Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Competition kinetics of OH radical reactions with oxygenated organic compounds in aqueous solution: Rate constants and internal optical absorption effects

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2-Propanone (Acetone)

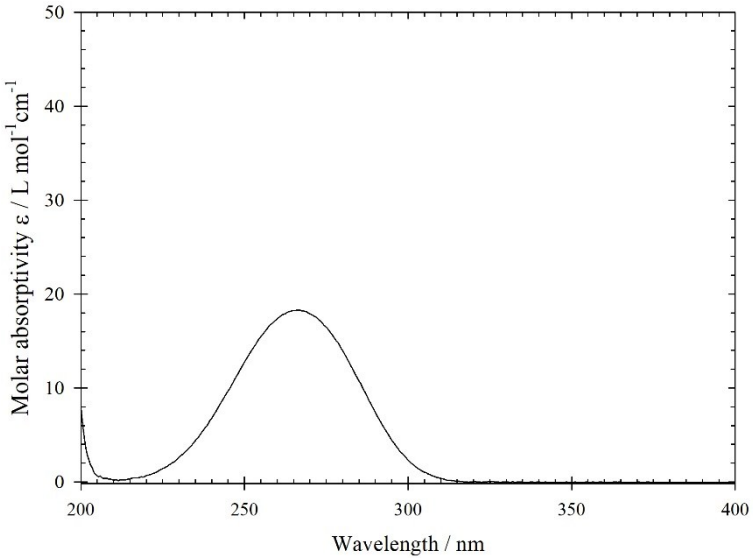

Figure ESM-1: The UV spectrum of 2-propanone as plot of the molar absorptivity ε against the wavelength in neutral aqueous solution.

In Figure ESM-1 the UV spectrum of 2-propanone is shown. The molar absorptivity ε of acetone can be given with $\varepsilon_{248\,nm}$ = 11.5 L mol^{-1} cm^{-1}. This data set is shown in Table 3 in the manuscript and was used to obtain the Arrhenius-Plot displayed in Figure ESM-2.

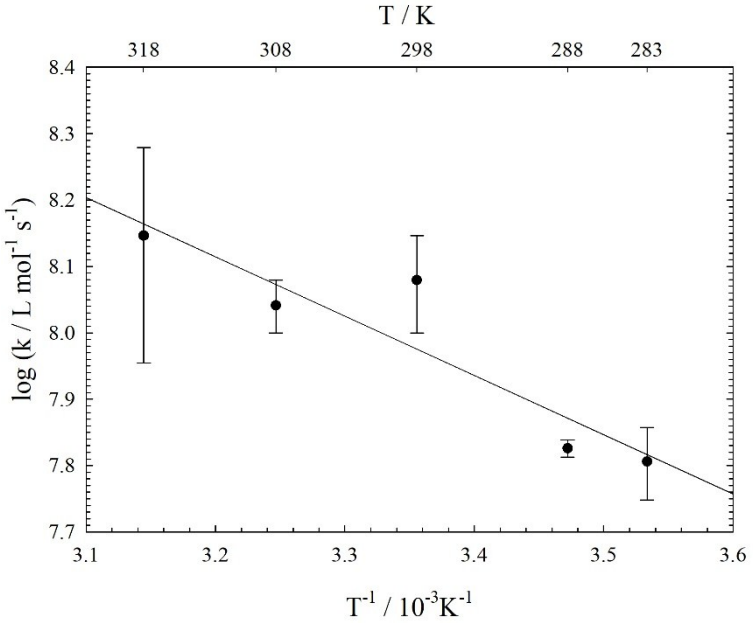

Figure ESM-2: Arrhenius plot of the OH radical reaction with 2-propanone considering the internal UV light absorption (data taken from Ervens et al. (2003)[1]).

