

**Supplementary Materials for**

**Catalytic sulfate formation mechanism influenced by important**

**constituents of cloud water via the reaction of SO<sub>2</sub> oxidized by**

**hypobromic acid in marine areas**

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**Contents**

Section 1. Theoretical method .....	3
1.1 Aqueous concentration of S(IV) .....	3
1.2 Aqueous concentration of hypobromic acid .....	3
Section 2. Figures .....	5
Section 3. Results.....	13
3.1 The reaction rates between HOBr and HOSO <sub>2</sub> <sup>-</sup> leading to sulfate formation. 13	
3.1.1 The reaction rate via Pathway 1(HOBr + HOSO <sub>2</sub> <sup>-</sup> ) .....	13
3.1.2 The reaction rate via Pathway 2(HOBr + HOSO <sub>2</sub> <sup>-</sup> ) .....	15
3.1.3 S(IV) oxidation rates, related reaction rate constants and S(IV) lifetimes through Pathway 1(HOBr + HOSO <sub>2</sub> <sup>-</sup> ) and Pathway 2(HOBr + HOSO <sub>2</sub> <sup>-</sup> ) .....	17
3.2 The reaction rates between HOBr and SO <sub>3</sub> <sup>2-</sup> leading to sulfate formation .....	19
3.2.1 The reaction rate via Pathway 1(HOBr + SO <sub>3</sub> <sup>2-</sup> ) .....	19
3.2.2 The reaction rate via Pathway 2(HOBr + SO <sub>3</sub> <sup>2-</sup> ) .....	23
3.2.3 S(IV) oxidation rates, related reaction rate constants and S(IV) lifetimes through Pathway 1(HOBr + SO <sub>3</sub> <sup>2-</sup> ) and Pathway 2(HOBr + SO <sub>3</sub> <sup>2-</sup> ) .....	24
3.3 The reaction rates between OBr <sup>-</sup> and SO <sub>3</sub> <sup>2-</sup> leading to sulfate formation .....	27

3.3.1 The reaction rate via Pathway 1(OBr <sup>-</sup> and SO <sub>3</sub> <sup>2-</sup> ).....	27
3.3.2 The reaction rate via Pathway 2(OBr <sup>-</sup> and SO <sub>3</sub> <sup>2-</sup> ).....	32
3.3.3 S(IV) oxidation rates, related reaction rate constants and S(IV) lifetimes through Pathway 1(OBr <sup>-</sup> + SO <sub>3</sub> <sup>2-</sup> ) and Pathway 2(OBr <sup>-</sup> + SO <sub>3</sub> <sup>2-</sup> ).....	34
<b>Section 4. Cartesian coordinates of the structures.....</b>	<b>36</b>
4.1 Cartesian coordinates of the structures involving in the reaction of HOBr with HOSO <sub>2</sub> <sup>-</sup> .....	36
4.2 Cartesian coordinates of the structures involving in the reaction of HOBr with SO <sub>3</sub> <sup>2-</sup> .....	42
4.3 Cartesian coordinates of the structures involving in the reaction of OBr <sup>-</sup> with SO <sub>3</sub> <sup>2-</sup> .....	46

## Section 1. Theoretical method

### 1.1 Aqueous concentration of S(IV)

For reactant S(IV), the ratio of the distribution of different forms ( $\text{HOSO}_2^-$ ,  $\text{SO}_3^{2-}$ ) is important for identifying the possible oxidation reaction, and thus should be calculated. The corresponding computational methods about the ratio of the distribution of different forms ( $\text{HOSO}_2^-$ ,  $\text{SO}_3^{2-}$ ) has been discussed in our previous work.<sup>1</sup>

### 1.2 Aqueous concentration of hypobromic acid

For the reactant HOBr, the aqueous [HOBr] can also estimate based on the gas-phase mixing ratio using Henry's law

$$[\text{HOBr}] = p(\text{HOBr}) \times H(\text{HOBr}) \quad (1)$$

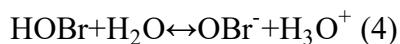
where  $p(\text{HOBr})$  is the partial pressure of HOBr in the gas phase and  $H(\text{HOBr})$  is the Henry's constant which has been measured from laboratory experiment and reported to be about  $1900 \text{ M}^1 \text{atm}^{-1}$ .<sup>2</sup>

Moreover, according to measurement results, the gas phase ground-level mixing ratio HOBr varies between about 0.01 ppbv and 0.310 ppbv. The corresponding partial pressures  $p(\text{HOBr})$  are  $1.00 \times 10^{-11} \text{ atm}$ - $3.10 \times 10^{-10} \text{ atm}$

$$[\text{HOBr}] = 1.00 \times 10^{-11} \text{ atm} \times 1900 \text{ M}^1 \text{atm}^{-1} = 1.90 \times 10^{-8} \text{ M} \quad (2)$$

$$[\text{HOBr}] = 3.10 \times 10^{-10} \text{ atm} \times 1900 \text{ M}^1 \text{atm}^{-1} = 5.89 \times 10^{-7} \text{ M} \quad (3)$$

we thus obtain a range of  $1.90 \times 10^{-8}$ - $5.89 \times 10^{-7} \text{ M}$  for [HOBr]. The concentration of  $\text{OBr}^-$  anion can be obtained from the equilibrium expression:



$$\frac{[\text{HOBr}]}{[\text{OBr}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{a3}} \quad (5)$$

$$[\text{OBr}^-] = K_{a3} \times [\text{HOBr}] / [\text{H}_3\text{O}^+] \quad (6)$$

where  $K_{a3}$  ( $10^{-8.9}$ ) is the acidity constant for HOBr. Concentrations of  $\text{OBr}^-$  corresponding to the [HOBr] range given above at different pH are shown in Table S2.

The distributions fraction of the two anions can be computed as:

$$\delta_{\text{HOBr}} = [\text{HOBr}] / ([\text{HOBr}] + [\text{OBr}^-]) \quad (7)$$

$$= [\text{HOBr}]/([\text{HOBr}] + K_{a3} \times [\text{HOBr}]/[\text{H}_3\text{O}^+]) \quad (8)$$

$$= 1/(1 + K_{a3}/[\text{H}_3\text{O}^+]) = [\text{H}_3\text{O}^+]/([\text{H}_3\text{O}^+] + K_{a3}) \quad (9)$$

$$\delta_{\text{OBr}^-} = [\text{OBr}^-]/([\text{HOBr}] + [\text{OBr}^-]) \quad (10)$$

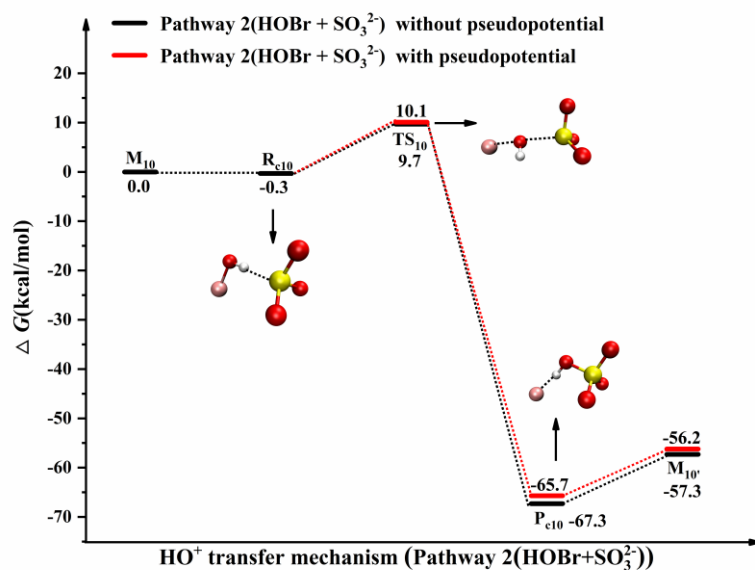
$$= [\text{OBr}^-]/([\text{OBr}^-] + [\text{H}_3\text{O}^+] \times [\text{OBr}^-]/K_{a3}) \quad (11)$$

$$= 1/(1 + [\text{H}_3\text{O}^+]/K_{a3}) = K_{a3}/([\text{H}_3\text{O}^+] + K_{a3}) \quad (12)$$

Table S1. Calculated aqueous  $[\text{OBr}^-]$  under the different aqueous  $[\text{HOBr}]$  ( $[\text{HOBr}] = 1.90 \times 10^{-8} \text{ M}$  and  $[\text{HOBr}] = 5.89 \times 10^{-7} \text{ M}$ ) and pH.

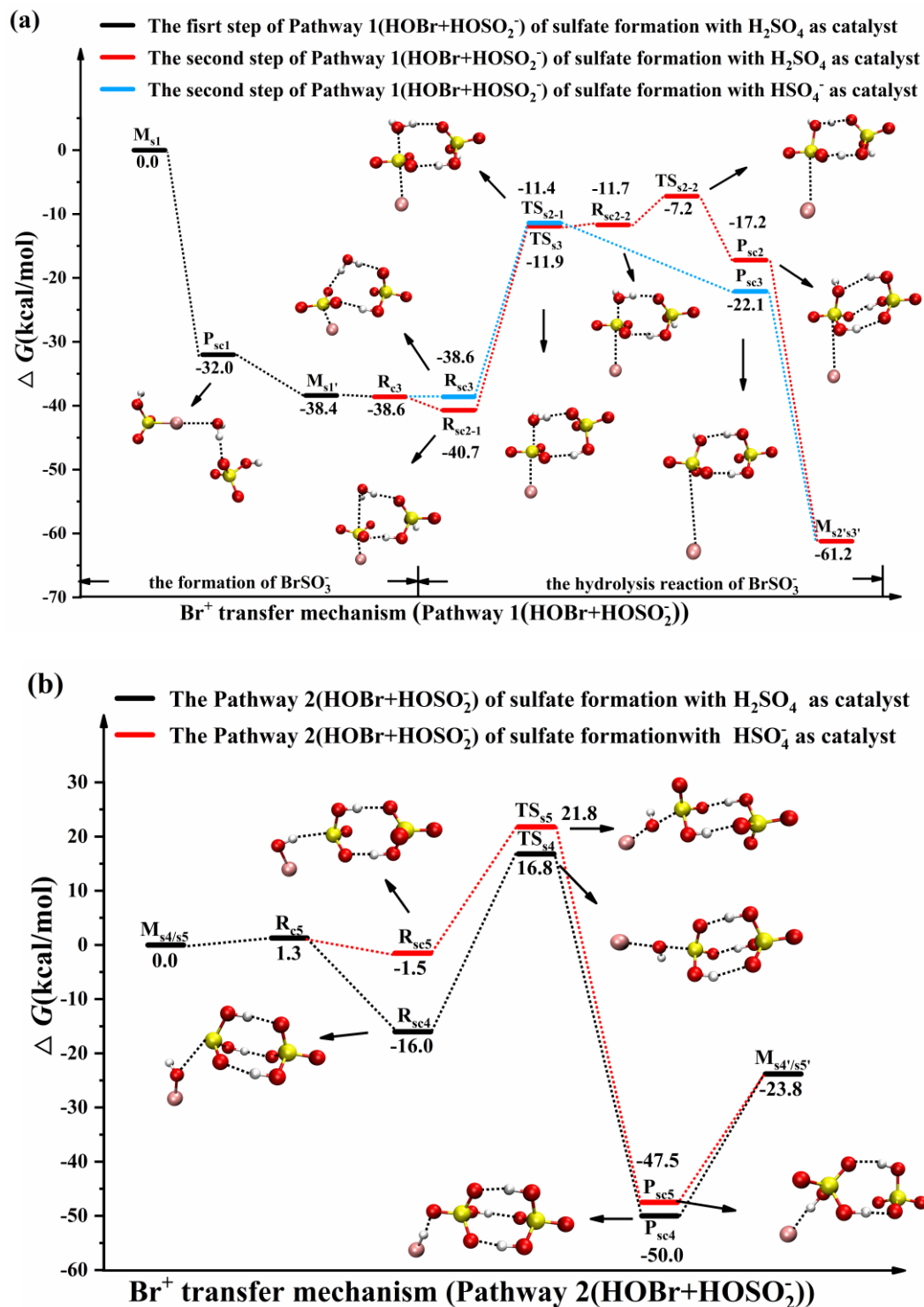
pH	$[\text{OBr}^-]$	$[\text{OBr}^-]$
3	$2.39 \times 10^{-14}$	$7.42 \times 10^{-13}$
4	$2.39 \times 10^{-13}$	$7.42 \times 10^{-12}$
5	$2.39 \times 10^{-12}$	$7.42 \times 10^{-11}$
6	$2.39 \times 10^{-11}$	$7.42 \times 10^{-10}$
6.97	$2.23 \times 10^{-10}$	$6.92 \times 10^{-9}$
7	$2.39 \times 10^{-10}$	$7.42 \times 10^{-9}$
7.5	$2.39 \times 10^{-9}$	$7.42 \times 10^{-8}$
8	$1.90 \times 10^{-8}$	$5.89 \times 10^{-7}$
9	$2.39 \times 10^{-8}$	$7.42 \times 10^{-7}$

## Section 2. Figures



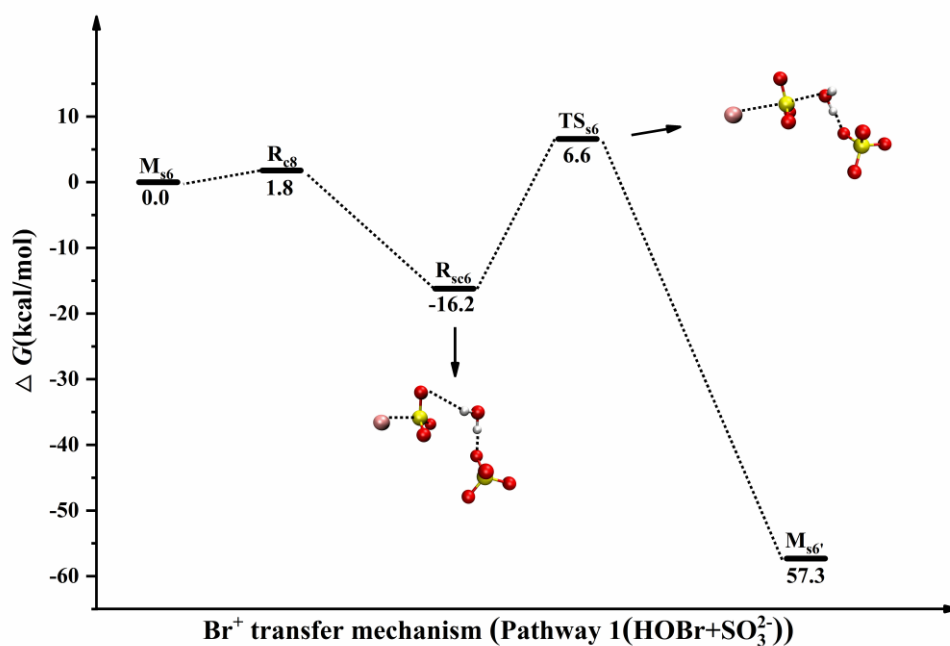
**Fig. S1** The Gibbs free energy profile (kcal/mol, at 298.15 K and a reference concentration of 1 mol/L) for the reaction of HOBr with SO<sub>3</sub><sup>2-</sup> through Pathway 2(HOBr + SO<sub>3</sub><sup>2-</sup>) at the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G (3df, 3pd) level of theory with or without pseudopotential. Solvent corrections are included in the M06-2X calculations using the SMD model. The white, pink, red, and yellow spheres represent H, Br, O, and S atoms, respectively.

