Atmospheric
Chemistry
and Physics

Supplement of

Towards a chemical mechanism of the oxidation of aqueous sulfur dioxide via isoprene hydroxyl hydroperoxides (ISOPOOH)

Eleni Dovrou et al.

Correspondence to: Eleni Dovrou (dovrouel@gmail.com) and Frank Keutsch (keutsch@seas.harvard.edu)
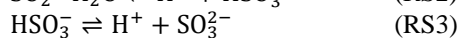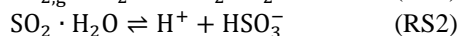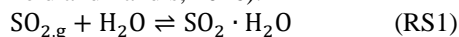
Supplement

1. Sulfur dioxide

Sulfur dioxide (SO_2) has a Henry's law constant of H_{SO_2}=1.3 M atm^{-1} and mass accommodation coefficient of γ_{SO_2}=0.11, which does not significantly change with temperature (Worsnop et al., 1989). Thus, SO_2 can dissolve ($SO_{2,aq}$) into cloud and fog water, where it can be rapidly oxidized to form sulfate.(Lind et al., 1987; Hegg and Hobbs, 1982; Shen et al., 2012; Harris et al., 2014; Dovrou et al., 2019b) $SO_{2,aq}$ reacts with water to form bisulfite (HSO_3^-) at pH$\gtrsim$2, which dissociates to form sulfite (SO_3^{2-}) at pH$\gtrsim$6 (RS1-RS3, Fig. S1) (Seinfeld and Pandis, 2016).

$$SO_{2,g} + H_2O \rightleftharpoons SO_2 \cdot H_2O \qquad \text{(RS1)}$$
$$SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^- \qquad \text{(RS2)}$$
$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \qquad \text{(RS3)}$$

2 Calculation of uncertainty

Weighted nonlinear regression was applied to the data and the Monte Carlo analysis was performed for the calculation of uncertainty. 5000 runs were used for the Monte Carlo simulation. A set of values were randomly sampled considering normal distribution and 95% confidence interval was selected. The standard deviation represents the uncertainty. The uncertainty in this work represents the precision of the measurements and not the accuracy, due to unknown systemic errors.

The standard deviation, S_i, is defined as $S_i = \frac{1}{N-1} \cdot \sum_{i=1}^{N} |C_i - \mu|^2$, where N is the number of the experimental concentrations, C_i is the concentration i and μ is the mean value of the concentrations and is equal to $\mu = \frac{1}{N} \cdot \sum_{i=1}^{N} C_i$.

3 Calculation of diffusion coefficient and time

Using the Wilke-Chang equation for diffusivity in liquids the diffusion coefficient, D, is calculated and assuming cloud relevant mean diffusivity distances, x, of 0-50 microns, (Miyabe and Isogai, 2011; Sitaraman et al., 1963),:

$$\frac{D \cdot \mu}{T} = \frac{7.4 \cdot 10^{-8} \cdot (\Phi_{air} \cdot M_{air})^{1/2}}{V_{b,A}^{0.6}} \qquad (1)$$

35   Where D is the diffusivity in $cm^2 \cdot s^{-1}$, μ is the viscosity of water in $Pa \cdot s$, T is the temperature in Kelvin, $\Phi_{air}=1$, M_{air} is the molecular weight of air and $V_{b,A}$ is the solute molar volume of MVK which is equal to $\frac{Molar\ weight}{density}$=83.4 $cm^3 \cdot mol^{-1}$.

The diffusion time is estimated as, (Mainardi et al., 2007),:

$$t = \frac{<x^2>}{q_i \cdot D} \qquad (2)$$

Where x is the mean diffusivity distance, q_i is a numerical constant which depends on dimensionality and is equal to 2, 4, or
40   6 for 1, 2, or 3-dimensional diffusion and D is the diffusivity in $cm^2 \cdot s^{-1}$. For the examined x values the diffusion time was in the range of 0-25 seconds.