1-Hydroxypropan-2-one (Hydroxyacetone, Acetol)

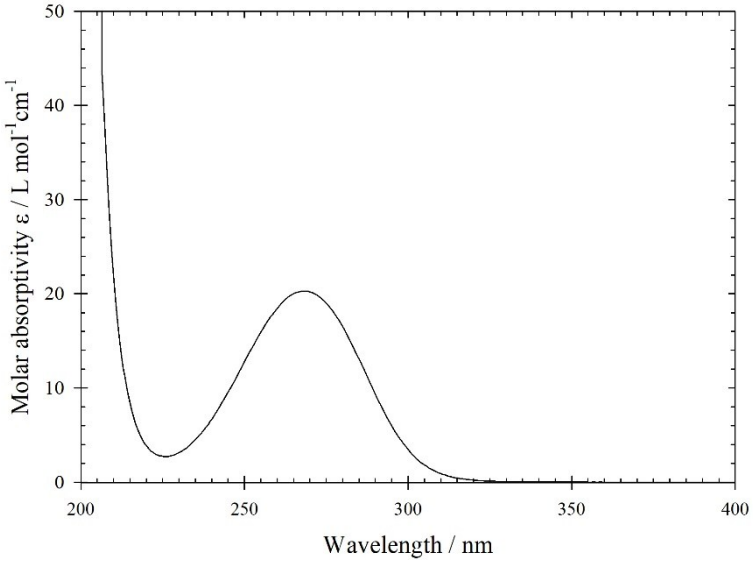

Figure ESM-3: The UV spectrum of 1-hydroxypropan-2-one as plot of the molar absorptivity ε against the wavelength in neutral aqueous solution.

The UV spectrum of the reactant 1-hydroxypropan-2-one is shown in Figure ESM-3. The molar absorptivity was determined with $\varepsilon_{248\,nm}$ = 11.4 L mol^{-1} cm^{-1} in neutral aqueous solution.

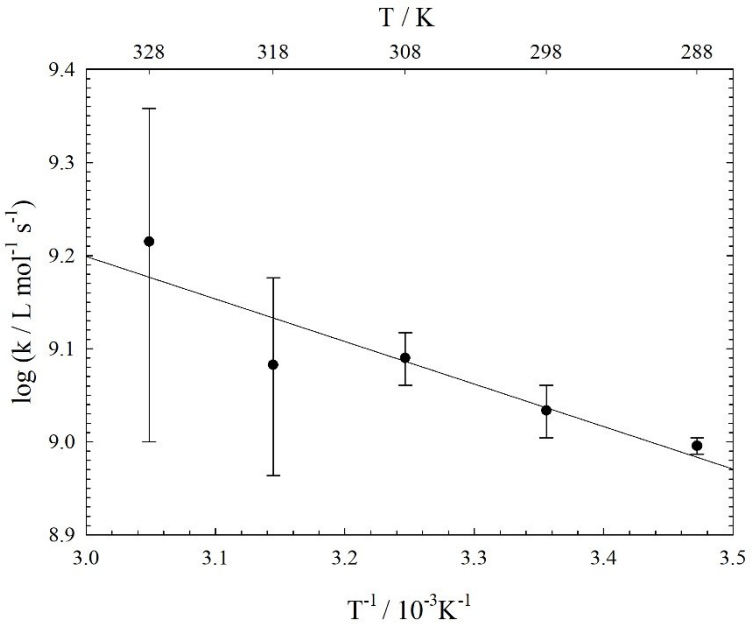

Figure ESM-4: Arrhenius plot of the OH radical reaction with 1-hydroxy-propan-2-one considering the internal UV light absorption.

Table ESM 1: Calculated rate constants without and with considering the internal UV absorption by the reactant 1-hydroxy-propan-2-one.

Temperature / K	$k_{not\ corrected}$ / L mol^{-1} s^{-1}	$k_{corrected}$ / L mol^{-1} s^{-1}	relative change / %
288	$(9.94 \pm 0.43) \cdot 10^8$	$(9.47 \pm 0.47) \cdot 10^8$	4.7
298	$(1.12 \pm 0.07) \cdot 10^9$	$(1.08 \pm 0.07) \cdot 10^9$	3.6
308	$(1.27 \pm 0.08) \cdot 10^9$	$(1.23 \pm 0.08) \cdot 10^9$	3.1
318	$(1.29 \pm 0.31) \cdot 10^9$	$(1.22 \pm 0.29) \cdot 10^9$	5.7
328	$(1.73 \pm 0.61) \cdot 10^9$	$(1.64 \pm 0.64) \cdot 10^9$	5.2

1,3-Dihydroxypropan-2-one (Dihydroxyacetone)

