

1 **Atmospheric aqueous phase radical chemistry of the isoprene
2 oxidation products methacrolein, methyl vinyl ketone, methacrylic
3 acid and acrylic acid – kinetics and product studies**

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11 **Electronic Supplemental Material (ESM)**

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1 **Basic assumptions of the reversed-rates method**

2 The chain-radical mechanism of the autoxidation of S(IV) catalysed by Fe(III) and inhibited
3 by an organic scavenger of sulfate radical anions used by the reversed-rates method contains
4 the following reactions:

5 *Chain initiation*



7 *Chain propagation*



13 *Formation of sulfate*



15 *Regeneration of the initiator*



19 *Termination*

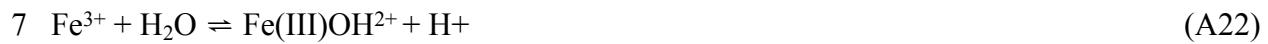


23 *Inhibition*



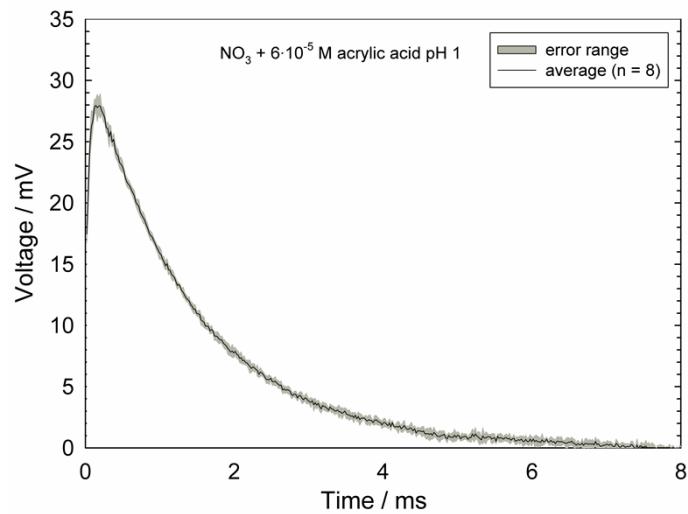
25 *Speciation and hydrolytic equilibria*



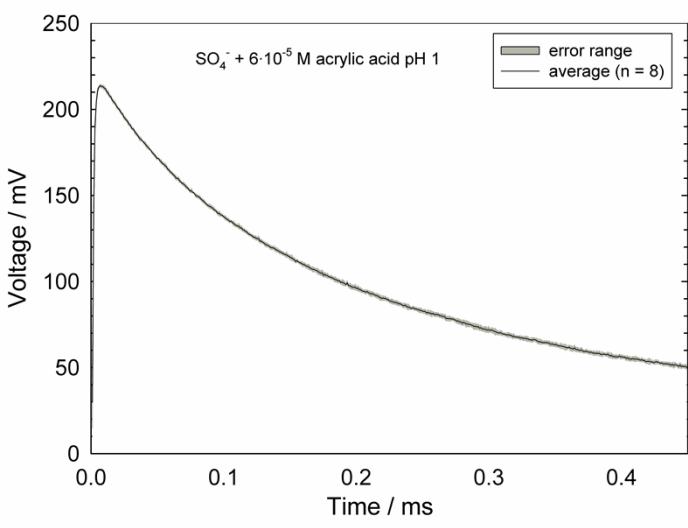


10 The assumptions underlying the pseudo-stationary analysis of the autoxidation of S(IV)
11 catalysed by Fe(III) and inhibited by organic scavenger of sulphate radical anions are (i) the
12 rate of autoxidation is controlled by the reaction of bisulfite ions with peroxymonosulfate
13 radical anions (A7), (ii) chain termination is dominated by reactions of ferrous ions with
14 peroxymonosulfate radicals (A8) and (A9), as well as by reaction of sulphate radical anions
15 with an organic inhibitor (A14); (iii) the chain initiation occurs by the reaction of ferric ions
16 with bisulfite ions (A1); (iv) rate of chain termination (by dominating reactions) is equal to
17 the rate of chain initiation.

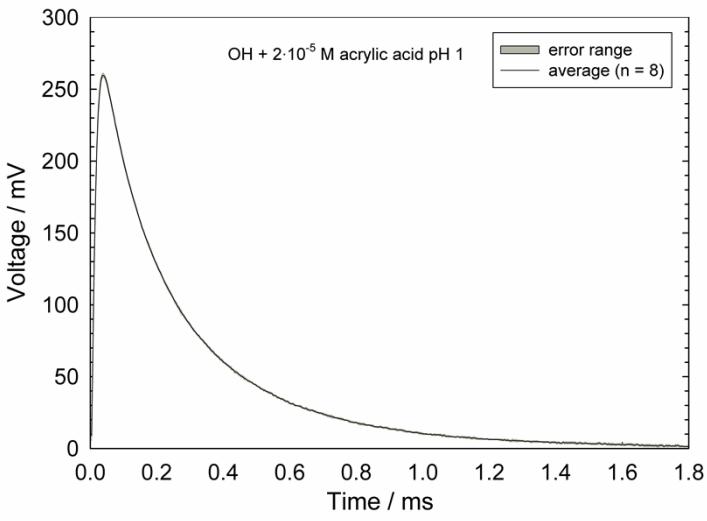
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4 Fig. A0.

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6 Temporal profiles of the reaction of acrylic acid (pH 1) with NO_3 (top), SO_4^- (middle) and OH radicals (bottom). Grey areas correspond to error range resulting from the standard deviation of eight signals.

