

Reactivity of polyfunctional alcohols towards atmospheric radicals in the aqueous solution

D. Hoffmann and H. Herrmann

Leibniz Institut für Troposphärenforschung, Permoserstr. 15, 04318 Leipzig, Germany (hoffmann@tropos.de)

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Motivation

- Poly-alcohols are wide-spread compounds used in many applications as antifreeze agent, engine coolant, moisturizer and plasticizer. [1]
- The oxidation of poly-alcohols by free radicals could represent an important process for the formation of dicarboxylic acids such as oxalic acid and succinic acid. These acids are known components of the water soluble organic carbon (WSOC) fraction on atmospheric particles. [2,3]
- Due to the high water solubility of alcohols oxidation reactions of these compounds will take place mainly in the aqueous solution. A fast conversion of alcohols to acids by aqueous phase oxidation reactions might influence the organic particle mass production and the aqueous solution acidity.
- Using the laser-flash photolysis setup, the reactivity of OH, NO₃ and SO₄⁻ radicals in aqueous solution was studied as a function of the temperature. The results will be used to better describe the atmospheric multiphase chemistry of poly-alcohols.

Experimental

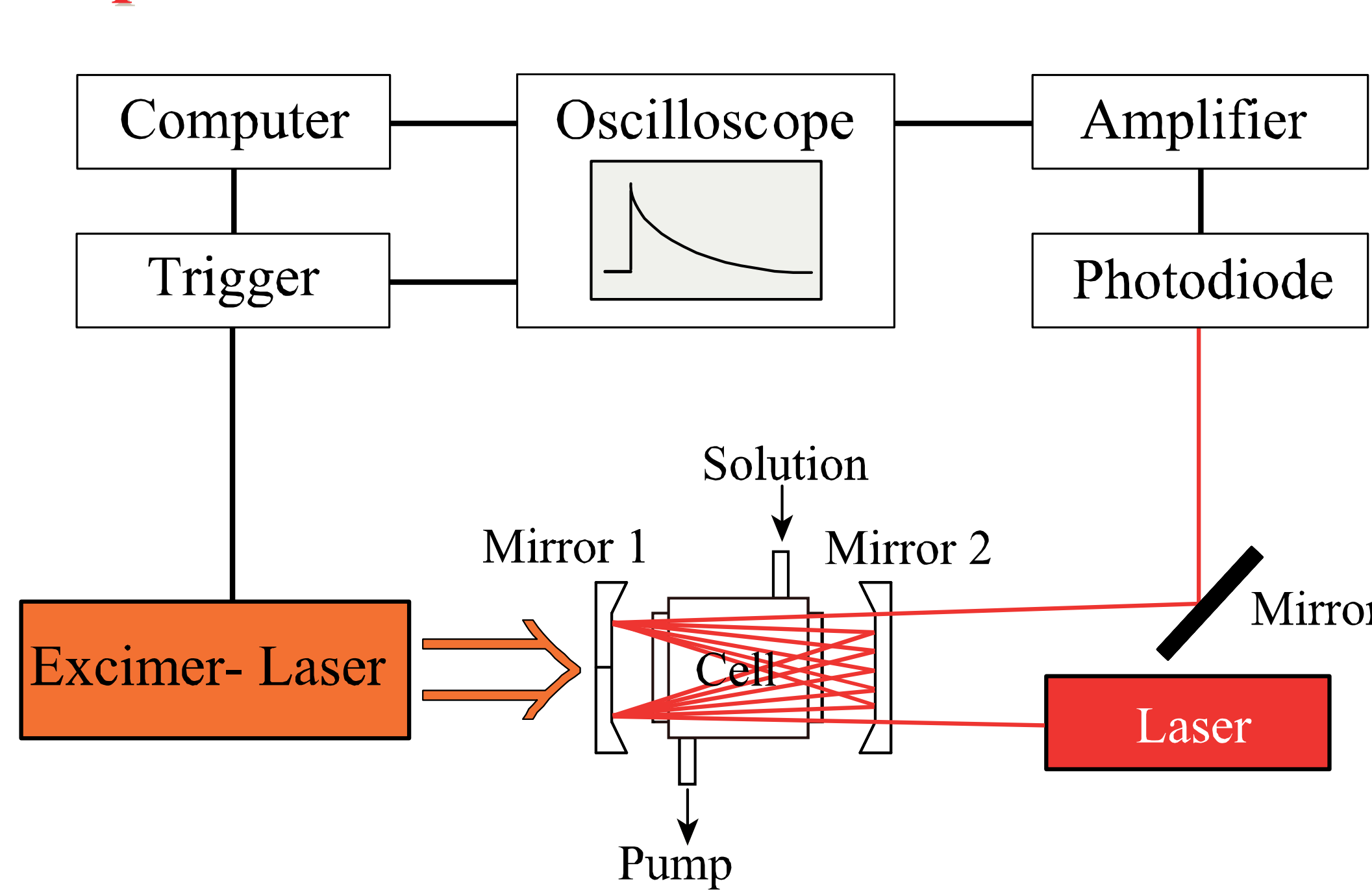
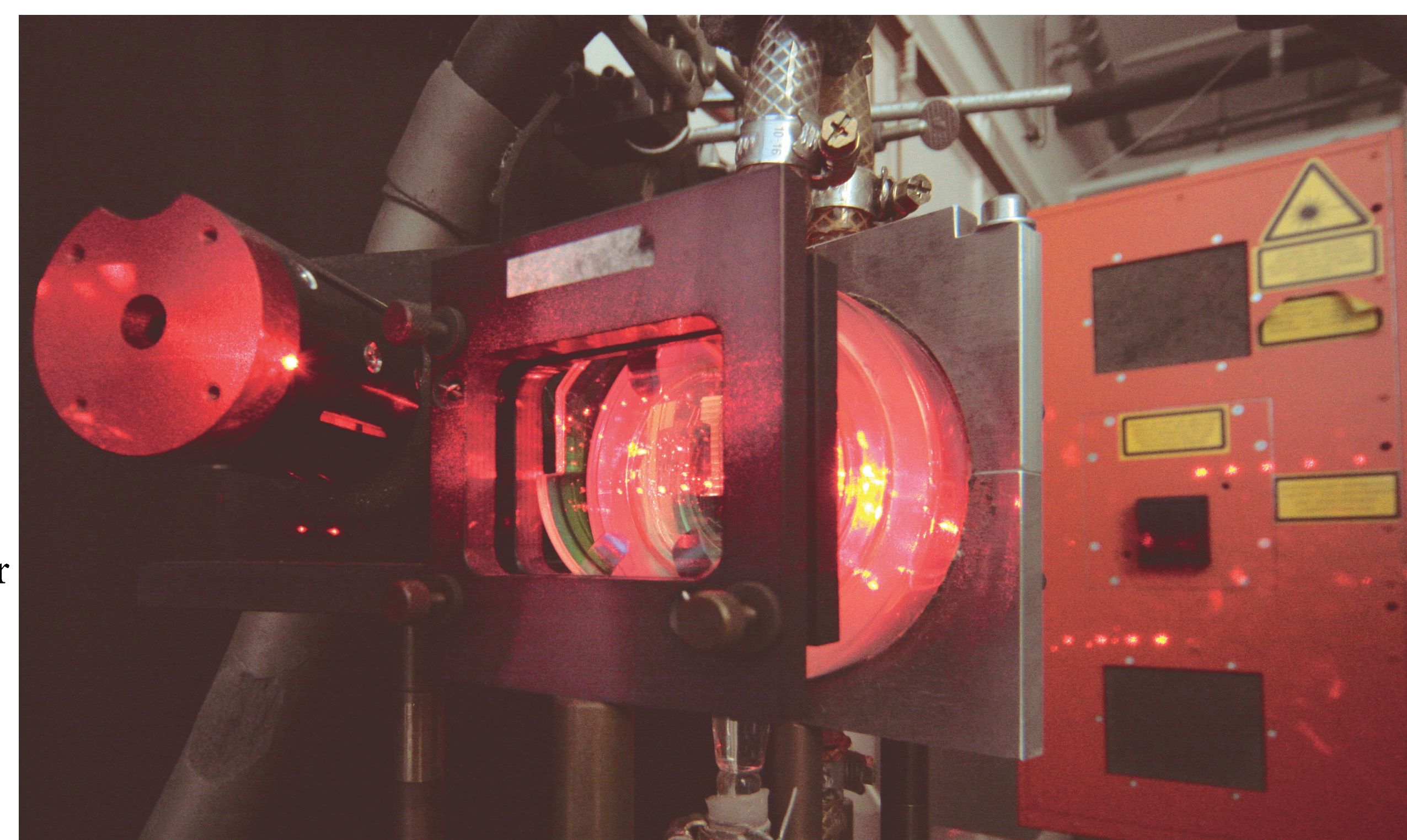


Fig. 1: Scheme of the Laser Photolysis Long Path Absorption set-up.



Results and Discussion

Table 1: Summary of aqueous phase rate constants, activation parameters, number of most easily abstractable H-atoms (n_H) and bond dissociation energies (BDE) of poly-alcohols from this work and literature studies.