In order to investigate the effect of pseudopotential on the reactions studied in the present work, we calculated the energy barrier of Pathway 2 between HOBr and SO<sub>3</sub><sup>2-</sup>, the most competitive mechanism in the studied system, with and without pseudopotential. As shown in Fig. S1, the reaction energy barrier with pseudopotential at the M06-2X/6-311++G(3df,3pd)//DLPNO-CCSD(T)/aug-cc-pVTZ (aug-cc-pVTZ-PP for the optimization of Br) level of theory is 10.4 kcal/mol, and that without pseudopotential at the M06-2X/6-311++G(3df,3pd)//DLPNO-CCSD(T)/aug-cc-pVTZ level of theory is 10.0 kcal/mol, with a low deviation of 0.4 kcal/mol. It is suggested that the effect of ignoring pseudopotential on the reaction energy barrier is very unobvious.

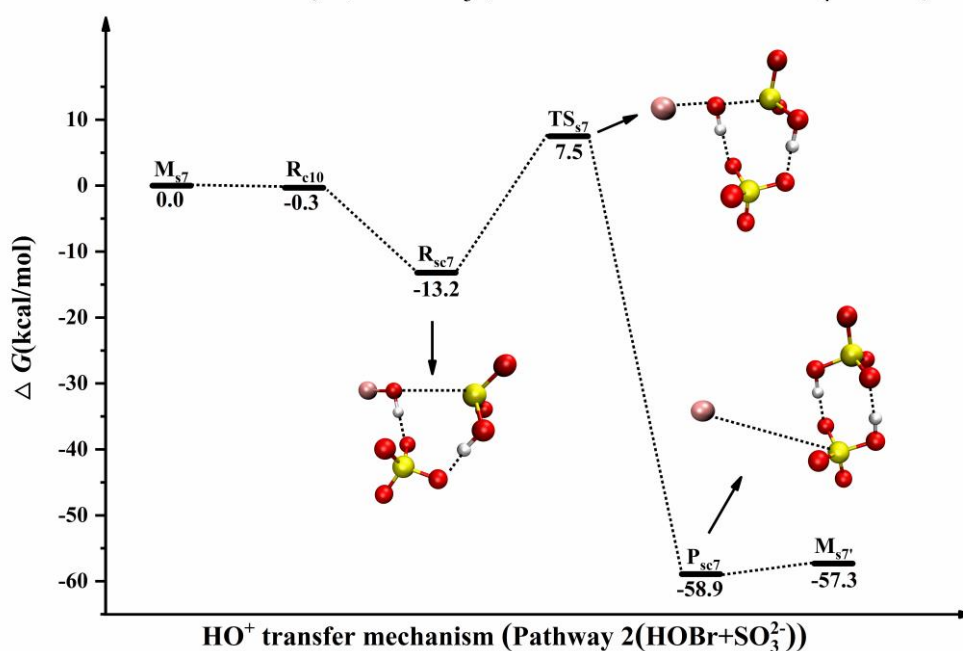


**Fig. S2** The Gibbs free energy profile (kcal/mol, at 298.15 K and a reference concentration of 1 mol/L) for the reaction of HOBr with HOSO<sub>2</sub><sup>-</sup> through (a) Pathway 1(HOBr + HOSO<sub>2</sub><sup>-</sup>) and (b) Pathway 2(HOBr + HOSO<sub>2</sub><sup>-</sup>) at the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G (3df, 3pd) level of theory. Solvent corrections are included in the M06-2X calculations using the SMD model. The white, pink, red, and yellow spheres represent H, Br, O, and S atoms, respectively.

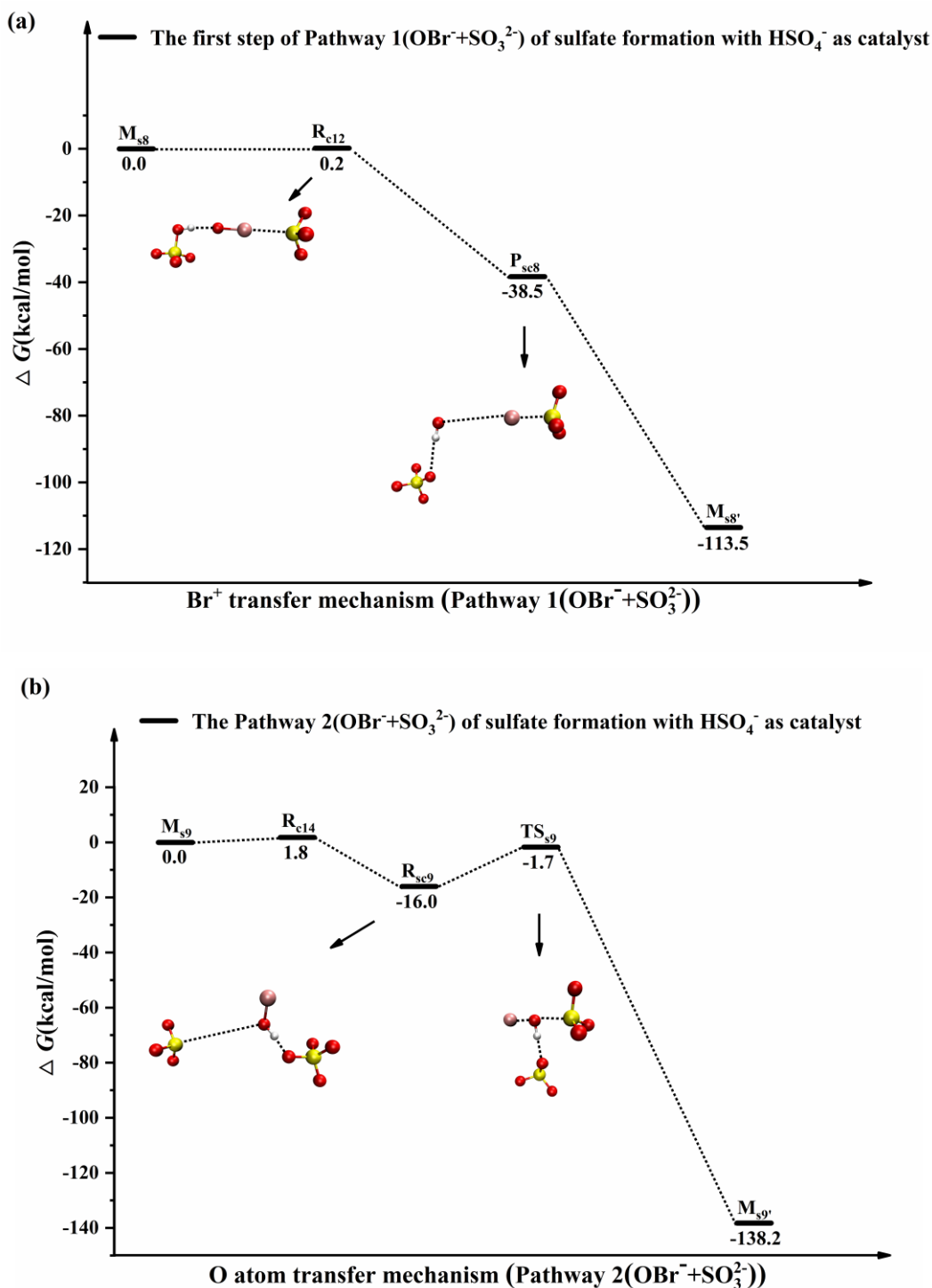
(a) — The second step of Pathway 1( $\text{HOBr} + \text{SO}_3^{2-}$ ) of sulfate formation with  $\text{HSO}_4^-$  as catalyst



(b) — The Pathway 2( $\text{HOBr} + \text{SO}_3^{2-}$ ) of sulfate formation with  $\text{HSO}_4^-$  as catalyst



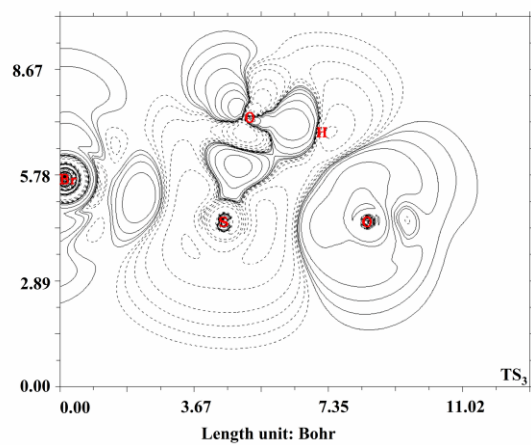
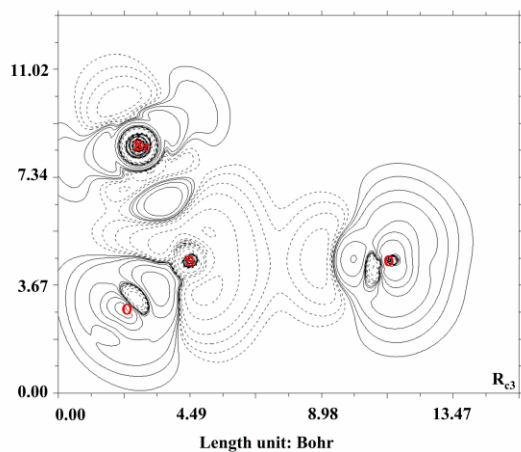
**Fig. S3** The Gibbs free energy profile (kcal/mol, at 298.15 K and a reference concentration of 1 mol/L) for the reaction of HOBr with  $\text{SO}_3^{2-}$  through (a) Pathway 1( $\text{HOBr} + \text{SO}_3^{2-}$ ) and (b) Pathway 2( $\text{HOBr} + \text{SO}_3^{2-}$ ) at the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G (3df, 3pd) level of theory. Solvent corrections are included in the M06-2X calculations using the SMD model. The white, pink, red, and yellow spheres represent H, Br, O, and S atoms, respectively.



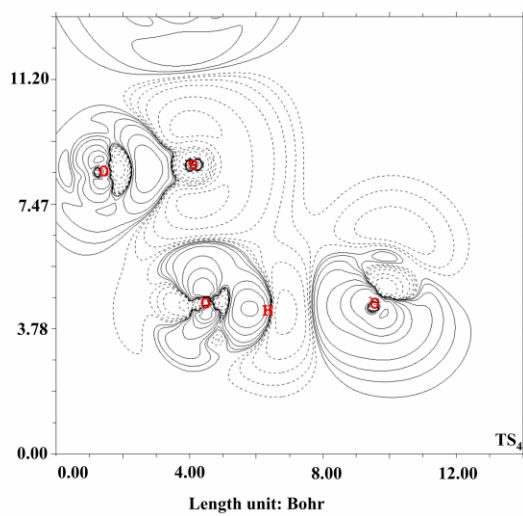
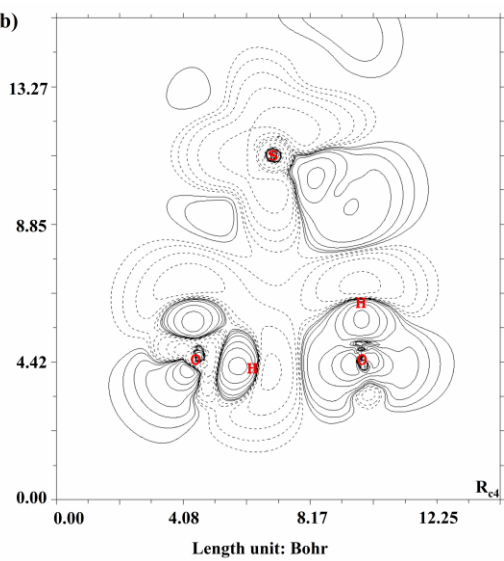
**Fig. S4** The Gibbs free energy profile (kcal/mol, at 298.15 K and a reference concentration of 1 mol/L) for the reaction of  $\text{OBr}^-$  with  $\text{SO}_3^{2-}$  through (a) Pathway 1( $\text{OBr}^- + \text{SO}_3^{2-}$ ) and (b) Pathway 2( $\text{OBr}^- + \text{SO}_3^{2-}$ ) at the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G (3df, 3pd) level of theory. Solvent corrections are included in the M06-2X calculations using the SMD model. The white, pink, red, and yellow spheres represent H, Br, O, and S atoms, respectively.



