



Supplement of

Temperature-dependent aqueous OH kinetics of C₂–C₁₀ linear and terpenoid alcohols and diols: new rate coefficients, structure–activity relationship, and atmospheric lifetimes

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S1. Materials and reagents

Hydrogen peroxide solution in water ($\geq 30\%$, ultra-trace, no stabilizers added), (-)-Menthol ($\geq 99\%$), (\pm)-exo,exo-2,3-Camphanediol ($\geq 97\%$), (+)-Borneol ($\geq 98\%$), 1,2-Butanediol ($\geq 98\%$), 1,2-Propanediol ($\geq 99\%$), 1,4-Butanediol ($\geq 97\%$), 1,6-Hexanediol ($\geq 99\%$), 1-Butanol ($\geq 99\%$), 1-Heptanol ($\geq 99\%$), 2-Butanol ($\geq 99\%$),
40 *cis*-2-Methylcyclohexanol ($\geq 98\%$), 1-Decanol ($\geq 99\%$), Dimethyl phthalate ($\geq 99\%$), 1,2-Ethandiol ($\geq 99\%$), 1-Hexanol ($\geq 98\%$), 1-Octanol ($\geq 99\%$), 1,3-propanediol ($\geq 98\%$), 3-ethyl-3-pentanol ($\geq 97\%$) and Sodium sulfate, anhydrous fine powder was purchased from Sigma-Merck (Schnelldorf, Germany). 1-Propanol ($\geq 98\%$) and Ethanol ($\geq 99\%$) were purchased from Avantor Performance Materials (Gliwice, Poland).
45 (+)-Fenchol ($\geq 96\%$), and 1-Nonanol ($\geq 99\%$) were purchased from Alfa Aesar; Chemat (Gdańsk, Poland). 1,5-Pentanediol ($\geq 95\%$) was purchased from AmBeed; Chemat (Gdańsk, Poland). 1,10-Decanediol ($\geq 98\%$), 1,7-Heptanediol ($\geq 98\%$), 1,8-Octanediol ($\geq 98\%$), 1,9-Nonanediol ($\geq 98\%$), *trans*-1,2-Cyclohexanediol ($\geq 99\%$) were purchased from Angene; Chemat (Gdańsk, Poland). 1-Pentanol (99%) was purchased from Aros; Chemat (Gdańsk, Poland). (1S,2S,3R,5S)-(+)-Pinanediol ($\geq 99\%$) and sodium chloride, extra pure were purchased from Thermo;
50 Chemat (Gdańsk, Poland)

Deionized (DI) water ($18 \text{ M}\Omega \times \text{cm}^{-1}$) was prepared using the Direct - Q3 Ultrapure Water System (Millipore). UHP gases: synthetic zero-air ($\leq 3 \text{ ppm}$ of H_2O and $\leq 0.1 \text{ ppm}$ of hydrocarbons), hydrogen ($\geq 99.999 \%$), and, helium ($\geq 99.999 \%$) were supplied by Multax (Stare Babice, Poland).

S2. Gas chromatography analysis conditions

55 S2.1. Gas chromatography coupled with the mass spectrometry

GC/MS analyses were carried out using a GC/MS-QP2010 Ultra gas chromatograph coupled with a single quadrupole mass spectrometer (Shimadzu) equipped with the electron ionization (70 eV) ion source. The instrument was equipped with an AOC-5000 autosampler (Shimadzu). This instrument was used to analyze two sets of cyclic and terpene alcohols and diols (Table S1).
60 The first group of alcohols was analyzed using VF-WAXms column (Agilent); 30 m, 0.25mm, 0.5 μm stationary phase. The column head pressure was 32.3 kPa, the total flow of the carrier gas (He) was 16.1 ml/min, the column flow was 0.67 ml/min (30 cm/sec), purge flow was 2 ml/min. The linear velocity flow control mode was used and the split ratio was 20. The injector, ion source, and mass spectrometer transfer line temperatures were 250°C. The following temperature program was used: initially, 70 °C was held for 4 min, then linear increase at the rate of 150
65 °C/min to 250°C, kept for 6 min, and analysis time was 22 min.

The second group of cyclic and terpene alcohols, containing (\pm)-exo,exo-2,3-camphanediol, and pinanediol was analyzed using the ZB-5MSplus column (Zebron); 30 m, 0.25mm, 0.5 μm stationary phase. The column head pressure was 27.2 kPa, the total flow of the carrier gas (He) was 16.4 ml/min, the column flow was 0.68 ml/min (30 cm/sec), purge flow was 2 ml/min. The linear velocity flow control mode was used and the split ratio was 20.
70 The injector, ion source, and mass spectrometer transfer line temperatures were 280°C. The following temperature program was used: initially, 50 °C was held for 2 min, then linear increase at the rate of 16 °C/min to 70°C, kept for 8 min, then linear increase at the rate of 10°C/min to 250°C, kept for 1 min analysis time was 30 min.

S2.2. Gas chromatography with the flame-ionization detector

75 GC/FID analyses were carried out using a GC17A capillary gas chromatography coupled with the flame-ionization detector (FID) and equipped with the AOC20i autosampler (Shimadzu). This instrument was used to analyze two groups of AAs (Table S2).

The temperatures of the injector and detector were 250°C. Analytes were separated with a ZB-Waxplus capillary column (Phenomenex), 30 m, 0.25mm, 0.5 µm stationary phase. The column was connected (from the injector side) with a 1 m retention gap (pre-column) of 0.25mm, untreated fused silica (no stationary phase). The retention gap was used to protect the length of the column placed in the injector from degradation and activation by water vapor combined with a high injector temperature.

80 1 µl of the ethyl acetate extracts (C₅-C₁₀ linear alcohols and diols, cyclic and terpene alcohols) were injected into the instrument. The column head pressure was 101 kPa, the column flow of the carrier gas (He) was 1.4 ml/min (30 cm/s), purge flow was 2 ml/min. The linear velocity flow control mode was used. Samples were injected in splitless mode (sampling time 0.5 min, then split ratio 1:14). The following temperature program was used: initially, 40°C was held for 3 min, then linear increase at the rate of 15 °C/min to 150°C, kept for 5 min, then linear increase at the rate of 20°C/min to 230°C, held for 4 min, then linear increase at the rate of 20°C/min to 250°C, held for 3 min; analysis time was 27.4 min.