No.	Compound	Radical	k _{298K} M ⁻¹ s ⁻¹	A M ⁻¹ s ⁻¹	E _A kJ/mol	Technique	Method	Ref.	n _H	BDE* kJ/mol
1	1,2-ethanediol	OH	(17±0.3)·10 ⁸	(9.0±0.3)·10 ¹⁰	9.9±2.0	LFP	OH + SCN ⁻	this work	4	385
		OH	2.4·10 ⁹			PR	OH + Fe(CN) ₆ ⁴⁺	[4]		
		OH	1.7·10 ⁹			PR	OH + Fe(CN) ₆ ⁴⁺	[4]		
		OH	1.7·10 ⁹			PR	OH + CO ₃ ²⁻	[4]		
		OH	1.4·10 ⁹			PR	OH + SCN ⁻	[4]		
		NO ₃	(6.6±2.8)·10 ⁶	(7.1±1.1)·10 ⁹	17.6±8.3	LFP	Direct	this work		
		NO ₃	1.6·10 ⁶			PR	Direct	[4]		
		NO ₃	7.6·10 ⁵			FP	Direct	[4]		
2	1,2-propanediol	OH	(1.7±0.3)·10 ⁹	(1.9±0.2)·10 ¹¹	11.5±8.6	LFP	OH + SCN ⁻	this work	1	380
		OH	1.7·10 ⁹			PR	OH + SCN ⁻	[4]		
		NO ₃	(9.9±0.8)·10 ⁶	(6.8±0.2)·10 ¹⁰	21.8±2.3	LFP	Direct	this work		
		SO ₄ ⁻	(4.3±0.9)·10 ⁷	(1.2±0.1)·10 ¹⁰	13.8±3.2	LFP	Direct	this work		
3	1,3-propanediol	OH	(2.7±0.2)·10 ⁹	(2.5±0.2)·10 ¹¹	11.4±6.3	LFP	OH + SCN ⁻	this work	4	383
		OH	2.5·10 ⁹			GR	OH + C ₂ H ₅ OH	[4]		
4	1,2,3-propanetriol	OH	(1.9±0.3)·10 ⁹	(2.8±0.2)·10 ¹¹	12.3±4.0	LFP	OH + SCN ⁻	this work	1	380
		OH	2.0·10 ⁹			PR	OH + SCN ⁻	[4]		
		OH	1.8·10 ⁹			PR	OH + Fe(CN) ₆ ⁴⁺	[4]		
		OH	2.1·10 ⁹			PR	OH + Fe(CN) ₆ ⁴⁺	[4]		
		OH	1.9·10 ⁹			PR	OH + CO ₃ ²⁻	[4]		
		OH	1.5·10 ⁹			PR	OH + SCN ⁻	[4]		
		OH	2.1·10 ⁹			PR	OH + CO ₃ ²⁻	[4]		
		NO ₃	(1.3±0.2)·10 ⁷	(1.4±0.1)·10 ¹²	28.7±2.4	LFP	Direct	this work		
5	1,2-butanediol	OH	(2.3±0.4)·10 ⁹	(5.2±0.5)·10 ¹¹	13.3±7.0	LFP	OH + SCN ⁻	this work	1	380
		OH	1.3·10 ⁹			PR	OH + SCN ⁻	[4]	2	380
		OH	2.2·10 ⁹			PR	OH + SCN ⁻	[4]	1	380
		OH	3.5±0.1)·10 ⁹	(2.0±0.1)·10 ¹¹	10.0±1.8	LFP	OH + SCN ⁻	this work	4	383
7	2,4-butanediol	OH	3.2·10 ⁹			PR	OH + SCN ⁻	[4]		
		OH	3.2·10 ⁹			PR	OH + SCN ⁻	[4]		
9	2,5-pentanediol	OH	2.2·10 ⁹			PR	OH + SCN ⁻	[4]	1	380
		OH	2.2·10 ⁹			PR	OH + SCN ⁻	[4]		
10	1,5-pentanediol	OH	(4.4±0.7)·10 ⁹	(3.1±0.1)·10 ¹¹	10.6±2.8	LFP	OH + SCN ⁻	this work	4	383
		OH	3.6·10 ⁹			GR	OH + C ₂ H ₅ OH	[4]		
11	1,6-hexanediol	OH	4.7·10 ⁹			GR	OH + C ₂ H ₅ OH	[4]	4	383

PR = pulse radiolysis, LFP = laser flash photolysis, GR = gamma radiolysis, FP = flash photolysis
* calculated using Benson incremental method [5]

- Good agreement with data from pulse and gamma radiolysis studies.
- Reactivity order: OH ≫ SO₄⁻ > NO₃
- Reactivity of the reactants increases linearly with the temperature (Fig. 1).
- Compounds with two terminal OH-groups reacts faster than the vicinal diols.
- Reactivity of compounds with terminal hydroxyl-groups increases linearly with the number of carbon atoms in the molecule (Fig. 2). The same applies to the reactivity of primary alcohols (Fig. 2).

