

Electronic Supplementary Material

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 ($\geq 99\%$), cis-2-Methylcyclohexanol ($\geq 98\%$), 1-Decanol ($\geq 99\%$), Dimethyl phthalate ($\geq 99\%$), 1,2-Ethanediol ($\geq 99\%$), 1-Heptanol ($\geq 98\%$), 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). (+)-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; Chemat (Gdańsk, Poland). Deionized (DI) water ($18 \text{ M}\Omega \times \text{cm}^{-1}$) was prepared using Direct - Q3 Ultrapure Water System (Millipore). UHP gases: 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).

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S2. Gas chromatography analysis conditions

S2.1. Gas chromatography coupled with the mass spectrometry

80 GC/MS analyses were carried out using 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).

85 The first group of alcohols was analyzed using VF-WAXms column (Agilent); 30 m, 0.25mm, 0.5 μ m 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 °C/min to 250°C, kept for 6 min, and analysis time was 22 min.

90 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 μ m 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. 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
95 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

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.

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.

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 held 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 quantified with the 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			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
1-Heptanol	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	GC/MS (WAX), ethyl acetate	1-Heptanol	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	extracts		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	Internal standard	17.8			162, 163, 134, 133, 120, 105, 104, 92, 77, 76, 50, 49

125 **Table S1.** Retention times and ions monitored in SIM mode for aliphatic alcohols quantified with the GC/MS instrument, continued...

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			55, 60, 67, 69, 79, 81, 84, 95, 99, 119, 121, 123, 137, 139, 152
(+)-Fenchol	C ₁₀ H ₁₈ O	18.2	GC/MS (ZB-5 column), ethyl acetate extracts	(+)-Fenchol	154, 139, 136, 125, 123, 121, 111, 107, 105, 97, 91, 85, 84, 81, 80, 72, 71, 69, 67, 57, 55, 53
Dimethyl phthalate	Internal standard	23.6			162, 163, 134, 133, 120, 105, 104, 92, 77, 76, 50, 49

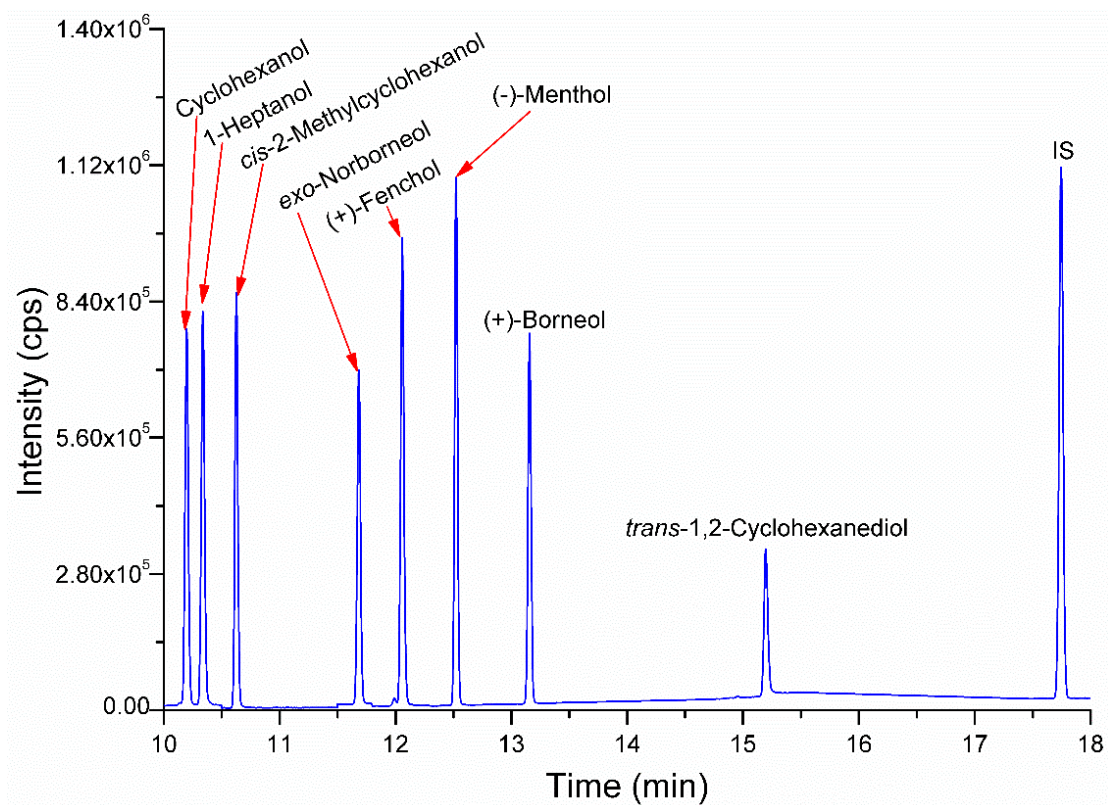
Table S2. Retention times of aliphatic alcohols quantified with the GC/FID instrument