90 C₂-C₅ linear alcohols and diols were analyzed by directly injecting 0.2 µl of the aqueous reaction mixture into the instrument. Such an approach was used due to the very low extraction recoveries obtained for the C₂-C₅ linear alcohols when liquid-liquid extraction with ethyl acetate was carried out (results now shown). The injector and detector were kept at 120 and 140°C for analyzing the aqueous samples, respectively. The column head pressure was 102 kPa, the column flow of the carrier gas (He) was 1.4 ml/min (31 cm/s), the purge flow was 2 ml/min, and the split ratio was 25. The column was initially kept at 35°C for 5 min, then linear increase at the rate of 20°C/min to 220°C, kept for 3 min; the analysis time was 17.3 min.

S3. List of the aliphatic alcohols investigated, retention times, and instruments used

Table S1. Retention times and ions monitored in SIM mode for aliphatic alcohols included in group 1 (GC/MS instrument)

Name	Elemental composition	Retention time (min)	Instrument (column)	Kinetic reference	Ions monitored in selected SIM mode (m/z)
Cyclohexanol	C ₆ H ₁₂ O	10.2	GC/MS (WAX), ethyl acetate extracts	1-Heptanol	100, 99, 85, 83, 82, 81, 72, 71, 70, 68, 67, 58, 57, 56, 55, 54, 53, 42, 41, 39
<i>exo</i> -Norborneol	C ₇ H ₁₂ O	10.4			113, 112, 97, 95, 94, 84, 83, 81, 70, 79, 77, 70, 69, 68, 67, 66, 65, 57, 56, 55, 54, 53, 41, 40, 39

Table S1. Retention times and ions monitored in SIM mode for aliphatic alcohols included in group 1 (GC/MS instrument), continued...

Name	Elemental composition	Retention time (min)	Instrument (column)	Kinetic reference	Ions monitored in selected SIM mode (m/z)
<i>1-Heptanol (ref.)</i>	C ₇ H ₁₆ O	10.6			98, 87, 83, 70, 69, 68, 57, 56, 55, 54
(+)-Fenchol	C ₁₀ H ₁₈ O	12.5			154, 139, 136, 125, 123, 121, 111, 107, 105, 97, 91, 85, 84, 81, 80, 72, 71, 69, 67, 57, 55, 53
(1S)-(-)-Borneol	C ₁₀ H ₁₈ O	13.2	GC/MS (WAX), ethyl acetate extracts	1-Heptanol	140, 139, 136, 121, 111, 110, 96, 95, 83, 81, 82, 83, 79, 77, 71, 69, 67, 57, 55, 53
(-)-Menthol	C ₁₀ H ₂₀ O	15.2			139, 138, 123, 110, 109, 96, 95, 83, 82, 81, 80, 71, 69, 68, 67, 57, 56, 55
Dimethyl phthalate	ISTD	17.8			162, 163, 134, 133, 120, 105, 104, 92, 77, 76, 50, 49

Table S2. Retention times and ions monitored in SIM mode for aliphatic alcohols included in group 2 (GC/MS instrument)

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Name	Elemental composition	Retention time (min)	Instrument (column)	Kinetic reference	Ions monitored in selected SIM mode (m/z)
cis-2-Methylcyclohexanol	C ₇ H ₁₄ O	12.7			56, 67, 70, 83, 84, 85, 97, 112, 113.
trans-1,2-Cyclohexanediol	C ₆ H ₁₂ O ₂	16.7			57, 69, 70, 83, 97, 98, 116.
Pinanediol	C ₁₀ H ₁₈ O ₂	22.01			55, 69, 71, 72, 81, 83, 93, 99, 108, 111, 119, 121, 126, 137.
(±)-exo,exo-2,3-Camphanediol	C ₁₀ H ₁₈ O ₂	23.0	GC/MS (ZB-5 column), ethyl acetate extracts	(+)-Fenchol	55, 60, 67, 69, 79, 81, 84, 95, 99, 119, 121, 123, 137, 139, 152.
(+)-Fenchol (ref.)	C ₁₀ H ₁₈ O	18.2			53, 55, 57, 67, 69, 71, 72, 80, 81, 84, 85, 91, 97, 105, 107, 111, 121, 123, 125, 136, 139, 154
Dimethyl phthalate	ISTD	23.6			49, 50, 76, 77, 92, 104, 105, 120, 133, 134, 162, 163

Table S3. Retention times of aliphatic alcohols included in group 3 (GC/FID instrument)

Name	Elemental composition	Retention time (min)	Group	Instrument (column)	Kinetic reference
Ethanol	C ₂ H ₆ O	5.8			
2-Butanol	C ₄ H ₁₀ O	7.4			
1-Propanol	C ₃ H ₈ O	7.6			
1-Butanol	C ₄ H ₁₀ O	8.9	C ₂ -C ₄ linear	GC/FID	1,4-
1,2-Propanediol	C ₃ H ₈ O ₂	12.7	alcohols and	(WAX column),	Butanediol
1,2-Ethanediol	C ₂ H ₆ O ₂	12.8	diols	aqueous injection	
1,2-Butanediol	C ₄ H ₁₀ O ₂	13.2			
1,4-Butanediol (ref.)	C ₄ H ₁₀ O ₂	14.6			

Table S4 Retention times of aliphatic alcohols included in group 4 (GC/FID instrument)