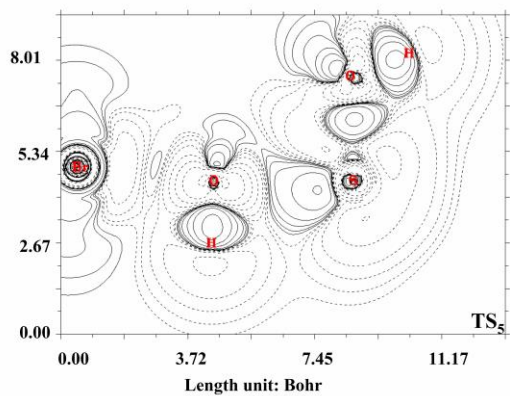
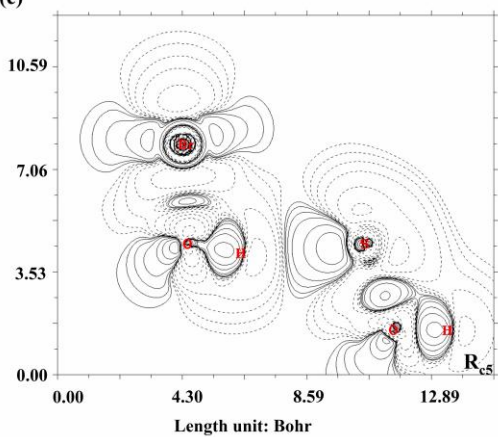
(a)



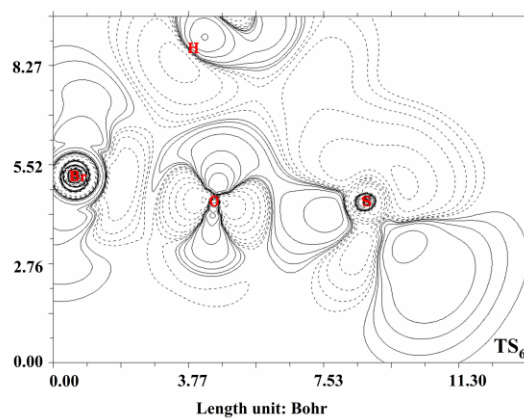
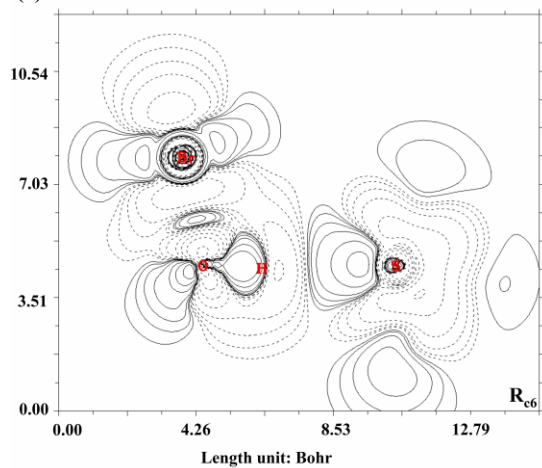
(b)



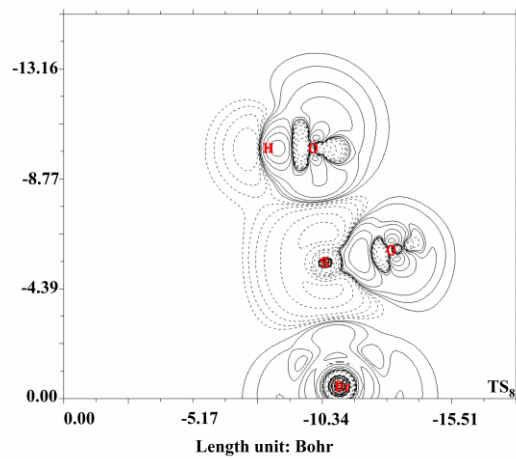
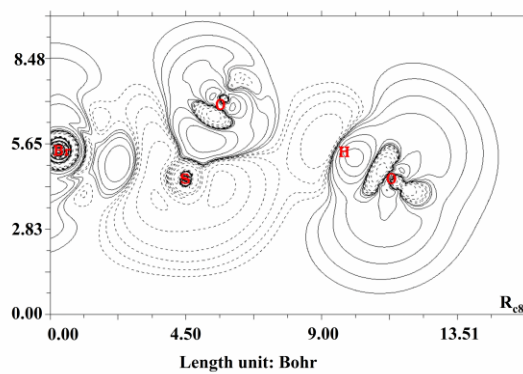
(c)



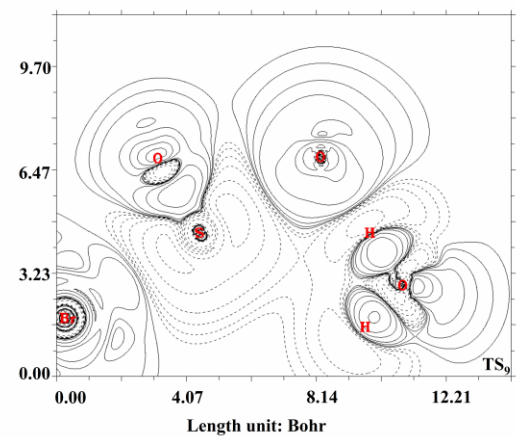
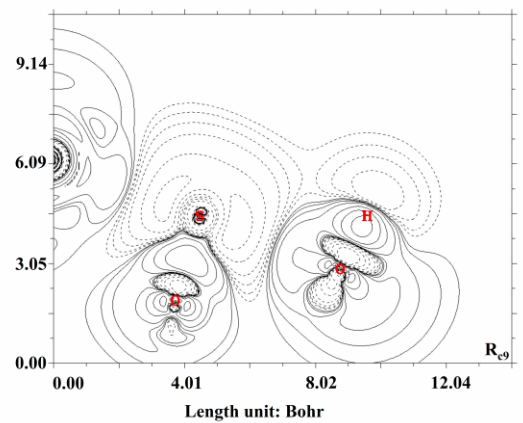
(d)



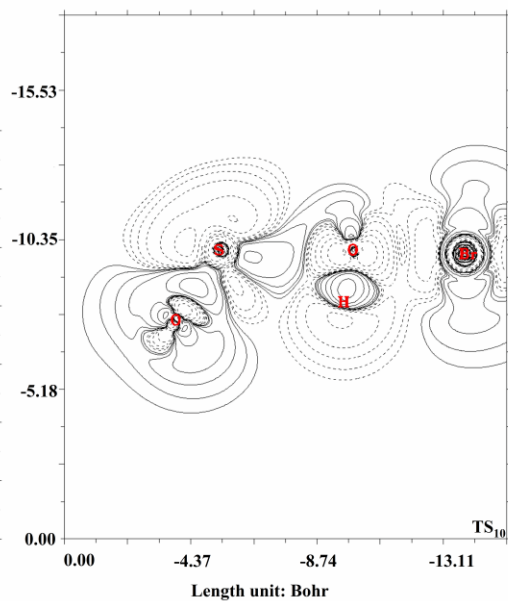
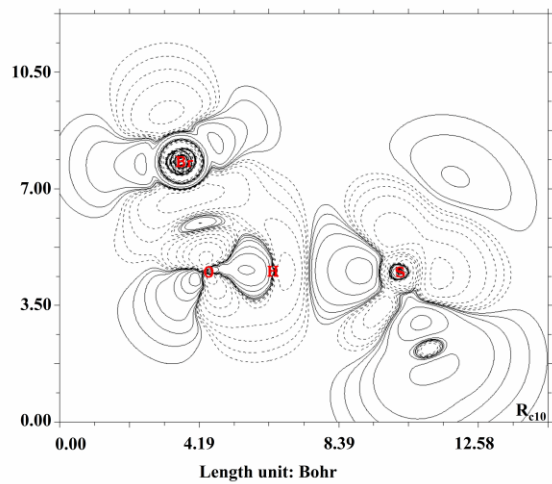
(e)



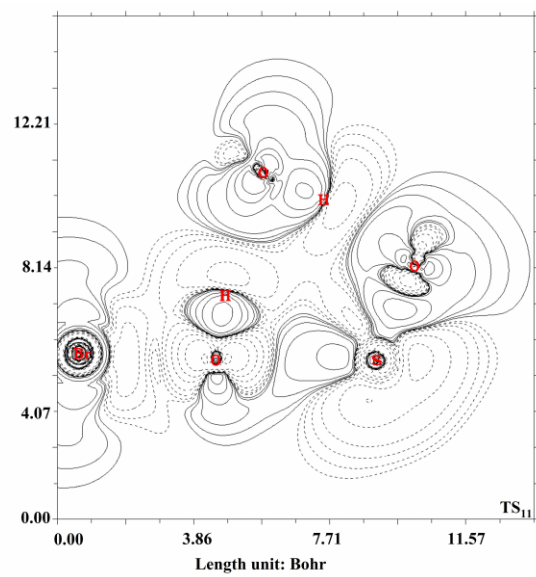
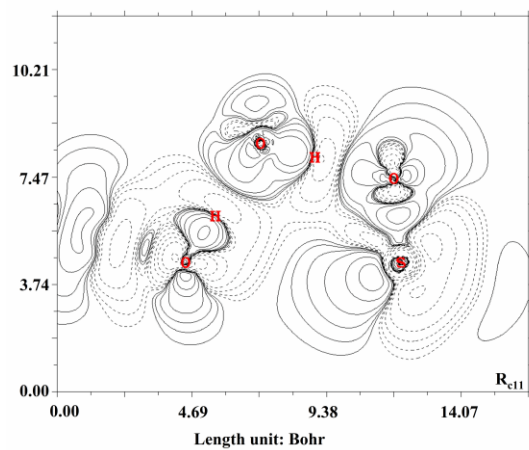
(f)



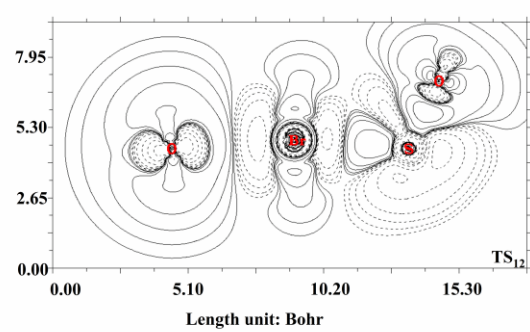
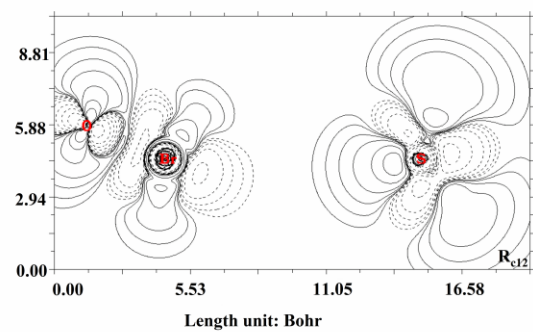
(g)



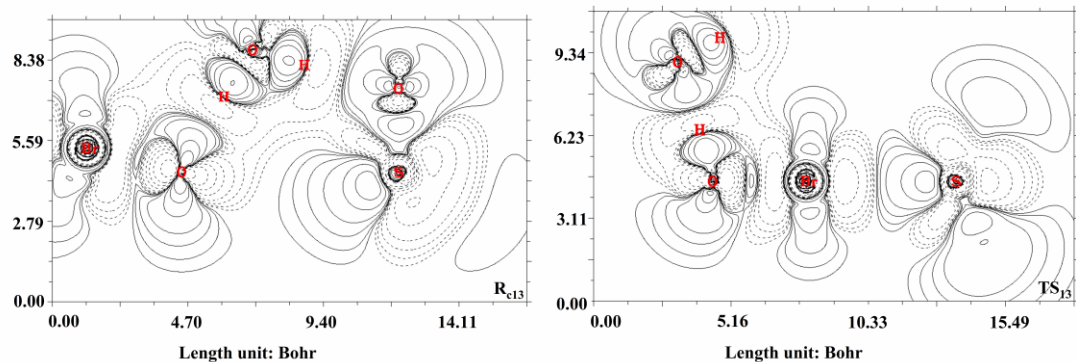
(h)



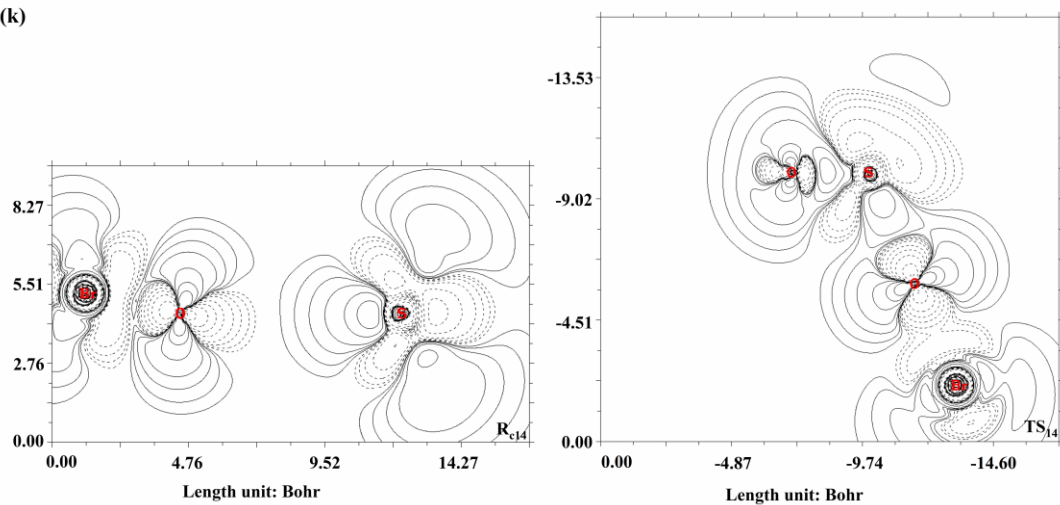
(i)



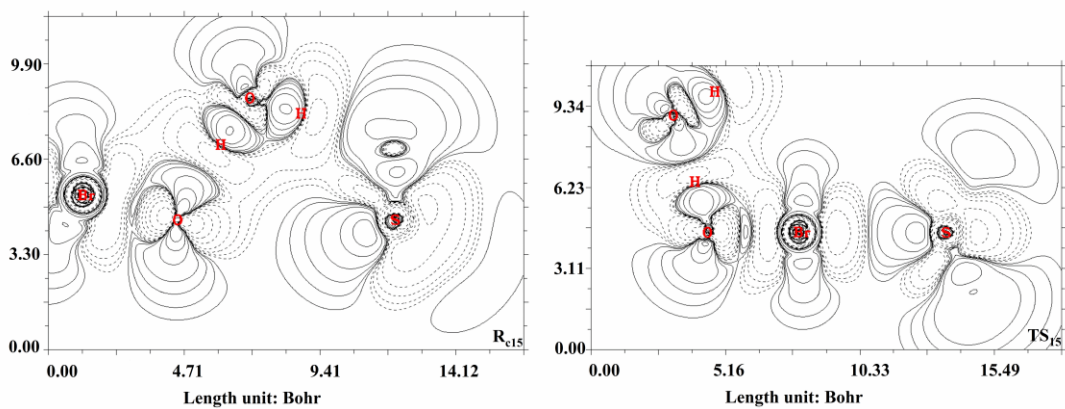
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(k)



(l)



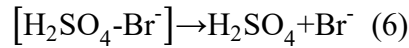
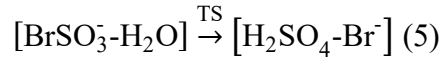
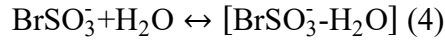
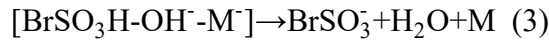
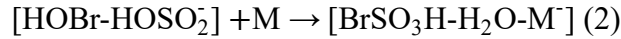
**Fig. S5.** Contour maps of the electron density differences between (a)  $R_{c3}$  and  $TS_3$ , (b)  $R_{c4}$  and  $TS_4$ , (c)  $R_{c5}$  and  $TS_5$  (d)  $R_{c6}$  and  $TS_6$ , (e)  $R_{c8}$  and  $TS_8$ , (f)  $R_{c9}$  and  $TS_9$ , (g)  $R_{c10}$  and  $TS_{10}$ , (h)  $R_{c11}$  and  $TS_{11}$ , (i)  $R_{c12}$  and  $TS_{12}$ , (j)  $R_{c13}$  and  $TS_{13}$ , (k)  $R_{c14}$  and  $TS_{14}$ , (l)  $R_{c15}$  and  $TS_{15}$ . Solid and dashed lines represent areas where electron density increases and decreases, respectively.

