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pH regulates the formation of organosulfates and inorganic sulfate from organic peroxide reaction with dissolved SO_2 in aquatic media

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S1 Calculation of the Gibbs free energy in aqueous phase

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

$$G=E^{\mathrm{CCSD(T)}} + E_{SMD}^{\omega B97XD} - E_{Gas}^{\omega B97XD} + G_{corr}^{\omega B97XD} + \Delta G_{\mathrm{1atm \to 1M}} \quad \text{(S1)}$$

where $E^{\mathrm{CCSD(T)}}$ 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 $\Delta G_{\mathrm{1atm \to 1M}}$ 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	**δ(SO_2•H_2O)**	**δ(HSO_3^-)**	**δ(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}

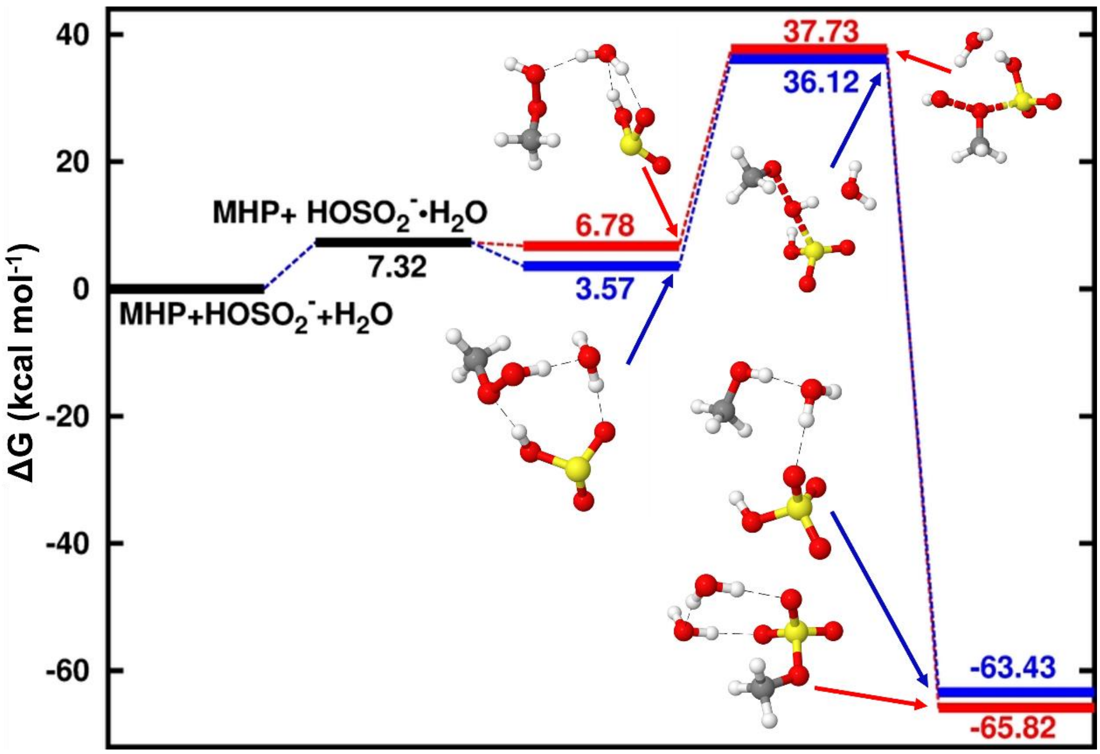

Figure S1: Gibbs free energy profile of the stationary points in the MHP+$HOSO_2^-$ reaction with the presence of an additional water molecule. The color coding is yellow for sulfur atom, red for oxygen atom, grey for carbon atom and white for hydrogen atom.

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