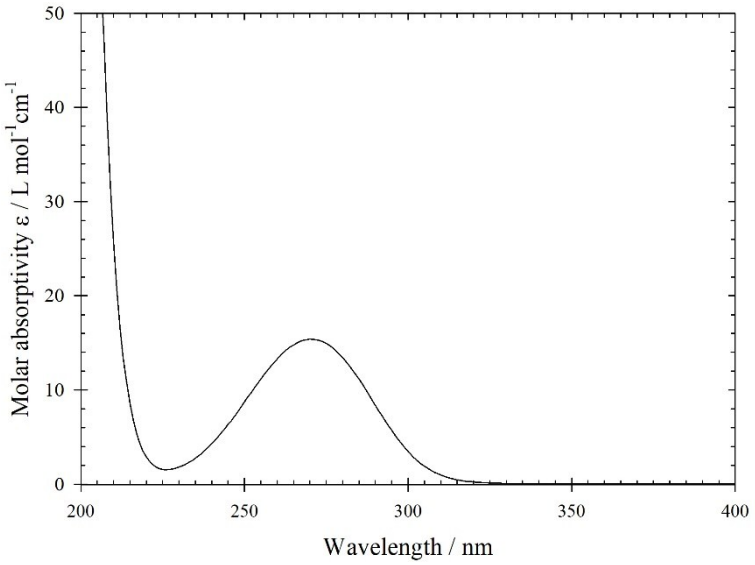

Figure ESM-5: The UV spectrum of 1,3-dihydroxypropan-2-one as plot of the molar absorptivity ε against the wavelength in neutral aqueous solution.

The UV spectrum of the reactant 1,3-dihydroxypropan-2-one is displayed in Figure ESM-5. The molar absorptivity was determined with $\varepsilon_{248\ nm} = 7.7$ L mol^{-1} cm^{-1} in neutral aqueous solution.

Table ESM 2: Calculated rate constants without and with considering the internal UV absorption of the reactant 1,3-dihydroxypropan-2-one.

Temperature / K	$k_{not\ corrected}$ / L mol^{-1} s^{-1}	$k_{corrected}$ / L mol^{-1} s^{-1}	relative change / %
278	$(1.20 \pm 0.57) \cdot 10^9$	$(1.14 \pm 0.57) \cdot 10^9$	5.0
288	$(1.31 \pm 0.09) \cdot 10^9$	$(1.25 \pm 0.07) \cdot 10^9$	4.6
298	$(1.57 \pm 0.13) \cdot 10^9$	$(1.50 \pm 0.11) \cdot 10^9$	4.5
308	$(2.01 \pm 0.16) \cdot 10^9$	$(1.92 \pm 0.14) \cdot 10^9$	4.5
318	$(2.26 \pm 0.21) \cdot 10^9$	$(2.16 \pm 0.17) \cdot 10^9$	4.4

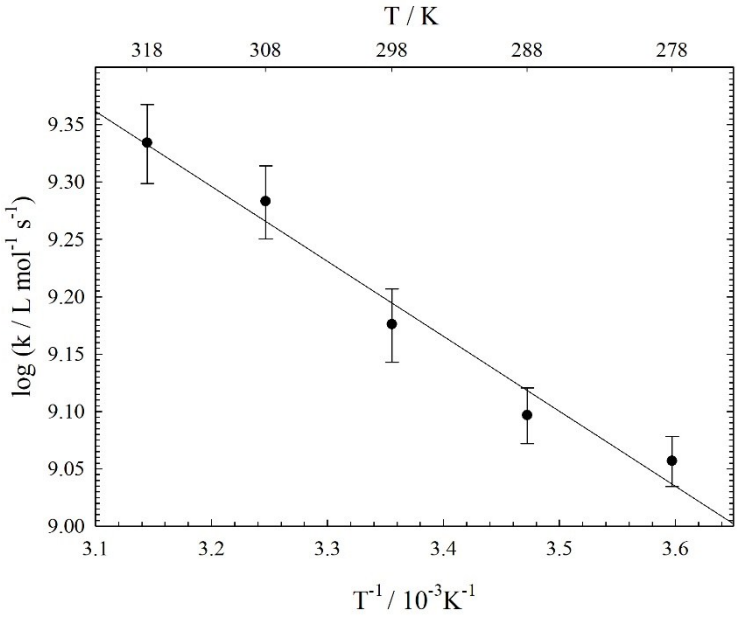

Figure ESM-6: Arrhenius plot of the OH radical reaction with 1,3-dihydroxypropan-2-one considering the internal UV light absorption.

