Supplement for

pH regulates the formation of organosulfates and inorganic sulfate from organic peroxides reaction with dissolved SO₂ in aquatic media

Lin Du, Xiaofan Lv, Makroni Lily, Kun Li and Narcisse Tsona Tchinda

Environment Research Institute, Shandong University, Qingdao, 266237, China

Correspondence to: Lin Du (lindu@sdu.edu.cn) and Narcisse Tsona Tchinda (tsonatch@sdu.edu.cn)

S1 Calculation of the Gibbs free energy in aqueous phase

For a given species, the Gibbs free energy in aqueous phase is calculated as:

$$G = E^{\text{CCSD(T)}} + E_{SMD}^{\omega B97XD} - E_{Gas}^{\omega B97XD} + G_{corr}^{\omega B97XD} + \Delta G_{1\text{atm} \rightarrow 1\text{M}} \quad (1)$$

where $E^{\text{CCSD(T)}}$ is the electronic energy obtained from DLPNO-CCSD(T)/aug-cc-pVTZ, $E_{SMD}^{\omega B97XD}$ and $E_{Gas}^{\omega B97XD}$ are electronic energies obtained from ωB97XD/6-31++G(d,p) calculations in aqueous-phase and in gas-phase, respectively, $G_{corr}^{\omega B97XD}$ is the thermal correction to Gibbs free energy obtained from ωB97XD/6-31++G(d,p) calculations at 298.15 K and 1 atm, and $\Delta G_{1\text{atm} \rightarrow 1\text{M}}$ is the term that converts the standard pressure of 1 atm in the gas-phase to the standard concentration of 1 M in aqueous-phase. The numerical value of this term is 1.89 kcal mol^{-1} (Marenich et al., 2009).

S2 Explicit effect of water

While the presence of additional water molecule could decrease the free energy barrier by 5.07 kcal mol^{-1} towards formation of methyl sulfate, this barrier is slightly increased (by 0.77 kcal mol^{-1}) in the formation of inorganic sulfate (see **Figure 3**). The consequence of this effect is that the presence of additional water has different impact on reactions (R5) and (R6) from a mechanistic point of view, with further implication in the kinetics. In principle, the additional water molecule plays different roles in the two processes, either by facilitating the hydrogen transfer from $HOSO_2^-$ to the HO fragment of MHP or by hindering the hydrogen transfer to the CH_3O fragment to form CH_3OH. Though these effects of water are not particularly significant to alter the overall MHP + S(IV) reaction, it is seen that the effect of explicit water is varied, as observed in various previous studies (Jara-Toro et al., 2018; Xu et al., 2019; Weber et al., 2020).

Table S1 Fractional population of different protonated states of SO_2 in the pH 1 – 10 range, calculated based on SO_2 partial vapor pressure of 3.96 atm and SO_2 Henry's law constant of 1.23 M atm^{-1} at 298.15 K.

pH	$\delta(SO_2 \cdot H_2O)$	$\delta(HSO_3^-)$	$\delta(SO_3^{2-})$
1	8.66×10^{-1}	1.34×10^{-1}	1.44×10^{-7}
1.81	5.00×10^{-1}	5.00×10^{-1}	3.46×10^{-6}
2	3.92×10^{-1}	6.08×10^{-1}	6.51×10^{-6}
3	6.06×10^{-2}	9.39×10^{-1}	1.01×10^{-4}
4	6.41×10^{-3}	9.93×10^{-1}	1.06×10^{-3}
4.5	2.03×10^{-3}	9.95×10^{-1}	3.37×10^{-3}
5	6.38×10^{-4}	9.89×10^{-1}	1.06×10^{-2}
6	5.83×10^{-5}	9.03×10^{-1}	9.68×10^{-2}
6.97	3.46×10^{-6}	5.00×10^{-1}	5.00×10^{-1}
7	3.12×10^{-6}	4.83×10^{-1}	5.17×10^{-1}
8	5.51×10^{-8}	8.54×10^{-2}	9.15×10^{-1}
9	5.97×10^{-10}	9.25×10^{-3}	9.91×10^{-1}
10	6.02×10^{-12}	9.32×10^{-4}	9.99×10^{-1}

Table S2 Effective rate constants (k_{eff}, M^{-1} s^{-1}) for the reactions of methyl hydroperoxide with S(IV) in the temperature range 240 – 340 K and pH 1 – 10.