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Reactant	T / K	OH	NO ₃	SO ₄ ⁻ (LFP)	SO ₄ ⁻ (KR)
methacrolein	278	(5.7 ± 0.4)·10 ⁹	(3.2 ± 1.1)·10 ⁷	(6.8 ± 4.8)·10 ⁷	
	288	(7.4 ± 0.3)·10 ⁹	(3.5 ± 0.8)·10 ⁷	(7.5 ± 2.7)·10 ⁷	(1.8 ± 1.2)·10 ⁷
	298	(9.4 ± 0.7)·10 ⁹	(4.0 ± 1.0)·10 ⁷	(9.9 ± 4.9)·10 ⁷	(5.5 ± 1.4)·10 ⁷
	308	(9.5 ± 0.4)·10 ⁹	(4.2 ± 1.4)·10 ⁷	(7.2 ± 2.0)·10 ⁷	(9.4 ± 1.9)·10 ⁷
	318	(1.0 ± 0.5)·10 ¹⁰	(1.5 ± 1.5)·10 ⁷	(5.4 ± 2.3)·10 ⁷	
methyl vinyl ketone	278	(5.1 ± 0.6)·10 ⁹	(7.7 ± 2.2)·10 ⁶	(8.1 ± 1.6)·10 ⁷	
	288	(6.3 ± 0.3)·10 ⁹	(1.0 ± 0.4)·10 ⁷	(5.3 ± 0.8)·10 ⁷	(1.2 ± 0.4)·10 ⁸
	298	(7.3 ± 0.5)·10 ⁹	(9.7 ± 3.4)·10 ⁶	(1.0 ± 0.2)·10 ⁸	(8.7 ± 2.2)·10 ⁷
	308	(8.5 ± 0.6)·10 ⁹	(1.0 ± 0.2)·10 ⁷	(9.0 ± 0.6)·10 ⁷	(8.6 ± 2.6)·10 ⁷
	313	(7.0 ± 0.6)·10 ⁹	---	---	
	318	(7.9 ± 0.4)·10 ⁹	(1.4 ± 0.5)·10 ⁷	(8.7 ± 2.6)·10 ⁷	
methacrylic acid	278	(7.9 ± 2.0)·10 ⁹	(9.3 ± 4.2)·10 ⁷	(1.1 ± 0.3)·10 ⁸	
	288	(9.0 ± 1.1)·10 ⁹	(1.1 ± 2.0)·10 ⁸	(1.4 ± 1.1)·10 ⁸	
	293	---	(1.1 ± 0.4)·10 ⁸	---	
	298	(1.1 ± 0.1)·10 ¹⁰	(9.2 ± 1.6)·10 ⁷	(2.5 ± 1.2)·10 ⁸	
	308	(1.2 ± 0.1)·10 ¹⁰	(8.3 ± 5.5)·10 ⁷	(1.7 ± 1.1)·10 ⁸	
	318	(1.5 ± 0.1)·10 ¹⁰	---	(2.0 ± 0.4)·10 ⁸	
methacrylate	278	(7.3 ± 0.4)·10 ⁹	(3.8 ± 0.5)·10 ⁸	(1.9 ± 0.9)·10 ⁸	
	288	(9.4 ± 0.4)·10 ⁹	(3.2 ± 0.5)·10 ⁸	(2.9 ± 1.3)·10 ⁸	
	298	(1.1 ± 0.1)·10 ¹⁰	(1.7 ± 1.2)·10 ⁸	(3.5 ± 1.1)·10 ⁸	
	303	---	---	(2.3 ± 0.7)·10 ⁸	
	308	(1.4 ± 0.2)·10 ¹⁰	(1.2 ± 0.4)·10 ⁸	(2.2 ± 1.1)·10 ⁸	
	318	(1.4 ± 0.3)·10 ¹⁰	(0.8 ± 1.9)·10 ⁷	(3.5 ± 1.6)·10 ⁸	
acrylic acid	278	(4.2 ± 0.5)·10 ⁹	(2.9 ± 0.9)·10 ⁶	(8.6 ± 1.1)·10 ⁷	
	288	(4.7 ± 0.3)·10 ⁹	(4.3 ± 0.5)·10 ⁶	(9.0 ± 3.3)·10 ⁷	
	298	(5.1 ± 0.8)·10 ⁹	(6.9 ± 1.0)·10 ⁶	(9.5 ± 0.8)·10 ⁷	
	303	---	---	(9.7 ± 2.5)·10 ⁷	
	308	(5.7 ± 0.7)·10 ⁹	(1.0 ± 0.4)·10 ⁷	(8.4 ± 2.0)·10 ⁷	
	318	(6.1 ± 0.7)·10 ⁹	(2.3 ± 0.3)·10 ⁷	(1.0 ± 0.2)·10 ⁸	
acrylate	278	(5.4 ± 1.0)·10 ⁹	(1.9 ± 0.3)·10 ⁷	(9.3 ± 0.9)·10 ⁷	
	288	(5.5 ± 0.5)·10 ⁹	(3.0 ± 0.7)·10 ⁷	(9.4 ± 2.2)·10 ⁷	
	298	(5.9 ± 0.9)·10 ⁹	(4.4 ± 0.6)·10 ⁷	(9.9 ± 2.0)·10 ⁷	
	308	(5.9 ± 1.2)·10 ⁹	(3.9 ± 1.6)·10 ⁷	(8.9 ± 2.3)·10 ⁷	
	318	(6.2 ± 0.4)·10 ⁹	(5.3 ± 1.6)·10 ⁷	(6.4 ± 1.7)·10 ⁷	

2 **Table A1.** Temperature dependent reaction rate constants for the conducted kinetic measurements.
3 Gray values were not used to calculate the activation parameters. LFP: Laser flash
4 photolysis. RR: Reversed-rates method.