2,3-Dihydroxypropanal (Glyceraldehyde)

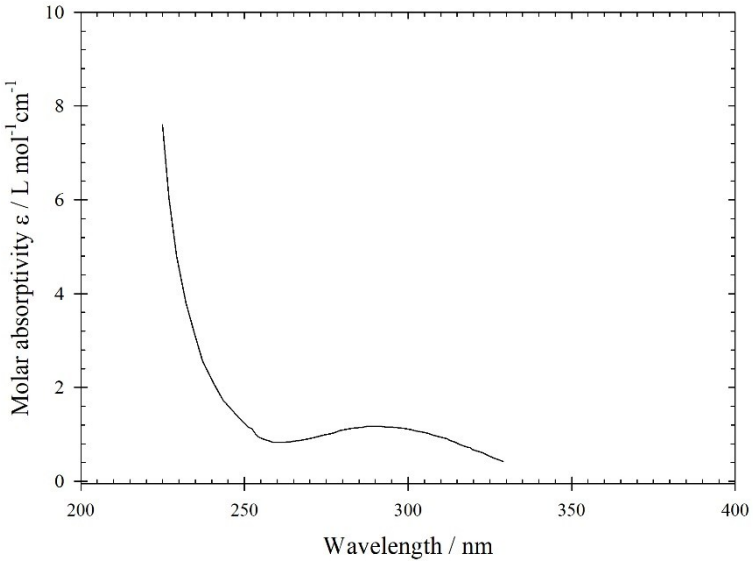

Figure ESM-7: The UV spectrum of 2,3-dihydroxypropanal as plot of the molar absorptivity ε against the wavelength in neutral aqueous solution, data taken from Berndt (1954)[2].

The UV spectrum of the reactant 2,3-dihydroxypropanal is displayed in Figure ESM-7. The molar absorptivity was determined with $\varepsilon_{248\,nm}$ = 1.4 L mol^{-1} cm^{-1} by Berndt (1954)[2] in neutral aqueous solution. The measurement conditions of the rate constant determination of the OH radical reaction with 2,3-dihydroxypropanal are given in table ESM-3.

Table ESM-3: Used concentrations for the measurement of the reactant 2,3-dihydroxypropanal.

Experiment	H_2O_2 / L mol^{-1}	KSCN / L mol^{-1}	Reactant / L mol^{-1}	$[OH]_0$ change / %
I	$2.0 \cdot 10^{-4}$	$2.2 \cdot 10^{-5}$	0	0
II	$2.0 \cdot 10^{-4}$	$2.2 \cdot 10^{-5}$	$1.02 \cdot 10^{-4}$	0.06
III	$2.0 \cdot 10^{-4}$	$2.2 \cdot 10^{-5}$	$2.04 \cdot 10^{-4}$	0.11
IV	$2.0 \cdot 10^{-4}$	$2.2 \cdot 10^{-5}$	$3.07 \cdot 10^{-4}$	0.17
V	$2.0 \cdot 10^{-4}$	$2.2 \cdot 10^{-5}$	$4.09 \cdot 10^{-4}$	0.23

The rate constants of the OH radical reaction with the reactant 2,3-dihydroxypropanal is not influenced by the internal UV absorption, shown in Table ESM-4. The Arrhenius-Plot of this reaction is displayed in Figure ESM-8.

Table ESM-4: Calculated rate constants without and with considering the internal UV absorption of the reactant 2,3-dihydroxypropanal.

