.

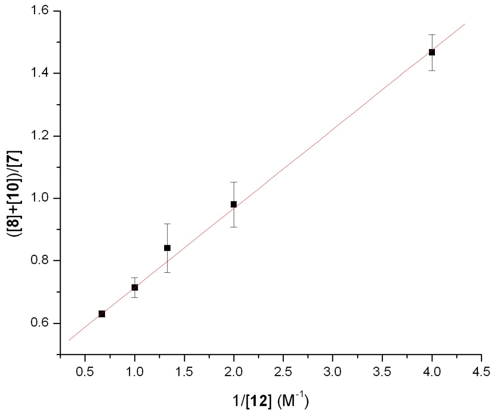

Figure SI-9. Ratio of (**8** + **10**) to **7** formed from the decomposition of **9** as a function of 1/[**12**] following 30 min irradiation (300 nm) at 25 °C in benzene.

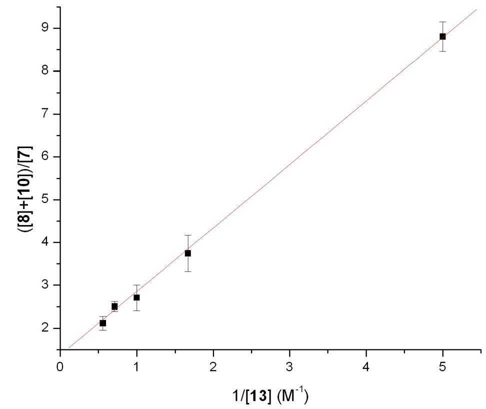

Figure SI-10. Ratio of (**8** + **10**) to **7** formed from the decomposition of **9** as a function of 1/[**13**] following 30 min irradiation (300 nm) at 25 °C in benzene.

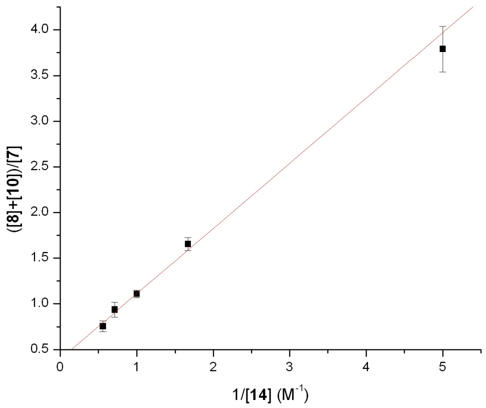

Figure SI-11. Clocking Ratio of (**8** + **10**) to **7** formed from the decomposition of **9** as a function of 1/[**14**] following 30 min irradiation (300 nm) at 25 °C in benzene.

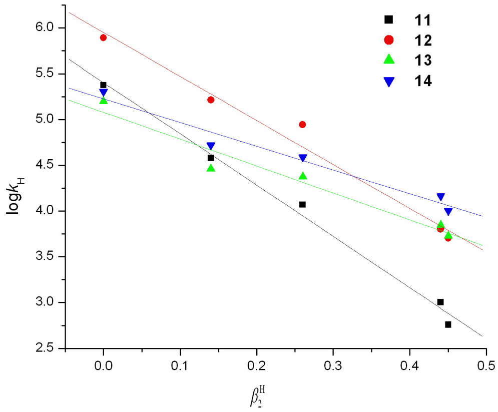

Figure SI-12. Correlation plot of logk_H as a function of hydrogen-bond acceptor (HBA, β_2^H) parameters of solvents; *p*-cresol (**11**, slope = -5.9 and R = 0.98); 2,4,6-trimethyl phenol (**12**, slope = -4.9 and R = 0.99); 2,6-di-*t*-butyl-4-methyl phenol (**13**, slope = -2.9 and R = 0.98) and diphenyl amine (**14**, slope = -2.5 and R = 0.99).

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[1] A. B. Smith III; B. H. Toder; S. J. Branca. *J. Am. Chem. Soc.,* 1984, **106**, 3995.

[2] P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, 1958, **80**, 1398.