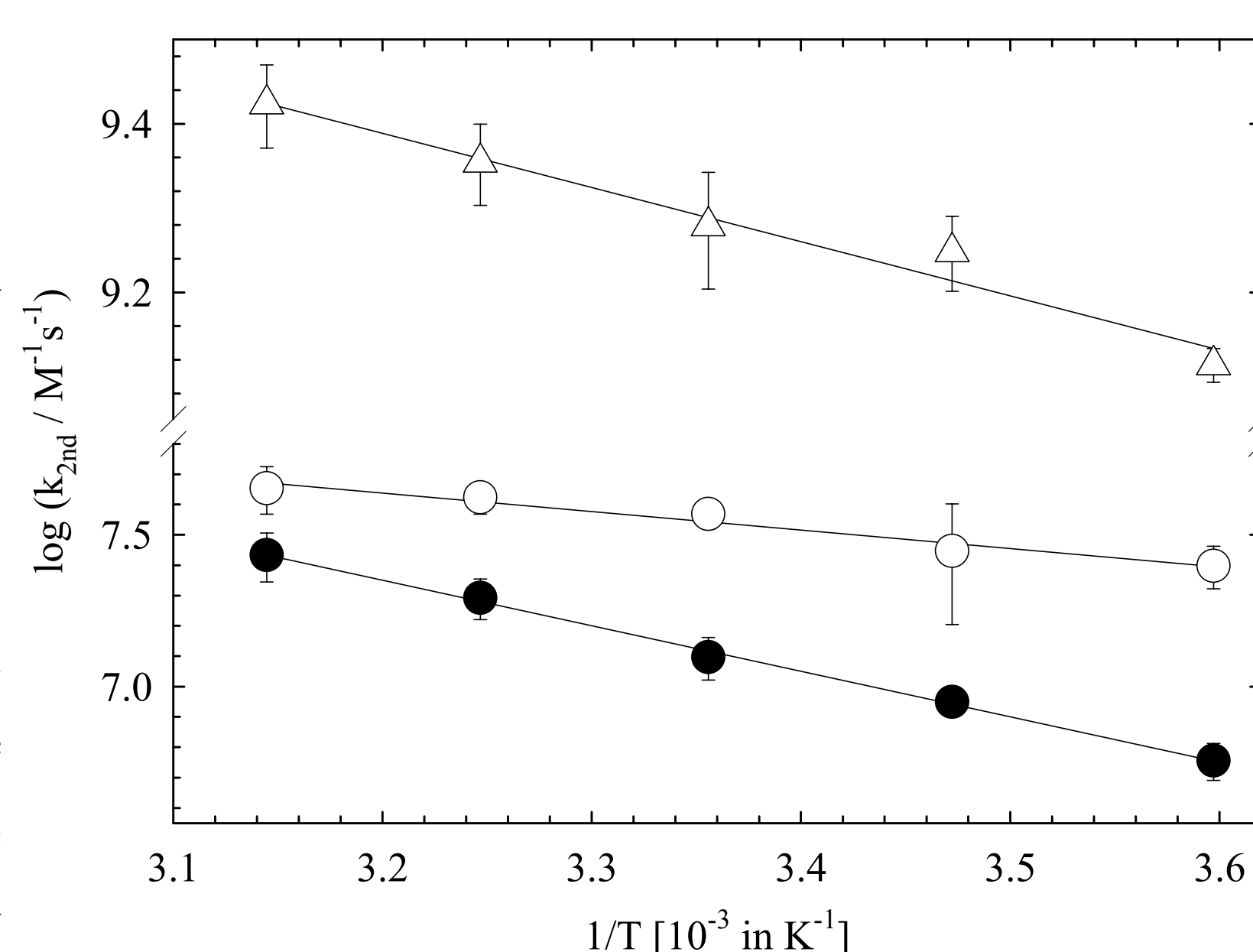


Figure 1: Arrhenius plots for the reactions of (●) NO₃, (○) SO₄⁻ and (Δ) OH radicals with 1,2,3-propanetriol in the aqueous solution.