4 NMR experiments

The MestReNova software was used to analyse the spectra of the NMR experiments. Experiments with (Table S1) and without (Fig. S4) standards were conducted with ISOPOOH synthesized according to the procedures described by Rivera-Rios (2018).
45   In the experiments conducted without and with standards the purity of ISOPOOH was 80% and 70%, respectively, and the relaxation delay of the experiments with standards was longer, 45 sec, compared to the experiments without standards, 17 sec. The use of standards and the longer relaxation delay of these experiments allows for quantitative analysis. However, the lower purity of ISOPOOH used in the experiments with standards increase the uncertainty of the calculations and the purity and relaxation delay affect the intensity and integration of the peaks. For example, in the experiments without standards (Fig. S4)
50   it is observed that the HMS peak (HMS1) has higher intensity and area, 1.14 integration at pH=5.5, the methyl group peak of MVK (M1), 1.00 integration at pH=5.5. In contrast, in the experiments with standards (Table S1) HMS1 has lower intensity and area, 0.13 and 1.05 integration at pH=5.5 when using 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt and DMSO, respectively, than M1, 0.20 and 1.50 integration at pH=5.5 when using 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt and DMSO, respectively. The main reason of this difference is due to the relaxation delay; thus, the values of Table S1 were
55   used for the calculations presented in this work.

2

References

Dovrou, E., Rivera-Rios, J. C., Bates, K. H. and Keutsch, F. N.: Sulfate Formation via Cloud Processing from Isoprene
60 Hydroxyl Hydroperoxides (ISOPOOH), Environ. Sci. Technol., 12476−12484, doi:10.1021/acs.est.9b04645, 2019b.

Harris, E., Sinha, B., Pinxteren, D. Van, Schneider, J., Poulain, L., Collett, J., Anna, B. D. and Fahlbusch, B.: In-cloud sulfate addition to single particles resolved with sulfur isotope analysis during HCCT-2010, Atmos. Chem. Phys., 4219–4235, doi:10.5194/acp-14-4219-2014, 2014.

Hegg, D. A. and Hobbs, P. V: Measurements of sulfate production in natural clouds, Atmos. Environ., 16(11), 2663–2668,
65 doi:10.1016/0004-6981(82)90348-1, 1982.

Lind, J. A., Lazrus, A. L. and Kok, G. L.: Aqueous Phase Oxidation of Sulfur(Iv) By Hydrogen-Peroxide, Methylhydroperoxide, and Peroxyacetic Acid, J. Geophys. Res., 92(D4), 4171–4177, doi:10.1029/JD092iD04p04171, 1987.

Mainardi, F., Luchko, Y. and Pagnini, G.: The fundamental solution of the space-time fractional diffusion equation, Fract. Calc. and Applied Anal., 4(2), 153–192, arXiv:cond-mat/0702419, 2007.

70 Miyabe, K. and Isogai, R.: Estimation of molecular diffusivity in liquid phase systems by the Wilke-Chang equation, J. Chromatogr. A, 1218(38), 6639–6645, doi:10.1016/j.chroma.2011.07.018, 2011.

Rivera-Rios, J. C.: Atmospheric Chemistry of Isoprene Hydroxyhydroperoxides, PhD dissertation. Harvard University, Cambridge MA, May 2018.

Seinfeld, J. H. and Pandis, S. N. (Eds): Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John
75 Wiley & Sons Publications, Hoboken, New Jersey, 2016

Shen, X., Lee, T., Guo, J., Wang, X., Li, P., Xu, P., Wang, Y., Ren, Y., Wang, W., Wang, T., Li, Y., Carn, S. A. and Collett, J. L.: Aqueous phase sulfate production in clouds in eastern China, Atmos. Environ., 62, 502–511, doi:10.1016/j.atmosenv.2012.07.079, 2012.

Sitaraman, R., Ibrahim, S. H. and Kuloor, N. R.: A Generalized Equation for Diffusion in Liquids, J. Chem. Eng. Data, 8(2),
80 198–201, doi:10.1021/je60017a017, 1963.