1 Calculation of activation parameters

2 The Arrhenius formula describes the temperature dependence of the rate constant $k(T)$.
3 Plotting the natural logarithm of k over the inverse temperature T , the preexponential factor A
4 and the activation energy E_A can be calculated.

$$5 \quad k(T) = A \exp\left(\frac{-E_A}{RT}\right) \quad (3)$$

6 For bimolecular reactions, the following applies:

$$7 \quad \Delta H^\ddagger = E_A - RT \quad (4)$$

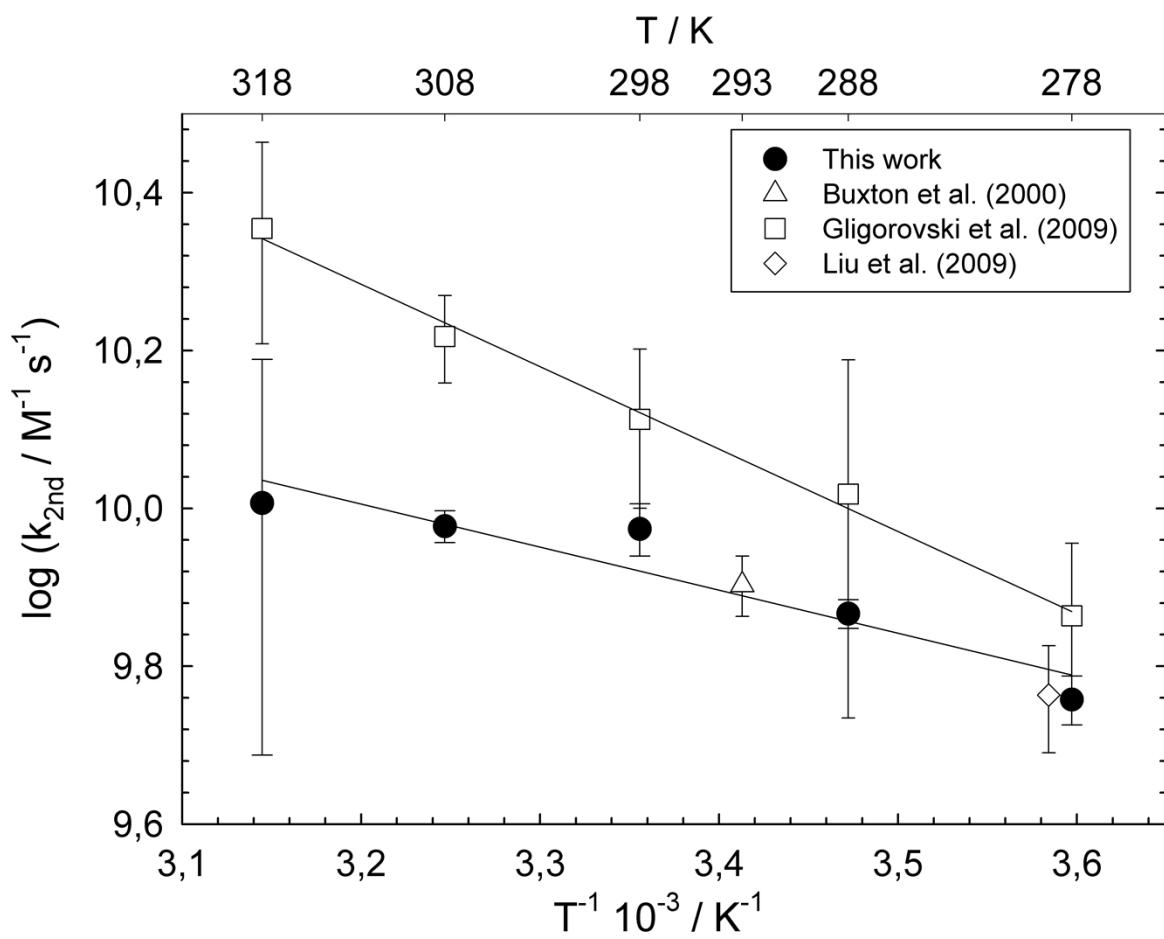
$$8 \quad \Delta S^\ddagger = R \left(\ln A - \ln \frac{k_B T}{h} - 1 \right) \quad (5)$$

