Supplement for

Atmospheric fate of organosulfates through gas-phase and aqueous-phase reaction with hydroxyl radicals: implications in inorganic sulfate formation

Narcisse Tsona Tchinda[1], Xiaofan Lv[1], Stanley Numbonui Tasheh[2], Julius Numbonui Ghogomu[2,3], Lin Du[1]

[1]Qingdao Key Laboratory for Prevention and Control of Atmospheric Pollution in Coastal Cities, Environment Research Institute, Shandong University, Qingdao, 266237, China

[2]Department of Chemistry, Faculty of Science, The University of Bamenda, P.O. Box 39 Bambili-Bamenda, Cameroon

[3]Research Unit of Noxious Chemistry and Environmental Engineering, Department of Chemistry, Faculty of Science, University of Dschang, P.O. Box 67 Dschang, Cameroon

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

Table S1: Electronic energy changes (*ΔE*) and Gibbs free energy changes (*ΔG*) for all intermediate species in the reaction of $H_2C^{\bullet}$-O-$SO_3H\cdots(H_2O)_{n+1}$ with NO_2. Energy units are kcal mol^{-1}. "RC" stands for intermediate reactant complex, "TS" stands for transition state, "PD" stands for product, "w" stands for water.

$H_2C^{\bullet}$-O-$SO_3H\cdots(H_2O)_{n+1}$ + NO_2 ↔ RC2-nw → TS2-nw → PD2-nw ($ON\cdots HSO_4^{\bullet}\cdots CH_2O\cdots(H_2O)_{n+1}$)

Species	***ΔG***	***ΔE***
n = 1		
RC2-1w	-54.85	-63.59
TS2-1w	18.55	11.94
PD2-1w	-52.45	-55.63
n = 2		
RC2-2w	-53.57	-63.48
TS2-2w	20.90	17.20
PD2-2w	-52.45	-54.56