Worsnop, D. R., Zahniser, M. S., Kolb, C. E., Gardner, J. A., Watson, L. R., Van Doren, J. M., Jayne, J. T. and Davidovits, P.: Temperature dependence of mass accommodation of SO2 and H2O2 on aqueous surfaces, J. Phys. Chem., 93(3), 1159–1172, doi:10.1021/j100340a027, 1989.
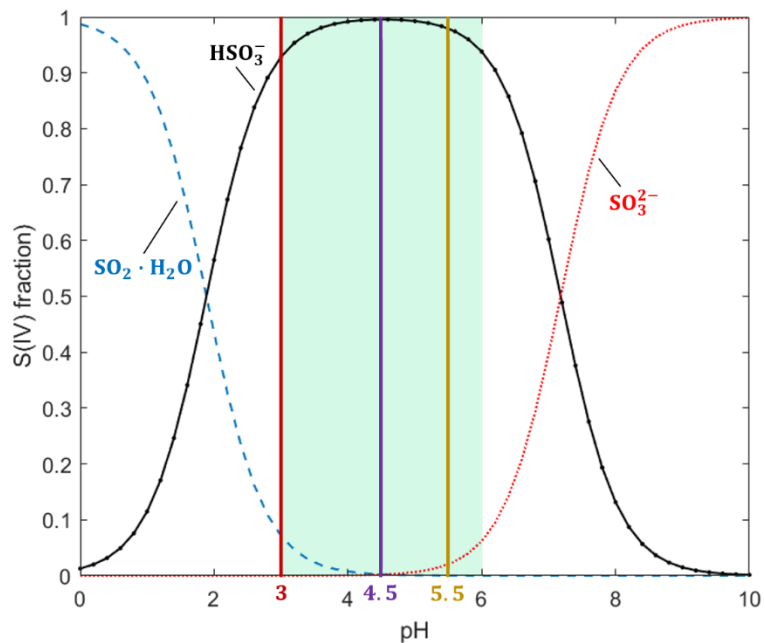
85

Figure S1. Mole fraction concentrations of S(IV) species vs pH. The green shaded area shows the pH range of 3-6 and the three pH values examined in the present work: pH=3 (crimson), pH=4.5 (purple) and pH=5.5 (dark yellow). The dominant form of $SO_{2,aq}$ under these conditions is bisulfite (HSO_3^-) (Seinfeld and Pandis, 2016).
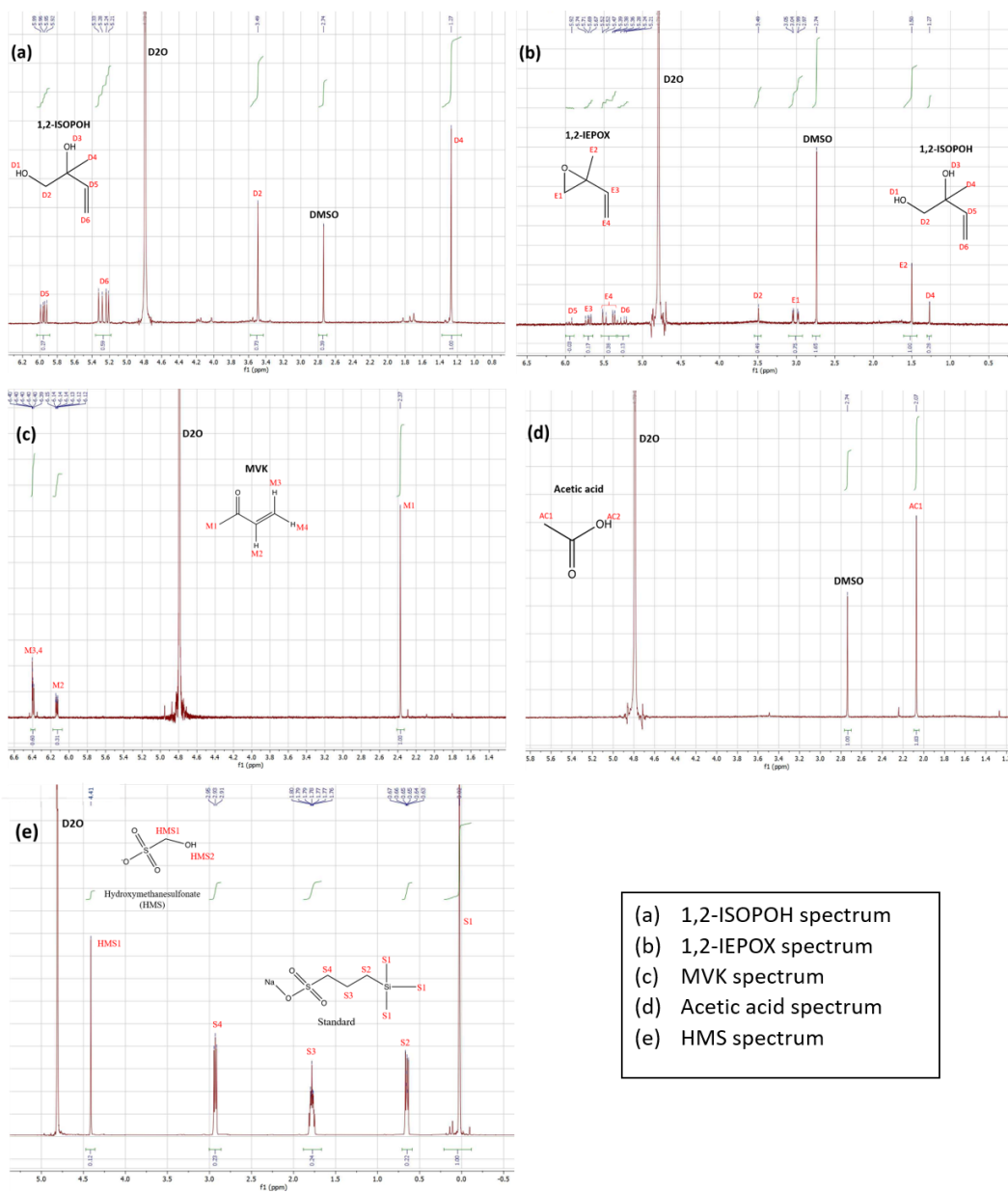
90