## Section 3. Results

### 3.1 The reaction rates between HOBr and HOSO<sub>2</sub><sup>-</sup> leading to sulfate formation

#### 3.1.1 The reaction rate via Pathway 1(HOBr + HOSO<sub>2</sub><sup>-</sup>)

The detailed formation process of sulfate from HOBr and HOSO<sub>2</sub><sup>-</sup> through Pathway 1(HOBr + HOSO<sub>2</sub><sup>-</sup>) is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex, and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the uncatalyzed formation reaction rate ( $v_{1\text{HOBr} + \text{HOSO}_2^-, \text{un}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{1\text{HOBr} + \text{HOSO}_2^-, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_5 [\text{BrSO}_3^- \text{-H}_2\text{O}] \quad (7)$$

$$k_4 [\text{BrSO}_3^-] [\text{H}_2\text{O}] - k_{-4} [\text{BrSO}_3^- \text{-H}_2\text{O}] - k_5 [\text{BrSO}_3^- \text{-H}_2\text{O}] = 0$$

$$[\text{BrSO}_3^- \text{-H}_2\text{O}] = \frac{k_4 [\text{BrSO}_3^-] [\text{H}_2\text{O}]}{k_{-4} + k_5} \quad (7-1)$$

$$k_3 [\text{BrSO}_3\text{H-OH}^- \text{-M}^-] - k_4 [\text{BrSO}_3^-] [\text{H}_2\text{O}] = 0$$

$$[\text{BrSO}_3^-] = \frac{k_3 [\text{BrSO}_3\text{H-OH}^- \text{-M}^-]}{k_4 [\text{H}_2\text{O}]} \quad (7-2)$$

$$k_2 [\text{HOBr-HOSO}_2^-] [\text{M}] - k_3 [\text{BrSO}_3\text{H-OH}^- \text{-M}^-] = 0$$

$$[\text{BrSO}_3\text{H-OH}^- \text{-M}^-] = \frac{k_2 [\text{HOBr-HOSO}_2^-] [\text{M}]}{k_3} \quad (7-3)$$

$$k_1 [\text{HOBr}] [\text{HOSO}_2^-] - k_{-1} [\text{HOBr-HOSO}_2^-] - k_2 [\text{HOBr-HOSO}_2^-] [\text{M}] = 0$$

$$[\text{HOBr-HOSO}_2^-] = \frac{k_1 [\text{HOBr}] [\text{HOSO}_2^-]}{k_{-1} + k_2 [\text{M}]} \quad (7-4)$$

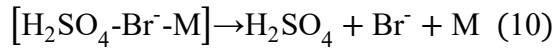
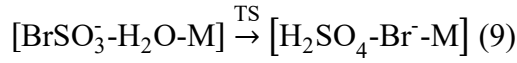
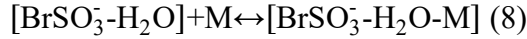
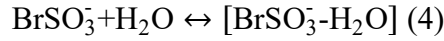
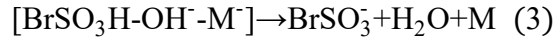
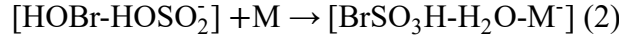
$$v_{1\text{HOBr} + \text{HOSO}_2^-, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_5}{k_{-4} + k_5} \times \frac{k_1 \times k_2}{k_{-1} + k_2 [\text{M}]} \times [\text{HOBr}] [\text{HOSO}_2^-] [\text{M}] \quad (7-5)$$

The pseudo-unimolecular uncatalyzed S(IV) oxidation rates through Pathway 1(HOBr + HOSO<sub>2</sub><sup>-</sup>) can then be written as

$$v_{1\text{HOBr}+\text{HOSO}_2^{\text{un-S(IV)}}} = \frac{k_5}{k_{-4} + k_5} \times \frac{k_1 \times k_2}{k_{-1} + k_2[\text{M}]} \times [\text{HOBr}][\text{M}] \quad (7-6)$$

where  $k_1/k_{-1}$  are the forward/reverse rate coefficients for the reaction 1,  $k_{-4}$  is the reverse rate coefficient for the reaction 4,  $k_2$  is the diffusion rate constant for the reaction 2, and  $k_5$  is the unimolecular rate constants for the uncatalyzed reaction 5. [M] is the concentration of catalyst M.

The catalyzed formation process of sulfate from HOBr and HOSO<sub>2</sub><sup>-</sup> through Pathway 1(HOBr + HOSO<sub>2</sub><sup>-</sup>) is similarly described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the catalyzed formation reaction rate ( $v_{1\text{HOBr}+\text{HOSO}_2^{\text{cat}}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{1\text{HOBr}+\text{HOSO}_2^{\text{cat}}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_9[\text{BrSO}_3^- \text{-H}_2\text{O-M}] \quad (10)$$

$$k_8[\text{BrSO}_3^- \text{-H}_2\text{O}][\text{M}] - k_{-8}[\text{BrSO}_3^- \text{-H}_2\text{O-M}] - k_9[\text{BrSO}_3^- \text{-H}_2\text{O-M}] = 0$$

$$[\text{BrSO}_3^- \text{-H}_2\text{O-M}] = \frac{k_8[\text{BrSO}_3^- \text{-H}_2\text{O}][\text{M}]}{k_{-8} + k_9} \quad (11-1)$$

$$k_4[\text{BrSO}_3^-][\text{H}_2\text{O}] - k_{-4}[\text{BrSO}_3^- \text{-H}_2\text{O}] - k_8[\text{BrSO}_3^- \text{-H}_2\text{O}][\text{M}] = 0$$

$$[\text{BrSO}_3^- \text{-H}_2\text{O}] = \frac{k_4[\text{BrSO}_3^-][\text{H}_2\text{O}]}{k_{-4} + k_8[\text{M}]} \quad (11-2)$$

$$k_3[\text{BrSO}_3\text{H-OH}^- \text{-M}^-] - k_4[\text{BrSO}_3^-][\text{H}_2\text{O}] = 0$$

$$[\text{BrSO}_3^-] = \frac{k_3[\text{BrSO}_3\text{H-OH}^- \text{-M}^-]}{k_4[\text{H}_2\text{O}]} \quad (11-3)$$

$$k_2[\text{HOBr-HOSO}_2^-][\text{M}] - k_3[\text{BrSO}_3\text{H-OH}^- \cdot \text{M}^-] = 0$$

$$[\text{BrSO}_3\text{H-OH}^- \cdot \text{M}^-] = \frac{k_2[\text{HOBr-HOSO}_2^-][\text{M}]}{k_3} \quad (11-4)$$

$$k_1[\text{HOBr}][\text{HOSO}_2^-] - k_{-1}[\text{HOBr-HOSO}_2^-] - k_2[\text{HOBr-HOSO}_2^-][\text{M}] = 0$$

$$[\text{HOBr-HOSO}_2^-] = \frac{k_1[\text{HOBr}][\text{HOSO}_2^-]}{k_{-1} + k_2[\text{M}]} \quad (11-5)$$

$$v_{1\text{HOBr+HOSO}_2^-, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt}$$

$$= \frac{k_9 \times k_8}{k_{-8} + k_9} \times \frac{1}{k_{-4} + k_8[\text{M}]} \times \frac{k_1 \times k_2}{k_{-1} + k_2[\text{M}]} [\text{HOBr}][\text{HOSO}_2^-][\text{M}][\text{M}] \quad (11-6)$$

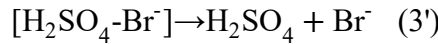
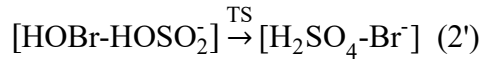
The pseudo-unimolecular uncatalyzed S(IV) oxidation rates through Pathway 1 (HOBr + HOSO<sub>2</sub><sup>-</sup>) can then be written as

$$v_{1\text{HOBr+HOSO}_2^-, \text{un-S(IV)}} = \frac{k_9 \times k_8}{k_{-8} + k_9} \times \frac{1}{k_{-4} + k_8[\text{M}]} \times \frac{k_1 \times k_2}{k_{-1} + k_2[\text{M}]} [\text{HOBr}][\text{M}][\text{M}] \quad (11-7)$$

where  $k_8/k_{-8}$  symbolize the forward/reverse rate coefficients for the reaction 8 and  $k_9$  is the unimolecular rate constant for the catalyzed reaction 9. [M] is the concentration of catalysts M.

### 3.1.2 The reaction rate via Pathway 2 (HOBr + HOSO<sub>2</sub><sup>-</sup>)

The detailed formation process of sulfate from HOBr and HOSO<sub>2</sub><sup>-</sup> through Pathway 2 (HOBr + HOSO<sub>2</sub><sup>-</sup>) is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the uncatalyzed formation reaction rate ( $v_{2\text{HOBr} + \text{HOSO}_2^-, \text{un}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{2\text{HOBr+HOSO}_2^-, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_{2'}[\text{HOBr-HOSO}_2^-] \quad (4')$$

$$k_{1'}[\text{HOBr}][\text{HOSO}_2^-] - k_{-1'}[\text{HOBr-HOSO}_2^-] - k_{2'}[\text{HOBr-HOSO}_2^-] = 0$$

$$[\text{HOBr-HOSO}_2^-] = \frac{k_{1'}}{k_{-1'} + k_{2'}} [\text{HOBr}][\text{HOSO}_2^-] \quad (4'-1)$$

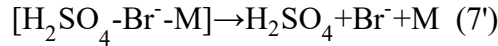
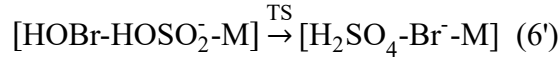
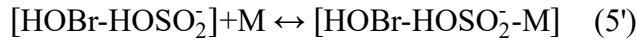
$$v_{2\text{HOBr+HOSO}_2^-, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_{1'} \times k_{2'}}{k_{-1'} + k_{2'}} [\text{HOBr}][\text{HOSO}_2^-] \quad (4'-2)$$

The pseudo-unimolecular uncatalyzed S(IV) oxidation rate through Pathway 2(HOBr + HOSO<sub>2</sub><sup>-</sup>) can be written as

$$v_{2\text{HOBr}+\text{HOSO}_2^{\text{un-S(IV)}}} = \frac{k_{1'} \times k_{2'}}{k_{-1'} + k_{2'}} [\text{HOBr}] \quad (4'-3)$$

where  $k_{1'}/k_{-1'}$  symbolize the forward/reverse rate coefficients for the reaction 1' and  $k_{2'}$  is the unimolecular rate constant for the uncatalyzed reaction 2'.

The catalyzed formation process of sulfate from HOBr and HOSO<sub>2</sub><sup>-</sup> through Pathway 2(HOBr + HOSO<sub>2</sub><sup>-</sup>) is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the catalyzed formation reaction rate ( $v_{2\text{HOBr}+\text{HOSO}_2^{\text{cat}}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{2\text{HOBr}+\text{HOSO}_2^{\text{cat}}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_6' [\text{HOSO}_2^-\text{-HOBr-M}] \quad (8')$$

$$k_5' [\text{HOBr-HOSO}_2^-] [\text{M}] - k_{-5}' [\text{HOSO}_2^-\text{-HOBr-M}] - k_6' [\text{HOSO}_2^-\text{-HOBr-M}] = 0$$

$$[\text{HOSO}_2^-\text{-HOBr-M}] = \frac{k_5' [\text{HOBr-HOSO}_2^-] [\text{M}]}{k_{-5}' + k_6'} \quad (8'-1)$$

$$k_1' [\text{HOBr}] [\text{HOSO}_2^-] - k_{-1}' [\text{HOBr-HOSO}_2^-] - k_5' [\text{HOBr-HOSO}_2^-] [\text{M}] = 0$$

$$[\text{HOBr-HOSO}_2^-] = \frac{k_1'}{k_{-1}' + k_5' [\text{M}]} [\text{HOBr}] [\text{HOSO}_2^-] \quad (8'-2)$$

$$v_{2\text{HOBr}+\text{HOSO}_2^{\text{cat}}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_1'}{k_{-1}' + k_5' [\text{M}]} \times \frac{k_5' \times k_6'}{k_{-5}' + k_6'} [\text{M}] [\text{HOBr}] [\text{HOSO}_2^-] \quad (8'-3)$$

The pseudo-unimolecular catalyzed S(IV) oxidation rate through Pathway 2(HOBr + HOSO<sub>2</sub><sup>-</sup>) can be written as

$$v_{2\text{HOBr}+\text{HOSO}_2^{\text{cat-S(IV)}}} = \frac{k_1'}{k_{-1}' + k_5' [\text{M}]} \times \frac{k_5' \times k_6'}{k_{-5}' + k_6'} [\text{M}] [\text{HOBr}] \quad (8'-4)$$

where  $k_5'/k_{-5}'$  symbolize the forward/reverse rate coefficients for the reaction 5' and  $k_6'$  is the unimolecular rate constant for the catalyzed reaction 6'. [M] is the concentration



of catalyst M.

### 3.1.3 S(IV) oxidation rates, related reaction rate constants and S(IV) lifetimes through Pathway 1(HOBr + HOSO<sub>2</sub><sup>-</sup>) and Pathway 2(HOBr + HOSO<sub>2</sub><sup>-</sup>)

Table S2. Calculated forward/reverse rate coefficients ( $k_1/k_{-1}$ ,  $k_4/k_{-4}$ ,  $k_8/k_{-8}$ ), diffusion rate constant  $k_2$ , the unimolecular rate constants ( $k_5$ ,  $k_9$ ) for the sulfate formation between HOBr and HOSO<sub>2</sub><sup>-</sup> through Pathway 1(HOBr + HOSO<sub>2</sub><sup>-</sup>).

Catalyst	Rate constants		Rate constants	
Without catalyst	$k_1$	$7.44 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-1}$	$5.65 \times 10^{10} \text{ s}^{-1}$
	$k_4$	$7.81 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-4}$	$5.57 \times 10^9 \text{ s}^{-1}$
	$k_5$	$8.05 \times 10^{-28} \text{ s}^{-1}$		
(H <sub>2</sub> O-catalyzed)	$k_8$	$7.81 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-8}$	$1.38 \times 10^{11} \text{ s}^{-1}$
	$k_9$	$2.27 \times 10^{-8} \text{ s}^{-1}$		
(H <sub>2</sub> SO <sub>4</sub> -catalyzed)	$k_2$	$7.48 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$		
	$k_8$	$7.44 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-8}$	$2.14 \times 10^8 \text{ s}^{-1}$
	$k_9$	$4.96 \times 10^{-9} \text{ s}^{-1}$		
(HSO <sub>4</sub> <sup>-</sup> -catalyzed)	$k_2$	$3.24 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$		
	$k_8$	$3.23 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-8}$	$3.23 \times 10^9 \text{ s}^{-1}$
	$k_9$	$7.39 \times 10^{-8} \text{ s}^{-1}$		

Table S3. Calculated forward/reverse rate coefficients ( $k_1'/k_{-1}'$ ,  $k_5'/k_{-5}'$ ), the unimolecular rate constants ( $k_2'$ ,  $k_6'$ ) for the sulfate formation between HOBr and HOSO<sub>2</sub><sup>-</sup> through Pathway 2(HOBr + HOSO<sub>2</sub><sup>-</sup>).