9 with ΔH^\ddagger and ΔS^\ddagger denoting the enthalpy and entropy of activation as well as
10 $k_B = 1.381 \cdot 10^{23} \text{ J K}^{-1}$ and $h = 6.626 \cdot 10^{-34} \text{ J s}$ the Boltzmann and Planck constants, respectively.
11 According to the Gibbs-Helmholtz equation, Gibbs' free energy, enthalpy and entropy of
12 activation are linked by

$$13 \quad \Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (6)$$

14 From these equations, all activation parameters can be calculated.

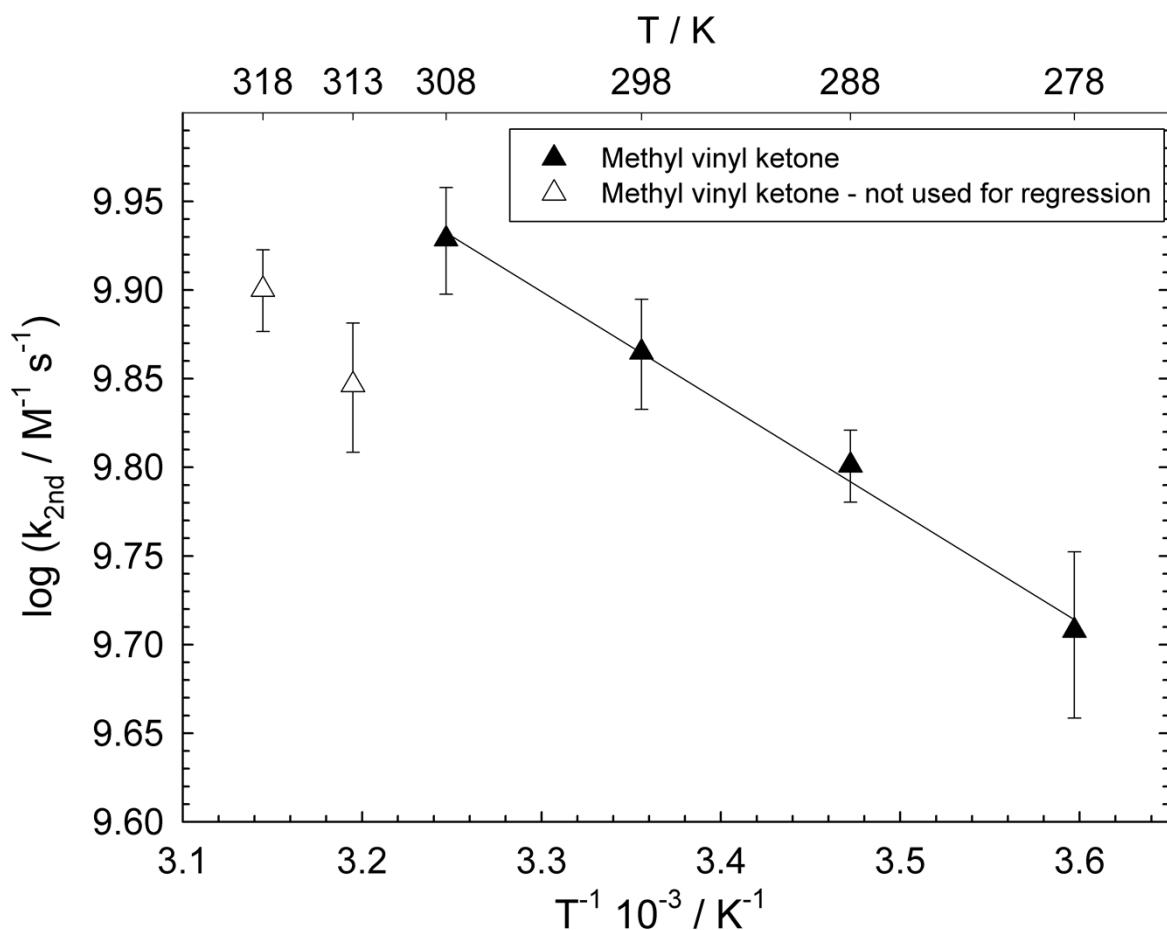
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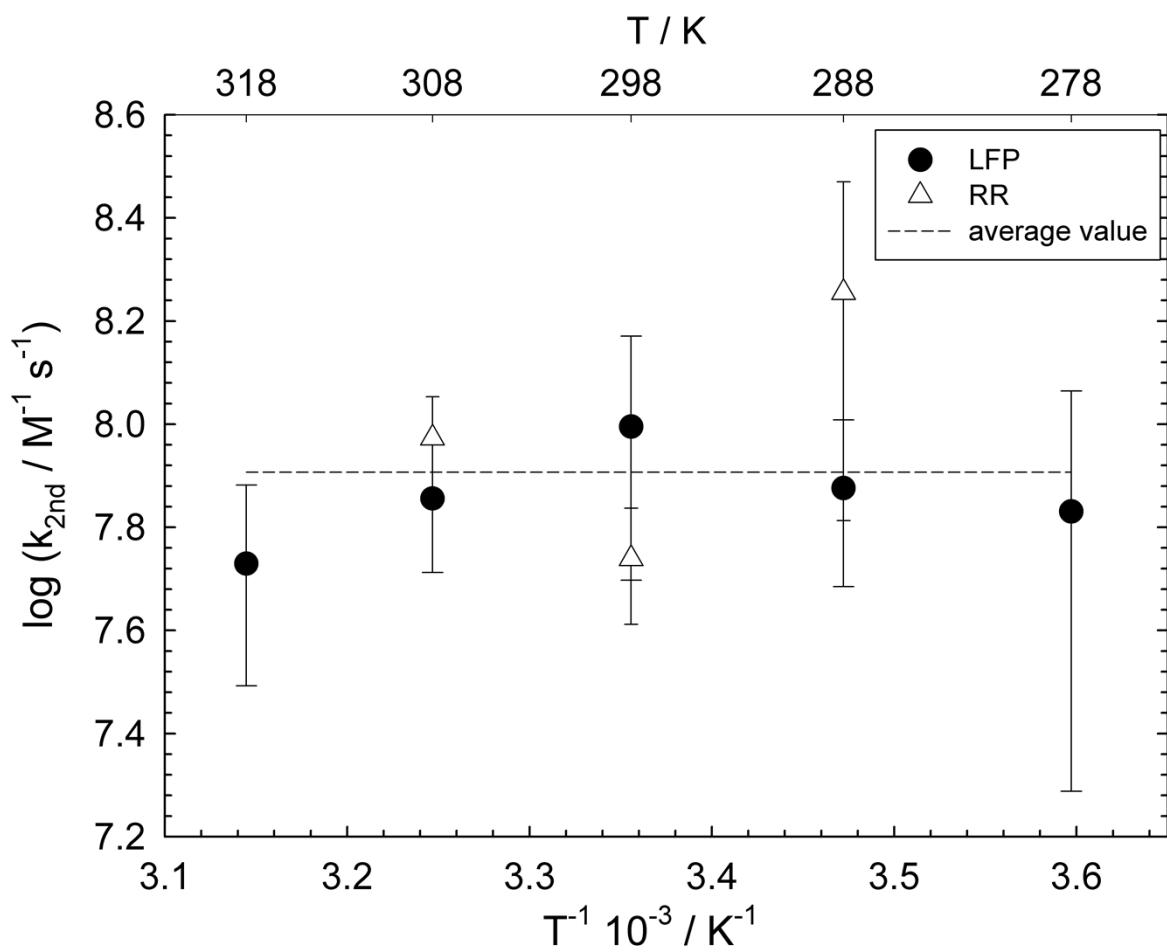
2 Fig. A1. Arrhenius plot for the reaction of methacrolein with OH including literature data.