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 ₅ linear alcohols and	GC/FID (WAX column),	1,4-Butanediol
1,2-Propanediol	C ₃ H ₈ O ₂	12.7	diols	aqueous injection	
1,2-Ethandiol	C ₂ H ₆ O ₂	12.8			
1,2-Butanediol	C ₄ H ₁₀ O ₂	13.2			
1,4-Butanediol	C ₄ H ₁₀ O ₂	14.6			

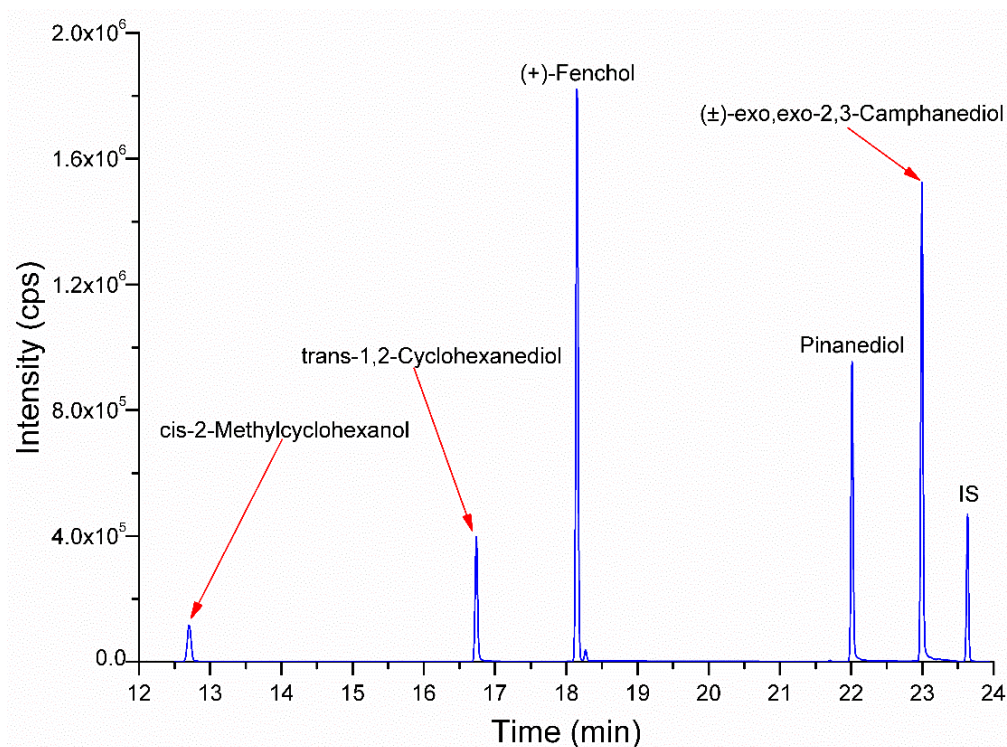
Table S2 Retention times of aliphatic alcohols quantified with the GC/FID instrument, continued...