Figure S2. Proton NMR spectra (^{1}H-NMR, 400MHz, D$_2$O) of (a) 1,2-ISOPOH, (b) 2-Methyl-2-vinyloxirane, (c) MVK, (d) Acetic acid with DMSO and (e) HMS with standard, 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt. (b)Hydrolysis of the epoxide to the diol was observed in the spectrum. The concentrations of these control samples were [1,2-ISOPOH]=0.1 mM, [2-Methyl-2-vinyloxirane]=0.1 mM, [standard]=4.6 mM, [HMS]=20 mM [DMSO]=0.03 mM and [Acetic acid]=0.1 mM. The labels at each peak represent the hydrogens of the compounds. The samples were at pH=5.5. D2O shift at 4.8 ppm.
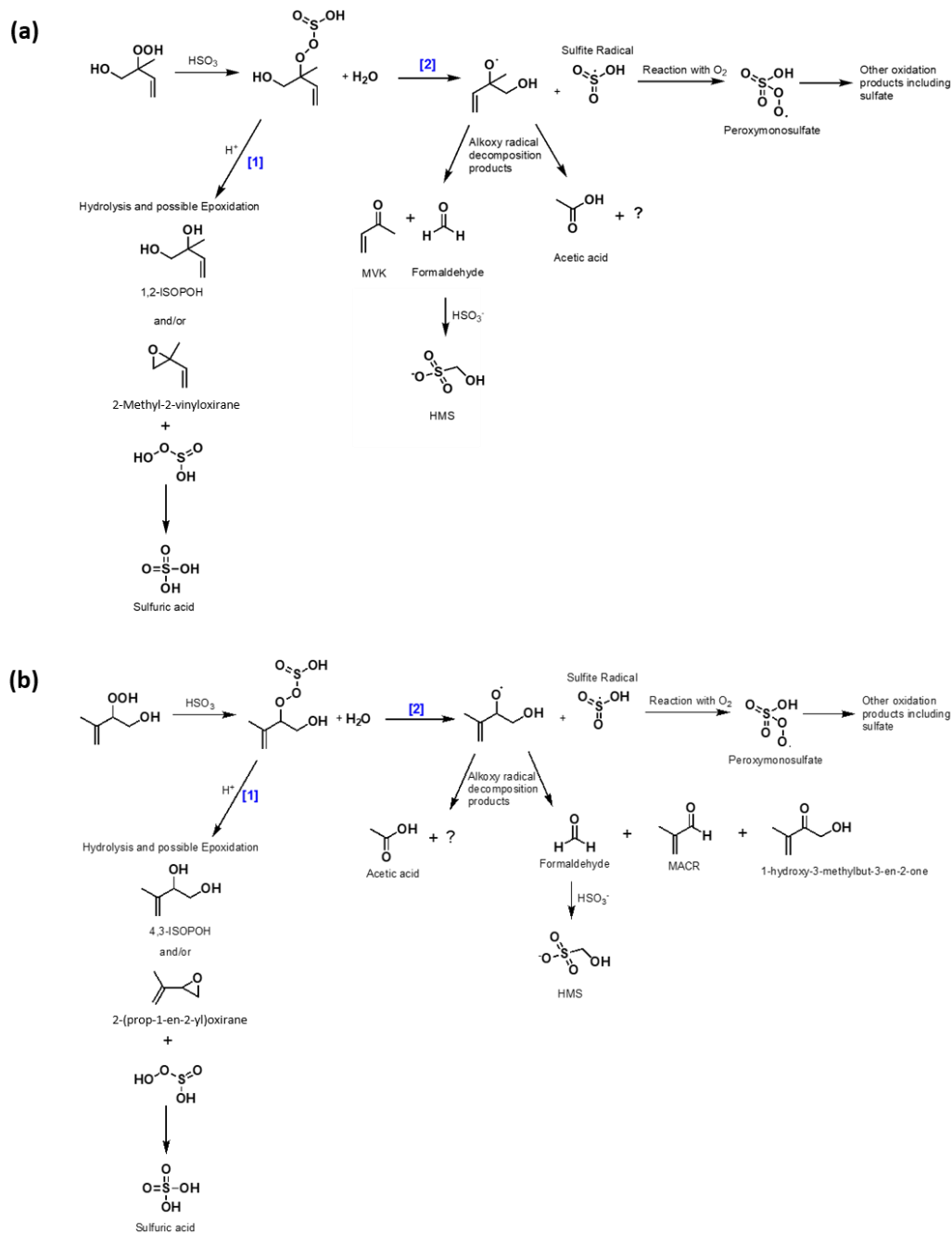
Figure S3. Proposed detailed chemical mechanisms of the oxidation of $SO_{2,aq}$ by a) 1,2-ISOPOOH and b) 4,3-ISOPOOH. There are two competing mechanisms: after ISOPOOH reacts with $SO_{2,aq}$, displacing water, a hydrolysis reaction is taking place [1] or an O-O bond breakage [2]. In mechanism [1], the product hydrolysis results in the same intermediate that the reaction of $SO_{2,aq}$ with H_2O_2 is forming and either a formation of a diol or an epoxide is being generated. In mechanism [2], an alkoxy radical and sulfite radical are formed leading to the production of MVK, MACR, HCHO and other products.

