Scavenging of dpph• radicals by Vitamin E is accelerated by its partial ionization. The role of Sequential Proton Loss Electron Transfer.

M. Musialik and G. Litwinienko

Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

SUPPORTING MATERIAL

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Table S1. Bimolecular rate constant, k^S, for the reaction of **dpph•** with PMHC in 1,4-dioxane– water and acetonitrile – water mixtures.

1.4-dioxane				MeCN			
$[H_2O]$ / %[a]	$[H_2O]$ /M	ε_r [b]	k^S /$M^{-1}s^{-1}$	$H_2O]$ / %[a]	[H2O] /M	ε_r [c]	k^S /$M^{-1}s^{-1}$
0	0	2	95	0	0.0	36.0	310
5	2.8		85	6	2.8	37.6	550
10	5.6	5	98	13	7.2	40.3	680
20	11.1	10	150	20	11.1	43.0	880
30	16.7	16	250	25	13.9	44.7	950
40	22.2	25	500	40	22.2	50.8	1400
50	27.8	32	1140				

[a] % vol/vol. [b] Values of ε_r for dioxane-water mixtures are from: Landolt-Bornstein: Zahlenwerte und Funktionen, 6th ed., Germany, Springer-Verlag, **1959**, p. 613. [c] Values of ε_r for MeCN-water mixtures from: Moreau, C., Douheret, G., *J. Chem. Thermodynamics*, **1976**, *8*, 403-410.

Table S2. Bimolecular rate constant, k^S, for the reaction of **dpph•** with BHT in 1,4-dioxane – water and acetonitrile – water mixtures.

1.4-dioxane				MeCN			
$[H_2O]$ / %[a]	$[H_2O]$ /M	ε_r [b]	k^S /$M^{-1}s^{-1}$	$H_2O]$ / %[a]	[H2O] /M	ε_r [c]	k^S /$M^{-1}s^{-1}$
0	0	2	0.044	0	0.0	36.0	0.21
5	2.8		0.076	5	2.8	37.6	1.0
10	5.6	5	0.090	10	5.6	39.3	2.2
20	11.1	10	0.13	20	11.1	43.0	3.95
30	16.7	16	0.24	30	16.7	47.1	5.9
40	22.2	25	0.45	40	22.2	50.8	9.6
50	27.8	32	1.1	50	27.8		12.8

[a] % vol/vol. [b] Values of ε_r for dioxane-water mixtures are from: Landolt-Bornstein: Zahlenwerte und Funktionen, 6th ed., Germany, Springer-Verlag, **1959**, p. 613. [c] Values of ε_r for MeCN-water mixtures from: Moreau, C., Douheret, G., *J. Chem. Thermodynamics*, **1976**, *8*, 403-410.

Determination of parameter α_2^H for PMHC.

In general, the method used for determination of α_2^H parameter was the same as used previously (ref. 8 and 9 in the main text).

Plots for PMHC + DMSO are showed on the Figure S1. The sharp band at 3629 cm^{-1} (free OH group) has been used for calculations of equilibrium constant of HB 1:1 complex formation, K^i:

$$K = [ROH....HBA]_{H\text{-bonded}} / [ROH]_{free}[HBA]_{free}$$

Values α_2^H were calculated using equations:

$$\log K = L_{HBA} \log K_A^H + D_{HBA}$$

$$\alpha_2^H = (\log K_A^H + 1.1) / 4.636$$

Our measurements gave K=13.90 (see Figure S2 and Table S3). For DMSO L_B=1.24 and D_B=0.266 (ref 6), hence $\log K_A^H$ =0.723, and α_2^H =0.39.