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	C ₅ -C ₁₀ linear alcohols and diols	GC/FID (WAX column), ethyl acetate extracts	1,5-Pentanediol
Nonanol	C ₉ H ₂₀ O	14.0			
Decanol	C ₁₀ H ₂₂ O	16.2			
1,5-Pentanediol	C ₅ H ₁₂ O ₂	19.4			
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	Internal standard	22.1			

Sample chromatograms for the alcohols under investigation are presented in Fig. S1-S4.



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



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

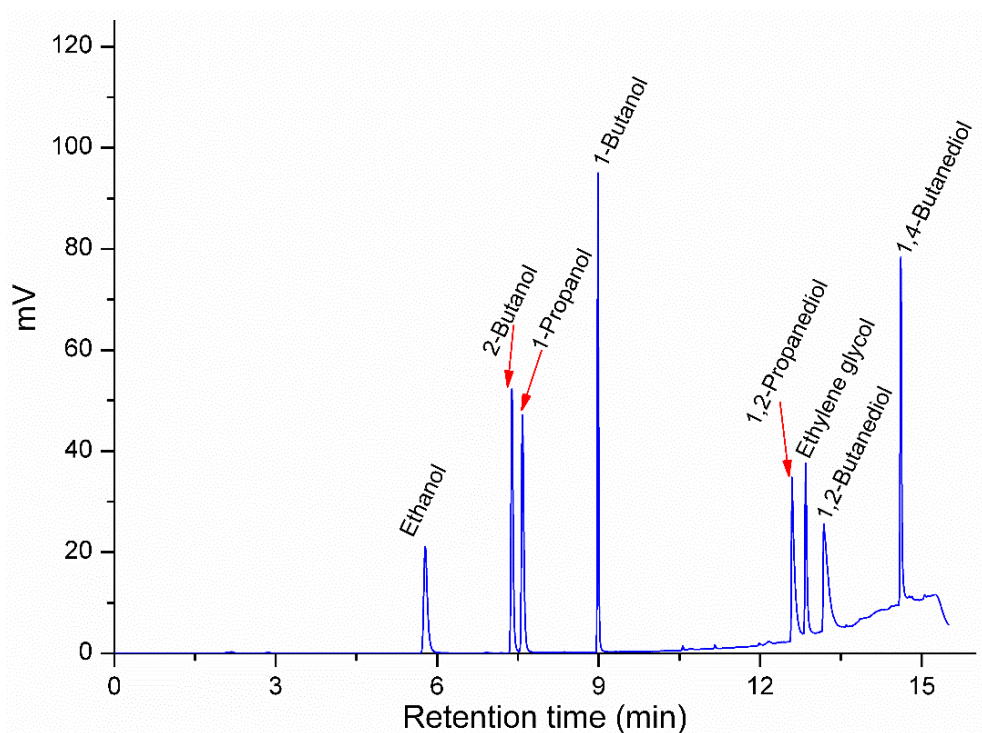


Figure S3: Sample chromatogram of the compounds listed in Table S2 (first set) acquired with the GC/FID instrument.