pH	240 K	260 K	280 K	300 K	320 K	340 K
1	1.24×10^{-17}	1.85×10^{-15}	1.35×10^{-13}	5.62×10^{-12}	1.47×10^{-10}	2.64×10^{-9}
2	6.30×10^{-17}	8.94×10^{-15}	6.39×10^{-13}	2.62×10^{-11}	6.81×10^{-10}	1.21×10^{-8}
3	2.00×10^{-16}	2.27×10^{-14}	1.39×10^{-12}	5.17×10^{-11}	1.26×10^{-9}	2.14×10^{-8}
4	1.30×10^{-15}	1.17×10^{-13}	5.75×10^{-12}	1.73×10^{-10}	3.49×10^{-9}	5.09×10^{-8}
5	1.21×10^{-14}	1.05×10^{-12}	4.83×10^{-11}	1.35×10^{-9}	2.51×10^{-8}	3.33×10^{-7}
6	1.10×10^{-13}	9.46×10^{-12}	4.33×10^{-10}	1.20×10^{-8}	2.20×10^{-7}	2.88×10^{-6}
7	5.87×10^{-13}	5.05×10^{-11}	2.31×10^{-9}	6.39×10^{-8}	1.17×10^{-6}	1.53×10^{-5}
8	1.04×10^{-12}	8.93×10^{-11}	4.09×10^{-9}	1.13×10^{-7}	2.07×10^{-6}	2.70×10^{-5}
9	1.12×10^{-12}	9.67×10^{-11}	4.43×10^{-9}	1.22×10^{-7}	2.24×10^{-6}	2.93×10^{-5}
10	1.13×10^{-12}	9.75×10^{-11}	4.47×10^{-9}	1.23×10^{-7}	2.26×10^{-6}	2.95×10^{-5}

Table S3 Effective rate constants (k_{eff}, M^{-1} s^{-1}) for the reactions of peracetic acid with S(IV) in the temperature range 240 – 340 K and pH 1 – 10.

pH	240 K	260 K	280 K	300 K	320 K	340 K
1	2.07×10^{-5}	2.84×10^{-4}	3.21×10^{-3}	2.86×10^{-2}	2.00×10^{-1}	1.14×10^{0}
2	5.28×10^{-4}	4.39×10^{-3}	3.14×10^{-2}	2.03×10^{-1}	1.18×10^{0}	5.98×10^{0}
3	7.53×10^{-3}	5.48×10^{-2}	3.09×10^{-1}	1.45×10^{0}	5.95×10^{0}	2.22×10^{1}
4	7.89×10^{-2}	5.65×10^{-1}	3.08×10^{0}	1.35×10^{1}	5.00×10^{1}	1.61×10^{2}
5	7.85×10^{-1}	5.62×10^{0}	3.05×10^{1}	1.33×10^{2}	4.85×10^{2}	1.53×10^{3}
6	7.17×10^{0}	5.13×10^{1}	2.79×10^{2}	1.21×10^{3}	4.42×10^{3}	1.39×10^{4}
7	3.83×10^{1}	2.74×10^{2}	1.49×10^{3}	6.49×10^{3}	2.36×10^{4}	7.41×10^{4}
8	6.78×10^{1}	4.85×10^{2}	2.63×10^{3}	1.15×10^{4}	4.18×10^{4}	1.31×10^{5}
9	7.34×10^{1}	5.25×10^{2}	2.85×10^{3}	1.24×10^{4}	4.52×10^{4}	1.42×10^{5}

| 10 | 7.40×10^1 | 5.30×10^2 | 2.88×10^3 | 1.25×10^4 | 4.56×10^4 | 1.43×10^5 |

Table S4 Effective rate constants (k_{eff}, $M^{-1}\,s^{-1}$) for the reactions of benzoyl peroxide with S(IV) in the temperature range 240 – 340 K and pH 1 – 10.