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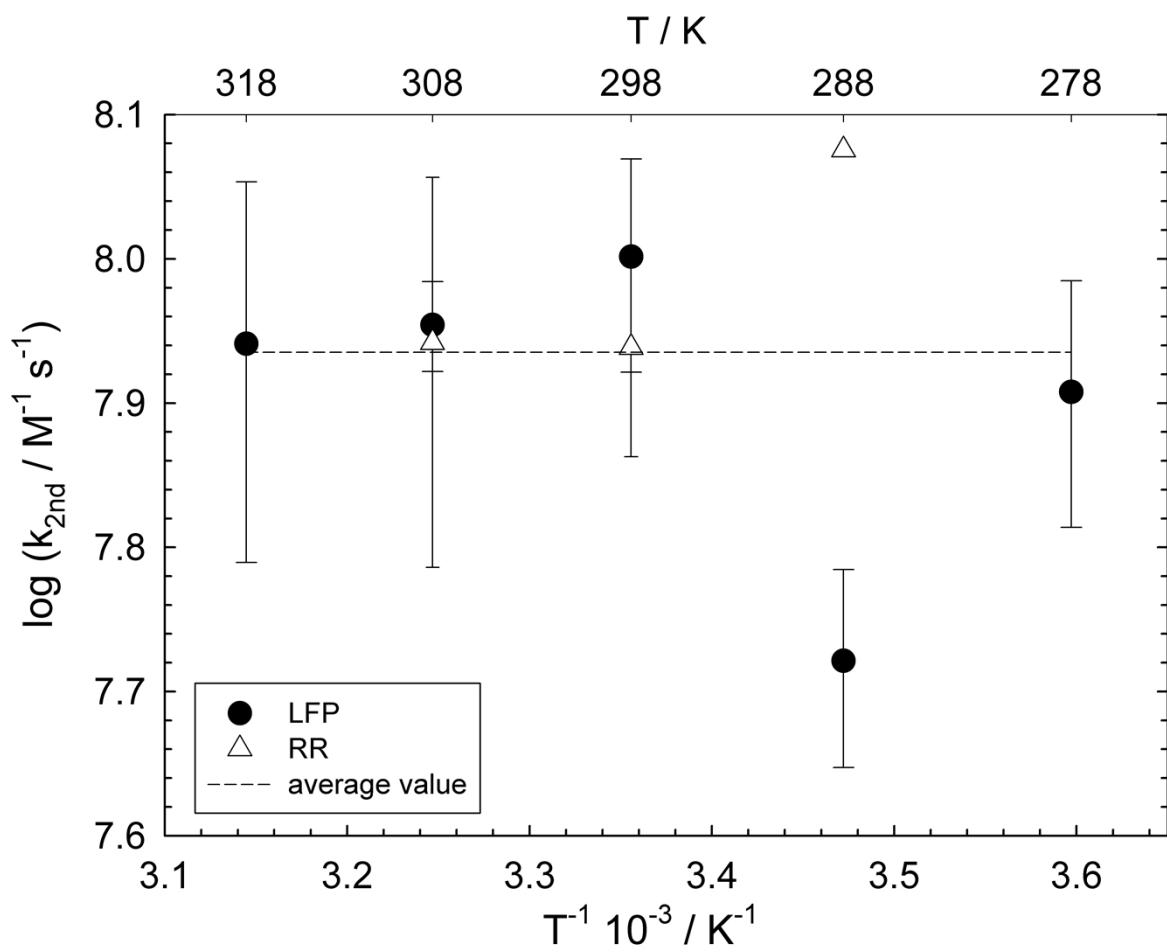
2 Fig. A2. Arrhenius plot for the reaction of methyl vinyl ketone with OH.