Temperature / K	$k_{not\ corrected}$ / L mol^{-1} s^{-1}	$k_{corrected}$ / L mol^{-1} s^{-1}	relative change / %
278	$(1.04 \pm 0.03) \cdot 10^9$	$(1.04 \pm 0.03) \cdot 10^9$	0.0
288	$(1.17 \pm 0.05) \cdot 10^9$	$(1.17 \pm 0.05) \cdot 10^9$	0.0
298	$(1.31 \pm 0.03) \cdot 10^9$	$(1.31 \pm 0.03) \cdot 10^9$	0.0
308	$(1.58 \pm 0.03) \cdot 10^9$	$(1.58 \pm 0.04) \cdot 10^9$	0.0
318	$(1.74 \pm 0.01) \cdot 10^9$	$(1.74 \pm 0.01) \cdot 10^9$	0.0

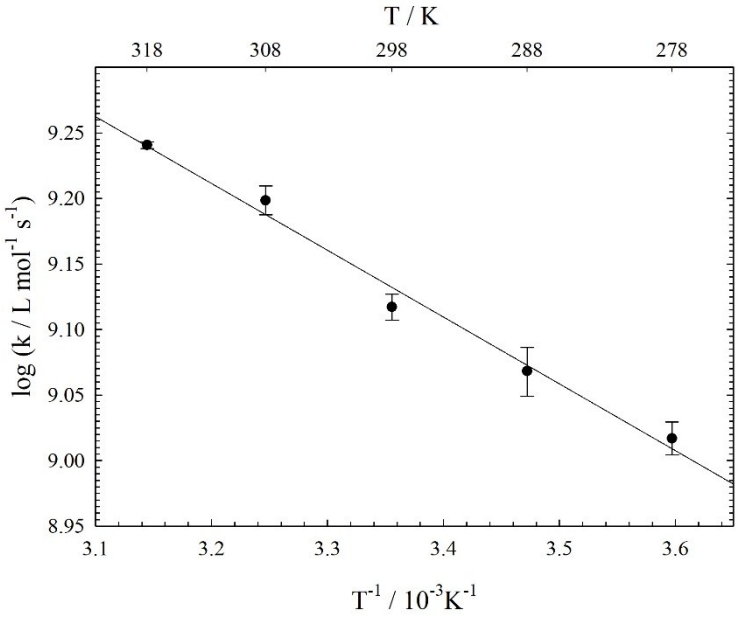

Figure ESM-8: Arrhenius plot of the OH radical reaction with 2,3-dihydroxypropanal considering the internal UV light absorption.

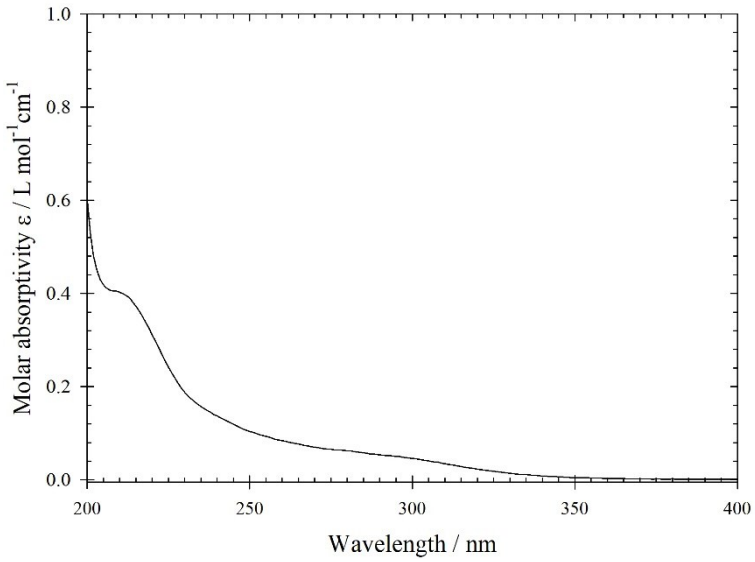

Figure ESM-9: The UV spectrum of butane-1,3-diol as plot of the molar absorptivity ε against the wavelength in neutral aqueous solution.

For butane-1,3-diol as reactant the obtained UV spectrum is shown in Figure ESM-10. The molar absorptivity was determined with $\varepsilon_{248\ nm}$ = 0.11 L mol^{-1} cm^{-1} by in neutral aqueous solution. The used measurement conditions of the reactant butane-1,3-diol are given in Table ESM-5.

Table ESM-5: Used concentrations for the measurement of the reactant butane-1,3-diol.