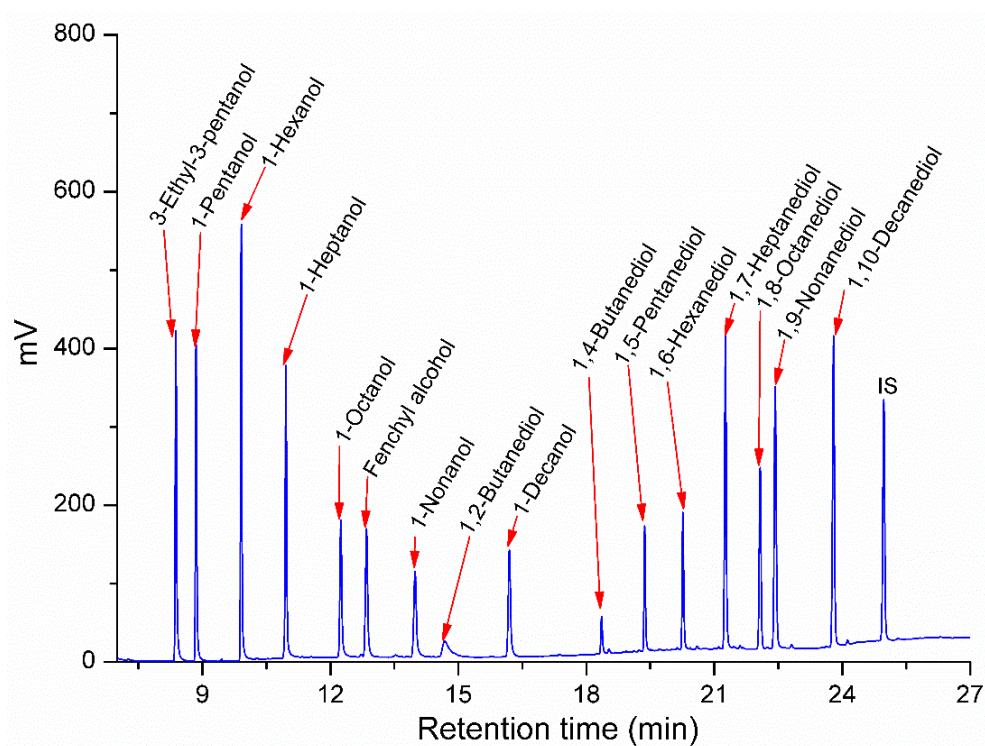


Figure S4: Sample chromatogram of the compounds listed in Table S2 (second set) acquired with the GC/FID instrument.

S4. Activation parameters

The E_a values obtained with eq. I (section 2.4 in the main text) were used to derive the activation parameters via eq. SI- SII:

$$150 \quad \Delta H^\ddagger = E_a - R \cdot T \quad (\text{SI})$$

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

$$\Delta G^\ddagger = \Delta H^\ddagger - \Delta S^\ddagger \cdot T \quad (\text{SIII})$$

In eq. SI-SIII, 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.

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S5. Estimating 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 – SIV.

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

The k_{diff} values are estimated with eq. SIV are listed in Table S3 together with the estimated diffusion contributions

Table S3. 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	1.95 \pm 0.07	14.1	14%
1-propanol	2.48 \pm 0.09	14.0	18%
2-butanol	2.45 \pm 0.11	14.0	18%
1-butanol	3.21 \pm 0.13	14.0	23%
1-Pentanol	4.50 \pm 0.06	14.1	32%
1-Hexanol	4.89 \pm 0.05	14.2	35%
1-Heptanol	4.98 \pm 0.06	14.3	35%
1-Octanol	5.66 \pm 0.09	14.4	39%
1-Nonanol	5.09 \pm 0.14	14.6	35%
1-Decanol	5.41 \pm 0.12	14.7	37%
3-ethyl-3-pentanol	2.52 \pm 0.11	14.3	18%
1,2-Ethanediol	1.86 \pm 0.04	14.0	13%
1,2-propanediol	1.80 \pm 0.07	14.0	13%
1,2-Butanediol	2.36 \pm 0.06	14.0	17%
1,6-Hexanediol	4.93 \pm 0.14	14.2	35%
1,7-Heptanediol	5.43 \pm 0.04	14.4	38%
1,8-Octanediol	5.51 \pm 0.08	14.5	38%
1,9-Nonanediol	6.37 \pm 0.05	14.6	44%
1,10-Decanediol	6.29 \pm 0.06	14.8	43%
Cyclohexanol	3.61 \pm 0.09	14.1	26%
trans-1,2-Cyclohexanediol	2.89 \pm 0.05	14.2	20%
exo-Norborneol	1.89 \pm 0.06	14.2	13%
cis-2-Methylcyclohexanol	4.78 \pm 0.52	14.2	34%

Table S3. Measured k_{OH} values, k_{diff} values at 298K, and the estimated diffusion contribution continued...