Name	Elemental composition	Retention time (min)	Group	Instrument (column)	Kinetic reference
3-ethyl-3-pentanol	C ₇ H ₁₆ O	8.4			
1-Pentanol	C ₅ H ₁₂ O	8.9			
Hexanol	C ₆ H ₁₄ O	9.9			
Heptanol	C ₇ H ₁₆ O	11.0			
Octanol	C ₈ H ₁₈ O	12.2			
Nonanol	C ₉ H ₂₀ O	14.0			
Decanol	C ₁₀ H ₂₂ O	16.2	C ₅ -C ₁₀ linear	GC/FID (WAX	1,5-
1,5-Pentanediol (ref.)	C ₅ H ₁₂ O ₂	19.4	alcohols and diols	column), ethyl acetate extracts	Pentanediol
1,6-Hexanediol	C ₆ H ₁₄ O ₂	20.3			
1,7-Heptanediol	C ₇ H ₁₆ O ₂	21.3			
1,8-Octanediol	C ₈ H ₁₈ O ₂	22.4			
1,9-Nonanediol	C ₉ H ₂₀ O ₂	23.8			
1,10-Decanediol	C ₁₀ H ₂₂ O ₂	25.0			
Dimethyl phthalate	ISTD	22.1			

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Sample chromatograms for the AAs under investigation are shown in Fig. S1-S4.

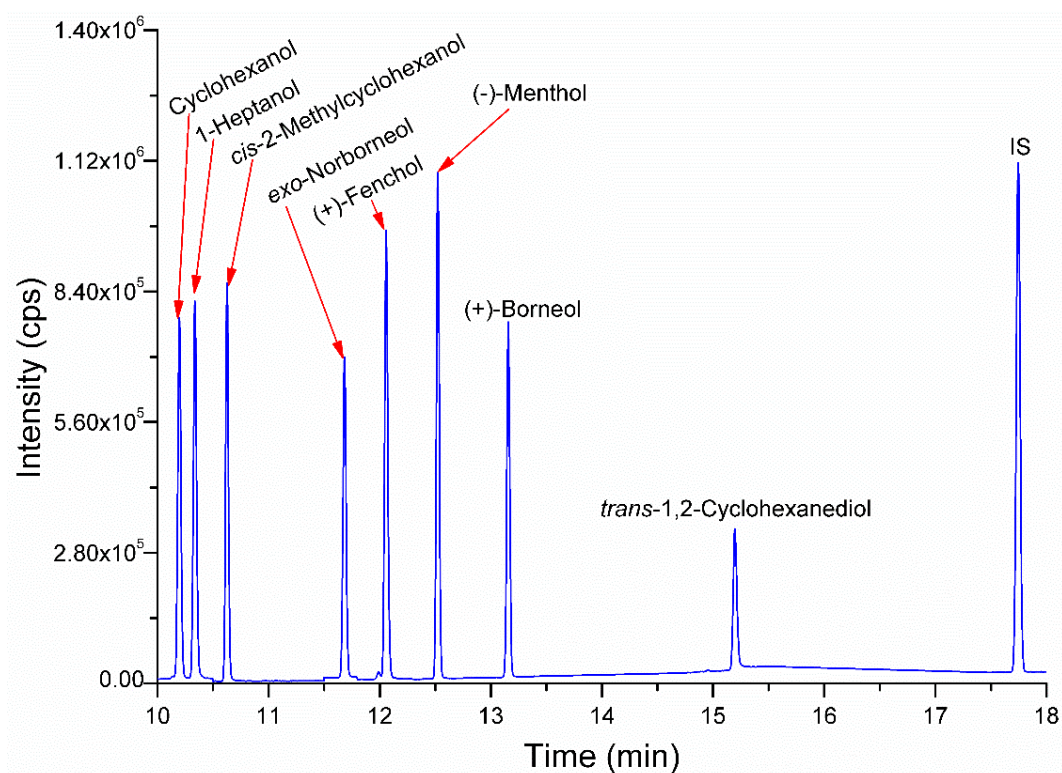


Figure S1: Sample chromatogram of the compounds listed in Table S1 (first set) acquired with the GC/MS instrument.