6
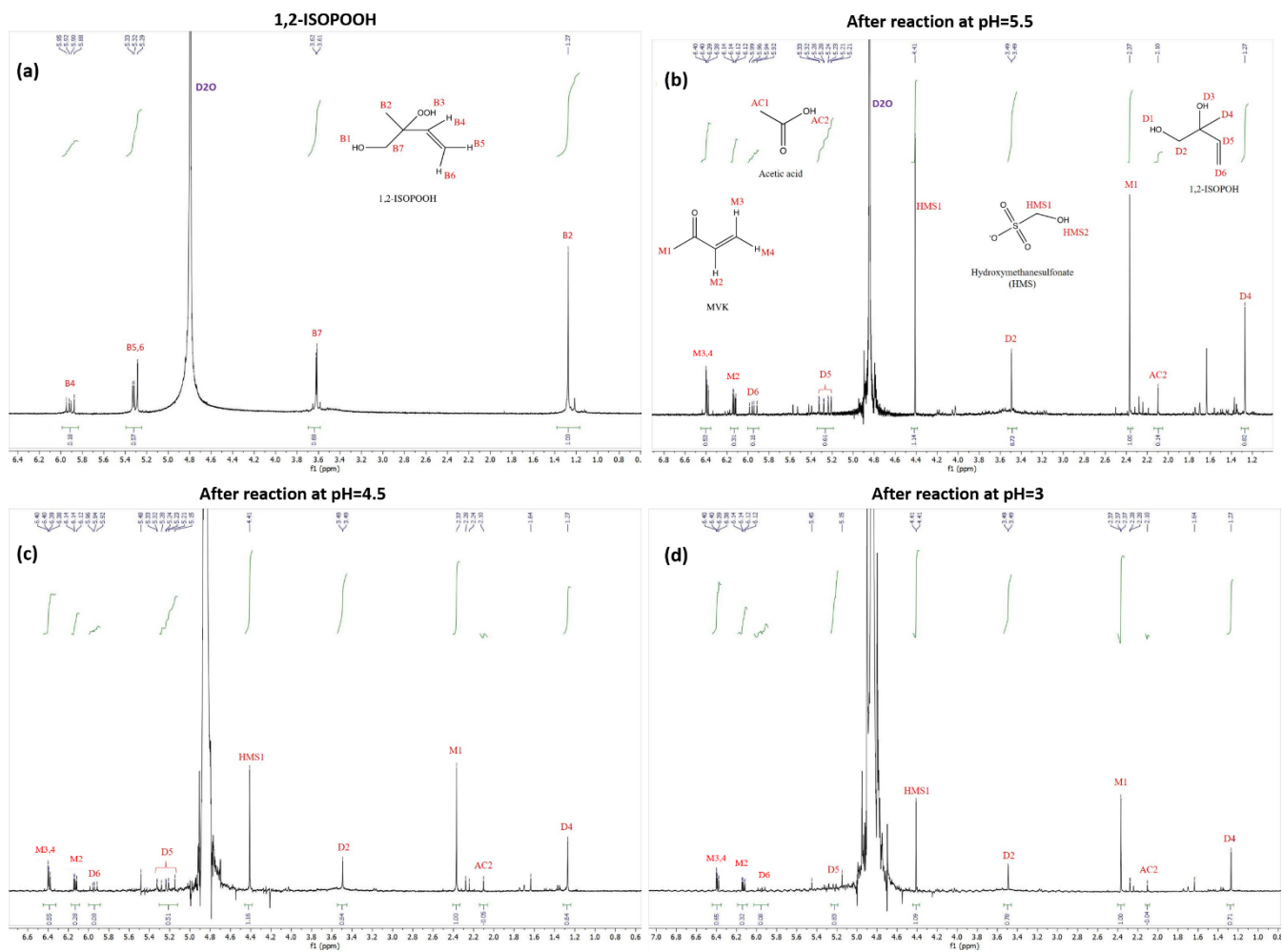
Figure S4. Proton NMR spectra (^{1}H-NMR, 400MHz, D$_2$O) of (a) 1,2-ISOPOOH and the products of the reaction of SO$_{2,aq}$+1,2-ISOPOOH at (b) pH=5.5, (c) pH=4.5 and (d) pH=3. The concentration of 1,2-ISOPOOH was 1 mM and the concentration of the diluted SO$_2$, HSO$_3^-$, was 2 mM. The labels at each peak represent the hydrogens of the compounds. D2O shift at 4.8 ppm.