Name	k_{OH} at 298 K, ($M^{-1}s^{-1}$) $\times 10^{-9}$		Diffusion contribution (%)
	Measured	k_{diff}	
(+)-Fenchol	2.99 \pm 0.05	14.6	20%
(+)-Borneol	3.32 \pm 0.11	14.3	23%
(-)-Menthol	3.99 \pm 0.09	14.5	27%
(\pm)-exo,exo-2,3-Camphanediol	4.07 \pm 0.07	14.6	28%
Pinanediol	3.63 \pm 0.12	14.6	25%

Table S4. The values of temperature-dependent rate coefficients measured in this work

Name/Temp (K)	$k_{OH_{aq}} \times 10^{-9}$							
	278	283	293	298	303	313	318	323
Ethanol	1.62±0.06	1.76±0.12	1.93±0.02	1.95±0.07	2.09±0.14	2.27±0.20	2.45±0.18	2.53±0.20
1-propanol	1.94±0.10	2.10±0.14	2.47±0.06	2.48±0.09	2.71±0.16	3.01±0.14	3.09±0.06	3.27±0.20
2-butanol	1.86±0.08	2.02±0.14	2.43±0.04	2.45±0.11	2.75±0.16	3.15±0.04	3.32±0.04	3.52±0.06
1-butanol	2.43±0.16	2.63±0.14	3.14±0.04	3.21±0.13	3.58±0.12	4.13±0.06	4.37±0.18	4.61±0.10
1-Pentanol	3.39±0.14	3.62±0.10	4.15±0.08	4.50±0.06	4.88±0.04	6.03±0.06	6.21±0.06	6.92±0.14
Hexanol	3.61±0.12	3.91±0.14	4.45±0.16	4.89±0.05	5.21±0.02	6.78±0.02	6.85±0.14	7.26±0.14
Heptanol	3.62±0.08	4.13±0.12	4.54±0.08	4.98±0.06	5.28±0.04	7.28±0.08	7.27±0.08	8.14±0.12
Octanol	3.76±0.18	4.28±0.12	4.66±0.08	5.66±0.09	6.42±0.18			
Nonanol	3.67±0.34	4.12±0.06	5.14±0.15	5.72±0.14	6.33±0.04			
Decanol	4.02±0.11	4.51±0.32	5.62±0.26	6.25±0.12	6.92±0.38			
3-ethyl-3-pentanol	1.58±0.12	1.92±0.18	2.05±0.20	2.52±0.11	2.70±0.04	3.09±0.22	3.44±0.06	3.85±0.16
ethylene glycol	1.50±0.08	1.56±0.18	1.64±0.18	1.86±0.04	2.08±0.12	2.20±0.10	2.21±0.16	2.32±0.12
1,2-propanediol	1.36±0.12	1.58±0.04	1.64±0.08	1.80±0.07	1.99±0.04	2.15±0.04	2.19±0.06	2.26±0.14
1,2-Butanediol	1.94±0.14	2.06±0.22	2.25±0.17	2.36±0.06	2.77±0.24	2.97±0.23	2.99±0.26	3.33±0.34
1,4-Butanediol	3.58±0.06	3.67±0.02	3.94±0.12	3.55±0.04	4.41±0.12	4.34±0.12	4.55±0.10	4.88±0.10
1,5-Pentanediol	3.21±0.31	3.49±0.32	4.08±0.29	4.40±0.26	4.90±0.29	5.42±0.45	5.60±0.47	6.16±0.54
1,6-Hexanediol	3.51±0.06	4.12±0.26	4.71±0.30	4.93±0.14	5.98±0.03	6.50±0.06	6.51±0.07	7.04±0.13
1,7-Heptanediol	3.98±0.18	5.13±0.04	5.41±0.10	5.43±0.04	6.68±0.20	7.21±0.06	7.60±0.06	7.99±0.08
1,8-Octanediol	3.71±0.12	4.47±0.04	4.98±0.04	5.51±0.08	5.80±0.06	8.35±0.06	8.89±0.06	9.50±0.40