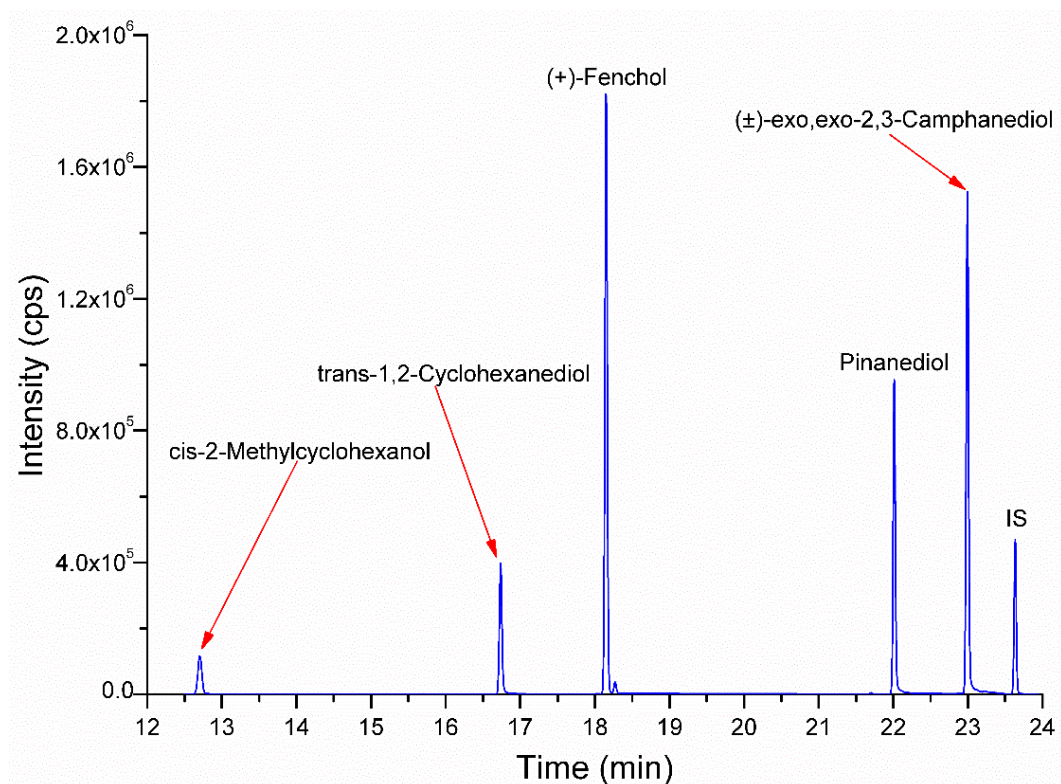
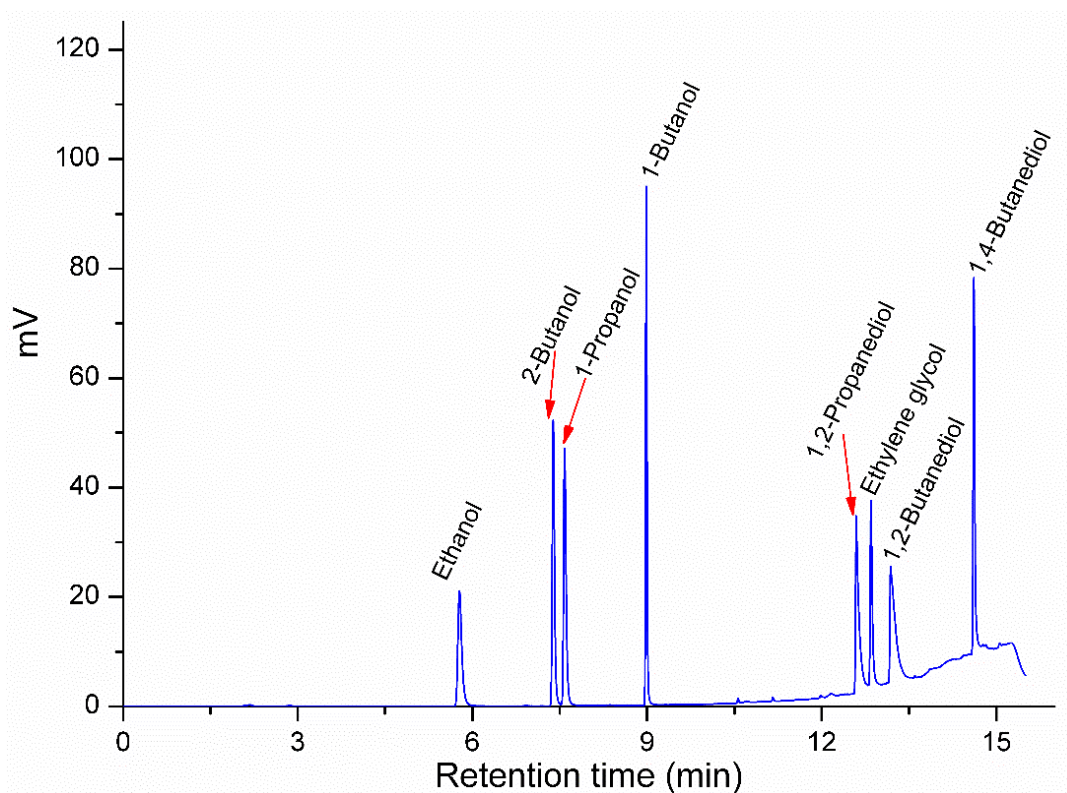


Figure S2: Sample chromatogram of the compounds listed in Table S1 (second set) acquired with the GC/MS instrument.



120 **Figure S3:** Sample chromatogram of the compounds listed in Table S2 (first set) acquired with the GC/FID instrument.

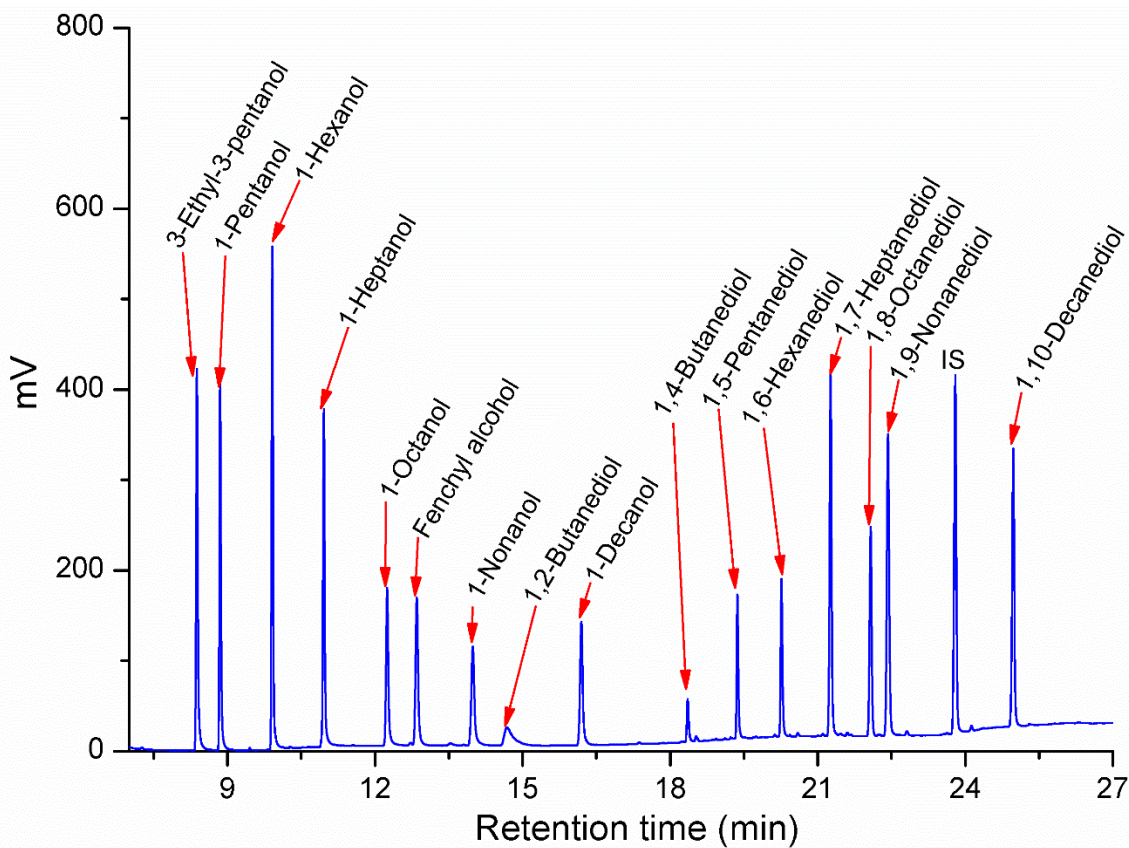


Figure S4: Sample chromatogram of the compounds listed in Table S2 (second set) acquired with the GC/FID instrument.