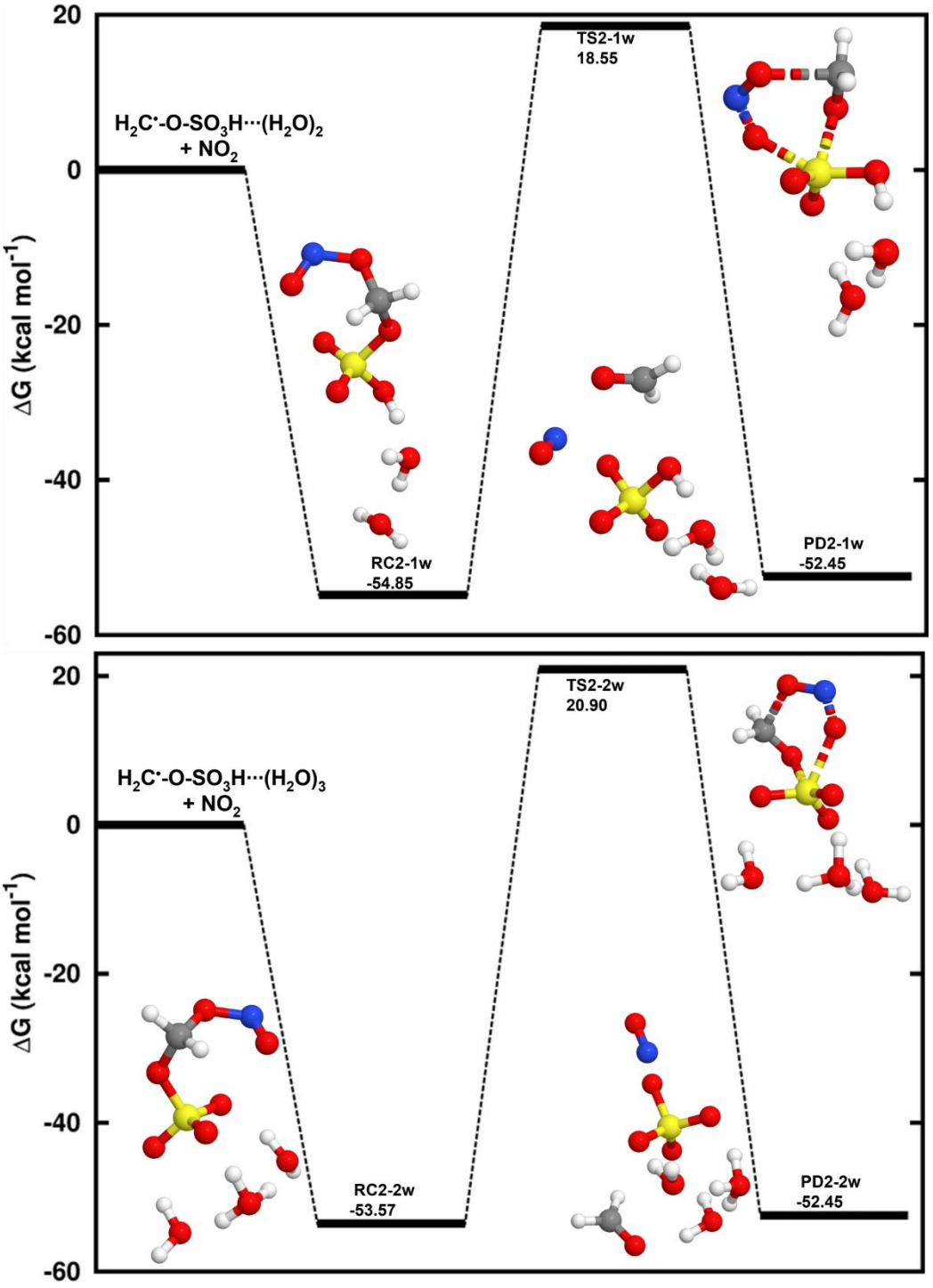

Figure S1 Gibbs free energy changes (in kcal mol^{-1}) and optimized structures of all stationary states in the reaction of $H_2C^{\bullet}$-O-$SO_3H\cdots(H_2O)_{2\text{-}3}$ with NO_2. The sulfur atom is in yellow, the oxygen atom is in red, the nitrogen atom is in blue, the carbon atom is in gray, and the hydrogen atom is in white. "RC" stands for intermediate reactant complex, "TS" stands for transition state, "PD" stands for product, "nw" stands for the number of added water molecules to the reaction of methyl sulfate with $HO^{\bullet}$ radicals.

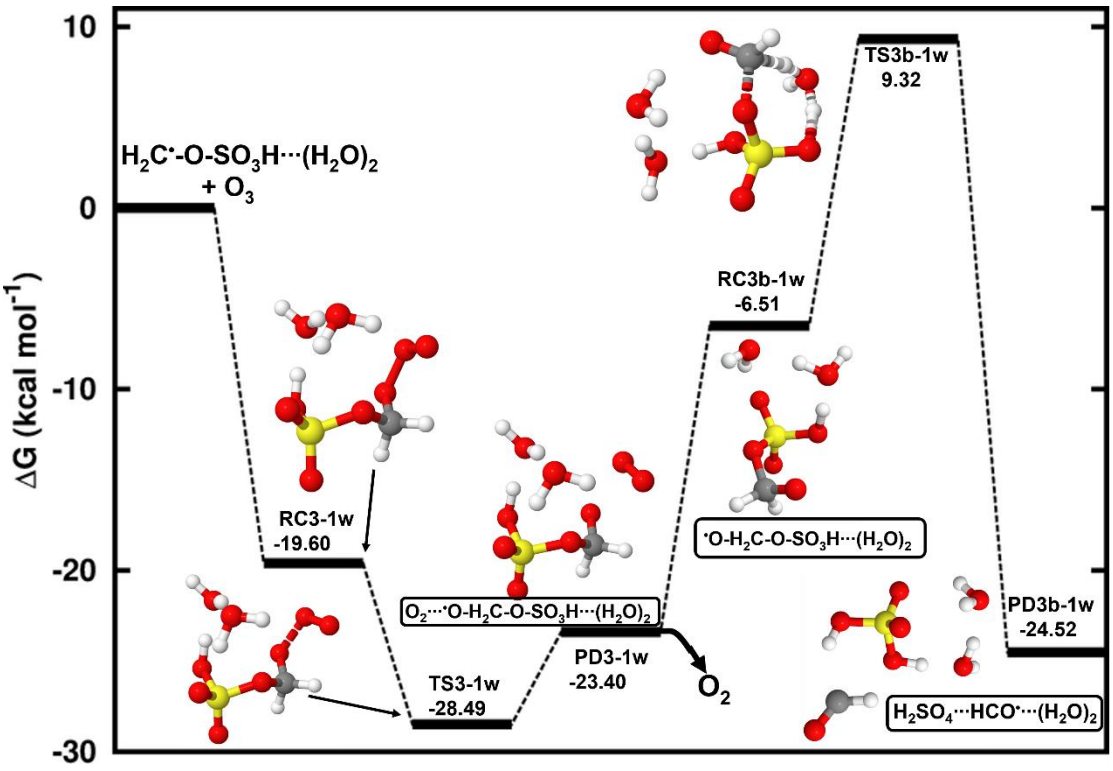

Figure S2 Gibbs free energy changes (in kcal mol^{-1}) and optimized structures for all intermediates in the reaction of $H_2C^{\bullet}$-O-SO_3H···$(H_2O)_2$ with O_3. The sulfur atom is in yellow, the oxygen atom is in red, the nitrogen atom is in blue, the carbon atom is in gray, and the hydrogen atom is in white.