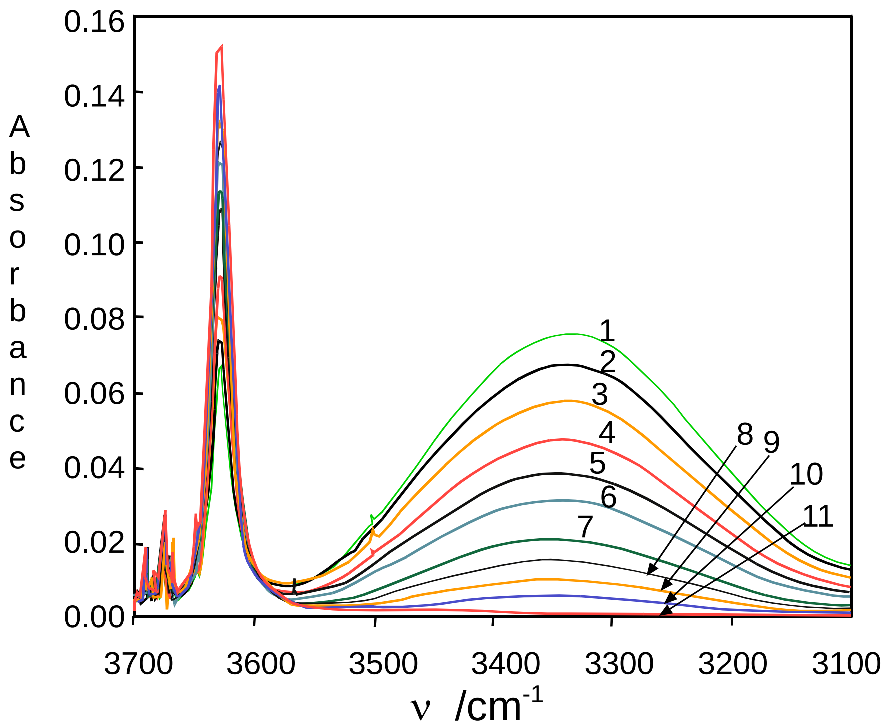

Figure S1. IR spectra of 11.1 mM of PMHC in CCl_4 containing DMSO at concentrations: 1) 98.4, 2) 76.6, 3) 57.4, 4) 43.0, 5) 32.0, 6) 24.0, 7)16.1, 8)10.8, 9) 7.2, 10) 4.3 and 11) 0.0 mM. The free OH stretching band having a maximum at 3626 cm^{-1} was used for calculation of the concentration of non-hydrogen bonded PMHC.

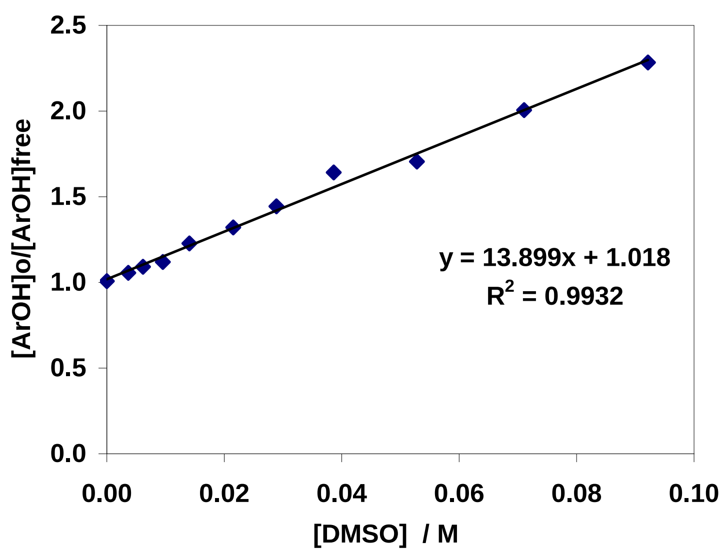

Figure S2. Plots of $[ArOH]_o/[ArOH]_{free}$ vs. $[DMSO]_{free}$ for PMHC. The slope of the straight line yields the HB equilibrium constant, *K*.

Table S3. Parameters used for calculation of the equilibrium constant *K* for HB complex formation between PMHC and DMSO. $[ArOH]_o$ = total concentration of phenol, $[ArOH]_{free}$ = concentration of non-hydrogen bonded phenol calculated from IR measurements, [HB] = $[ArOH]_o$ - $[ArOH]_{free}$, $[DMSO]_o$ = total concentration of DMSO in CCl_4, $[DMSO]_{free}$ = concentration of free (i.e. non-hydrogen bonded) DMSO. Plots of $[ArOH]_o/[ArOH]_{free}$ vs. $[DMSO]_{free}$ are presented in Figure S2. All concentrations are given in mM units.

$[ArOH]_o$	$[ArOH]_{free}$	[HB]	$[DMSO]_o$	$[DMSO]_{free}$	$[ArOH]_o/[ArOH]_{free}$
11.10	11.01	0.0	0.0	0.0	1.01
11.10	10.51	0.6	4.3	3.7	1.06
11.10	10.17	0.9	7.1	6.2	1.09
11.10	9.91	1.2	10.7	9.5	1.12
11.10	9.05	2.1	16.1	14.0	1.23
11.10	8.40	2.7	24.2	21.5	1.32
11.10	7.69	3.4	32.3	28.9	1.44
11.10	6.76	4.3	43.0	38.7	1.64
11.10	6.51	4.6	57.4	52.8	1.71
11.10	5.54	5.6	76.6	71.0	2.00
11.10	4.86	6.2	98.4	92.2	2.28

Experimental procedures for determination of rate constants

Materials. Because phenol/**dpph$^\bullet$** reaction kinetics in methanol, ethanol, and acetonitrile are sensitive to traces of acids and bases, these solvents were fractionally distilled over a small amount of **dpph$^\bullet$** and a few beads of an ion-exchange resin prior to use. All other solvents were of the highest commercially available purity and were used as received. Commercially available phenols were used as received.

Kinetic Measurements. The procedures were described previously (see refs 8 and 9 in the text). Decays of **dpph$^\bullet$** (initial concentrations 3-8 × 10^{-5} M) in the presence of excess ArOH at known concentrations were monitored at 517 nm on an Applied Photophysics stopped-flow spectrophotometer, SX 18 MV, equipped with a 150 W xenon lamp at ambient temperature. The rate constants presented in Table 1 are mean values from at least two independent sets of measurements of several pseudo-first-order rate constants, k_{ex}. Bimolecular rate constants in each solvent, k^S / $M^{-1}s^{-1}$, were calculated from the linear least-squares slopes derived from plots of k_{ex} vs. [ArOH]:

$$k_{ex} = \text{const} + k^S\,[ArOH]$$

Table S4. Kinetic data for the reaction of **dpph•** with α-Tocopherol in *n*-heptane, ethyl acetate and acetonitrile. Concentration [ArOH], pseudo-first-order rate constant, k_{ex}, and R^2 are given for each data set. The calculated mean bimolecular rate constant is denoted as (k^S ± absolute error).