S4. Activation parameters

The E_a values obtained with eq. 1 (section 2.4 in the main text) were used to derive the activation parameters with eq. S1- S3:

$$\Delta H^\ddagger = E_a - R \cdot T \quad (S1)$$

$$\Delta S^\ddagger = R \times \left(\ln(A) - \ln\left(\frac{k_B \cdot T}{h}\right) - 1 \right) \quad (S2)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - \Delta S^\ddagger \cdot T \quad (S3)$$

In eq. S1-S3, ΔG^\ddagger is Gibbs free energy of activation, ΔH^\ddagger is the enthalpy of activation and ΔS^\ddagger is the entropy of activation, k_B and h are Boltzmann and Plank constants, respectively.

S5. Calculating the rates of the completely diffusion-limited reactions

The rates of the completely diffusion-controlled reactions of the AAs under investigation with the OH in the aqueous phase (k_{diff} , $M^{-1}s^{-1}$) were estimated with the Smoluchowski equation as previously described (Schöne et al., 2014; Schaefer et al., 2020; Witkowski et al., 2021). Initially, the group-contribution method was used to estimate the critical volumes (V_c , cm^3) (Joback and Reid, 1987). The V_c obtained was then used to derive molar volumes (V_m) for each AA (Joback and Reid, 1987). The V_m values calculated were used to calculate the values of radii (r , cm^{-1}), which were utilized to calculate diffusivities using a modified version of the Stokes-Einstein equation (Wilke and Chang, 1955). Finally, the r and D ($cm^2 s^{-1}$) values were used to calculate the k_{diff} via the Smoluchowski equation – eq. S4.

$$k_{diff} = 4 \cdot 10^{-3} \cdot \pi \cdot N_A \cdot (r_{OH} + r_{acid}) \cdot (D_{OH} + D_{acid}) \quad (S4)$$

The k_{diff} values are estimated with eq. S4 are listed in Table S5 together with the estimated diffusion contributions.

Table S5 Measured k_{OH} values, k_{diff} values at 298K, and the estimated diffusion contribution

Name	k_{OH} at 298 K, ($M^{-1}s^{-1}$) $\times 10^{-9}$		Diffusion contribution (%)
	Measured	k_{diff}	
Ethanol	2.0 \pm 0.1	14.1	14%
1-propanol	2.5 \pm 0.2	14.0	18%
2-butanol	2.5 \pm 0.2	14.0	18%
1-butanol	3.2 \pm 0.2	14.0	23%
1-Pentanol	4.5 \pm 0.3	14.1	32%
1-Hexanol	4.9 \pm 0.4	14.2	35%
1-Heptanol	5.0 \pm 0.4	14.3	35%
1-Octanol	5.7 \pm 0.4	14.4	39%
1-Nonanol	5.4 \pm 0.4	14.6	35%
1-Decanol	6.2 \pm 0.5	14.7	37%
3-ethyl-3-pentanol	2.5 \pm 0.3	14.3	18%
1,2-Ethandiol	1.9 \pm 0.2	14.0	13%
1,2-propanediol	1.8 \pm 0.1	14.0	13%
1,2-Butanediol	2.4 \pm 0.2	14.0	17%

Table S5 Measured k_{OH} values, k_{diff} values at 298K, and the estimated diffusion contribution, continued...

1,6-Hexanediol	4.9±0.5	14.2	35%
1,7-Heptanediol	5.4±0.4	14.4	38%
1,8-Octanediol	5.5±0.4	14.5	38%
1,9-Nonanediol	6.4±0.4	14.6	44%
1,10-Decanediol	6.3±0.4	14.8	43%
Cyclohexanol	3.6±0.3	14.1	26%
trans-1,2-Cyclohexanediol	2.9±0.1	14.2	20%
exo-Norborneol	1.9±0.1	14.2	13%
cis-2-Methylcyclohexanol	4.8±0.5	14.2	34%
(+)-Fenchol	3.0±0.2	14.6	20%
(+)-Borneol	3.3±0.1	14.3	23%
(-)-Menthol	4.0±0.1	14.5	27%
(±)-exo,exo-2,3-Camphanediol	4.1±0.1	14.6	28%
Pinanediol	3.6±0.1	14.6	25%

150 **S6. Derivation of the uncertainty of the $k_{OH_{aq}}$ values measured in this work, taking into account the experimental uncertainties and the uncertainties of the k_{ref} values**

The uncertainties of the slopes of the relative kinetic plots ($\Delta slope$), corresponding the the k_{AA}/k_{ref} ratios were derived as two 2σ values from three or more separate measurements and, the uncertainties of the k_{ref} values (Δk_{ref}) reported in the literature both contributed to uncertainties of the $k_{OH_{aq}}$ measured in his work. In the relative rate technique, the unknown $k_{OH_{aq}}$ values are obtained by eq. S5.

155
$$k_{OH_{aq}} = slope \times k_{ref} \quad (S5)$$

In the exact differential method, $\Delta slope$ and Δk_{ref} are propagated, to obtain the uncertainties of the $k_{OH_{aq}}$ ($\Delta k_{OH_{aq}}$) are calculated using a general formula – eq. S6.