110

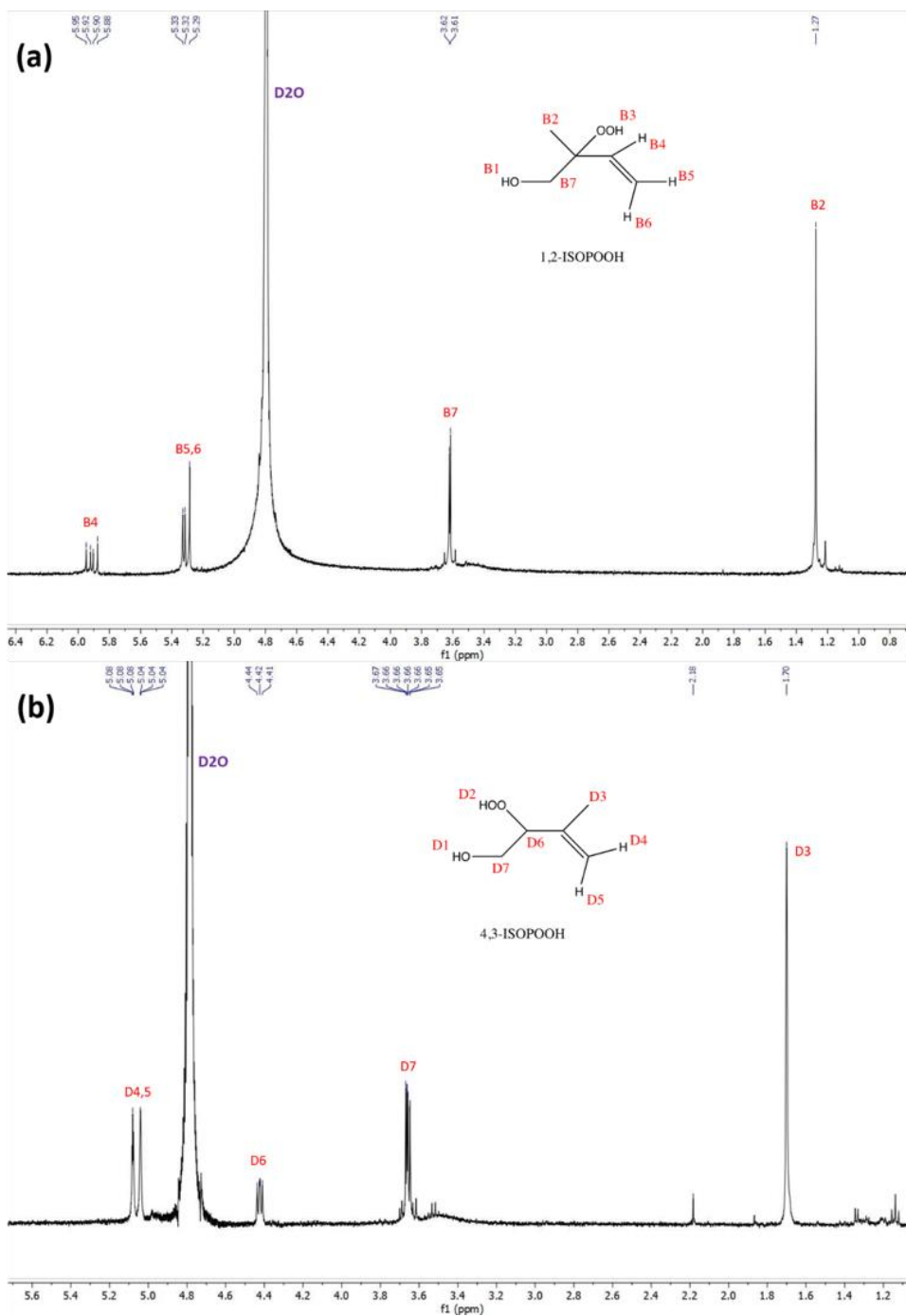**Figure S5. Proton NMR spectra (^{1}H-NMR, 400MHz, D$_2$O) of (a) 1,2-ISOPOOH and (b) 4,3-ISOPOOH. The concentration of both ISOPOOH isomers was 1 mM and the pH of the samples was pH=5.5. The labels at each peak represent the hydrogens of the compounds. D2O shift at 4.8 ppm.**