n-heptane		ethyl acetate		MeCN	
[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] / mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] / mM	$10^3 \times k_{ex}$ / s^{-1}
2.93	24.8	4.08	756.8	2.11	743
2.28	19.8	3.17	591.1	1.64	592
1.71	14.9	2.38	437.5	1.23	463
1.22	10.8	1.70	291.0	0.92	361
0.814	7.22	1.13	199.0	0.69	278
0.489	4.70	0.76	140.3	0.52	207
0.293	2.73	0.45	87.8	0.37	155
0.176	1.69	0.27	45.9	0.25	110
0.106	0.958			0.16	74
0.063	0.527				
k = 8500 $M^{-1}s^{-1}$		k = 186 $M^{-1}s^{-1}$		k = 344 $M^{-1}s^{-1}$	
Δk^a = 132 $M^{-1}s^{-1}$		Δk^a = 5 $M^{-1}s^{-1}$		Δk^a = 10 $M^{-1}s^{-1}$	
R^2 = 0.9994		R^2 = 0.9987		R^2 = 0.9982	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$k^{n\text{-}heptane}$ **= 8500 ± 200 $M^{-1}s^{-1}$**
$k^{Ethyl\ acetate}$ **= 190 ± 10 $M^{-1}s^{-1}$**
k^{MeCN} **= 340 ± 10 $M^{-1}s^{-1}$**

Table S5. Kinetic data for the reaction of **dpph•** with α-Tocopherol in methanol and acidified methanol. Symbols are the same as for Table S4.

Neat MeOH		MeOH / 10 mM CH_3CO_2H		MeOH / 100 mM CH_3CO_2H	
[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
2.76	1.16	1.78	472.9	1.78	467.2
2.07	0.867	1.38	410.2	1.38	411.2
1.48	0.654	1.04	323.7	1.04	312.0
0.99	0.490	0.74	238.4	0.74	238.4
0.59	0.310	0.49	172.2	0.49	172.7
0.30	0.178	0.30	120.8	0.30	120.0
		0.15	74.8	0.15	69.4
k = 388 $M^{-1}s^{-1}$		k = 251 $M^{-1}s^{-1}$		k = 249 $M^{-1}s^{-1}$	
Δk^a = 17 $M^{-1}s^{-1}$		Δk^a = 19		Δk^a = 20	
R^2 = 0.9981		R^2 = 0.9922		R^2 = 0.9908	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$k^{methanol}$ **= 390 ± 20 $M^{-1}s^{-1}$**
$k^{methanol\ /10\ mM\ CH3CO2H}$ **= 250 ± 20 $M^{-1}s^{-1}$**
$k^{methanol\ /100\ mM\ CH3CO2H}$ **= 250 ± 20 $M^{-1}s^{-1}$**

Table S6. . Kinetic data for the reaction of **dpph•** with α-Tocopherol in ethanol and acidified ethanol. Symbols are the same as for Table S4.

Neat EtOH		EtOH / 10 mM CH_3CO_2H		EtOH / 100 mM CH_3CO_2H	
[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
3.64	1.395	1.82	450.8	1.82	457.0
2.83	1.143	1.41	379.5	1.41	408.2
2.12	0.925	1.06	300.3	1.06	320.3
1.51	0.688	0.76	217.4	0.76	241.0
1.01	0.497	0.50	153.7	0.50	169.8
0.50	0.275	0.25	91.4	0.25	99.3
0.30	0.172	0.15	56.0	0.15	61.5
0.15	0.085	0.08	33.6	0.08	50.2
k **=** 375 $M^{-1}s^{-1}$		***k*** **=** 244 $M^{-1}s^{-1}$		***k*** **=** 247 $M^{-1}s^{-1}$	
Δ*k*[a]= 24 $M^{-1}s^{-1}$		**Δ*k*[a]=** 14		**Δ*k*[a]=** 22	
R^2 = 0.9930		R^2 = 0.9946		R^2 = 0.9869	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{ethanol} = 380 \pm 20\ M^{-1}s^{-1}}$
$\boldsymbol{k^{ethanol\ /10\ mM\ CH3CO2H} = 240 \pm 10\ M^{-1}s^{-1}}$
$\boldsymbol{k^{ethanol\ /100\ mM\ CH3CO2H} = 250 \pm 20\ M^{-1}s^{-1}}$

Table S7. Kinetic data for the reaction of **dpph•** with PMHC in n-heptane. Symbols are the same as for Table S4.

heptane		heptane	
[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	k_{ex} / s^{-1}
2.40	17.7	3.74	29.80
1.89	14.0	2.91	23.66
1.41	10.5	2.18	18.07
1.01	7.8	1.56	13.16
0.67	5.4	1.04	8.99
0.41	3.3	0.69	6.04
		0.46	3.98
		0.31	2.61
		0.20	1.82
		0.14	1.16
		0.09	0.78
		0.06	0.45
k **=** 7210 $M^{-1}s^{-1}$		***k*** **=** 8040 $M^{-1}s^{-1}$	
Δ*k*[a]= 136 $M^{-1}s^{-1}$		**Δ*k*[a]=** 130	
R^2 = 0.9996		R^2 = 0.9992	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{n\text{-}heptane} = 7600 \pm 400\ M^{-1}s^{-1}}$