160
$$\Delta k_{OH_{aq}} = \sqrt{\left(\frac{\partial k_{OH_{aq}}}{\partial slope} \times \Delta slope\right)^2 + \left(\frac{\partial k_{OH_{aq}}}{\partial k_{ref}} \times \Delta k_{ref}\right)^2} \quad (S6)$$

In eq. S6, the derivative of the formula (function) used to calculate the value of $k_{OH_{aq}}$ are calculated for $slope$ and k_{ref} . Because the derivative of a function $y=A \times x$ for x is equal to A , solving eq. 6S yields eq. 6 (given in the main text), which was used to obtain the $\Delta k_{OH_{aq}}$ listed in Tables 1 and S6.

Table S6 The $k_{OH_{aq}}$ values measured in this work

Name/Temp (K)	$k_{OH_{aq}} \times 10^{-9}$							
	278	283	293	298	303	313	318	323
Ethanol	1.6±0.2	1.8±0.2	1.9±0.1	2.0±0.1	2.1±0.2	2.3±0.2	2.5±0.3	2.5±0.3
1-propanol	1.9±0.2	2.1±0.3	2.5±0.1	2.5±0.2	2.7±0.2	3.0±0.2	3.1±0.3	3.3±0.3
2-butanol	1.9±0.2	2.0±0.2	2.4±0.1	2.5±0.2	2.7±0.2	3.2±0.1	3.3±0.3	3.5±0.3
1-butanol	2.4±0.3	2.6±0.3	3.1±0.1	3.2±0.2	3.6±0.2	4.1±0.1	4.4±0.5	4.6±0.4
1-Pentanol	3.4±0.3	3.6±0.3	4.1±0.3	4.5±0.3	4.9±0.7	6.0±0.4	6.2±0.6	6.9±0.5
Hexanol	3.6±0.3	3.9±0.3	4.4±0.3	4.9±0.4	5.2±0.8	6.8±0.5	6.9±0.7	7.3±0.5
Heptanol	3.6±0.2	4.1±0.3	4.5±0.3	5.0±0.4	5.3±0.8	7.3±0.5	7.3±0.7	8.1±0.6
Octanol	3.8±0.3	4.3±0.3	4.7±0.3	5.7±0.4	6.4±1.0			
Nonanol	3.7±0.4	4.1±0.3	5.1±0.4	5.4±0.4	6.3±1.0			
Decanol	4.0±0.3	4.5±0.4	5.6±0.5	6.2±0.5	6.9±1.1			
3-ethyl-3-pentanol	1.6±0.2	1.9±0.2	2.1±0.2	2.5±0.3	2.7±0.4	3.1±0.3	3.4±0.3	3.9±0.3
ethylene glycol	1.5±0.2	1.6±0.2	1.6±0.2	1.9±0.2	2.1±0.2	2.2±0.1	2.2±0.3	2.3±0.2
1,2-propanediol	1.4±0.2	1.6±0.2	1.6±0.1	1.8±0.1	2.0±0.1	2.1±0.1	2.2±0.2	2.3±0.2
1,2-Butanediol	1.9±0.2	2.1±0.3	2.3±0.2	2.4±0.2	2.8±0.3	3.0±0.3	3.0±0.4	3.3±0.4
1,6-Hexanediol	3.5±0.2	4.1±0.4	4.7±0.4	4.9±0.5	6.0±0.9	6.5±0.5	6.5±0.7	7.0±0.5
1,7-Heptanediol	4.0±0.3	5.1±0.4	5.4±0.4	5.4±0.4	6.7±1.0	7.2±0.5	7.6±0.8	8.0±0.6
1,8-Octanediol	3.7±0.3	4.5±0.3	5.0±0.4	5.5±0.4	5.8±0.9	8.3±0.6	8.9±0.9	9.5±0.8
1,9-Nonanediol	4.4±0.3	4.9±0.3	5.7±0.4	6.4±0.4	6.8±1.0	8.6±0.6	9.1±0.9	9.7±0.7
1,10-Decanediol	4.5±0.3	5.0±0.4	5.9±0.4	6.3±0.4	7.4±1.1	9.5±0.7	9.9±1.0	10.6±0.7
Cyclohexanol	2.6±0.1	2.9±0.2	3.3±0.3	3.6±0.3	3.9±0.1	5.5±0.3	5.6±0.2	6.4±0.1
trans-1,2-Cyclohexanediol	2.2±0.1	2.3±0.1	2.7±0.1	2.9±0.1	3.0±0.2	4.1±0.1	4.2±0.2	4.5±0.4
exo-Norborneol	1.4±0.1	1.6±0.1	1.7±0.1	1.9±0.1	1.9±0.1	2.9±0.1	2.8±0.3	3.3±0.3

Table S6 The values of temperature-dependent rate coefficients measured in this work, continued...

Name/Temp (K)	$k_{OH_{aq}} \times 10^{-9}$							
	278	283	293	298	303	313	318	323
cis-2-Methylcyclohexanol	3.7±0.1	3.7±0.1	4.9±0.1	4.8±0.5	5.2±0.1	7.4±0.5	7.8±0.2	8.2±0.3
(+)-Fenchol	2.0±0.2	2.2±0.2	2.6±0.1	3.0±0.2	3.2±0.2	4.5±0.1	4.5±0.1	5.2±0.2
(+)-Borneol	2.4±0.1	2.7±0.1	3.1±0.1	3.3±0.1	3.6±0.1	5.0±0.2	5.1±0.1	5.8±0.2
(-)-Menthol	2.6±0.1	3.0±0.1	3.6±0.1	4.0±0.1	4.2±0.1	5.0±0.3	6.4±0.1	7.2±0.1
(±)-exo,exo-2,3-Camphanediol	2.9±0.1	3.0±0.1	3.5±0.1	4.1±0.1	4.3±0.1	6.1±0.2	6.3±0.1	6.5±0.2
Pinanediol	2.4±0.1	3.0±0.1	3.4±0.1	3.6±0.1	4.6±0.3	6.2±0.2	6.4±0.3	6.7±0.2