Catalyst	Rate constants		Rate constants	
Without catalyst	$k_1'$	$7.44 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-1}'$	$6.68 \times 10^{10} \text{ s}^{-1}$
	$k_2'$	$1.21 \times 10^{-4} \text{ s}^{-1}$		
(H <sub>2</sub> O-catalyzed)	$k_5'$	$7.92 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-5}'$	$1.63 \times 10^8 \text{ s}^{-1}$
	$k_6'$	$1.61 \times 10^{-5} \text{ s}^{-1}$		
(H <sub>2</sub> SO <sub>4</sub> -catalyzed)	$k_5'$	$7.48 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-5}'$	$1.54 \times 10^{-3} \text{ s}^{-1}$
	$k_6'$	$7.00 \times 10^{-12} \text{ s}^{-1}$		
(HSO <sub>4</sub> <sup>-</sup> -catalyzed)	$k_5'$	$3.24 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-5}'$	$2.86 \times 10^7 \text{ s}^{-1}$
	$k_6'$	$6.43 \times 10^{-5} \text{ s}^{-1}$		

Table S4. Calculated overall rate constant, effective rate constant, S(IV) oxidation rate and the S(IV) lifetimes for Pathway 1(HOBr + HOSO<sub>2</sub><sup>-</sup>) and Pathway 2(HOBr + HOSO<sub>2</sub><sup>-</sup>) from HOSO<sub>2</sub><sup>-</sup> and HOBr respectively, assuming [HOBr] =  $5.89 \times 10^{-7} \text{ M}$  (corresponding to a Henry's law equilibrium with a gas phase HOBr mixing ratio of 0.31 ppbv), and [H<sub>2</sub>O] = 55.56 M (corresponding to the known bulk concentration of

H<sub>2</sub>O).

Rate constants	Catalysts	Overall rate constant M <sup>-2</sup> s <sup>-1</sup>	Effective rate constant <sup>c</sup> (M <sup>-1</sup> s <sup>-1</sup> )	S(IV) oxidation rate (s <sup>-1</sup> )	S(IV) lifetime (s)
Pathway1 (HOBr+HOSO <sub>2</sub> <sup>-</sup> )	Without catalyst	6.61×10 <sup>-36</sup>	6.61×10 <sup>-36</sup>	3.89×10 <sup>-42</sup>	2.57×10 <sup>41</sup>
	H <sub>2</sub> O-catalyzed	1.34×10 <sup>-19</sup>	7.43×10 <sup>-18</sup>	4.38×10 <sup>-24</sup>	2.28×10 <sup>23</sup>
	H <sub>2</sub> SO <sub>4</sub> -catalyzed <sup>a</sup>	7.06×10 <sup>-16</sup>	3.78×10 <sup>-23</sup>	2.23×10 <sup>-29</sup>	4.49×10 <sup>28</sup>
	HSO <sub>4</sub> <sup>-</sup> -catalyzed <sup>b</sup>	6.07×10 <sup>-16</sup>	6.50×10 <sup>-23</sup>	3.83×10 <sup>-29</sup>	2.61×10 <sup>28</sup>
Pathway 2 (HOBr+HOSO <sub>2</sub> <sup>-</sup> )	Without catalyst	1.35×10 <sup>-5</sup>	1.35×10 <sup>-5</sup>	7.94×10 <sup>-12</sup>	1.26×10 <sup>11</sup>
	H <sub>2</sub> O-catalyzed	1.15×10 <sup>-5</sup>	6.39×10 <sup>-4</sup>	3.76×10 <sup>-10</sup>	2.66×10 <sup>9</sup>
	H <sub>2</sub> SO <sub>4</sub> -catalyzed <sup>a</sup>	3.79×10 <sup>0</sup>	2.03×10 <sup>-7</sup>	1.20×10 <sup>-13</sup>	8.35×10 <sup>12</sup>
	HSO <sub>4</sub> <sup>-</sup> -catalyzed <sup>b</sup>	8.10×10 <sup>-4</sup>	8.68×10 <sup>-11</sup>	5.11×10 <sup>-17</sup>	1.96×10 <sup>16</sup>

<sup>a</sup> Assuming a half of general concentration of H<sup>+</sup> act as the possible high limit for the concentration of H<sub>2</sub>SO<sub>4</sub> in cloud water.

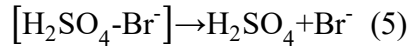
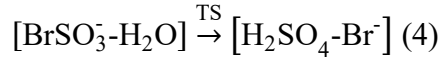
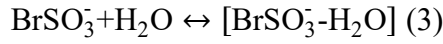
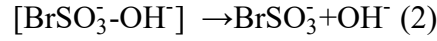
<sup>b</sup> Assuming a general concentration of H<sup>+</sup> act as the possible high limit for the concentration of HSO<sub>4</sub><sup>-</sup> in cloud water.

<sup>c</sup> Effective rate constant = Overall rate constant × [M], where [M] is the concentration of catalyst M.

### 3.2 The reaction rates between HOBr and SO<sub>3</sub><sup>2-</sup> leading to sulfate formation.

#### 3.2.1 The reaction rate via Pathway 1(HOBr + SO<sub>3</sub><sup>2-</sup>)

The detailed formation process of sulfate from HOBr and SO<sub>3</sub><sup>2-</sup> through the Pathway 1(HOBr + SO<sub>3</sub><sup>2-</sup>) is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the uncatalyzed formation reaction rate ( $v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{un}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_4 [\text{BrSO}_3^- \text{-H}_2\text{O}] \quad (6)$$

$$k_3 [\text{BrSO}_3^-] [\text{H}_2\text{O}] - k_{-3} [\text{BrSO}_3^- \text{-H}_2\text{O}] - k_4 [\text{BrSO}_3^- \text{-H}_2\text{O}] = 0$$

$$[\text{BrSO}_3^- \text{-H}_2\text{O}] = \frac{k_3 [\text{BrSO}_3^-] [\text{H}_2\text{O}]}{k_{-3} + k_4} \quad (6-1)$$

$$k_2 [\text{BrSO}_3^- \text{-OH}^-] - k_3 [\text{BrSO}_3^-] [\text{H}_2\text{O}] = 0$$

$$[\text{BrSO}_3^-] = \frac{k_2 [\text{BrSO}_3^- \text{-OH}^-]}{k_3 [\text{H}_2\text{O}]} \quad (6-2)$$

$$k_1 [\text{HOBr}] [\text{SO}_3^{2-}] - k_2 [\text{BrSO}_3^- \text{-OH}^-] = 0$$

$$[\text{BrSO}_3^- \text{-OH}^-] = \frac{k_1 [\text{HOBr}] [\text{SO}_3^{2-}]}{k_2} \quad (6-3)$$

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_4 \times k_1}{k_{-3} + k_4} [\text{HOBr}] [\text{SO}_3^{2-}] \quad (6-4)$$

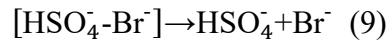
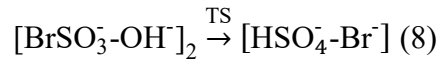
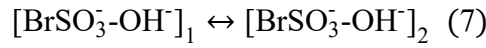
The pseudo-unimolecular uncatalyzed S(IV) oxidation rates through Pathway 1(HOBr + SO<sub>3</sub><sup>2-</sup>) can be written as

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{un-S(IV)}} = \frac{k_4 \times k_1}{k_{-3} + k_4} [\text{HOBr}] \quad (6-6)$$

where  $k_1$  is the diffusion rate constant between HOBr and SO<sub>3</sub><sup>2-</sup>,  $k_{-3}$  is the reverse rate

coefficients for the reaction 3 and  $k_4$  is the unimolecular rate constant for the uncatalyzed reaction 4.

The possible formation process of sulfate from  $\text{BrSO}_3^-$  and  $\text{OH}^-$  is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the uncatalyzed formation reaction rate ( $v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{un}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_8 [\text{BrSO}_3^- \text{-OH}^-] \quad (10)$$

$$k_7 [\text{BrSO}_3^- \text{-OH}^-]_1 - k_{-7} [\text{BrSO}_3^- \text{-OH}^-]_2 - k_8 [\text{BrSO}_3^- \text{-OH}^-]_2 = 0$$

$$[\text{BrSO}_3^- \text{-OH}^-]_2 = \frac{k_7 [\text{BrSO}_3^- \text{-OH}^-]_1}{k_{-7} + k_8} \quad (10-1)$$

$$k_1 [\text{HOBr}] [\text{SO}_3^{2-}] - k_7 [\text{BrSO}_3^- \text{-OH}^-]_1 = 0$$

$$[\text{BrSO}_3^- \text{-OH}^-]_1 = \frac{k_1 [\text{HOBr}] [\text{SO}_3^{2-}]}{k_7} \quad (10-2)$$

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_8 \times k_1}{k_{-7} + k_8} [\text{HOBr}] [\text{SO}_3^{2-}] \quad (10-3)$$

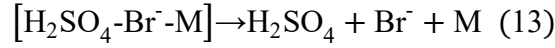
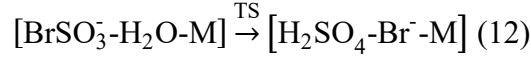
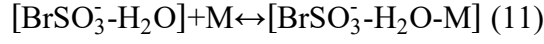
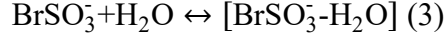
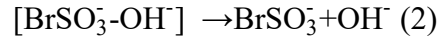
The pseudo-unimolecular uncatalyzed S(IV) oxidation rate through Pathway 1 ( $\text{HOBr} + \text{SO}_3^{2-}$ ) can be written as

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{un-S(IV)}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_8 \times k_1}{k_{-7} + k_8} [\text{HOBr}] \quad (10-4)$$

where  $k_7/k_{-7}$  symbolize the forward/reverse rate coefficients for the reaction 7 and  $k_8$  is the unimolecular rate constant for the reaction 8.

The catalyzed formation process of sulfate from HOBr and  $\text{SO}_3^{2-}$  through Pathway

1(HOBr + SO<sub>3</sub><sup>2-</sup>) is similarly described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the catalyzed formation reaction rate ( $v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{cat}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_{12}[\text{BrSO}_3\text{-H}_2\text{O-M}] \quad (14)$$

$$k_{11}[\text{BrSO}_3\text{-H}_2\text{O}][\text{M}] - k_{-11}[\text{BrSO}_3\text{-H}_2\text{O-M}] - k_{12}[\text{BrSO}_3\text{-H}_2\text{O-M}] = 0$$

$$[\text{BrSO}_3\text{-H}_2\text{O-M}] = \frac{k_{11}[\text{BrSO}_3\text{-H}_2\text{O}][\text{M}]}{k_{-11} + k_{12}} \quad (14-1)$$

$$k_3[\text{BrSO}_3][\text{H}_2\text{O}] - k_{-3}[\text{BrSO}_3\text{-H}_2\text{O}] - k_{11}[\text{BrSO}_3\text{-H}_2\text{O}][\text{M}] = 0$$

$$[\text{BrSO}_3\text{-H}_2\text{O}] = \frac{k_3[\text{BrSO}_3][\text{H}_2\text{O}]}{k_{-3} + k_{11}[\text{M}]} \quad (14-2)$$

$$k_2[\text{BrSO}_3\text{-OH}^-] - k_{-3}[\text{BrSO}_3][\text{H}_2\text{O}] = 0$$

$$[\text{BrSO}_3] = \frac{k_2[\text{BrSO}_3\text{-OH}^-]}{k_3[\text{H}_2\text{O}]} \quad (14-3)$$

$$k_1[\text{HOBr}][\text{SO}_3^{2-}] - k_2[\text{BrSO}_3\text{-OH}^-] = 0$$

$$[\text{BrSO}_3\text{-OH}^-] = \frac{k_1[\text{HOBr}][\text{SO}_3^{2-}]}{k_2} \quad (14-4)$$

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_{12} \times k_{11}}{k_{-11} + k_{12}} \times \frac{k_1}{k_{-3} + k_{11}[\text{M}]} \times [\text{HOBr}][\text{SO}_3^{2-}][\text{M}] \quad (14-5)$$

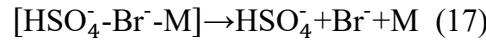
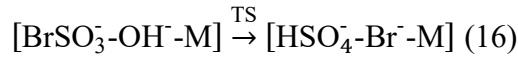
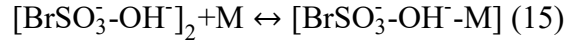
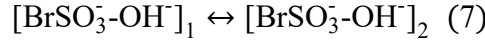
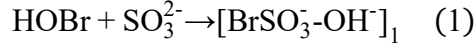
The pseudo-unimolecular catalyzed S(IV) oxidation rate through Pathway 1(HOBr + SO<sub>3</sub><sup>2-</sup>) can then be written as

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{cat-S(IV)}} = \frac{k_{12} \times k_{11}}{k_{-11} + k_{12}} \times \frac{k_1}{k_{-3} + k_{11}[\text{M}]} \times [\text{HOBr}][\text{M}] \quad (14-6)$$

where  $k_{11}/k_{-11}$  symbolize the forward/reverse rate coefficients for the reaction 11 and

$k_{12}$  is the unimolecular rate constant for the catalyzed reaction 12.