Table S8. . Kinetic data for the reaction of **dpph•** with PMHC in ethyl acetate and dioxane. Symbols are the same as for Table S4.

ethyl acetate		dioxane		dioxane	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
5.18	902	7.30	731.0	4.22	395.7
4.03	703	5.68	542.5	3.29	310.2
3.02	535	4.26	408.9	2.46	229.4
2.16	388	3.04	302.9	1.76	170.7
1.44	259	2.03	205.1	1.17	113.3
0.96	175	1.22	125.5	0.70	76.7
0.58	107	0.73	75.6	0.35	39.7
0.29	55.9	0.44	45.2		
		0.26	26.8		
$\boldsymbol{k}$ **=** 173 $M^{-1}s^{-1}$		$\boldsymbol{k}$ **=** 97.8 $M^{-1}s^{-1}$		$\boldsymbol{k}$ **=** 91.5 $M^{-1}s^{-1}$	
Δk^a = 2		Δk^a = 2.4		Δk^a = 1.6	
R^2 = 0.9999		R^2 = 0.9988		R^2 = 0.9995	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{Ethyl\ acetate} = 170 \pm 10\ M^{-1}s^{-1}}$
$\boldsymbol{k^{dioxane} = 95 \pm 10\ M^{-1}s^{-1}}$

Table S9. Kinetic data for the reaction of **dpph•** with PMHC in methanol and acidified methanol. Symbols are the same as for Table S4.

Neat MeOH		Neat MeOH		MeOH / 10 mM CH3CO2H	
[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
4.53	1.74	7.58	2.58	2.26	553.1
3.52	1.53	5.72	1.86	1.76	498.7
2.64	1.13	4.30	1.46	1.32	418.4
1.89	0.84	3.07	1.05	0.94	350.4
1.26	0.62	2.05	0.74	0.63	238.5
0.75	0.43	1.23	0.47	0.38	167.7
0.38	0.22			0.19	99.2
$\boldsymbol{k}$ **=** 370 $M^{-1}s^{-1}$		$\boldsymbol{k}$ **=** 330 $M^{-1}s^{-1}$		$\boldsymbol{k}$ **=** 221 $M^{-1}s^{-1}$	
Δk^a = 30 $M^{-1}s^{-1}$		Δk^a = 15		Δk^a = 38	
R^2 = 0.9911		R^2 = 0.9980		R^2 = 0.9614	

Table S9. *continued*.

MeOH / 10 mM CH3CO2H		MeOH / 100 mM CH3CO2H	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
2.26	671.4	2.26	545.5
1.76	652.3	1.76	507.9
1.32	521.6	1.32	413.1
0.94	403.4	0.94	321.7
0.63	289.7	0.63	218.6
0.38	193.6	0.38	155.5
0.19	109.1	0.19	92.7
$\boldsymbol{k}$ = 280 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 230 $M^{-1}s^{-1}$	
$\Delta\boldsymbol{k}^a$ = 50 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^a$ = 36	
R^2 = 0.9536		R^2 = 0.9672	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k}^{methanol}$ **= 350 ± 20 $M^{-1}s^{-1}$**
$\boldsymbol{k}^{methanol\ /10\ mM\ CH3CO2H}$ **= 280 ± 40 $M^{-1}s^{-1}$**
$\boldsymbol{k}^{methanol\ /100\ mM\ CH3CO2H}$ **= 230 ± 40 $M^{-1}s^{-1}$**

Table S10. . Kinetic data for the reaction of **dpph•** with PMHC in ethanol and acidified ethanol. Symbols are the same as for Table S4.

Neat EtOH		EtOH / 10 mM CH3CO2H		EtOH / 100 mM CH3CO2H		EtOH / 100 mM CH3CO2H	
[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
4.68	1.95	2.34	596.5	2.34	550.6	3.07	800.0
3.27	1.47	1.64	452.0	1.64	447.6	2.20	577.6
2.55	1.18	1.27	357.1	1.27	365.5	1.57	418.5
1.91	0.95	0.95	279.3	0.95	280.9	1.01	281.2
1.36	0.72	0.68	202.6	0.68	210.9	0.61	174.4
0.91	0.48	0.45	147.2	0.45	150.0	0.31	86.5
0.55	0.30	0.27	97.4	0.27	98.8		
0.27	0.16	0.14	57.2	0.14	66.8		
$\boldsymbol{k}$ = 407 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 248 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 228 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 256 $M^{-1}s^{-1}$	
$\Delta\boldsymbol{k}^a$ = 30 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^a$ = 10 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^a$ = 21 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^a$ = 5 $M^{-1}s^{-1}$	
R^2 = 0.9932		R^2 = 0.9971		R^2 = 0.9861		R^2 = 0.9997	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k}^{ethanol}$ **= 410 ± 30 $M^{-1}s^{-1}$**
$\boldsymbol{k}^{ethanol\ /10\ mM\ CH3CO2H}$ **= 250 ± 10 $M^{-1}s^{-1}$**
$\boldsymbol{k}^{ethanol\ /100\ mM\ CH3CO2H}$ **= 240 ± 20 $M^{-1}s^{-1}$**