Table S4. 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
1,9-Nonanediol	4.36±0.06	4.89±0.06	5.67±0.04	6.37±0.05	6.78±0.06	8.58±0.06	9.09±0.06	9.69±0.06
1,10-Decanediol	4.49±0.06	5.03±0.08	5.93±0.05	6.29±0.06	7.37±0.08	9.54±0.08	9.85±0.12	10.60±0.06
Cyclohexanol	2.63±0.14	2.95±0.16	3.32±0.30	3.61±0.09	3.93±0.06	5.51±0.30	5.61±0.18	6.40±0.12
trans-1,2-Cyclohexanediol	2.19±0.06	2.26±0.12	2.74±0.11	2.89±0.05	2.98±0.24	4.14±0.08	4.15±0.18	4.52±0.36
exo-Norborneol	1.37±0.04	1.56±0.10	1.74±0.07	1.89±0.06	1.93±0.04	2.93±0.06	2.84±0.26	3.35±0.34
cis-2-Methylcyclohexanol	3.65±0.08	3.71±0.04	4.94±0.11	4.78±0.52	5.22±0.13	7.44±0.48	7.75±0.19	8.24±0.30
(+)-Fenchol	1.95±0.20	2.19±0.25	2.64±0.01	2.99±0.05	3.15±0.04	4.52±0.10	4.54±0.12	5.20±0.20
(+)-Borneol	2.37±0.06	2.71±0.12	3.08±0.06	3.32±0.11	3.55±0.14	5.04±0.18	5.05±0.10	5.77±0.18
(-)-Menthol	2.58±0.08	3.04±0.12	3.62±0.06	3.99±0.09	4.20±0.06	5.00±0.32	6.42±0.14	7.25±0.12
(±)-exo,exo-2,3-Camphanediol	2.87±0.08	3.00±0.06	3.54±0.06	4.07±0.07	4.32±0.13	6.05±0.07	6.29±0.12	6.45±0.24
Pinanediol	2.44±0.10	3.01±0.06	3.37±0.08	3.63±0.12	4.57±0.28	6.21±0.08	6.38±0.30	6.66±0.15