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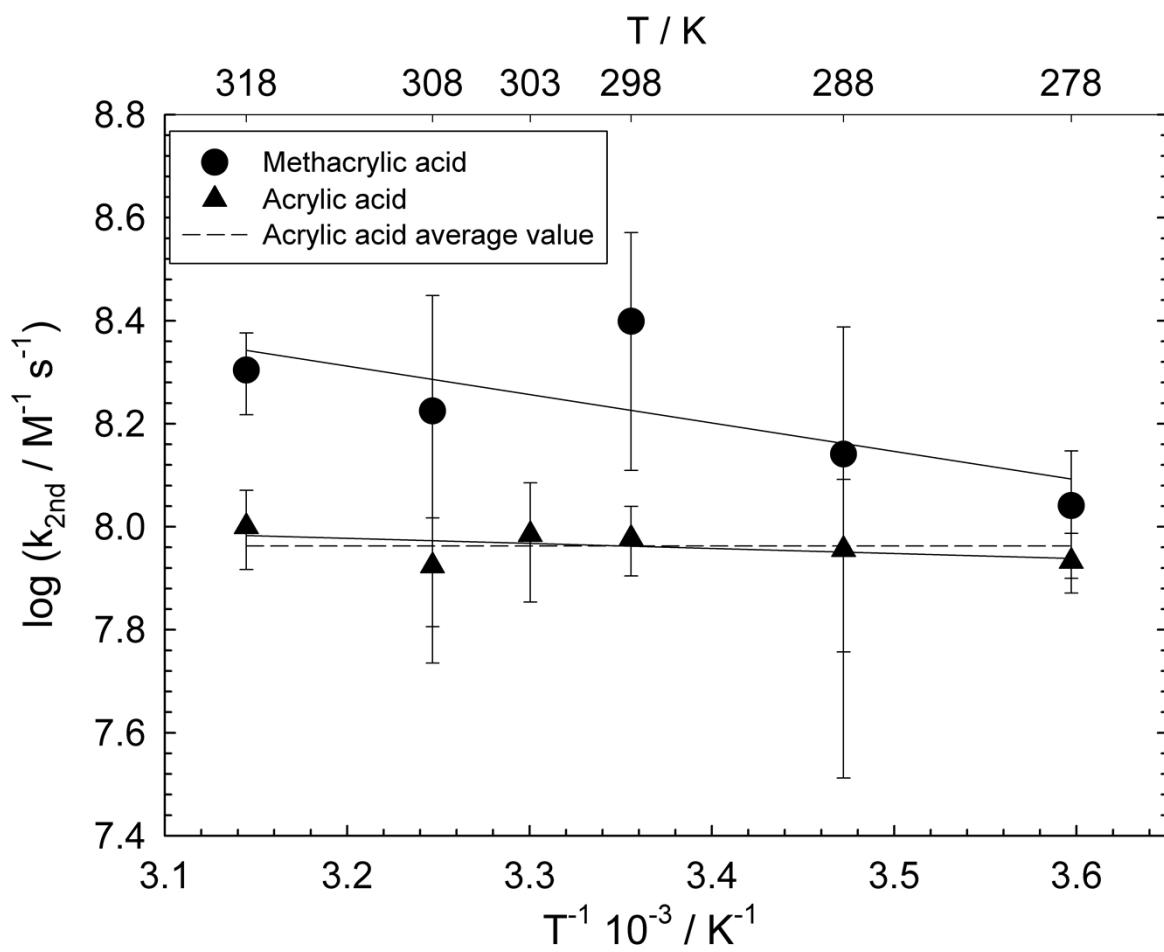
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2 Fig. A3. Arrhenius plot for the reaction of methacrolein with SO_4^- . LFP: Laser flash photolysis. RR:
3 reversed-rates method.

4



2 Fig. A4. Arrhenius plot for the reaction of methyl vinyl ketone with SO_4^- . LFP: Laser flash photolysis. RR:
3 reversed-rates method.