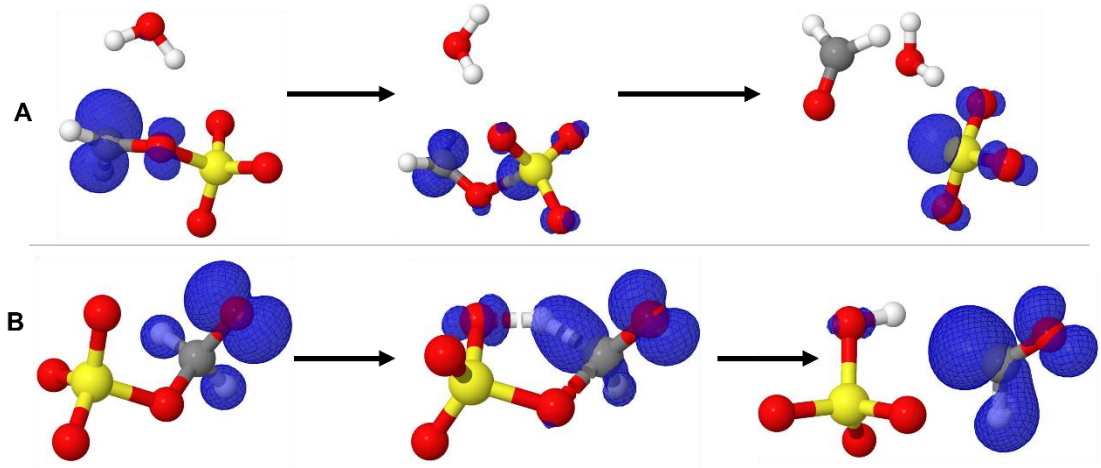

Figure S3 Representation of the spin density (blue color) on the electronic states of the decomposition of (A) $H_2C^{\bullet}$-O-SO_3^- and (B) $^{\bullet}O$-H_2C-O-SO_3^-. From left to right are the reactant, transition state and product complex, respectively. The sulfur atom is in yellow, the oxygen atom is in red, the nitrogen atom is in blue, the carbon atom is in gray, and the hydrogen atom is in white.

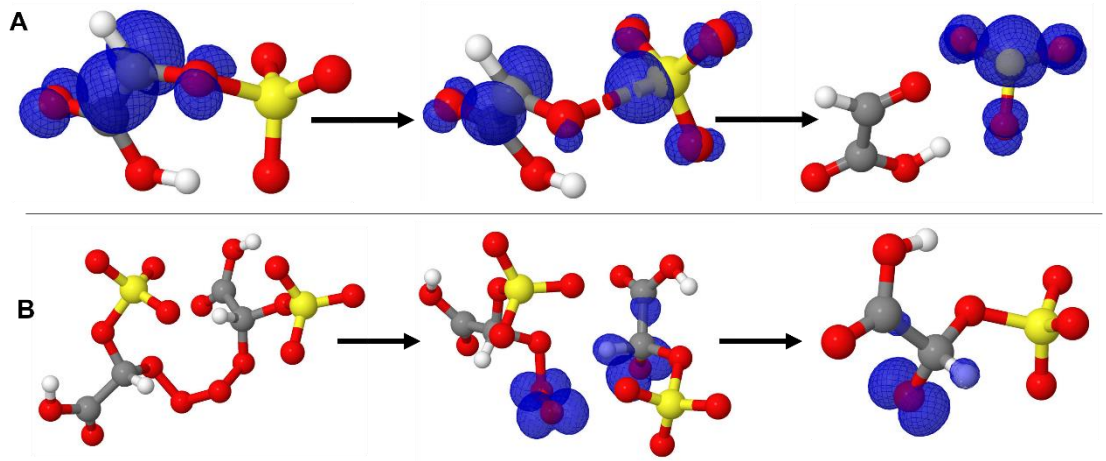

Figure S4 Representation of the spin density (blue color) on the electronic states of the decomposition of (A) HOOC-CH•-O-SO_3^- (where from left to right are the reactant, transition state and the product complex, respectively) and (B) O_3^-S-O-CH(COOH)-OO-OO-CH(COOH)-O-SO_3^- (where from left to right are the singlet state, triplet state and the decomposition product, respectively). The sulfur atom is in yellow, the oxygen atom is in red, the nitrogen atom is in blue, the carbon atom is in gray, and the hydrogen atom is in white.