Experiment	H_2O_2 / L mol^{-1}	KSCN / L mol^{-1}	Reactant / L mol^{-1}	$[OH]_0$ change / %
I	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	0	0
II	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	0.009
III	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$4.0 \cdot 10^{-4}$	0.017
IV	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$6.0 \cdot 10^{-4}$	0.026
V	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$8.0 \cdot 10^{-4}$	0.035

The rate constants of the OH radical reaction with the reactant butane-1,3-diol are not influenced by the internal UV absorption, shown in Table ESM-6. The Arrhenius-Plot of this reaction is given in Figure ESM-10.

Table ESM-6: Calculated rate constants without and with considering the internal UV absorption of the reactant butane-1,3-diol.

Temperature / K	$k_{not\ corrected}$ / L mol^{-1} s^{-1}	$k_{corrected}$ / L mol^{-1} s^{-1}	relative change / %
278	$(1.68 \pm 0.03) \cdot 10^9$	$(1.68 \pm 0.03) \cdot 10^9$	0.0
288	$(2.04 \pm 0.03) \cdot 10^9$	$(2.04 \pm 0.03) \cdot 10^9$	0.0
298	$(2.50 \pm 0.09) \cdot 10^9$	$(2.50 \pm 0.09) \cdot 10^9$	0.0
308	$(2.66 \pm 0.09) \cdot 10^9$	$(2.66 \pm 0.10) \cdot 10^9$	0.0
318	$(2.90 \pm 0.08) \cdot 10^9$	$(2.90 \pm 0.08) \cdot 10^9$	0.0

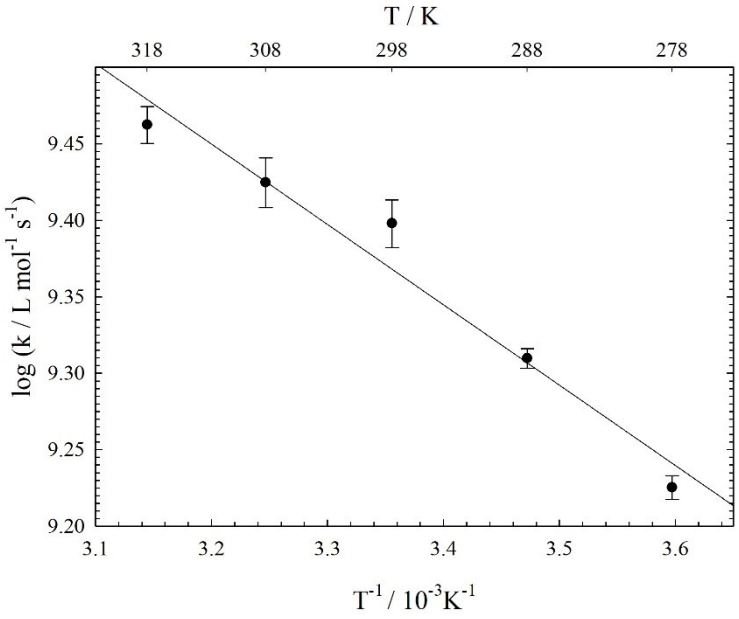

Figure ESM-10: Arrhenius plot of the OH radical reaction with butane-1,3-diol.

Butane-2,3-diol

Figure ESM-11: The UV spectrum of butane-2,3-diol as plot of the molar absorptivity ε against the wavelength in neutral aqueous solution.

Butane-2,3-diol has only a very small molar absorptivity, with $\varepsilon_{248\,nm}$ = 0.11 L mol^{-1} cm^{-1} in neutral aqueous solution. The internal filter of the excitation UV light is negligible. To study the reaction of the OH radicals with reactant butane-2,3-diol the following measurement conditions have been used (Table ESM 7).

Table ESM-7: Used concentrations for the measurement of the reactant butane-2,3-diol.

Experiment	H_2O_2 / L mol^{-1}	KSCN / L mol^{-1}	Reactant / L mol^{-1}	$[OH]_0$ change / %
I	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	0	0
II	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	0.009
III	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$4.0 \cdot 10^{-4}$	0.017
IV	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$6.0 \cdot 10^{-4}$	0.026
V	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$8.0 \cdot 10^{-4}$	0.035

For butane-2,3-diol as reactant the obtained rate constants of the OH radical reaction are not influenced by an internal UV absorption (Table ESM-8). The Arrhenius-Plot of this reaction is given in Figure ESM-12.