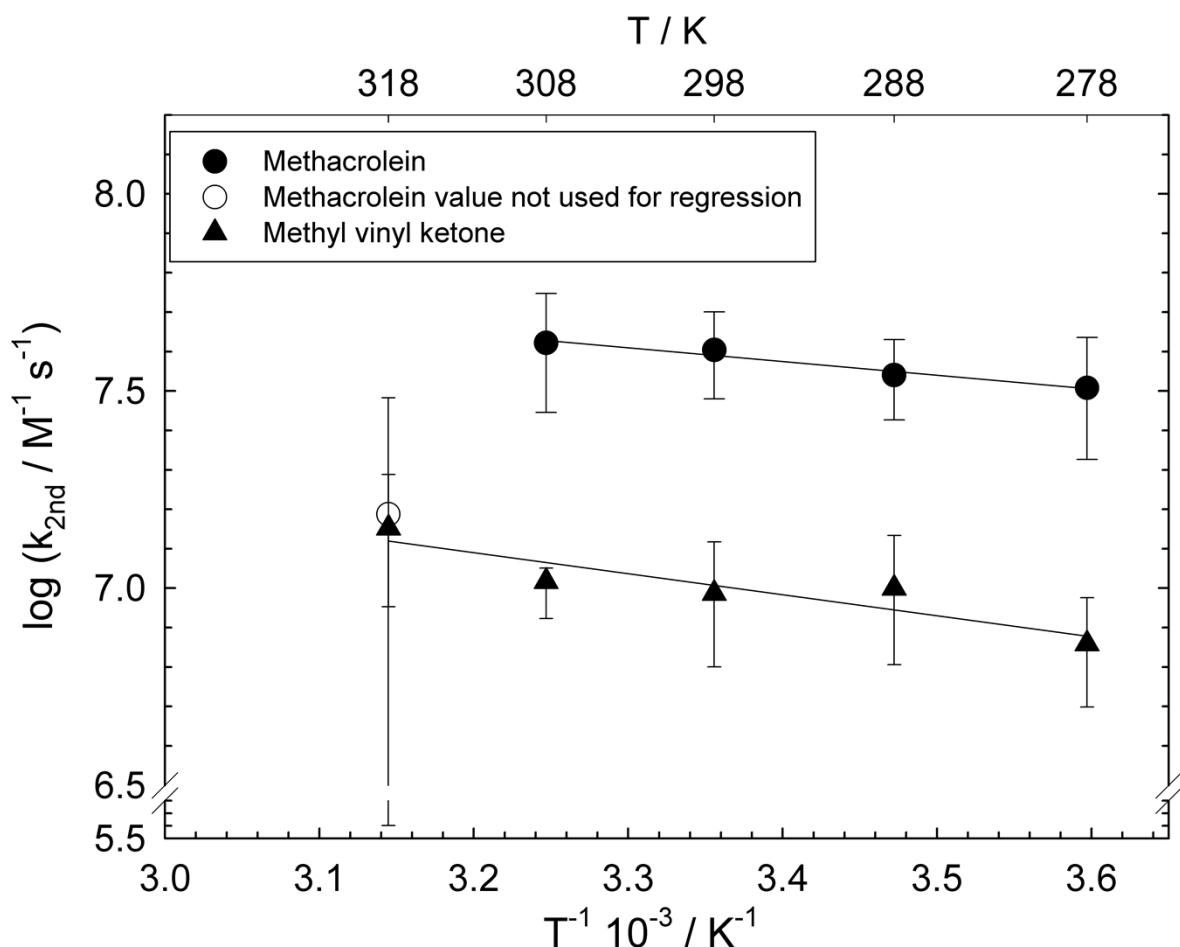
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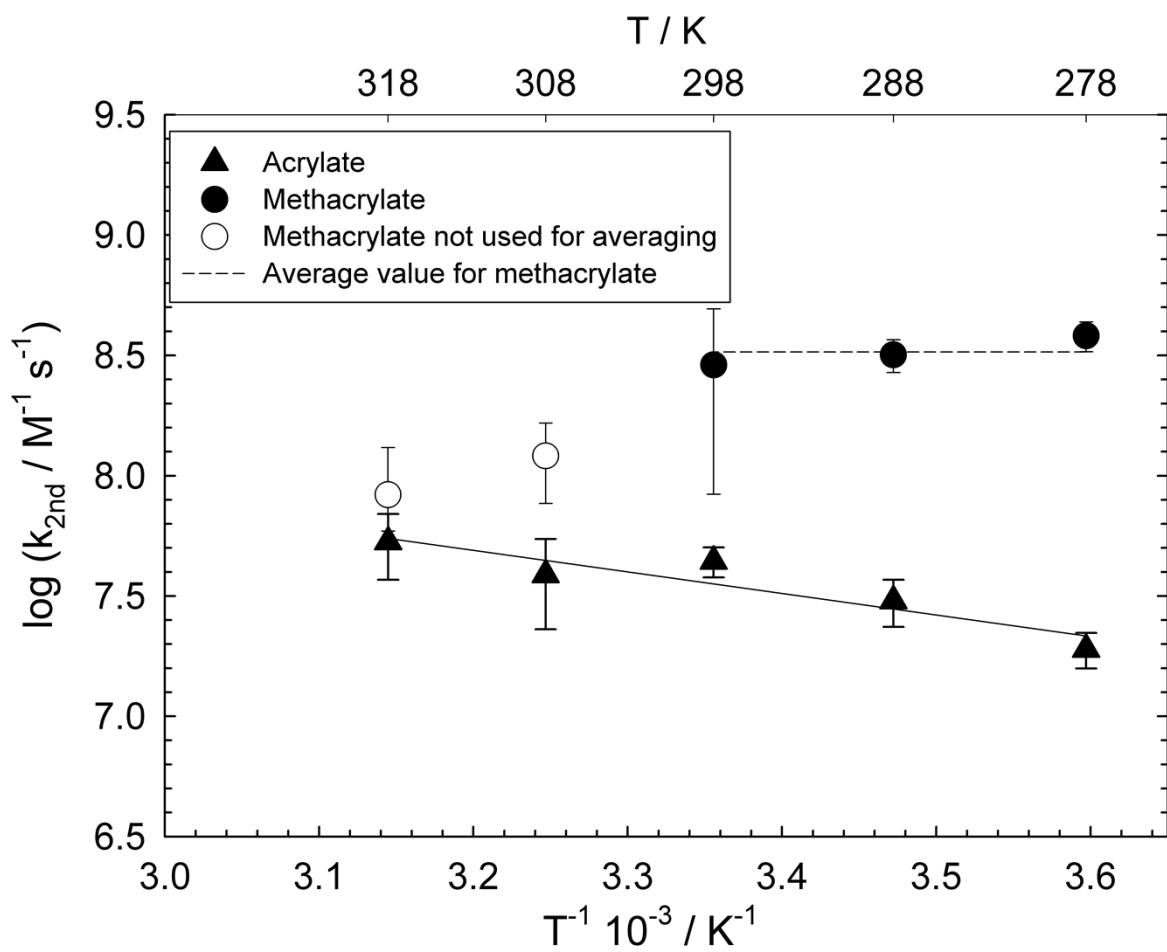
2 Fig. A5. Arrhenius plot for the reactions of methacrylic and acrylic acid at pH 1 with SO_4^- .