Table S11. Kinetic data for the reaction of **dpph**$^{\bullet}$ with PMHC in MeCN. Symbols are the same as for Table S4.

neat MeCN		neat MeCN	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
2.91	928.6	2.86	909.5
2.26	721.9	2.22	709.1
1.70	542.3	1.67	538.0
1.21	392.5	1.19	388.7
0.81	273.4	0.79	270.9
0.49	170.0	0.48	161.8
0.24	92.0	0.29	96.6
		0.17	58.2
		0.09	29.8
$\boldsymbol{k}$ = 312 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 317 $M^{-1}s^{-1}$	
$\Delta\boldsymbol{k}^a$ = 3 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^a$ = 4 $M^{-1}s^{-1}$	
R^2 = 0.9990		R^2 = 0.9997	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{MeCN}}$ **= 310 ± 10 $M^{-1}s^{-1}$**

Table S12. Kinetic data for the reaction of **dpph**$^{\bullet}$ with PMHC in MeCN-water mixtures. Symbols are the same as for Table S4.

6% H2O		13% H2O		20% H2O	
[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	k_{ex} / s^{-1}
2.91	1.60	2.91	1.96	2.86	2.50
2.26	1.28	2.26	1.60	2.22	2.02
1.70	0.99	1.70	1.27	1.67	1.60
1.21	0.73	1.27	0.98	1.19	1.15
0.81	0.50	0.85	0.65	0.79	0.80
0.49	0.31	0.51	0.40	0.48	0.52
0.24	0.17	0.25	0.19	0.29	0.26
0.12	0.09	0.13	0.10	0.17	0.19
				0.09	0.10
$\boldsymbol{k}$ = 544 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 676 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 877 $M^{-1}s^{-1}$	
$\Delta\boldsymbol{k}^a$ = 14 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^a$ = 36 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^a$ = 34 $M^{-1}s^{-1}$	
R^2 = 0.9989		R^2 = 0.9950		R^2 = 0.9968	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

Table S12. *continued*

25 % H2O		40 % H2O		50 % H2O	
[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	k_{ex} / s^{-1}
1.70	1.62	2.86	4.12	2.86	6.65
1.21	1.25	2.14	3.18	2.14	5.12
0.81	0.88	1.53	2.42	1.53	3.76
0.49	0.47	1.09	1.86	1.09	2.97
0.24	0.27	0.78	1.44	0.78	2.23
0.12	0.16	0.52	0.98	0.52	1.58
		0.31	0.66	0.31	1.03
		0.19	0.47	0.19	0.77
				0.11	0.56
$\boldsymbol{k}$ = 951 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 1358 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 2209 $M^{-1}s^{-1}$	
$\Delta \boldsymbol{k}^a$ = 72 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 53 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 59 $M^{-1}s^{-1}$	
R^2 = 0.9940		R^2 = 0.9974		R^2 = 0.9985	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{MeCN\,/\,6\%H2O}}$ **= 540 ± 10 $M^{-1}s^{-1}$**
$\boldsymbol{k^{MeCN\,/\,13\%H2O}}$ **= 680 ± 40 $M^{-1}s^{-1}$**
$\boldsymbol{k^{MeCN\,/\,20\%H2O}}$ **= 880 ± 40 $M^{-1}s^{-1}$**
$\boldsymbol{k^{MeCN\,/\,25\%H2O}}$ **= 950 ± 70 $M^{-1}s^{-1}$**
$\boldsymbol{k^{MeCN\,/\,40\%H2O}}$ **= 1400 ± 100 $M^{-1}s^{-1}$**
$\boldsymbol{k^{MeCN\,/\,50\%H2O}}$ **= 2200± 100 $M^{-1}s^{-1}$**

Table S13. Kinetic data for the reaction of **dpph•** with PMHC in dioxane. Symbols are the same as for Table S4.

neat dioxane		neat dioxane	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] / mM	$10^3 \times k_{ex}$ / s^{-1}
2.91	288.1	7.30	731.0
2.18	216.8	5.68	542.5
1.56	155.8	4.26	408.9
1.04	103.8	3.04	302.9
0.623	63.6	2.03	205.1
0.374	38.2	1.22	125.5
0.224	23.0	0.73	75.6
0.135	13.8	0.44	45.2
		0.26	26.8
$\boldsymbol{k}$ = 98.8 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 97.8 $M^{-1}s^{-1}$	
$\Delta \boldsymbol{k}^a$ = 0.4 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 2.5 $M^{-1}s^{-1}$	
R^2 = 1.000		R^2 = 0.9988	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{dioxane}}$ **= 98± 2 $M^{-1}s^{-1}$**

Table S14. Kinetic data for the reaction of **dpph•** with PMHC in dioxane-water mixtures. Symbols are the same as for Table S4.