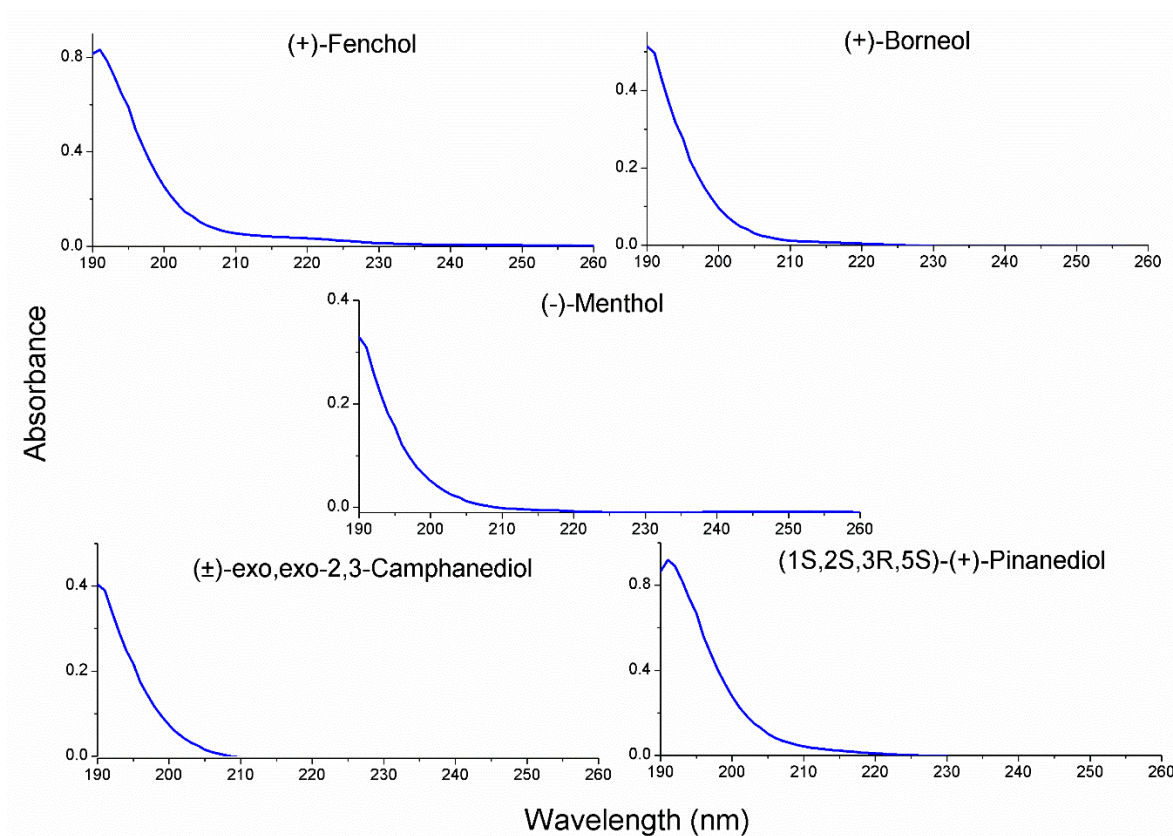


Figure S5: UV-Vis spectra of the terpenic alcohols in water (concentration approx. 0.5 g/L each) and diols (concentration approx.. 0.15 g/L each) investigated in this work.

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 direct photolysis in the photoreactors (see section 2.1 in the main text).

Table S5. The previously measured values of $k_{OH_{gas}}$ and $k_{OH_{aq}}$ for n-alcohols and n-alkanes

Number of carbon atoms	Name	$k_{OH_{gas}} \times 10^{11}$ ($cm^3 molec^{-1} s^{-1}$)	Ref.	Name	$k_{OH_{gas}} \times 10^{11}$ ($cm^3 molec^{-1} s^{-1}$)	Ref.	$k_{OH_{aq}} (M^{-1} s^{-1})$ $\times 10^{-9}$	Ref.
	n-Alcohols			Alkanes				
C ₂	Ethanol	0.33	(McGillen et al., 2020)	Ethane	0.02	(McGillen et al., 2020)	1.60	(Hickel, 1975; Buxton et al., 1988; Getoff, 1989)
C ₃	1-propanol	0.59	(McGillen et al., 2020)	Propane	0.11	(McGillen et al., 2020)	2.95	(Buxton et al., 1988; Getoff, 1991)
C ₄	1-butanol	0.91	(Sime et al., 2020)	Butane	0.24	(McGillen et al., 2020)	4.60	(Buxton et al., 1988)
C ₅	1-Pentanol	1.10	(Calvert et al., 2015)	Pentane	0.38	(McGillen et al., 2020)	5.40	(Buxton et al., 1988)
C ₆	1-Hexanol	1.30	(Calvert et al., 2015)	Hexane	0.50	(McGillen et al., 2020)	6.60	(Buxton et al., 1988)
C ₇	1-Heptanol	1.37	(Wallington et al., 1988; Nelson et al., 1990)	Heptane	0.62	(McGillen et al., 2020)	7.70	(Buxton et al., 1988)
C ₈	1-Octanol	1.38	(Nelson et al., 1990; Calvert et al., 2015)	Octane	0.85	(McGillen et al., 2020)	9.10	(Buxton et al., 1988)
C ₉				Nonane	1.02	(McGillen et al., 2020)		
C ₁₀				Decane	1.31	(McGillen et al., 2020)		

190 **Table S6.** Performance of SAR (Model 2) for aliphatic alcohols, carboxylic acids, and (di)carboxylate anions in the temperature range between 278-328K.

Temperature (K)	Slope	R ²
278	1.1	0.738
283	1.0	0.638
288	0.90	0.736
293	0.97	0.529
298	1.1	0.750
303	0.98	0.666
308	0.85	0.702
313	0.82	0.631
318	0.86	0.687
323	0.88	0.656
328	1.55	0.423

Note that for different temperatures, a different number of $k_{OH_{aq}}$ are available for some molecules; for instance, only three rate coefficients in the training set were measured at 328K (Hoffmann et al., 2009).