pH	240 K	260 K	280 K	300 K	320 K	340 K
1	1.09×10^{-2}	4.28×10^{-2}	1.35×10^{-1}	3.88×10^{-1}	9.55×10^{-1}	2.12×10^0
2	4.93×10^{-1}	1.94×10^0	6.30×10^0	1.76×10^1	4.33×10^1	9.61×10^1
3	7.63×10^0	3.00×10^1	9.73×10^1	2.71×10^2	6.69×10^2	1.49×10^3
4	8.06×10^1	3.17×10^2	1.03×10^3	2.87×10^3	7.06×10^3	1.57×10^4
5	8.03×10^2	3.15×10^3	1.02×10^4	2.87×10^4	7.04×10^4	1.56×10^5
6	7.33×10^3	2.88×10^4	9.36×10^4	2.61×10^5	6.43×10^5	1.43×10^6
7	3.92×10^4	1.54×10^5	5.00×10^5	1.40×10^6	3.44×10^6	7.64×10^6
8	6.93×10^4	2.72×10^5	8.84×10^5	2.47×10^6	6.08×10^6	1.35×10^7
9	7.51×10^4	2.95×10^5	9.58×10^5	2.67×10^6	6.58×10^6	1.46×10^7
10	7.57×10^4	2.97×10^5	9.66×10^5	2.69×10^6	6.64×10^6	1.47×10^7
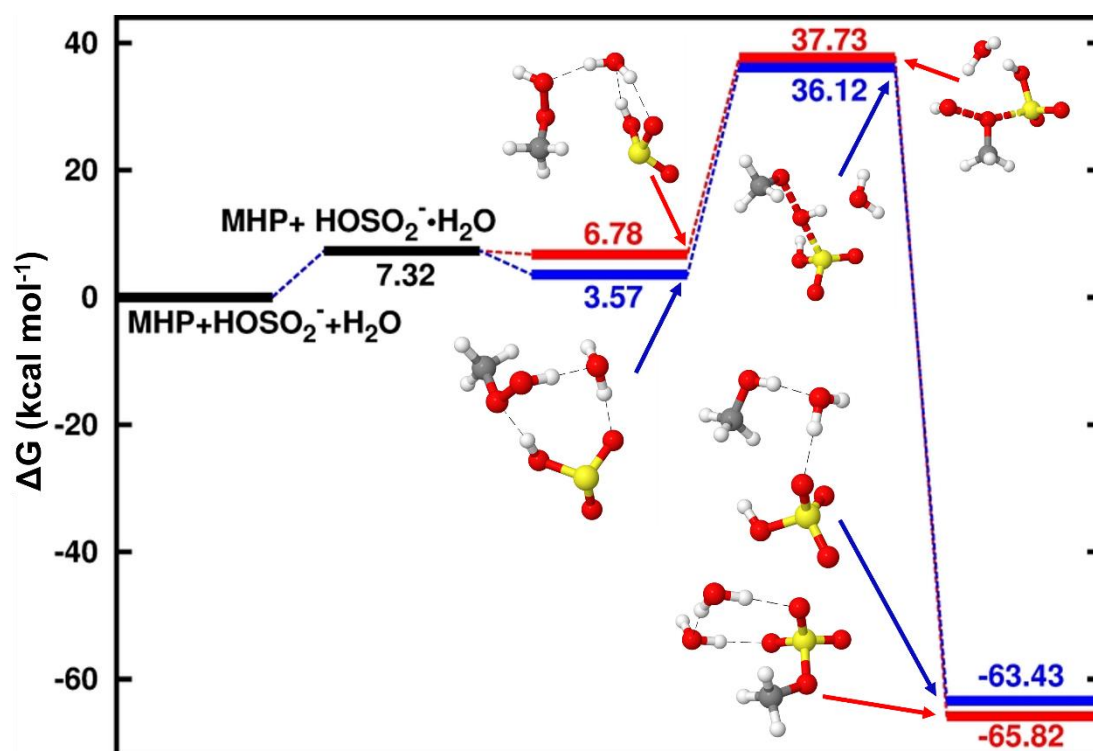
Figure S1: Gibbs free energy profile of the stationary points in the MHP+HOSO$_2^-$ reaction with the presence of an additional water molecule. The color coding is yellow for sulfur atom, red for oxygen atom, grey for carbon atom and white for hydrogen atom.

References

Jara-Toro, R. A., Hernández, F. J., Garavagno, M. d. l. A., Taccone, R. A., and Pino, G. A.: Water catalysis of the reaction between hydroxyl radicals and linear saturated alcohols (ethanol and n-propanol) at 294 K, Phy. Chem. Chem. Phys., 20, 27885-27896, doi:10.1039/C8CP05411H, 2018.

Marenich, A. V., Cramer, C. J., and Truhlar, D. G.: Performance of SM6, SM8, and SMD on the SAMPL1 Test Set for the Prediction of Small-Molecule Solvation Free Energies, J. Phys. Chem. B, 113, 4538-4543, doi:10.1021/jp809094y, 2009.

Weber, I., Bouzidi, H., Krumm, B., Schoemaecker, C., Tomas, A., and Fittschen, C.: Water does not catalyze the reaction of OH radicals with ethanol, Phys. Chem. Chem. Phys., 22, 7165-7168, doi:10.1039/D0CP00467G, 2020.

Xu, L., Tsona, N. T., Tang, S., Li, J., and Du, L.: Role of (H2O)n (n = 1–2) in the Gas-Phase Reaction of Ethanol with Hydroxyl Radical: Mechanism, Kinetics, and Products, ACS Omega, 4, 5805-5817, doi:10.1021/acsomega.9b00145, 2019.