5% H2O		5% H2O		10% H2O	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
5.5	455.4	4.2	378.8	5.4	528.9
4.3	361.7	3.3	284.3	4.2	407.4
3.2	274.8	2.5	205.6	3.2	311.7
2.3	198.3	1.8	161.0	2.3	225.4
1.5	133.9	1.2	117.8	1.5	151.0
0.9	80.5	0.8	74.0	0.9	92.4
0.6	49.9	0.5	43.4	0.5	58.7
0.3	30.8	0.3	26.7	0.3	35.6
0.2	19.6			0.2	22.2
$\boldsymbol{k}$ = 82.5 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 86.1 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 96.5 $M^{-1}s^{-1}$	
$\Delta \boldsymbol{k}^a$ = 1.1 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 4.1 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 1 $M^{-1}s^{-1}$	
R^2 = 0.9996		R^2 = 0.9950		R^2 = 0.9999	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

10% H2O		20% H2O		20% H2O	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
4.4	442.4	5.5	824.7	4.4	624.4
3.5	345.4	4.3	657.4	3.5	491.0
2.6	253.4	3.2	501.2	2.6	367.6
1.9	180.8	2.3	359.4	1.9	261.4
1.2	121.4	1.5	245.3	1.2	176.6
0.7	69.2	0.9	157.2	0.7	104.5
0.4	42.0	0.6	98.4	0.4	63.4
0.3	25.4	0.3	57.6	0.3	38.8
		0.2	35.8		
$\boldsymbol{k}$ = 100.1 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 148.6 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 141 $M^{-1}s^{-1}$	
$\Delta \boldsymbol{k}^a$ = 1.0 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 2.4 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 1 $M^{-1}s^{-1}$	
R^2 = 0.9998		R^2 = 0.9999		R^2 = 0.9999	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

Table S14. *continued*

30% H2O		40% H2O		50% H2O	
[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	k_{ex} / s^{-1}	[ArOH] /mM	k_{ex} / s^{-1}
4.45	1.12	4.45	2.29	4.45	5.17
3.46	0.88	3.46	1.71	3.46	4.15
2.59	0.66	2.59	1.39	2.59	3.21
1.85	0.49	1.85	1.05	1.85	2.44
1.24	0.33	1.24	0.73	1.24	1.71
0.74	0.21	0.74	0.48	0.74	1.10
0.44	0.14	0.44	0.30	0.44	0.75
0.27	0.09	0.27	0.20	0.27	0.49
		0.16	0.14	0.16	0.33
		0.10	0.10	0.10	0.21
***k* =** 246.1 $M^{-1}s^{-1}$		***k* =** 492 $M^{-1}s^{-1}$		***k* =** 1140 $M^{-1}s^{-1}$	
Δ*k*[a]= 2.2 $M^{-1}s^{-1}$		**Δ*k*[a]=** 17 $M^{-1}s^{-1}$		**Δ*k*[a]=** 33 $M^{-1}s^{-1}$	
R^2 = 0.9999		R^2 = 0.9972		R^2 = 0.9980	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{dioxane\ /\ 5\%H2O} = 85 \pm 3\ M^{-1}s^{-1}}$
$\boldsymbol{k^{dioxane\ /\ 10\%H2O} = 98 \pm 3\ M^{-1}s^{-1}}$
$\boldsymbol{k^{dioxane\ /\ 20\%H2O} = 150 \pm 10\ M^{-1}s^{-1}}$
$\boldsymbol{k^{dioxane\ /\ 30\%H2O} = 250 \pm 10\ M^{-1}s^{-1}}$
$\boldsymbol{k^{dioxane\ /\ 40\%H2O} = 500 \pm 20\ M^{-1}s^{-1}}$
$\boldsymbol{k^{dioxane\ /\ 50\%H2O} = 1140 \pm 40\ M^{-1}s^{-1}}$

Table S15. Kinetic data for the reaction of **dpph•** with BHT in neat MeCN. Symbols are the same as for Table S4.

[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
16.06	5.28	20.08	4.51
12.49	4.25	15.62	4.01
9.37	3.77	11.71	3.35
6.69	3.03	8.37	2.97
4.46	2.38	5.58	2.34
2.97	1.98	3.72	1.95
1.98	1.84	2.48	1.65
1.32	1.36	1.65	1.38
***k* =** 0.25 $M^{-1}s^{-1}$		***k* =** 0.17 $M^{-1}s^{-1}$	
Δ*k*[a]= 0.018 $M^{-1}s^{-1}$		**Δ*k*[a]=** 0.017	
R^2 = 0.9912		R^2 = 0.9819	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{MeCN} = 0.21 \pm 0.04\ M^{-1}s^{-1}}$

Table S16. Kinetic data for the reaction of **dpph•** with BHT in MeCN containing water. Symbols are the same as for Table S4.

5% H_2O		5% H_2O		5% H_2O	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
3.34	4.11	9.97	9.12	1.30	1.63
2.51	3.83	7.75	6.88	0.93	1.31
1.79	3.16	5.82	4.99	0.62	0.97
1.19	2.51	4.15	3.77	0.37	0.80
0.72	1.90	2.77	2.81	0.22	0.55
0.36	1.23	1.66	2.04	0.13	0.42
		0.83	1.37	0.08	0.31
$\boldsymbol{k}$ = 0.97 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 0.83 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 1.05 $M^{-1}s^{-1}$	
$\Delta \boldsymbol{k}^a$ = 0.20 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 0.10		$\Delta \boldsymbol{k}^a$ = 0.11	
R^2 = 0.9486		R^2 = 0.9930		R^2 = 0.9849	