195 **References**

- Buxton, G. V., Greenstock, C. L., Helman, W. P., and Ross, A. B.: Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}^-$ in Aqueous Solution, 17, 513-886, <https://doi.org/10.1063/1.555805>, 1988.
- Calvert, J. G., Orlando, J. J., Stockwell, W. R., and Wallington, T. J.: The Mechanisms of Reactions Influencing Atmospheric Ozone, Oxford University Press, <https://doi.org/10.1093/oso/9780190233020.001.0001>, 2015.
- Getoff, N.: Advancements of radiation induced degradation of pollutants in drinking and waste water, 40, 585-594, [https://doi.org/10.1016/0883-2889\(89\)90114-7](https://doi.org/10.1016/0883-2889(89)90114-7), 1989.
- Getoff, N.: Radiation- and photoinduced degradation of pollutants in water. A comparative study, 37, 673-680, [https://doi.org/10.1016/1359-0197\(91\)90166-Y](https://doi.org/10.1016/1359-0197(91)90166-Y), 1991.
- Hickel, B.: Absorption spectra and kinetics of methyl and ethyl radicals in water, 79, 1054-1059, <https://doi.org/10.1021/j100578a003>, 1975.
- Hoffmann, D., Weigert, B., Barzaghi, P., and Herrmann, H.: Reactivity of poly-alcohols towards OH, NO₃ and SO₄⁻ in aqueous solution, 11, 9351-9363, <https://doi.org/10.1039/B908459B>, 2009.
- Joback, K. G. and Reid, R. C.: Estimation of pure-component properties from group-contributions, 57, 233-243, <https://doi.org/10.1080/00986448708960487>, 1987.
- McGillen, M. R., Carter, W. P. L., Mellouki, A., Orlando, J. J., Picquet-Varrault, B., and Wallington, T. J.: Database for the kinetics of the gas-phase atmospheric reactions of organic compounds, 12, 1203-1216, <https://doi.org/10.5194/essd-12-1203-2020>, 2020.
- Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J., and Nielsen, O. J.: Absolute and relative rate constants for the reactions of hydroxyl radicals and chlorine atoms with a series of aliphatic alcohols and ethers at 298 K, 22, 1111-1126, <https://doi.org/10.1002/kin.550221102>, 1990.
- Onori, G.: Ultraviolet absorption study of aqueous mixtures of monohydric alcohols: Water structural effects, 9, 507-515, <https://doi.org/10.1007/BF02667946>, 1987.
- Schaefer, T., Wen, L., Estelmann, A., Maak, J., and Herrmann, H.: pH- and Temperature-Dependent Kinetics of the Oxidation Reactions of OH with Succinic and Pimelic Acid in Aqueous Solution, 11, 320, <https://doi.org/10.3390/atmos11040320>, 2020.
- Schöne, L., Schindelka, J., Szeremeta, E., Schaefer, T., Hoffmann, D., Rudzinski, K. J., Szmigielski, R., and Herrmann, H.: Atmospheric aqueous phase radical chemistry of the isoprene oxidation products methacrolein, methyl vinyl ketone, methacrylic acid and acrylic acid – kinetics and product studies, 16, 6257-6272, <https://doi.org/10.1039/C3CP54859G>, 2014.
- Sime, S. L., Blitz, M. A., and Seakins, P. W.: Rate coefficients for the reactions of OH with butanols from 298 K to temperatures relevant for low-temperature combustion, 52, 1046-1059, <https://doi.org/10.1002/kin.21422>, 2020.
- Wallington, T. J., Dagaut, P., Liu, R., and Kurylo, M. J.: Rate constants for the gas phase reactions of OH with C₅ through C₇ aliphatic alcohols and ethers: Predicted and experimental values, 20, 541-547, <https://doi.org/10.1002/kin.550200704>, 1988.
- Wilke, C. R. and Chang, P.: Correlation of diffusion coefficients in dilute solutions, 1, 264-270, <https://doi.org/10.1002/aic.690010222>, 1955.
- Witkowski, B., Chi, J., Jain, P., Błaziak, K., and Gierczak, T.: Aqueous OH kinetics of saturated C₆–C₁₀ dicarboxylic acids under acidic and basic conditions between 283 and 318 K; new structure-activity relationship parameters, 267, 118761, <https://doi.org/10.1016/j.atmosenv.2021.118761>, 2021.