The catalyzed formation process of sulfate from  $\text{BrSO}_3^-$  and  $\text{OH}^-$  is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the catalyzed formation reaction rate ( $v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{cat}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_{16} [\text{BrSO}_3^- \text{-OH}^- \text{-M}] \quad (18)$$

$$k_{15} [\text{BrSO}_3^- \text{-OH}^-]_2 [\text{M}] - k_{15} [\text{BrSO}_3^- \text{-OH}^- \text{-M}] - k_{16} [\text{BrSO}_3^- \text{-OH}^- \text{-M}] = 0$$

$$[\text{BrSO}_3^- \text{-OH}^- \text{-M}] = \frac{k_{15} [\text{BrSO}_3^- \text{-OH}^-]_2 [\text{M}]}{k_{15} + k_{16}} \quad (18-1)$$

$$k_7 [\text{BrSO}_3^- \text{-OH}^-]_1 - k_{-7} [\text{BrSO}_3^- \text{-OH}^-]_2 - k_{15} [\text{BrSO}_3^- \text{-OH}^-]_2 [\text{M}]$$

$$[\text{BrSO}_3^- \text{-OH}^-]_2 = \frac{k_7 [\text{BrSO}_3^- \text{-OH}^-]_1}{k_{-7} + k_{15} [\text{M}]} \quad (18-2)$$

$$k_1 [\text{HOBr}] [\text{SO}_3^{2-}] - k_7 [\text{BrSO}_3^- \text{-OH}^-]_1 = 0$$

$$[\text{BrSO}_3^- \text{-OH}^-]_1 = \frac{k_1 [\text{HOBr}] [\text{SO}_3^{2-}]}{k_8} \quad (18-3)$$

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_{16} \times k_{15}}{k_{15} + k_{16}} \times \frac{k_1}{k_{-7} + k_{15} [\text{M}]} \times [\text{HOBr}] [\text{SO}_3^{2-}] [\text{M}] \quad (18-4)$$

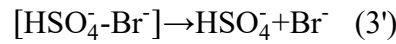
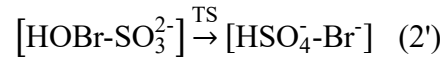
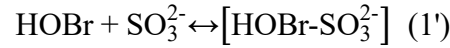
The pseudo-unimolecular catalyzed S(IV) oxidation rate through Pathway 1 ( $\text{HOBr} + \text{SO}_3^{2-}$ ) can be written as

$$v_{1\text{HOBr} + \text{SO}_3^{2-}, \text{cat-S(IV)}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_{16} \times k_{15}}{k_{15} + k_{16}} \times \frac{k_1}{k_{-7} + k_{15} [\text{M}]} \times [\text{HOBr}] [\text{M}] \quad (18-5)$$

where  $k_{15}/k_{-15}$  symbolize the forward/reverse rate coefficients for the reaction 15 and  $k_{16}$  is the unimolecular rate constant for the reaction 16.

### 3.2.2 The reaction rate via Pathway 2(HOBr + SO<sub>3</sub><sup>2-</sup>)

The detailed formation process of sulfate from HOBr and SO<sub>3</sub><sup>2-</sup> through the Pathway 2(HOBr + SO<sub>3</sub><sup>2-</sup>) is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the formation reaction rate ( $v_{2\text{HOBr} + \text{SO}_3^{2-}, \text{un}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{2\text{HOBr} + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_2 [\text{HOBr-SO}_3^{2-}] \quad (4')$$

$$k_{1'} [\text{HOBr}] [\text{SO}_3^{2-}] - k_{-1'} [\text{HOBr-SO}_3^{2-}] - k_2 [\text{HOBr-SO}_3^{2-}] = 0$$

$$[\text{HOBr-SO}_3^{2-}] = \frac{k_{1'} [\text{HOBr}] [\text{SO}_3^{2-}]}{k_{-1'} + k_2} \quad (4'-1)$$

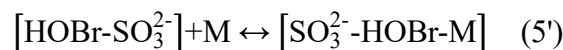
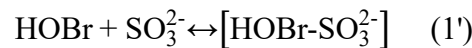
$$v_{2\text{HOBr} + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_1 \times k_2}{k_{-1'} + k_2} [\text{HOBr}] [\text{SO}_3^{2-}] \quad (4'-2)$$

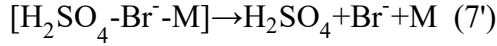
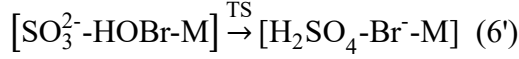
The pseudo-unimolecular catalyzed S(IV) oxidation rates through Pathway 2(HOBr + SO<sub>3</sub><sup>2-</sup>) can be written as

$$v_{2\text{HOBr} + \text{SO}_3^{2-}, \text{un-S(IV)}} = \frac{k_1 \times k_2}{k_{-1'} + k_2} [\text{HOBr}] \quad (4'-3)$$

where  $k_{1'}/k_{-1'}$  symbolize the forward/reverse rate coefficients for the reaction 1', and  $k_2$  is the unimolecular rate constant for the reaction 2'.

The catalyzed formation process of sulfate from HOBr and SO<sub>3</sub><sup>2-</sup> through Pathway 2(HOBr + SO<sub>3</sub><sup>2-</sup>) is described by the following reaction equations:





Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the catalyzed formation reaction rate ( $v_{2\text{HOBr} + \text{SO}_3^{2-}, \text{cat}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{2\text{HOBr} + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_6' [\text{SO}_3^{2-}\text{-HOBr-M}] \quad (8')$$

$$k_5' [\text{HOBr-SO}_3^{2-}] [\text{M}] - k_{-5}' [\text{SO}_3^{2-}\text{-HOBr-M}] - k_6' [\text{SO}_3^{2-}\text{-HOBr-M}] = 0$$

$$[\text{SO}_3^{2-}\text{-HOBr-M}] = \frac{k_5' [\text{HOBr-SO}_3^{2-}] [\text{M}]}{k_{-5}' + k_6'} \quad (8'-1)$$

$$k_1' [\text{HOBr}] [\text{SO}_3^{2-}] - k_{-1}' [\text{HOBr-SO}_3^{2-}] - k_5' [\text{HOBr-SO}_3^{2-}] [\text{M}] = 0$$

$$[\text{HOBr-SO}_3^{2-}] = \frac{k_1' [\text{HOBr}] [\text{SO}_3^{2-}]}{k_{-1}' + k_5' [\text{M}]} \quad (8'-2)$$

$$v_{2\text{HOBr} + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_5' \times k_6'}{k_{-5}' + k_6'} \times \frac{k_1'}{k_{-1}' + k_5' [\text{M}]} \times [\text{M}] [\text{HOBr}] [\text{SO}_3^{2-}] \quad (8'-3)$$

The pseudo-unimolecular catalyzed S(IV) oxidation rate through Pathway 2(HOBr+SO<sub>3</sub><sup>2-</sup>) can be written as

$$v_{2\text{HOBr} + \text{SO}_3^{2-}, \text{cat-S(IV)}} = \frac{k_5' \times k_6'}{k_{-5}' + k_6'} \times \frac{k_1'}{k_{-1}' + k_5' [\text{M}]} \times [\text{M}] [\text{HOBr}] \quad (8'-4)$$

where  $k_5'/k_{-5}'$  symbolize the forward/reverse rate coefficients for the reaction 5' and  $k_6'$  is the unimolecular rate constant for the catalyzed reaction 6'. [M] is the concentration of catalyst M.

### 3.2.3 S(IV) oxidation rates, related reaction rate constants and S(IV) lifetimes through Pathway 1(HOBr + SO<sub>3</sub><sup>2-</sup>) and Pathway 2(HOBr + SO<sub>3</sub><sup>2-</sup>)

Table S5. Calculated diffusion rate constant ( $k_1$ ) between HOBr and SO<sub>3</sub><sup>2-</sup>, the forward/reverse rate coefficients ( $k_3/k_{-3}$ ,  $k_7/k_{-7}$ ,  $k_{11}/k_{-11}$ ,  $k_{15}/k_{-15}$ ), and the unimolecular rate constants ( $k_4$ ,  $k_8$ ,  $k_{12}$ ,  $k_{16}$ ) for the sulfate formation between HOBr and SO<sub>3</sub><sup>2-</sup> through Pathway 1(HOBr + SO<sub>3</sub><sup>2-</sup>).



Catalyst	Rate constants		Rate constants	
Without	$k_1$	$7.45 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$		
	$k_3$	$7.81 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-3}$	$5.57 \times 10^9 \text{ s}^{-1}$
	$k_4$	$8.05 \times 10^{-28} \text{ s}^{-1}$		
	$k_7$	$1.44 \times 10^9 \text{ s}^{-1}$	$k_{-7}$	$3.34 \times 10^9 \text{ s}^{-1}$
(H <sub>2</sub> O-catalyzed)	$k_8$	$1.03 \text{ s}^{-1}$		
	$k_{11}$	$7.81 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-11}$	$1.38 \times 10^{11} \text{ s}^{-1}$
	$k_{12}$	$2.27 \times 10^{-8} \text{ s}^{-1}$		
	$k_{15}$	$7.98 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-15}$	$1.26 \times 10^{12} \text{ s}^{-1}$
(HSO <sub>4</sub> <sup>-</sup> -catalyzed)	$k_{16}$	$4.70 \text{ s}^{-1}$		
	$k_{11}$	$3.23 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-11}$	$3.23 \times 10^9 \text{ s}^{-1}$
	$k_{12}$	$7.39 \times 10^{-8} \text{ s}^{-1}$		
	$k_{15}$	$3.25 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-15}$	$2.04 \times 10^{-4} \text{ s}^{-1}$
	$k_{16}$	$1.25 \times 10^{-4} \text{ s}^{-1}$		

Table S6. Calculated forward/reverse rate coefficients ( $k_1/k_{-1}$ ,  $k_5/k_{-5}$ ), and the unimolecular rate constant ( $k_2$ ,  $k_6$ ) for the sulfate formation between HOBr and SO<sub>3</sub><sup>2-</sup> through Pathway 2 (HOBr + SO<sub>3</sub><sup>2-</sup>).

Catalyst	Rate constants		Rate constants	
Without catalyst	$k_1$	$7.45 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-1}$	$4.49 \times 10^9 \text{ s}^{-1}$
	$k_2$	$3.50 \times 10^5 \text{ s}^{-1}$		
(H <sub>2</sub> O-catalyzed)	$k_5$	$7.96 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-5}$	$3.42 \times 10^9 \text{ s}^{-1}$
	$k_6$	$4.18 \times 10^5 \text{ s}^{-1}$		
(HSO <sub>4</sub> <sup>-</sup> -catalyzed)	$k_5$	$3.24 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-5}$	$1.12 \text{ s}^{-1}$
	$k_6$	$5.19 \times 10^{-3} \text{ s}^{-1}$		

Table S7. Calculated overall rate constant, effective rate constant, S(IV) oxidation rate and the S(IV) lifetimes for Pathway 1 (HOBr + SO<sub>3</sub><sup>2-</sup>) and Pathway 2 (HOBr + SO<sub>3</sub><sup>2-</sup>) from SO<sub>3</sub><sup>2-</sup> and HOBr respectively, assuming [HOBr] =  $5.89 \times 10^{-7} \text{ M}$  (corresponding to a Henry's law equilibrium with a gas phase HOBr mixing ratio of 0.31 ppbv), and [H<sub>2</sub>O] =  $55.56 \text{ M}$  (corresponding to the known bulk concentration of H<sub>2</sub>O).

Rate constants	Catalysts	Overall rate constant $\text{M}^{-2} \text{ s}^{-1}$	Effective rate constant <sup>d</sup> ( $\text{M}^{-1} \text{ s}^{-1}$ )	S(IV) oxidation rate ( $\text{s}^{-1}$ )	S(IV) lifetime (s)
Pathway 1 <sup>a</sup> (HOBr + SO <sub>3</sub> <sup>2-</sup> )	Without catalyst	$1.08 \times 10^{-27}$	$1.08 \times 10^{-27}$	$6.34 \times 10^{-34}$	$1.58 \times 10^{33}$
	H <sub>2</sub> O-catalyzed	$2.18 \times 10^{-11}$	$1.21 \times 10^{-9}$	$7.13 \times 10^{-16}$	$1.40 \times 10^{15}$
	HSO <sub>4</sub> <sup>-</sup> -catalyzed <sup>c</sup>	$9.88 \times 10^{-8}$	$1.24 \times 10^{-16}$	$7.33 \times 10^{-23}$	$1.36 \times 10^{22}$
Pathway 1 <sup>b</sup> (HOBr + SO <sub>3</sub> <sup>2-</sup> )	Without catalyst	2.30	2.30	$1.35 \times 10^{-6}$	$7.39 \times 10^5$
	H <sub>2</sub> O-catalyzed	$1.24 \times 10^1$	$6.90 \times 10^2$	$4.07 \times 10^{-4}$	$2.46 \times 10^3$
	HSO <sub>4</sub> <sup>-</sup> -catalyzed <sup>c</sup>	$2.74 \times 10^9$	$3.45 \times 10^0$	$2.03 \times 10^{-6}$	$4.92 \times 10^5$
Pathway 2 (HOBr + SO <sub>3</sub> <sup>2-</sup> )	Without catalyst	$5.80 \times 10^5$	$5.80 \times 10^5$	$3.42 \times 10^{-1}$	$2.93 \times 10^0$
	H <sub>2</sub> O-catalyzed	$1.62 \times 10^4$	$9.01 \times 10^5$	$5.31 \times 10^{-1}$	$1.88 \times 10^0$

HSO <sub>4</sub> <sup>-</sup> -catalyzed <sup>c</sup>	2.48×10 <sup>7</sup>	3.12×10 <sup>-2</sup>	1.84×10 <sup>-8</sup>	5.44×10 <sup>7</sup>
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<sup>a</sup> The second step of Pathway 1(HOBr + SO<sub>3</sub><sup>2-</sup>) leading to sulfate formation through the hydrolysis reaction.

<sup>b</sup> The second step of Pathway 1(HOBr + SO<sub>3</sub><sup>2-</sup>) leading to sulfate formation through the reaction of BrSO<sub>3</sub><sup>-</sup> intermediate with OH<sup>-</sup>.

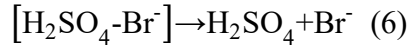
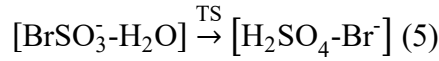
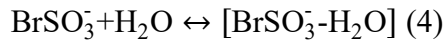
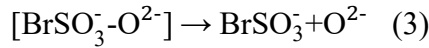
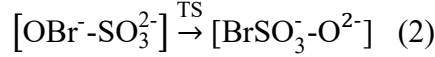
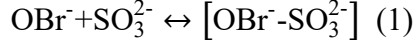
<sup>c</sup> Assuming a general concentration of H<sup>+</sup> act as the possible high limit for the concentration of HSO<sub>4</sub><sup>-</sup> in cloud water.

<sup>d</sup> Effective rate constant = Overall rate constant × [M], where [M] is the concentration of catalyst M.