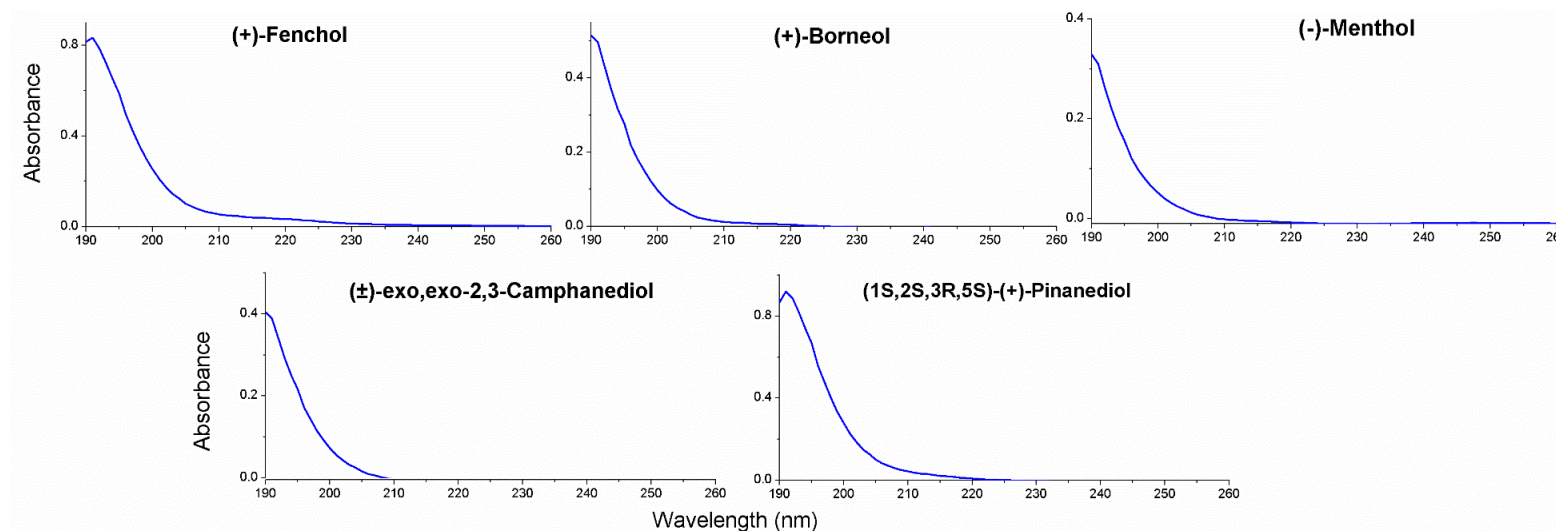
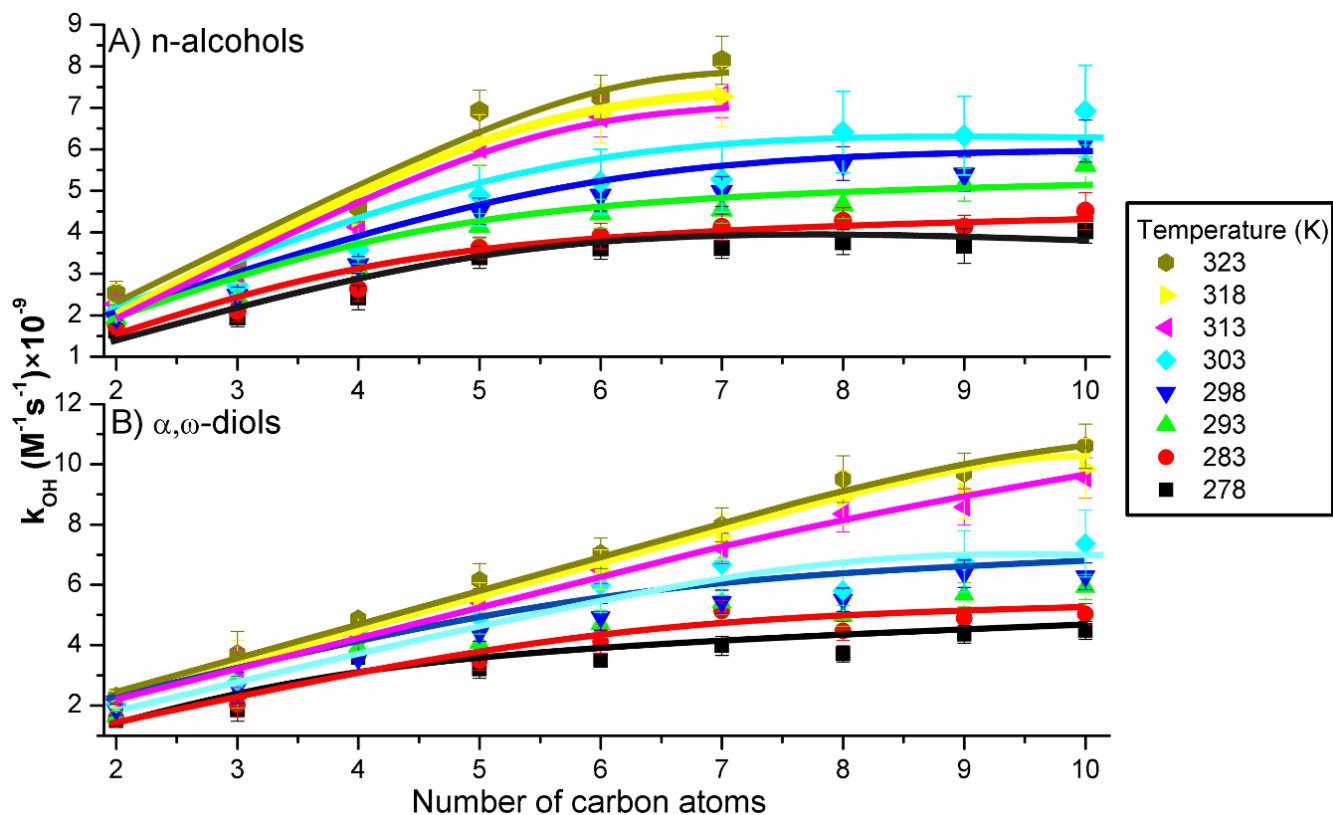


Figure S5: UV-Vis spectra of the terpenic alcohols in water (concentration approx. 0.5 g/L each) and diols (concentration approx. 0.15 g/L each) investigated in this work

170 As presented in Fig. S5, the terpenic alcohols, and diols investigated in this work did not exhibit any absorbance above 220 nm, which is characteristic of other aliphatic alcohols and diols (Onori, 1987). Hence, it is reasonable to assume that these molecules did not undergo any direct photolysis in the photoreactors under the experimental conditions used ($\lambda_{\max}=254$ nm).