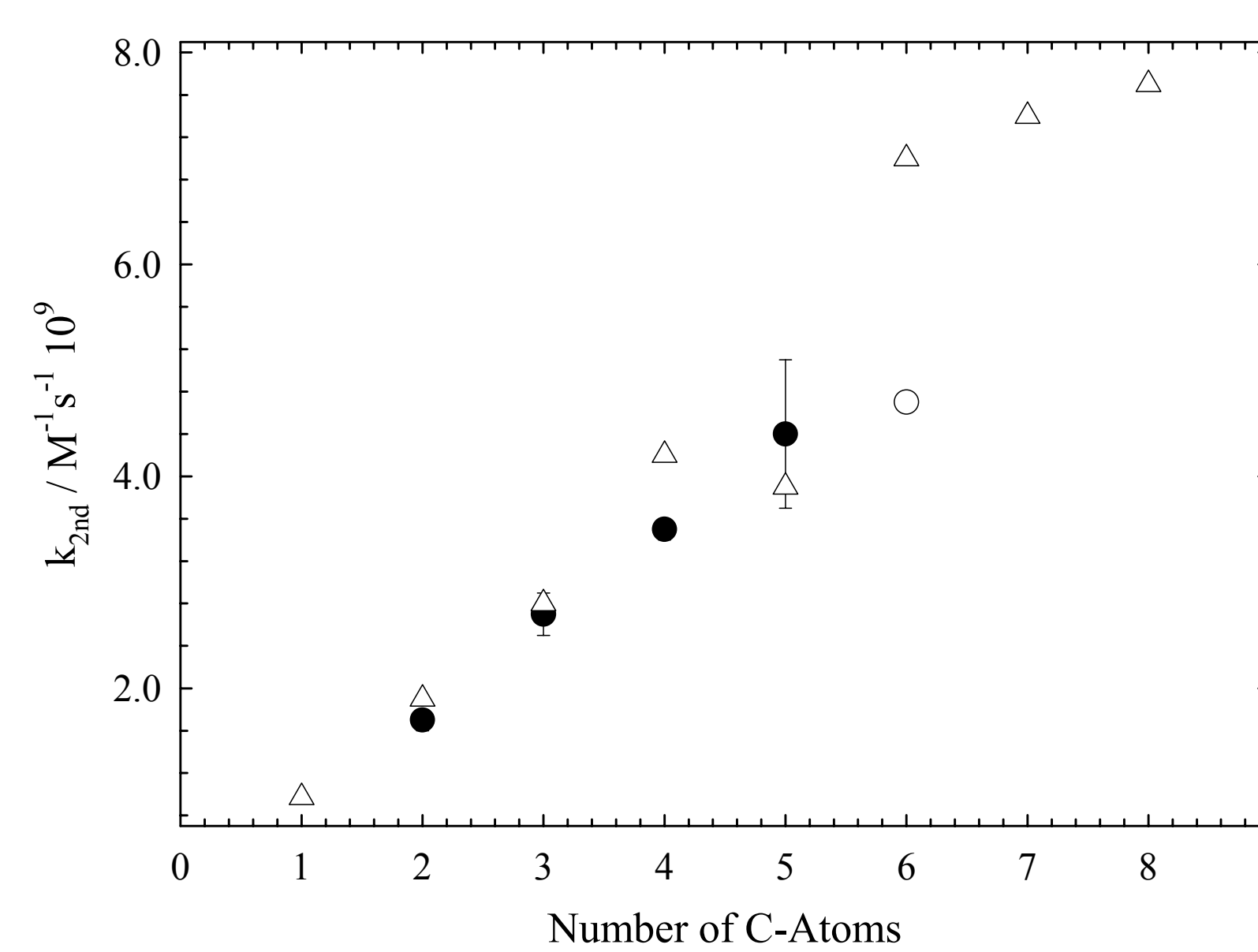
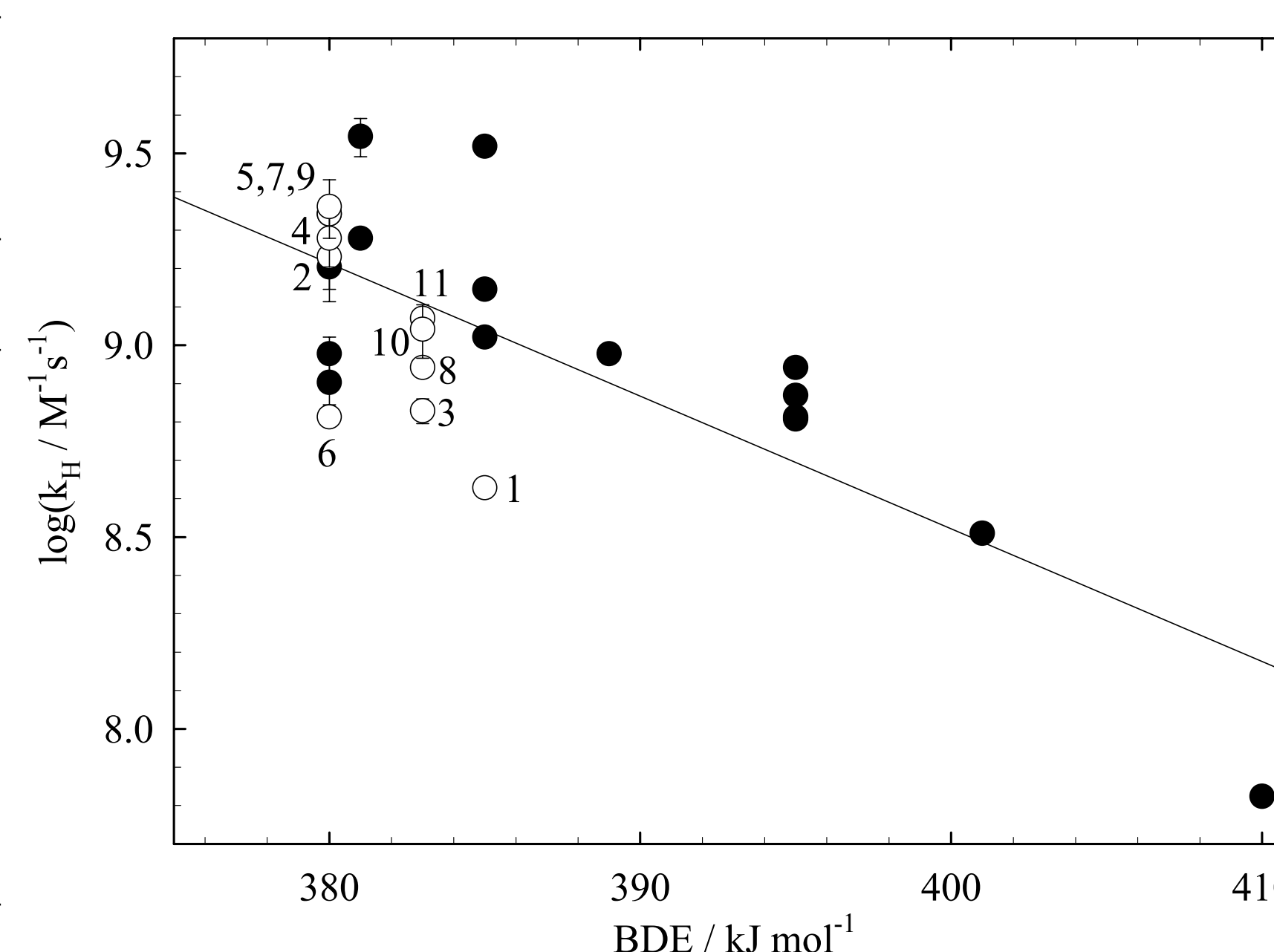