10% H_2O		10% H_2O		5% H_2O	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
8.13	16.62	9.97	22.80	1.73	4.96
6.32	11.47	7.75	15.45	1.30	3.75
4.74	9.12	5.82	11.77	0.93	2.73
3.39	6.94	4.15	8.93	0.62	1.94
2.26	5.00	2.77	6.25	0.37	1.26
1.35	3.48	1.66	4.18	0.22	0.80
0.68	2.10	0.83	2.63	0.13	0.59
				0.08	0.47
$\boldsymbol{k}$ = 1.85 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 2.1 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 2.71 $M^{-1}s^{-1}$	
$\Delta \boldsymbol{k}^a$ = 0.20 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 0.20		$\Delta \boldsymbol{k}^a$ = 0.05	
R^2 = 0.9878		R^2 = 0.9842		R^2 = 0.9998	

Table S16. *continued*

20 % H_2O		20 % H_2O		20 % H_2O	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
1.73	7.25	4.88	23.42	6.44	27.89
1.30	4.54	3.79	15.98	5.01	23.67
0.93	3.64	2.84	12.45	3.76	18.56
0.62	2.65	2.03	9.57	2.68	14.60
0.37	1.85	1.35	6.99	1.79	10.69
0.22	1.38	0.81	4.86	1.07	7.14
0.13	0.85	0.41	2.92		
0.08	0.68				
$\boldsymbol{k}$ = 3.67 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 4.32 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 3.87 $M^{-1}s^{-1}$	
$\Delta \boldsymbol{k}^a$ = 0.40 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 0.50		$\Delta \boldsymbol{k}^a$ = 0.30	
R^2 = 0.9799		R^2 = 0.9845		R^2 = 0.9943	

30 % H_2O		30 % H_2O		30 % H_2O	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
2.71	15.69	1.11	7.68	0.89	5.75
1.35	10.54	0.87	5.57	0.69	4.26
0.81	8.10	0.65	4.02	0.52	3.29
0.54	4.28	0.46	2.97	0.37	2.53
0.36	2.88	0.31	2.18	0.27	2.03
0.22	1.78	0.19	1.49	0.19	1.65
0.11	1.03	0.11	1.14	0.13	1.28
		0.07	0.87	0.08	1.02
				0.06	0.87
$\boldsymbol{k}$ = 5.72 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 6.3 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 5.6 $M^{-1}s^{-1}$	
$\Delta \boldsymbol{k}^a$ = 1.2 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 0.50		$\Delta \boldsymbol{k}^a$ = 0.30	
R^2 = 0.9444		R^2 = 0.9898		R^2 = 0.9947	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

Table S16. *continued*

40 % H_2O		50 % H_2O		50 % H_2O	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
0.67	7.67	2.23	30.70	2.15	30.13
0.52	5.98	1.73	23.43	1.67	26.28
0.39	4.75	1.30	16.80	1.25	20.90
0.28	3.81	0.93	11.97	0.89	16.20
0.20	3.13	0.62	8.42	0.60	11.98
0.14	2.57	0.37	5.56	0.36	8.34
0.09	2.04	0.22	3.73		
0.06	1.55	0.13	2.67		
k **=**9.6 $M^{-1}s^{-1}$		***k*** **=**13.2 $M^{-1}s^{-1}$		***k*** **=**12.4 $M^{-1}s^{-1}$	
Δ***k***[a]**=**0.4 $M^{-1}s^{-1}$		Δ***k***[a]**=**0.6		Δ***k***[a]**=**1.2	
R^2 =0.9974		R^2 =0.9968		R^2 =0.9902	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{MeCN / 5\%H2O} = 1.0 \pm 0.1\ M^{-1}s^{-1}}$
$\boldsymbol{k^{MeCN / 10\%H2O} = 2.2 \pm 0.5\ M^{-1}s^{-1}}$
$\boldsymbol{k^{MeCN / 20\%H2O} = 3.95 \pm 0.4\ M^{-1}s^{-1}}$
$\boldsymbol{k^{MeCN / 30\%H2O} = 5.9 \pm 0.4\ M^{-1}s^{-1}}$
$\boldsymbol{k^{MeCN / 40\%H2O} = 9.6 \pm 0.4\ M^{-1}s^{-1}}$
$\boldsymbol{k^{MeCN / 50\%H2O} = 13 \pm 1\ M^{-1}s^{-1}}$

Table S17. Kinetic data for the reaction of **dpph•** with BHT in dioxane. Symbols are the same as for Table S4.

[ArOH] /mM	$10^4 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^4 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^4 \times k_{ex}$ / s^{-1}
10.68	4.55	6.29	3.44	15.57	6.15
8.55	3.92	4.89	2.40	12.45	5.10
6.65	2.94	3.67	1.96	9.69	3.94
4.98	2.38	2.75	1.43	7.27	3.01
3.56	1.54	2.06	1.17	5.19	2.13
2.37	1.08	1.55	1.00	3.46	1.79
		1.16	0.08		
		0.87	0.05		
k **=**0.0428 $M^{-1}s^{-1}$		***k*** **=**0.0505 $M^{-1}s^{-1}$		***k*** **=**0.0374 $M^{-1}s^{-1}$	
Δ***k***[a]**=**0.0037 $M^{-1}s^{-1}$		Δ***k***[a]**=**0.0042		Δ***k***[a]**=**0.0024	
R^2 =0.9922		R^2 =0.9982		R^2 =0.9958	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{dioxane} = 0.044 \pm 0.010\ M^{-1}s^{-1}}$

Table S18. Kinetic data for the reaction of **dpph•** with BHT in dioxane containing water. Symbols are the same as for Table S4.

