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

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Basic assumptions of the reversed-rates method

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

Chain initiation

6 $\text{Fe(III)OH} + \text{HSO}_3^- \rightarrow \text{Fe(II)} + \text{SO}_3^{2-} + \text{H}_2\text{O}$ (A1)

7 Chain propagation

8 $\text{SO}_3^{2-} + \text{O}_2 \rightarrow \text{SO}_5^{2-}$ (A2)

9 $\text{SO}_5^{2-} + \text{HSO}_3^- \rightarrow \text{HSO}_5^- + \text{SO}_3^{2-}$ (A3)

10 $\text{SO}_5^{2-} + \text{HSO}_3^- \rightarrow \text{SO}_4^{2-} + \text{SO}_3^{2-} + \text{H}^+$ (A4)

11 $\text{SO}_4^{2-} + \text{HSO}_3^- \rightarrow \text{SO}_4^{2-} + \text{SO}_3^{2-} + \text{H}^+$ (A5)

12 $\text{SO}_5^{2-} + \text{SO}_5^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{O}_2$ (A6)

13 Formation of sulfate

14 $\text{HSO}_5^- + \text{HSO}_3^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + 2 \text{H}^+$ (A7)

Regeneration of the initiator

15

16 $\text{SO}_5^{2-} + \text{Fe(II)} \rightarrow \text{SO}_4^{2-} + \text{Fe(III)}$ (A8)

17 $\text{SO}_5^{2-} + \text{Fe(II)} \rightarrow \text{SO}_4^{2-} + \text{Fe(III)} (+ \text{OH}^-)$ (A9)

18 $\text{SO}_4^{2-} + \text{Fe(II)} \rightarrow \text{SO}_4^{2-} + \text{Fe(III)}$ (A10)

Termination

19

20 $\text{SO}_3^{2-} + \text{SO}_3^{2-} \rightarrow \text{S}_2\text{O}_6^{2-}$ (A11)

21 $\text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_6^{2-}$ (A12)

22 $\text{SO}_5^{2-} + \text{SO}_3^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2$ (A13)

Inhibition

23

24 Organic $+ \text{SO}_4^{2-} \rightarrow \text{Products}$ (A14)

25 Speciation and hydrolytic equilibria

26 $\text{H}_2\text{SO}_3 \leftrightarrow \text{H}^+ + \text{HSO}_3^-$ (A15)
1 \[ \text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-} \] \hspace{1cm} (A16)

2 \[ \text{S}_2\text{O}_5^{2-} \rightleftharpoons \text{HSO}_3^- + \text{HSO}_3^- \] \hspace{1cm} (A17)

3 \[ \text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} \] \hspace{1cm} (A18)

4 \[ \text{Fe}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{Fe(II)SO}_4 \] \hspace{1cm} (A19)

5 \[ \text{Fe}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{Fe(III)SO}_4^+ \] \hspace{1cm} (A20)

6 \[ \text{Fe}^{3+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Fe(III)(SO}_4^2\] \hspace{1cm} (A21)

7 \[ \text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(III)OH}^{2+} + \text{H}^- \] \hspace{1cm} (A22)

8 \[ \text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe(III)(OH)}^{2+} + 2\text{H}^+ \] \hspace{1cm} (A23)

9 \[ \frac{[\text{Fe(II)}]_{\text{total}}}{[\text{Fe(III)}]_{\text{total}}} = 3 \] \hspace{1cm} (A24)

10 The assumptions underlying the pseudo-stationary analysis of the autoxidation of S(IV) catalysed by Fe(III) and inhibited by organic scavenger of sulphate radical anions are (i) the rate of autoxidation is controlled by the reaction of bisulfite ions with peroxymonosulfate radical anions (A7), (ii) chain termination is dominated by reactions of ferrous ions with peroxymonosulfate radicals (A8) and (A9), as well as by reaction of sulphate radical anions with an organic inhibitor (A14); (iii) the chain initiation occurs by the reaction of ferric ions with bisulfite ions (A1); (iv) rate of chain termination (by dominating reactions) is equal to the rate of chain initiation.
Fig. A0. Temporal profiles of the reaction of acrylic acid (pH 1) with NO$_3^-$ (top), SO$_4^{2-}$ (middle) and OH radicals (bottom). Grey areas correspond to error range resulting from the standard deviation of eight signals.
<table>
<thead>
<tr>
<th>Reactant</th>
<th>T / K</th>
<th>OH</th>
<th>NO$_3$</th>
<th>SO$_4^-$ (LFP)</th>
<th>SO$_4^-$ (KR)</th>
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<td>methacrolein</td>
<td>278</td>
<td>(5.7 ± 0.4) × 10$^8$</td>
<td>(3.2 ± 1.1) × 10$^7$</td>
<td>(6.8 ± 4.8) × 10$^7$</td>
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Table A1. Temperature dependent reaction rate constants for the conducted kinetic measurements. Gray values were not used to calculate the activation parameters. LFP: Laser flash 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 $A$ and the activation energy $E_A$ can be calculated.

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

6 For bimolecular reactions, the following applies:

7 \[ \Delta H^\ddagger = E_A - RT \] (4)

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

9 with $\Delta H^\ddagger$ and $\Delta S^\ddagger$ denoting the enthalpy and entropy of activation as well as

10 $k_B = 1.381 \cdot 10^{23}$ J K$^{-1}$ and $h = 6.626 \cdot 10^{-34}$ 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 \[ \Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \] (6)

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

15
Fig. A1. Arrhenius plot for the reaction of methacrolein with OH including literature data.
Fig. A2. Arrhenius plot for the reaction of methyl vinyl ketone with OH.
Fig. A3. Arrhenius plot for the reaction of methacrolein with SO₄⁻. LFP: Laser flash photolysis. RR: reversed-rates method.
Fig. A4. Arrhenius plot for the reaction of methyl vinyl ketone with SO$_4^-$.

Fig. A5. Arrhenius plot for the reactions of methacrylic and acrylic acid at pH 1 with SO$_4^{2-}$.
Fig. A6. Arrhenius plot for the reaction of methacrolein and methyl vinyl ketone with NO₃.
Fig. A7. Arrhenius plot for the reaction of acrylate and methacrylate at pH 8 with NO$_3$. 
Fig. A8. Temperature dependent determination of second order rate constants for the reaction of acrylic acid + NO<sub>3</sub> at pH 1. Error bars for $k_{1st}$ correspond to the standard deviation (1σ) of the eightfold averaged absorption signals, including the student-t-factor for the 95% confidence interval.
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 $k_{\text{diff}}$ (eq. 7) were
6 calculated according to the equations listed below. The resulting errors in $k_{\text{diff}}$ are 4.6\%.
7 It has to be noted, that the exact differential method usually overestimates the experimental
8 errors.

\[
\Delta r = \frac{1}{(4\pi N_A)^{1/3}(3V_m)^{2/3}} \Delta V_m \tag{A25}
\]

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

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