Table ESM-8: Calculated rate constants without and with considering the internal UV absorption of the reactant butane-2,3-diol.

Temperature / K	$k_{not\ corrected}$ / L mol^{-1} s^{-1}	$k_{corrected}$ / L mol^{-1} s^{-1}	relative change / %
278	$(1.39 \pm 0.03) \cdot 10^9$	$(1.39 \pm 0.03) \cdot 10^9$	0.0
288	$(1.73 \pm 0.04) \cdot 10^9$	$(1.73 \pm 0.04) \cdot 10^9$	0.0
298	$(1.99 \pm 0.02) \cdot 10^9$	$(1.99 \pm 0.02) \cdot 10^9$	0.0
308	$(2.20 \pm 0.04) \cdot 10^9$	$(2.20 \pm 0.04) \cdot 10^9$	0.0
318	$(2.45 \pm 0.04) \cdot 10^9$	$(2.44 \pm 0.04) \cdot 10^9$	0.0

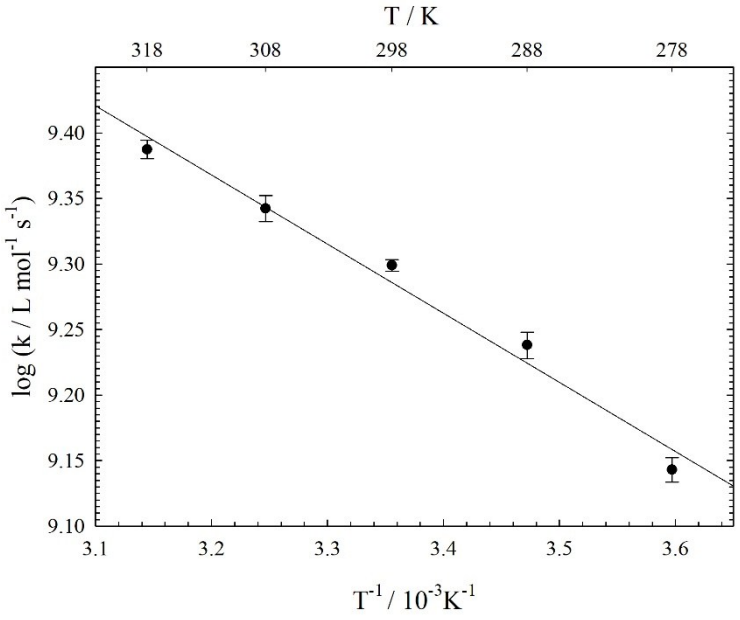

Figure ESM-12: Arrhenius plot of the OH radical reaction with butane-2,3-diol.

Hexane-1,2-diol

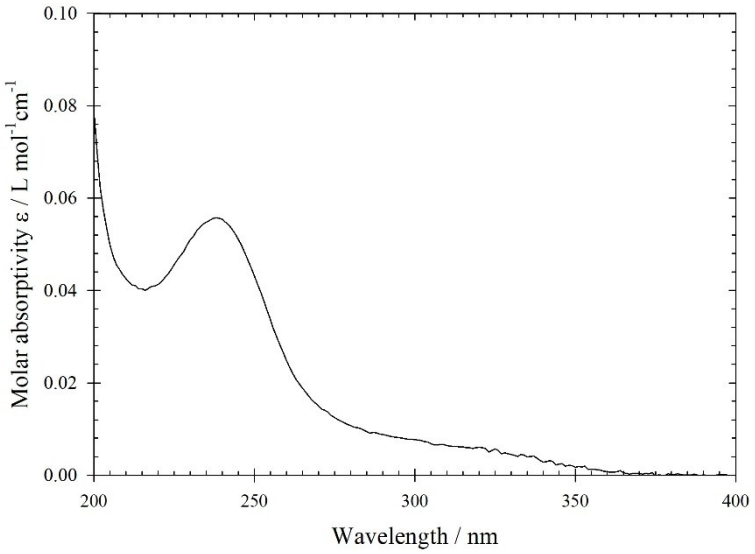

Figure ESM-13: The UV spectrum of hexane-1,2-diol as plot of the molar absorptivity ε against the wavelength in neutral aqueous solution.