Table S1. Shifts and peak integration of 1,2-ISOPOOH and the products of HSO_3^-+1,2-ISOPOOH at the pH range of 3-6. D2O shift at 4.8 ppm. The standards used was 0.5 mM of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt ($(CH_3)_3Si(CH_2)_3SO_3Na$) and 0.1 mM DMSO.

	Standard $(CH_3)_3Si(CH_2)_3SO_3Na$				1,2-ISOPOOH				MVK			HMS	1,2-ISOPOH				Acetic Acid
	S1	S2	S3	S4	B4	B5,6	B7	B2	M1	M3,4	M2	HMS1	D4	D2	D6	D5	AC1
Shift (ppm)	0.02	0.63-0.67	1.76-1.80	2.91-2.95	5.88-5.95	5.29-5.33	3.61-3.62	1.27	2.37	6.38-6.40	6.12-6.14	4.41	1.27	3.49	5.21-5.33	5.92-5.99	2.10
Integration pH=5.5	1	0.22	0.24	0.23	0.22	0.47	0.42	0.68	0.20	0.13	0.07	0.13	0.15	0.10	0.10	0.05	0.03
Integration pH=4.5	1	0.22	0.24	0.23	0.26	0.45	0.40	0.67	0.13	0.10	0.04	0.09	0.09	0.06	0.05	0.03	0.00
Integration pH=3.0	1	0.22	0.24	0.23	0.23	0.44	0.43	0.65	0.13	0.10	0.04	0.10	0.11	0.07	0.08	0.04	0.01

	Standard $(CH_3)_2SO$ DMSO	1,2-ISOPOOH				MVK			HMS	1,2-ISOPOH				Acetic Acid
		B4	B5,6	B7	B2	M1	M3,4	M2	HMS1	D4	D2	D6	D5	AC1
Shift (ppm)	2.74	5.88-5.95	5.29-5.33	3.61-3.62	1.27	2.37	6.38-6.40	6.12-6.14	4.41	1.27	3.49	5.21-5.33	5.92-5.99	2.10
Integration pH=5.5	1	1.67	3.22	3.01	4.98	1.50	0.95	0.50	1.05	1.10	0.73	0.81	0.44	0.23
Integration pH=4.5	1	1.67	3.22	3.01	4.98	1.00	0.63	0.33	0.70	0.71	0.47	0.51	0.28	0.02
Integration pH=3.0	1	1.67	3.22	3.01	4.98	1.00	0.63	0.34	0.81	0.79	0.53	0.59	0.32	0.05