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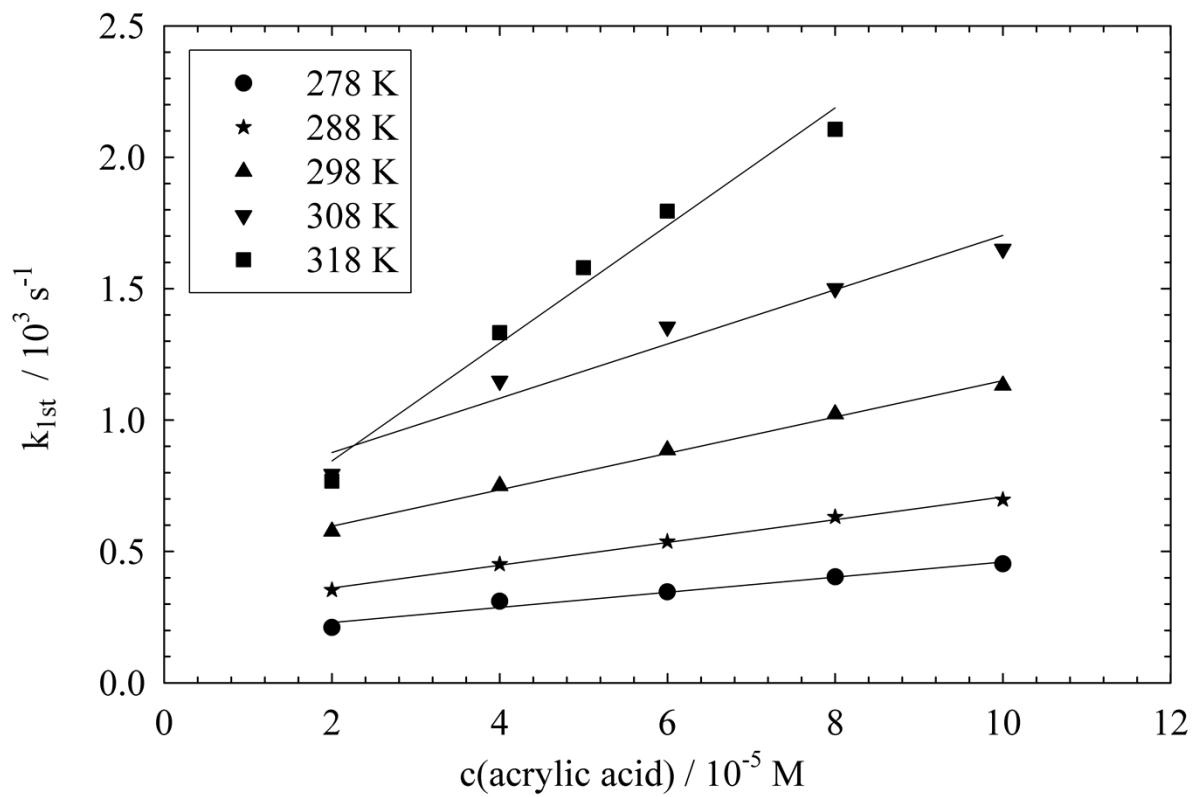
2 Fig. A6. Arrhenius plot for the reaction of methacrolein and methyl vinyl ketone with NO_3 .

3



2 Fig. A7. Arrhenius plot for the reaction of acrylate and methacrylate at pH 8 with NO_3^- .

3



2 Fig. A8. Temperature dependent determination of second order rate constants for the reaction of acrylic
3 acid + NO_3 at pH 1. Error bars for $k_{1\text{st}}$ correspond to the standard deviation (1σ) of the eightfold
4 averaged absorption signals, including the student-t-factor for the 95 % confidence interval.

5

1 **Errors on diffusion limits**

2 The errors on diffusion limits can be calculated using the exact differential method starting
 3 with the Tyn and Calus formula. According to Poling et al., (2000), the error of V_m is
 4 $\Delta V_m = 2.8\%$ whereas $\Delta \eta = 2\%$ is the error of the tabulated values and $\Delta T = 0.1\text{ K}$,
 5 respectively. The error on r (eq. 9), D (eq. 8) and, finally, the errors on k_{diff} (eq. 7) were
 6 calculated according to the equations listed below. The resulting errors in k_{diff} are 4.6 %. It
 7 has to be noted, that the exact differential method usually overestimates the experimental
 8 errors.

9
$$\Delta r = \frac{1}{(4\pi N_A)^{1/8} (3V_m)^{2/8}} \Delta V_m \quad (\text{A25})$$

10
$$\Delta D = 4.44 \times 10^{-8} \frac{(XM)^{0.5} T}{(\eta V_m)^{1.6}} \Delta V_m + 7.4 \times 10^{-8} \frac{(XM)^{0.5}}{(\eta V_m)^{0.6}} \left(\Delta T + \frac{T}{\eta} \Delta \eta \right) \quad (\text{A26})$$

11
$$\Delta k_{\text{diff}} = 4 \times 10^3 \pi N_A [(r_{\text{radical}} + r_{\text{reactant}})(\Delta D_{\text{radical}} + \Delta D_{\text{reactant}}) + (D_{\text{radical}} + D_{\text{reactant}})(\Delta r_{\text{radical}} + \Delta r_{\text{reactant}})] \quad (\text{A27})$$

12