Table S7. The measured values of $k_{OH_{gas}}$ and $k_{OH_{aq}}$ for n-alcohols and n-alkanes

Number of carbon atoms	Name	$k_{OH_{gas}} \times 10^{11}$	Ref.	Name	$k_{OH_{gas}} \times 10^{11}$	Ref.	$k_{OH_{aq}}$	Ref.
		($cm^3 molec^{-1} s^{-1}$)			($cm^3 molec^{-1} s^{-1}$)		$\times 10^{-9}$ ($M^{-1} s^{-1}$)	
<i>n-Alcohols</i>				<i>Alkanes</i>				
C₁	Methanol	0.09±0.01	(McGillen et al., 2020; McGillen et al., 2021)	Methane	0.0007±0.0001	(McGillen et al., 2020; McGillen et al., 2021)	0.11	(Buxton et al., 1988a)
C₂	Ethanol	0.33±0.03	(McGillen et al., 2020; McGillen et al., 2021)	Ethane	0.025±0.002	(McGillen et al., 2020; McGillen et al., 2021)	1.60	(Hickel, 1975; Buxton et al., 1988b; Getoff, 1989)
C₃	1-propanol	0.59±0.06	(McGillen et al., 2020; McGillen et al., 2021)	Propane	0.11±0.01	(McGillen et al., 2020; McGillen et al., 2021)	2.95	(Buxton et al., 1988b; Getoff, 1991)
C₄	1-butanol	0.91±0.14	(Sime et al., 2020)	Butane	0.24±0.02	(McGillen et al., 2020; McGillen et al., 2021)	4.60	(Buxton et al., 1988b)
C₅	1-Pentanol	1.10±0.17	(Calvert et al., 2015)	Pentane	0.38±0.04	(McGillen et al., 2020; McGillen et al., 2021)	5.40	(Buxton et al., 1988b)
C₆	1-Hexanol	1.30±0.33	(Calvert et al., 2015)	Hexane	0.50±0.08	(McGillen et al., 2020; McGillen et al., 2021)	6.60	(Buxton et al., 1988b)
C₇	1-Heptanol	1.37±0.34	(Wallington et al., 1988; Nelson et al., 1990)	Heptane	0.62±0.09	(McGillen et al., 2020; McGillen et al., 2021)	7.70	(Buxton et al., 1988b)
C₈	1-Octanol	1.38±0.41	(Nelson et al., 1990; Calvert et al., 2015)	Octane	0.85±0.01	(McGillen et al., 2020; McGillen et al., 2021)	9.10	(Buxton et al., 1988b)
C₉				Nonane	1.02±0.15	(McGillen et al., 2020; McGillen et al., 2021)		
C₁₀				Decane	1.31±0.32	(McGillen et al., 2020; McGillen et al., 2021)		



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Figure S6: The values of $k_{OH_{aq}}$ for the C₂-C₁₀ homolog series of n-alcohols (A) and α,ω -diols (B) measured in this work in the temperature range between 278 and 323K. Experimental data are represented by points; lines are provided to guide the eye

Table S8. The $k_{OH_{aq}}$ values measured at 298K for 1-propanol, 1, and 2-butanols using ethanol as a kinetic reference compound. The uncertainties listed were derived with eq. 6 (main text)

Name	$k_{OH_{aq}}$ at 298K ($M^{-1}s^{-1}) \times 10^{-9}$	k_{ref} value (ethanol) at 298K ($M^{-1}s^{-1}) \times 10^{-9}$
1-Propanol	2.6±0.1	
1-Butanol	3.4±0.2	2.0±0.3
2-Butanol	2.6±0.2	

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Table S9. Results of the linear regression analysis of the measured (independent variable) vs predicted (dependent variable) $k_{OH_{aq}}$ for the compounds used to optimize SAR factors at different temperatures – these data are presented in Fig. 11 in the main text

<i>Temperature</i>	Mono alcohols		Diols and glycerine		Cyclic alcohols		Carboxylic acids		(di)Carboxylate anions	
	<i>Slope</i>	<i>R</i> ²	<i>Slope</i>	<i>R</i> ²	<i>Slope</i>	<i>R</i> ²	<i>Slope</i>	<i>R</i> ²	<i>Slope</i>	<i>R</i> ²
278	0.868	0.734	0.961	0.868	1.334	0.433	0.712	0.867	0.787	0.726
283	0.898	0.773	0.847	0.814	1.418	0.429	0.727	0.870	0.864	0.922
288	1.041	0.878	0.957	0.879	1.286	0.426	0.751	0.889	0.861	0.941
293	0.917	0.889	0.933	0.868	1.217	0.478	0.682	0.932	0.828	0.963
298	0.966	0.952	0.923	0.906	1.202	0.662	0.772	0.874	1.041	0.857
303	0.917	0.957	0.900	0.843	0.949	0.293	0.670	0.715	0.733	0.774
308	0.984	0.923	0.898	0.896	0.974	0.363	0.709	0.714	0.838	0.958
313	0.698	0.897	0.836	0.902	0.717	0.235	0.658	0.808	0.714	0.783
318	0.794	0.908	0.860	0.905	0.767	0.303	0.655	0.713	0.745	0.963
323	0.773	0.917	0.882	0.913	0.902	0.371	0.638	0.802	0.696	0.789
328	0.761	0.901	0.816	0.842	0.728	0.281	0.628	0.897	0.681	0.790

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