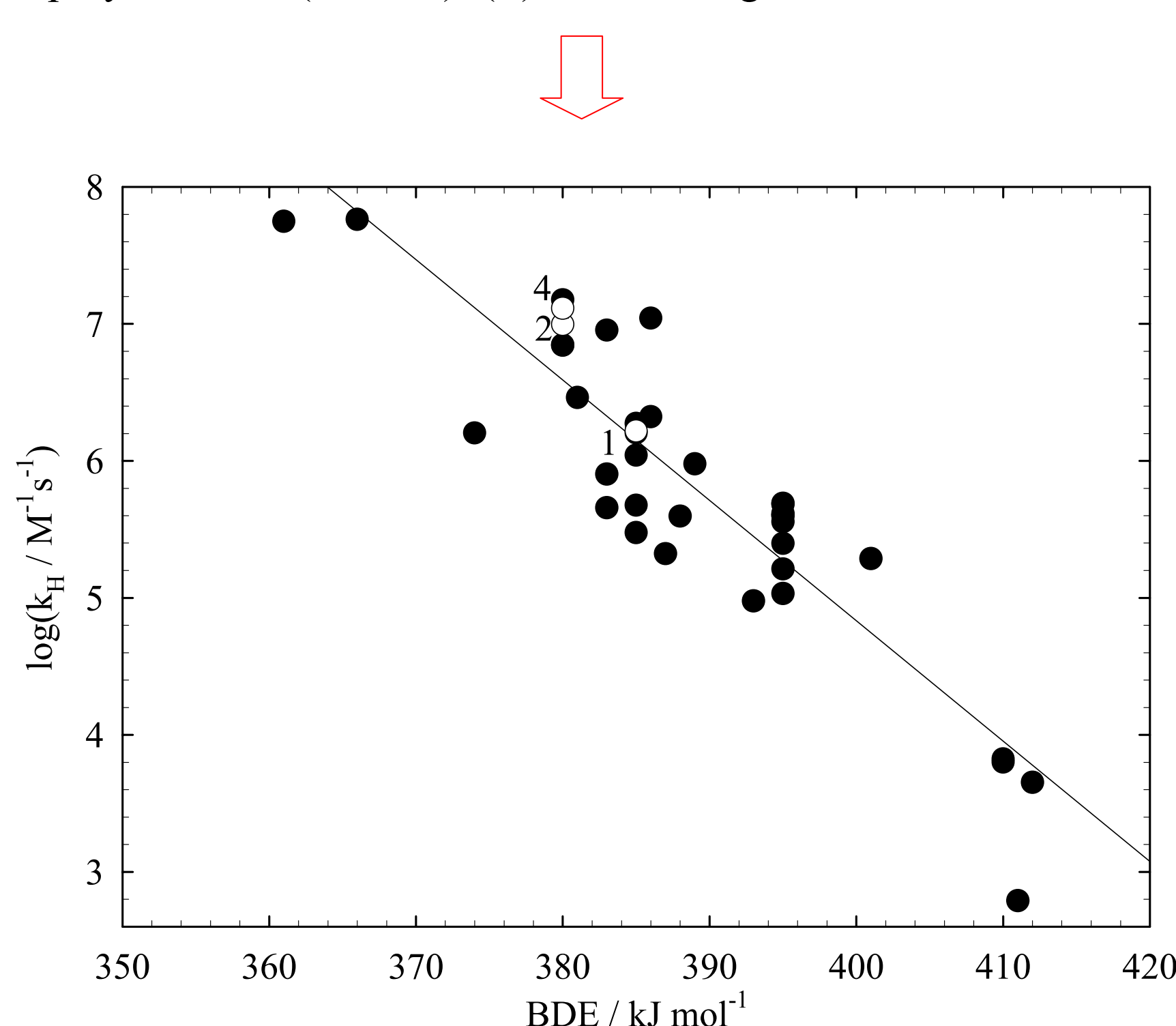