Diols have a very small molar absorptivity at λ= 248 nm $\varepsilon_{248\ nm}$ = 0.34 L mol^{-1} cm^{-1} in neutral aqueous solution, due to this the internal filter of the excitation UV light is negligible. The following measurement conditions have been used (Table ESM-9).

Table ESM-9: Used concentrations for the measurement of the reactant hexane-1,2-diol.

Experiment	H_2O_2 / L mol^{-1}	KSCN / L mol^{-1}	Reactant / L mol^{-1}	$[OH]_0$ change / %
I	$2.0 \cdot 10^{-4}$	$1.78 \cdot 10^{-5}$	0	0
II	$2.0 \cdot 10^{-4}$	$1.78 \cdot 10^{-5}$	$5.0 \cdot 10^{-5}$	0.053
III	$2.0 \cdot 10^{-4}$	$1.78 \cdot 10^{-5}$	$1.0 \cdot 10^{-4}$	0.107
IV	$2.0 \cdot 10^{-4}$	$1.78 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$	0.160
V	$2.0 \cdot 10^{-4}$	$1.78 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	0.213

The obtained rate constants of the OH radical reaction are also not influenced by an internal UV absorption (Table ESM-10), like in the case of butane-1,3-diol and butane-2,3-diol. The obtained Arrhenius-Plot is given in Figure ESM-14.

Table ESM-10: Calculated rate constants of the OH radical reaction with the reactant hexane-1,2-diol.

Temperature / K	$k_{not\ corrected}$ / L mol^{-1} s^{-1}	$k_{corrected}$ / L mol^{-1} s^{-1}	relative change / %
278	$(3.36 \pm 0.09) \cdot 10^9$	$(3.35 \pm 0.09) \cdot 10^9$	0.3
288	$(4.23 \pm 0.21) \cdot 10^9$	$(4.22 \pm 0.20) \cdot 10^9$	0.2
298	$(4.60 \pm 0.41) \cdot 10^9$	$(4.59 \pm 0.41) \cdot 10^9$	0.2
308	$(5.49 \pm 0.48) \cdot 10^9$	$(5.48 \pm 0.48) \cdot 10^9$	0.2
318	$(7.47 \pm 1.18) \cdot 10^9$	$(7.45 \pm 1.17) \cdot 10^9$	0.3

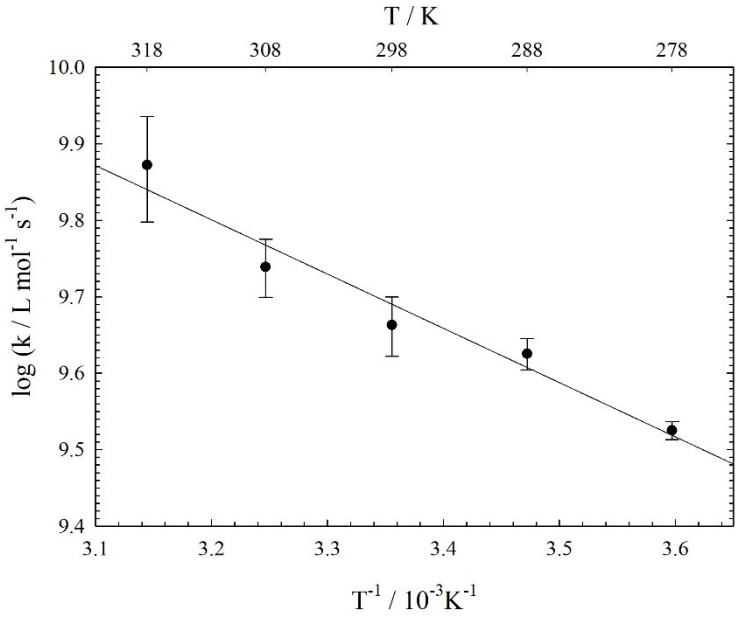

Figure ESM-14: Arrhenius plot of the rate constants of the OH radical reaction with hexane-1,2-diol

References (Electronic Supplementary Information)

1. B. Ervens, S. Gligorovski and H. Herrmann, *Physical Chemistry Chemical Physics*, 2003, 5, 1811-1824.
2. W. Berndt, *Monatshefte der Chemie*, 1954, 85, 387-392.