5% H_2O		10 % H_2O		20 % H_2O	
[ArOH] /mM	$10^4 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^4 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^4 \times k_{ex}$ / s^{-1}
2.52	1.99	1.96	1.89	2.52	3.60
1.96	1.67	1.47	1.53	1.96	3.12
1.47	1.24	1.10	1.33	1.47	2.33
1.10	0.97	0.83	0.98	1.10	1.98
0.83	0.72	0.62	0.73	0.83	1.45
0.62	0.62			0.62	1.35
				0.46	0.10
				0.23	0.08
k **=**0.076 $M^{-1}s^{-1}$		***k*** **=**0.0901 $M^{-1}s^{-1}$		***k*** **=**0.128 $M^{-1}s^{-1}$	
Δ*k*[a]=0.0039 $M^{-1}s^{-1}$		**Δ*k*[a]=**0.014		**Δ*k*[a]=**0.0084	
R^2 =0.9983		R^2 =0.9738		R^2 =0.9925	

30% H_2O		40 % H_2O		50 % H_2O	
[ArOH] /mM	$10^4 \times k_{ex\,x}$ / s^{-1}	[ArOH] /mM	$10^4 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^4 \times k_{ex}$ / s^{-1}
2.52	6.68	2.52	13.30	2.52	30.10
1.96	5.08	1.96	10.70	1.96	27.45
1.47	4.04	1.47	9.32	1.47	21.15
1.10	3.43	1.10	7.26	1.10	17.80
0.83	2.62	0.83	6.03	0.83	14.60
0.62	2.16	0.62	5.00	0.62	10.32
0.41	0.14	0.41	0.39	0.41	0.95
0.25	0.11	0.25	0.30	0.25	0.75
k **=**0.24 $M^{-1}s^{-1}$		***k*** **=**0.45 $M^{-1}s^{-1}$		***k*** **=**1.06 $M^{-1}s^{-1}$	
Δ*k*[a]=0.013 $M^{-1}s^{-1}$		**Δ*k*[a]=**0.026		**Δ*k*[a]=**0.11	
R^2 =0.9951		R^2 =0.9941		R^2 =0.9817	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$k^{dioxane\,/\,5\%H2O}$= 0.076 ± 0.004 $M^{-1}s^{-1}$
$k^{dioxane\,/\,10\%H2O}$ = 0.090 ± 0.01 $M^{-1}s^{-1}$
$k^{dioxane\,/\,20\%H2O}$ = 0.13 ± 0.010 $M^{-1}s^{-1}$
$k^{dioxane\,/\,30\%H2O}$ = 0.24 ± 0.01 $M^{-1}s^{-1}$
$k^{dioxane\,/\,40\%H2O}$ = 0.45 ± 0.0.03 $M^{-1}s^{-1}$
$k^{dioxane\,/\,50\%H2O}$ = 1.1± 0.1 $M^{-1}s^{-1}$

Table S19. Kinetic data for the reaction of **dpph•** with BHT in acidified ethanol. Symbols are the same as for Table S4.

EtOH / 10 mM CH_3CO_2H		EtOH / 100 mM CH_3CO_2H		EtOH / 1000 mM CH_3CO_2H	
[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}	[ArOH] /mM	$10^3 \times k_{ex}$ / s^{-1}
19.59	10.16	19.59	6.55	19.59	6.33
15.24	8.22	15.24	5.65	15.24	5.42
11.43	6.57	11.43	4.62	11.43	4.56
8.16	5.32	8.16	3.80	8.16	3.75
5.44	3.92	5.44	3.03	5.44	3.03
3.63	3.04	3.63	2.46	3.63	2.45
2.42	2.33	2.42	2.00	2.42	1.95
1.61	1.81				
1.07	1.44				
$\boldsymbol{k}$ = 0.46 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 0.26 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 0.25 $M^{-1}s^{-1}$	
$\Delta \boldsymbol{k}^a$ = 0.020 $M^{-1}s^{-1}$		$\Delta \boldsymbol{k}^a$ = 0.016		$\Delta \boldsymbol{k}^a$ = 0.019	
R^2 = 0.9943		R^2 = 0.9949		R^2 = 0.9924	

[a] Calculated as the confidence interval of the slope for the 90% confidence level.

$\boldsymbol{k^{EtOH} = 0.86\ M^{-1}s^{-1}}$ (from ref 8 in the text)
$\boldsymbol{k^{EtOH\ /\ 10\ mM\ CH3CO2H} = 0.46 \pm 0.02\ M^{-1}s^{-1}}$
$\boldsymbol{k^{EtOH\ /\ 100\ mM\ CH3CO2H} = 0.26 \pm 0.02\ M^{-1}s^{-1}}$
$\boldsymbol{k^{EtOH\ /\ 1000\ mM\ CH3CO2H} = 0.25 \pm 0.02\ M^{-1}s^{-1}}$