Figure 2: Reactivity of several primary alcohols and diols with two terminal hydroxyl-groups towards OH radicals in aqueous solution at room temperature. (●) diols - laser flash photolysis (this work); (○) diol - gamma radiolysis (Table 1); (Δ) primary alcohols - pulse radiolysis



Figures 3 and 4: Evans-Polanyi type correlation (log(k_H) vs. BDE) for H-abstraction reactions of OH radicals (left picture) and NO₃ radicals (right picture, [6]) in aqueous solution. (○) poly-alcohols (Table 1); (●) data coming from the literature.



$$\log k_{H, OH} = (22.4 \pm 4.5) - (0.035 \pm 0.012) \cdot \text{BDE} [\text{kJ mol}^{-1}] \quad (n = 26; r = 0.77) \quad \text{Eqn. 1}$$

$$\log k_{H, NO_3} = (39.9 \pm 5.4) - (0.087 \pm 0.014) \cdot \text{BDE} [\text{kJ mol}^{-1}] \quad (n = 38; r = 0.90) \quad \text{Eqn. 2}$$

- Rate constants of OH reactions in Table 2 (k_{2nd,SAR,calc.}) were calculated applying a structure activity method (SAR) published by Monod and Doussin [7]. The obtained data for different alcohols were compared to measured rate constants as well as rate constants derived based on equation 2 and the corresponding C-H bond strengths of the compounds (k_{2nd,Benson,calc.}).