### 3.3 The reaction rates between $\text{OBr}^-$ and $\text{SO}_3^{2-}$ leading to sulfate formation.

#### 3.3.1 The reaction rate via Pathway 1( $\text{OBr}^- + \text{SO}_3^{2-}$ )

The detailed formation process of sulfate from  $\text{OBr}^-$  and  $\text{SO}_3^{2-}$  through Pathway 1( $\text{OBr}^- + \text{SO}_3^{2-}$ ) is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the uncatalyzed formation reaction rate ( $v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{un}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_5[\text{BrSO}_3^- - \text{H}_2\text{O}] \quad (7)$$

$$k_4[\text{BrSO}_3^-][\text{H}_2\text{O}] - k_{-4}[\text{BrSO}_3^- - \text{H}_2\text{O}] - k_5[\text{BrSO}_3^- - \text{H}_2\text{O}] = 0$$

$$[\text{BrSO}_3^- - \text{H}_2\text{O}] = \frac{k_4[\text{BrSO}_3^-][\text{H}_2\text{O}]}{k_{-4} + k_5} \quad (7-1)$$

$$k_3[\text{BrSO}_3^- - \text{O}^{2-}] - k_4[\text{BrSO}_3^-][\text{H}_2\text{O}] = 0$$

$$[\text{BrSO}_3^-] = \frac{k_3[\text{BrSO}_3^- - \text{O}^{2-}]}{k_4[\text{H}_2\text{O}]} \quad (7-2)$$

$$k_2[\text{OBr}^- - \text{SO}_3^{2-}] - k_3[\text{BrSO}_3^- - \text{O}^{2-}] = 0$$

$$[\text{BrSO}_3^- - \text{O}^{2-}] = \frac{k_2[\text{OBr}^- - \text{SO}_3^{2-}]}{k_3} \quad (7-3)$$

$$k_1[\text{OBr}^-][\text{SO}_3^{2-}] - k_{-1}[\text{OBr}^- - \text{SO}_3^{2-}] - k_2[\text{OBr}^- - \text{SO}_3^{2-}] = 0$$

$$[\text{OBr}^- - \text{SO}_3^{2-}] = \frac{k_1[\text{OBr}^-][\text{SO}_3^{2-}]}{k_{-1} + k_2} \quad (7-4)$$

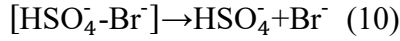
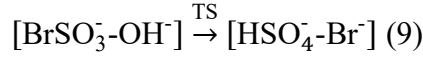
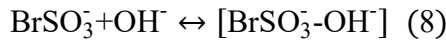
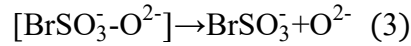
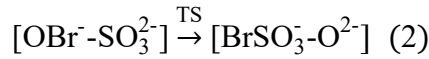
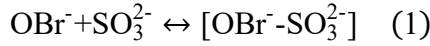
$$v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_5}{k_{-4} + k_5} \times \frac{k_2 \times k_1}{k_{-1} + k_2} [\text{OBr}^-][\text{SO}_3^{2-}] \quad (7-6)$$

The pseudo-unimolecular uncatalyzed S(IV) oxidation rate through Pathway 1(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) can be written as

$$v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{un-S(IV)}} = \frac{k_5}{k_{-4} + k_5} \times \frac{k_2 \times k_1}{k_{-1} + k_2} [\text{OBr}^-][\text{SO}_3^{2-}] \quad (7-7)$$

where  $k_1/k_{-1}$  and  $k_{-4}$  symbolize the forward/reverse and reverse rate coefficients for the reactions 1 and 4, respectively, as well as  $k_2$  and  $k_5$  are the unimolecular rate constants for the uncatalyzed reactions 2 and 5.

The possible formation process of sulfate from BrSO<sub>3</sub><sup>-</sup> and OH<sup>-</sup> is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the uncatalyzed formation reaction rate ( $v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{un}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_9 [\text{BrSO}_3^- - \text{OH}^-] \quad (11)$$

$$k_8 [\text{BrSO}_3^-][\text{OH}^-] - k_{-8} [\text{BrSO}_3^- - \text{OH}^-] - k_9 [\text{BrSO}_3^- - \text{OH}^-] = 0$$

$$[\text{BrSO}_3^- - \text{OH}^-] = \frac{k_8 [\text{BrSO}_3^-][\text{OH}^-]}{k_{-8} + k_9} \quad (11-1)$$

$$k_3 [\text{BrSO}_3^- - \text{O}^{2-}] - k_8 [\text{BrSO}_3^-][\text{OH}^-] = 0$$

$$[\text{BrSO}_3^-] = \frac{k_3 [\text{BrSO}_3^- - \text{O}^{2-}]}{k_8 [\text{OH}^-]} \quad (11-2)$$

$$k_2 [\text{OBr}^- - \text{SO}_3^{2-}] - k_3 [\text{BrSO}_3^- - \text{O}^{2-}] = 0$$

$$[\text{BrSO}_3^- \text{O}^{2-}] = \frac{k_2[\text{OBr}^- \text{SO}_3^{2-}]}{k_3} \quad (11-3)$$

$$k_1[\text{OBr}^-][\text{SO}_3^{2-}] - k_{-1}[\text{OBr}^- \text{SO}_3^{2-}] - k_2[\text{OBr}^- \text{SO}_3^{2-}] = 0$$

$$[\text{OBr}^- \text{SO}_3^{2-}] = \frac{k_1[\text{OBr}^-][\text{SO}_3^{2-}]}{k_{-1} + k_2} \quad (11-4)$$

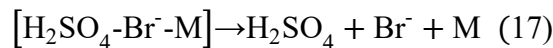
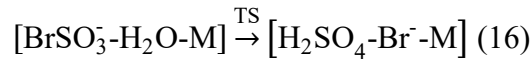
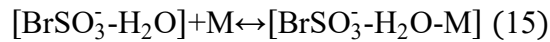
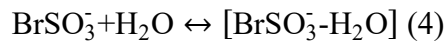
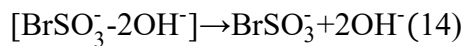
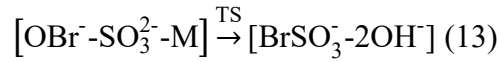
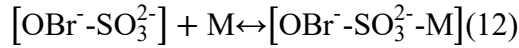
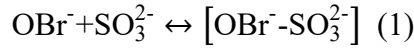
$$v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_9}{k_{-8} + k_9} \times \frac{k_2 \times k_1}{k_{-1} + k_2} [\text{OBr}^-][\text{SO}_3^{2-}] \quad (11-5)$$

The pseudo-unimolecular catalyzed S(IV) oxidation rate through Pathway 1(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) can be written as

$$v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{un-S(IV)}} = \frac{k_9}{k_{-8} + k_9} \times \frac{k_2 \times k_1}{k_{-1} + k_2} [\text{OBr}^-] \quad (11-6)$$

where  $k_{-8}$  symbolizes the reverse rate coefficients for the reaction 8, and  $k_9$  is the unimolecular rate constant for the reaction 9.

The detailed catalyzed formation process of sulfate from OBr<sup>-</sup> and SO<sub>3</sub><sup>2-</sup> through Pathway 1(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) is similarly described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the catalyzed formation reaction rate ( $v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{cat}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{\text{OBr}^- + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_{16}[\text{BrSO}_3^- \text{H}_2\text{O} \cdot \text{M}] \quad (18)$$

$$k_{15}[\text{BrSO}_3^- \text{H}_2\text{O}] [\text{M}] - k_{-15}[\text{BrSO}_3^- \text{H}_2\text{O} \cdot \text{M}] - k_{16}[\text{BrSO}_3^- \text{H}_2\text{O} \cdot \text{M}] = 0$$

$$[\text{BrSO}_3^- \text{H}_2\text{O} \cdot \text{M}] = \frac{k_{15}[\text{BrSO}_3^- \text{H}_2\text{O}] [\text{M}]}{k_{-15} + k_{16}} \quad (18-1)$$

$$k_4[\text{BrSO}_3^-] [\text{H}_2\text{O}] - k_{-4}[\text{BrSO}_3^- \text{H}_2\text{O}] - k_{15}[\text{BrSO}_3^- \text{H}_2\text{O}] [\text{M}] = 0$$

$$[\text{BrSO}_3^- \text{H}_2\text{O}] = \frac{k_4 [\text{BrSO}_3^-] [\text{H}_2\text{O}]}{k_{-4} + k_{15} [\text{M}]} \quad (18-2)$$

$$k_{14}[\text{BrSO}_3^- \cdot 2\text{OH}^-] - k_4[\text{BrSO}_3^-] [\text{H}_2\text{O}] = 0$$

$$[\text{BrSO}_3^-] = \frac{k_{14}[\text{BrSO}_3^- \cdot 2\text{OH}^-]}{k_4 [\text{H}_2\text{O}]} \quad (18-3)$$

$$k_{13}[\text{OBr}^- \cdot \text{SO}_3^{2-} \cdot \text{M}] - k_{14}[\text{BrSO}_3^- \cdot 2\text{OH}^-] = 0$$

$$[\text{BrSO}_3^- \cdot 2\text{OH}^-] = \frac{k_{13}[\text{OBr}^- \cdot \text{SO}_3^{2-} \cdot \text{M}]}{k_{14}} \quad (18-4)$$

$$k_{12}[\text{OBr}^- \cdot \text{SO}_3^{2-}] [\text{M}] - k_{-12}[\text{OBr}^- \cdot \text{SO}_3^{2-} \cdot \text{M}] - k_{13}[\text{OBr}^- \cdot \text{SO}_3^{2-} \cdot \text{M}] = 0$$

$$[\text{OBr}^- \cdot \text{SO}_3^{2-} \cdot \text{M}] = \frac{k_{12}[\text{OBr}^- \cdot \text{SO}_3^{2-}] [\text{M}]}{k_{-12} + k_{13}} \quad (18-5)$$

$$k_1[\text{OBr}^-] [\text{SO}_3^{2-}] - k_{-1}[\text{OBr}^- \cdot \text{SO}_3^{2-}] - k_{12}[\text{OBr}^- \cdot \text{SO}_3^{2-}] [\text{M}] = 0$$

$$[\text{OBr}^- \cdot \text{SO}_3^{2-}] = \frac{k_1[\text{OBr}^-] [\text{SO}_3^{2-}]}{k_{-1} + k_{12} [\text{M}]} \quad (18-6)$$

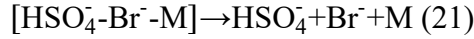
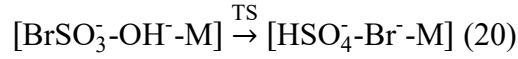
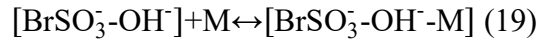
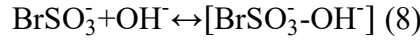
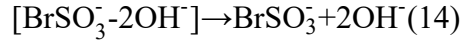
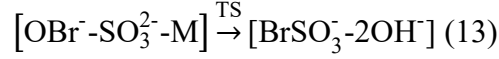
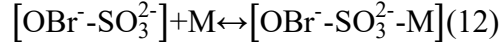
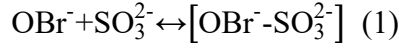
$$= \frac{k_{16} \times k_{15}}{k_{-15} + k_{16}} \times \frac{1}{k_{-4} + k_{15} [\text{M}]} \times \frac{k_{12} \times k_{13}}{k_{-12} + k_{13}} \times \frac{k_1}{k_{-1} + k_{12} [\text{M}]} [\text{OBr}^-] [\text{SO}_3^{2-}] [\text{M}] [\text{M}] \quad (18-7)$$

The pseudo-unimolecular catalyzed S(IV) oxidation rate through Pathway 1 (OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) can be written as

$$v_{\text{OBr}^- + \text{SO}_3^{2-}, \text{cat-S(IV)}} = \frac{k_{16} \times k_{15}}{k_{-15} + k_{16}} \times \frac{1}{k_{-4} + k_{15} [\text{M}]} \times \frac{k_{12} \times k_{13}}{k_{-12} + k_{13}} \times \frac{k_1}{k_{-1} + k_{12} [\text{M}]} [\text{OBr}^-] [\text{M}] [\text{M}] \quad (18-8)$$

where  $k_{12}/k_{-12}$  and  $k_{15}/k_{-15}$  symbolize the forward/reverse rate coefficients for the reactions 12 and 15, respectively, as well as  $k_{13}$  and  $k_{16}$  are the unimolecular rate constants for the catalyzed reactions 13 and 16. In addition,  $[\text{M}]$  is the concentration of catalyst M.

The catalyzed formation process of sulfate from  $\text{BrSO}_3^-$  and  $\text{OH}^-$  is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the catalyzed formation reaction rate ( $v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{cat}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_{20} [\text{BrSO}_3^- - \text{OH}^- - \text{M}] \quad (22)$$

$$k_{19} [\text{BrSO}_3^- - \text{OH}^-] [\text{M}] - k_{-19} [\text{BrSO}_3^- - \text{OH}^- - \text{M}] - k_{20} [\text{BrSO}_3^- - \text{OH}^- - \text{M}] = 0$$

$$[\text{BrSO}_3^- - \text{OH}^- - \text{M}] = \frac{k_{19} [\text{BrSO}_3^- - \text{OH}^-] [\text{M}]}{k_{-19} + k_{20}} \quad (22-1)$$

$$k_8 [\text{BrSO}_3^-] [\text{OH}^-] - k_{-8} [\text{BrSO}_3^- - \text{OH}^-] - k_{19} [\text{BrSO}_3^- - \text{OH}^-] [\text{M}] = 0$$

$$[\text{BrSO}_3^- - \text{OH}^-] = \frac{k_8 [\text{BrSO}_3^-] [\text{OH}^-]}{k_{-8} + k_{19} [\text{M}]} \quad (22-2)$$

$$k_{14} [\text{BrSO}_3^- - 2\text{OH}^-] - k_8 [\text{BrSO}_3^-] [\text{OH}^-] = 0$$

$$[\text{BrSO}_3^-] = \frac{k_{14} [\text{BrSO}_3^- - 2\text{OH}^-]}{k_8 [\text{OH}^-]} \quad (22-3)$$

$$k_{13} [\text{OBr}^- - \text{SO}_3^{2-} - \text{M}] - k_{14} [\text{BrSO}_3^- - 2\text{OH}^-] = 0$$

$$[\text{BrSO}_3^- - 2\text{OH}^-] = \frac{k_{13} [\text{OBr}^- - \text{SO}_3^{2-} - \text{M}]}{k_{14}} \quad (22-4)$$

$$k_{12} [\text{OBr}^- - \text{SO}_3^{2-}] [\text{M}] - k_{-12} [\text{OBr}^- - \text{SO}_3^{2-} - \text{M}] - k_{13} [\text{OBr}^- - \text{SO}_3^{2-} - \text{M}] = 0$$

$$[\text{OBr}^- \cdot \text{SO}_3^{2-} \cdot \text{M}] = \frac{k_{12}[\text{OBr}^- \cdot \text{SO}_3^{2-}][\text{M}]}{k_{-12} + k_{13}} \quad (22-5)$$

$$k_1[\text{OBr}^-][\text{SO}_3^{2-}] - k_{-1}[\text{OBr}^- \cdot \text{SO}_3^{2-}] - k_{12}[\text{OBr}^- \cdot \text{SO}_3^{2-}][\text{M}] = 0$$

$$[\text{OBr}^- \cdot \text{SO}_3^{2-}] = \frac{k_1[\text{OBr}^-][\text{SO}_3^{2-}]}{k_{-1} + k_{12}[\text{M}]} \quad (22-6)$$

$$v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_{20} \times k_{19}}{k_{-19} + k_{20}} \times \frac{1}{k_{-8} + k_{19}[\text{M}]} \times \frac{k_{13} \times k_{12}}{k_{-12} + k_{13}} \\ \times \frac{k_1}{k_{-1} + k_{12}[\text{M}]} [\text{OBr}^-][\text{SO}_3^{2-}][\text{M}][\text{M}] \quad (22-7)$$

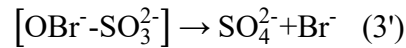
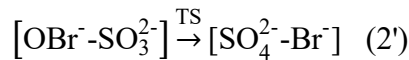
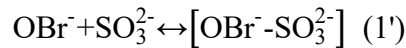
The pseudo-unimolecular catalyzed S(IV) oxidation rate through Pathway 1 (OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) can be written as

$$v_{1\text{OBr}^- + \text{SO}_3^{2-}, \text{cat-S(IV)}} = \frac{k_{20} \times k_{19}}{k_{-19} + k_{20}} \times \frac{1}{k_{-8} + k_{19}[\text{M}]} \times \frac{k_{13} \times k_{12}}{k_{-12} + k_{13}} \\ \times \frac{k_1}{k_{-1} + k_{12}[\text{M}]} [\text{OBr}^-][\text{M}][\text{M}] \quad (22-8)$$

where  $k_{19}/k_{-19}$  symbolize the forward/reverse rate coefficients for the reaction 19 and  $k_{20}$  is the unimolecular rate constant for the catalyzed reaction 20. In addition, [M] is the concentration of catalyst M.