compound	k _{2nd,meas.} M ⁻¹ s ⁻¹	k _{2nd,SAR,calc.} M ⁻¹ s ⁻¹	%	k _{2nd,Benson,calc.} M ⁻¹ s ⁻¹	%
mono-alcohols					
ethanol	1.9·10 ⁹	2.10·10 ⁹	10	1.22·10 ⁹	-36
1-propanol	2.8·10 ⁹	2.95·10 ⁹	5	1.68·10 ⁹	-40
1-butanol	4.2·10 ⁹	4.02·10 ⁹	-4	3.37·10 ⁹	-20
2-propanol	1.9·10 ⁹	2.25·10 ⁹	18	1.16·10 ⁹	-39
2-butanol	3.5·10 ⁹	3.08·10 ⁹	-12	1.16·10 ⁹	-67
t-butanol	6.0·10 ⁸	7.43·10 ⁸	24	1.01·10 ⁹	68
1-pentanol	3.9·10 ⁹	5.21·10 ⁹	34	2.26·10 ⁹	-42
1-hexanol	7.0·10 ⁹	6.36·10 ⁹	-9	3.01·10 ⁹	-57
1-heptanol	7.4·10 ⁹	7.51·10 ⁹	2	3.76·10 ⁹	-49
1-octanol	7.7·10 ⁹	8.67·10 ⁹	13	4.51·10 ⁹	-41
iso-butanol	3.3·10 ⁹	3.60·10 ⁹	9	8.41·10 ⁸	-75
average			13		49
poly-alcohols					
1,2-ethanediol	1.7·10 ⁹	1.60·10 ⁹	-6	3.37·10 ⁹	98
1,2-propanediol	1.7·10 ⁹	1.85·10 ⁹	9	1.26·10 ⁹	-26
1,3-propanediol	2.7·10 ⁹	4.00·10 ⁹	48	3.95·10 ⁹	46
1,2,3-propanetriol	1.9·10 ⁹	2.00·10 ⁹	5	1.26·10 ⁹	-34
1,2-butanediol	2.3·10 ⁹	2.60·10 ⁹	13	1.26·10 ⁹	-45
2,3-butanediol	1.3·10 ⁹	2.00·10 ⁹	54	2.52·10 ⁹	94
2,4-butanediol	2.2·10 ⁹	4.10·10 ⁹	86	1.26·10 ⁹	-43
1,4-butanediol	3.5·10 ⁹	4.70·10 ⁹	34	3.95·10 ⁹	13
2,5-pentanediol	2.2·10 ⁹	4.90·10 ⁹	123	1.26·10 ⁹	-43
1,5-pentanediol	4.4·10 ⁹	5.90·10 ⁹	34	3.95·10 ⁹	-10
1,6-hexanediol	4.7·10 ⁹	7.00·10 ⁹	49	3.95·10 ⁹	-16
erythritol	1.9·10 ⁹	2.30·10 ⁹	21	2.52·10 ⁹	33
arabitol	1.6·10 ⁹	2.50·10 ⁹	56	1.26·10 ⁹	-21
mannitol	1.6·10 ⁹	2.70·10 ⁹	69	2.52·10 ⁹	57
average			43		41
average (all)			30		45

Table 2: Comparison between measured rate constants at T = 298 K with calculated values using the SAR method and the incremental method of Benson [5] applying Equation 1.

- Mono-functional alcohols are well described by the SAR approach.
- The reactivity of poly-alcohols is in general overestimated by the SAR.
- Largest deviations from the measured data are shown by the non-vicinal diols.

Summary and Conclusion

- Poly-alcohols can act as effective radical scavengers in the tropospheric aqueous phase and subsequently influence the overall tropospheric oxidation budget.
- Aqueous phase oxidation reactions of alcohols are potential precursors for particle-bound acids such as oxalic acid, pyruvic acid, malonic acid, succinic acid and glyoxylic acid.
- Model simulations with CAPRAM 3.0i shows that the aqueous phase conversion of ethylene glycol can contribute considerably to the formation of oxalic acid under remote (up to 1.7%) and urban (up to 9.5%) conditions. [3]
- The SAR method appears to be a very useful tool in addition to established Evans-Polanyi correlations to estimate rate constants for OH radical reactions in aqueous solution.

References

- [1] C.A. Staples, J.B. Williams, G.R. Craig and K.M. Roberts, *Chemosphere*, 2001, **43**, 377-383; [2] P. Warneck, *Atmos. Environ.*, 2003, **37**, 2423-2427; [3] A. Tilgner, R. Wolke and H. Herrmann, CAPRAM modelling of the physico-chemical cloud processing of tropospheric aerosols, in *Environmental simulation chambers - Application to atmospheric chemical processes: Proceedings of the NATO Advanced Research Workshop on Simulation and Assessment of Chemical Processes in a Multiphase Environment Alushta, Ukraine 1 September 2007*, edited by I. Barnes and M. Kharytonov, Springer, Berlin; Heidelberg; New York, 2008, p. 540; [4] NIST Solution Kinetics Database Version 3.0, National Institute of Standards and Technology, Gaithersburg, 1998; [5] S.W. Benson, *Thermochemical Kinetics*, Wiley, New York, 2nd edn., 1976; [6] P. Gaillard de Semainville, D. Hoffmann, C. George and H. Herrmann, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1-11; [7] A. Monod and J.F. Doussin, *Atmos. Environ.*, 2008, **42**, 7611-7622