### 3.3.2 The reaction rate via Pathway 2(OBr<sup>-</sup>+SO<sub>3</sub><sup>2-</sup>)

The detailed formation process of sulfate from OBr<sup>-</sup> and SO<sub>3</sub><sup>2-</sup> through Pathway 2(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the uncatalyzed formation reaction rate ( $v_{2\text{OBr}^- + \text{SO}_3^{2-}, \text{un}}$ ) of (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{2\text{OBr}^- + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_2' [\text{OBr}^- \cdot \text{SO}_3^{2-}] \quad (4')$$



$$k_{1'}[\text{OBr}^-][\text{SO}_3^{2-}] - k_{-1'}[\text{OBr}^-][\text{SO}_3^{2-}] - k_2[\text{OBr}^- - \text{SO}_3^{2-}] = 0$$

$$[\text{OBr}^- - \text{SO}_3^{2-}] = \frac{k_{1'}[\text{OBr}^-][\text{SO}_3^{2-}]}{k_{-1'} + k_2} \quad (4'-1)$$

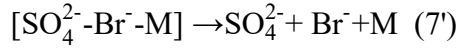
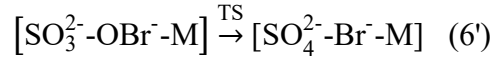
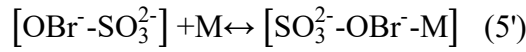
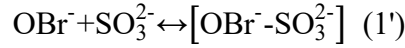
$$v_{2\text{OBr}^- + \text{SO}_3^{2-}, \text{un}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_{1'} \times k_2'}{k_{-1'} + k_2'} [\text{OBr}^-][\text{SO}_3^{2-}] \quad (4'-2)$$

The pseudo-unimolecular uncatalyzed S(IV) oxidation rates through Pathway 2(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) can be written as

$$v_{2\text{OBr}^- + \text{SO}_3^{2-} - \text{S(IV)}} = \frac{k_{1'} \times k_2'}{k_{-1'} + k_2'} [\text{OBr}^-] \quad (4'-3)$$

where  $k_{1'}/k_{-1'}$  symbolizes the forward/reverse rate coefficients for the reaction 1' and  $k_2'$  is the unimolecular rate constant for the uncatalyzed reaction 2'.

The detailed catalyzed formation process of sulfate from OBr<sup>-</sup> and SO<sub>3</sub><sup>2-</sup> through Pathway 2(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) is described by the following reaction equations:



Applying the steady-state approximation to the pre-reactive complex and assuming that the complex is in equilibrium with the reactant, we obtain the following expressions for the catalyzed formation reaction rate ( $v_{2\text{OBr}^- + \text{SO}_3^{2-}, \text{cat}}$ ) of sulfate (where  $k_n$  is the rate constant for reaction n in the scheme given above):

$$v_{2\text{OBr}^- + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = k_6' [\text{SO}_3^{2-} - \text{OBr}^- - \text{M}] \quad (8')$$

$$k_5' [\text{OBr}^- - \text{SO}_3^{2-}] [\text{M}] - k_{-5}' [\text{SO}_3^{2-} - \text{OBr}^- - \text{M}] - k_6' [\text{SO}_3^{2-} - \text{OBr}^- - \text{M}] = 0$$

$$[\text{SO}_3^{2-} - \text{OBr}^- - \text{M}] = \frac{k_5' [\text{OBr}^- - \text{SO}_3^{2-}] [\text{M}]}{k_{-5}' + k_6'} \quad (8'-1)$$

$$k_{1'} [\text{OBr}^-] [\text{SO}_3^{2-}] - k_{-1'} [\text{OBr}^- - \text{SO}_3^{2-}] - k_5' [\text{OBr}^- - \text{SO}_3^{2-}] [\text{M}] = 0$$

$$[\text{OBr}^- - \text{SO}_3^{2-}] = \frac{k_{1'} [\text{OBr}^-] [\text{SO}_3^{2-}]}{k_{-1'} + k_5' [\text{M}]} \quad (8'-2)$$

$$v_{2\text{OBr}^- + \text{SO}_3^{2-}, \text{cat}} = \frac{d[\text{SO}_4^{2-}]}{dt} = \frac{k_6' \times k_5'}{k_{-5'} + k_6'} \times \frac{k_1'}{k_{-1'} + k_5'[\text{M}]} \times [\text{OBr}^-][\text{SO}_3^{2-}][\text{M}] \quad (8'-3)$$

The pseudo-unimolecular catalyzed S(IV) oxidation rate through Pathway 1(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) can be written as

$$v_{2\text{OBr}^- + \text{SO}_3^{2-}, \text{cat-S(IV)}} = \frac{k_6' \times k_5'}{k_{-5'} + k_6'} \times \frac{k_1'}{k_{-1'} + k_5'[\text{M}]} \times [\text{OBr}^-][\text{M}] \quad (8'-4)$$

where  $k_5'/k_{-5'}$  symbolizes the forward/reverse rate coefficients for the reaction 5' and  $k_6'$  is the unimolecular rate constant for the catalyzed reaction 6'.

### 3.3.3 S(IV) oxidation rate, related reaction rate constants and S(IV) lifetimes through Pathway 1(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>) and Pathway 2(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>)

Table S8. Calculated forward/reverse rate coefficients ( $k_1/k_{-1}$ ,  $k_4/k_{-4}$ ,  $k_8/k_{-8}$ ,  $k_{12}/k_{-12}$ ,  $k_{15}/k_{-15}$ ,  $k_{19}/k_{-19}$ ), and the unimolecular rate constants ( $k_2$ ,  $k_5$ ,  $k_9$ ,  $k_{13}$ ,  $k_{16}$ ,  $k_{20}$ ) for the sulfate formation between OBr<sup>-</sup> and SO<sub>3</sub><sup>2-</sup> through Pathway 1(OBr<sup>-</sup> + SO<sub>3</sub><sup>2-</sup>).

Catalyst	Rate constants		Rate constants	
Without catalyst	$k_1$	$3.23 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-1}$	$4.53 \times 10^9 \text{ s}^{-1}$
	$k_2$	$1.88 \times 10^{-3} \text{ s}^{-1}$		
	$k_4$	$7.81 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-4}$	$5.57 \times 10^9 \text{ s}^{-1}$
	$k_5$	$8.05 \times 10^{-28}$		
	$k_8$	$7.69 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-8}$	$1.61 \times 10^{11} \text{ s}^{-1}$
	$k_9$	$1.03 \text{ s}^{-1}$		
(H <sub>2</sub> O-catalyzed)	$k_{12}$	$8.00 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-12}$	$4.53 \times 10^8 \text{ s}^{-1}$
	$k_{13}$	$3.67 \times 10^2 \text{ s}^{-1}$		
	$k_{15}$	$7.81 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-15}$	$1.38 \times 10^{11} \text{ s}^{-1}$
	$k_{16}$	$2.27 \times 10^{-8}$		
	$k_{19}$	$7.98 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-19}$	$5.03 \times 10^7 \text{ s}^{-1}$
	$k_{20}$	$4.70 \text{ s}^{-1}$		
(HSO <sub>4</sub> <sup>-</sup> -catalyzed)	$k_{12}$	$3.23 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-12}$	$4.53 \times 10^9 \text{ s}^{-1}$
	$k_{13}$	$3.25 \times 10^9 \text{ s}^{-1}$		
	$k_{15}$	$3.23 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-15}$	$1.64 \times 10^9 \text{ s}^{-1}$
	$k_{16}$	$7.39 \times 10^{-8}$		
	$k_{19}$	$3.25 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-19}$	$2.04 \times 10^{-4} \text{ s}^{-1}$
	$k_{20}$	$1.25 \times 10^{-4} \text{ s}^{-1}$		

Table S9. Calculated forward/reverse rate coefficients ( $k_1'/k_{-1}'$ ,  $k_5'/k_{-5}'$ ), and the unimolecular rate constants ( $k_2'$ ,  $k_6'$ ) for the sulfate formation between OBr<sup>-</sup> and SO<sub>3</sub><sup>2-</sup>

through Pathway 2( $\text{OBr}^- + \text{SO}_3^{2-}$ ).

Rate constant	Rate constants		Rate constants	
(H <sub>2</sub> O-catalyzed)	$k_1$	$3.23 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-1}$	$6.75 \times 10^{10} \text{ s}^{-1}$
	$k_2$	$3.32 \times 10^{-5} \text{ s}^{-1}$		
	$k_5$	$8.03 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-5}$	$3.19 \times 10^5 \text{ s}^{-1}$
(HSO <sub>4</sub> <sup>-</sup> -catalyzed)	$k_6$	$2.54 \times 10^{-4}$		
	$k_5$	$3.25 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{-5}$	$2.87 \times 10^{-4} \text{ s}^{-1}$
	$k_6$	$2.46 \times 10^2 \text{ s}^{-1}$		

Table S10. Calculated overall rate constant, effective rate constant, S(IV) oxidation rate and the S(IV) lifetimes for Pathway 1( $\text{OBr}^- + \text{SO}_3^{2-}$ ) and Pathway 2( $\text{OBr}^- + \text{SO}_3^{2-}$ ) from  $\text{SO}_3^{2-}$  and  $\text{OBr}^-$  respectively, assuming  $[\text{OBr}^-] = 7.42 \times 10^{-7} \text{ M}$  (corresponding to a Henry's law equilibrium with a gas phase HOBr mixing ratio of 0.31 ppbv at pH=9), and  $[\text{H}_2\text{O}] = 55.56 \text{ M}$  (corresponding to the known bulk concentration of H<sub>2</sub>O).

Rate constants	Catalysts	Overall rate constant $\text{M}^{-2} \text{s}^{-1}$	Effective rate constant <sup>d</sup> ( $\text{M}^{-1} \text{s}^{-1}$ )	S(IV) oxidation rate ( $\text{s}^{-1}$ )	S(IV) lifetime (s)
Pathway 1 <sup>a</sup> ( $\text{OBr}^- + \text{SO}_3^{2-}$ )	Without catalyst	$1.94 \times 10^{-40}$	$1.94 \times 10^{-40}$	$1.44 \times 10^{-46}$	$6.96 \times 10^{45}$
	H <sub>2</sub> O-catalyzed	$1.36 \times 10^{-19}$	$4.21 \times 10^{-16}$	$3.12 \times 10^{-22}$	$3.20 \times 10^{21}$
	HSO <sub>4</sub> <sup>-</sup> -catalyzed <sup>c</sup>	$2.51 \times 10^{-8}$	$2.51 \times 10^{-26}$	$1.86 \times 10^{-32}$	$5.37 \times 10^{31}$
Pathway 1 <sup>b</sup> ( $\text{OBr}^- + \text{SO}_3^{2-}$ )	Without catalyst	$6.80 \times 10^{-15}$	$6.80 \times 10^{-15}$	$5.05 \times 10^{-21}$	$1.98 \times 10^{20}$
	H <sub>2</sub> O-catalyzed	$4.44 \times 10^{-8}$	$1.37 \times 10^{-4}$	$1.02 \times 10^{-10}$	$9.83 \times 10^9$
	HSO <sub>4</sub> <sup>-</sup> -catalyzed <sup>c</sup>	$1.76 \times 10^7$	$1.76 \times 10^{-11}$	$1.31 \times 10^{-17}$	$7.64 \times 10^{16}$
Pathway 2 ( $\text{OBr}^- + \text{SO}_3^{2-}$ )	Without catalyst	$1.59 \times 10^{-6}$	$1.59 \times 10^{-6}$	$1.18 \times 10^{-12}$	$8.49 \times 10^{11}$
	H <sub>2</sub> O-catalyzed	$4.01 \times 10^{-2}$	2.23	$1.65 \times 10^{-6}$	$6.04 \times 10^5$
	HSO <sub>4</sub> <sup>-</sup> -catalyzed <sup>c</sup>	$1.56 \times 10^8$	$1.56 \times 10^{-1}$	$1.15 \times 10^{-7}$	$8.66 \times 10^6$

<sup>a</sup> The second step of Pathway 1 ( $\text{OBr}^- + \text{SO}_3^{2-}$ ) leading to sulfate formation through the hydrolysis reaction.

<sup>b</sup> The second step of Pathway 1 ( $\text{OBr}^- + \text{SO}_3^{2-}$ ) leading to sulfate formation through the reaction of  $\text{BrSO}_3^-$  intermediate with  $\text{OH}^-$ .

<sup>c</sup> Assuming a general concentration of  $\text{H}^+$  act as the possible higher limit for the concentration of  $\text{HSO}_4^-$  in cloud water.

<sup>d</sup> Effective rate constant = Overall rate constant  $\times [\text{M}]$ , where  $[\text{M}]$  is the concentration of catalyst M.

## Section 4. Cartesian coordinates of the structures.

### 4.1 Cartesian coordinates of the structures involving in the reaction of HOBr with HOSO<sub>2</sub><sup>-</sup>.

Table S11. Coordinates of HOBr. Units are in angstrom.

atom	X	Y	Z
O	0.021200	1.437606	0.000000
H	-0.911587	1.678685	0.000000
Br	0.021200	-0.376558	0.000000

Table S12. Coordinates of HOSO<sub>2</sub><sup>-</sup>. Units are in angstrom.

atom	X	Y	Z
S	0.174133	0.000070	-0.381367
O	-1.480647	-0.001124	0.046825
H	-1.462594	-0.000264	1.013624
O	0.658589	-1.218452	0.294668
O	0.656617	1.219468	0.294537

Table S13. Coordinates of BrSO<sub>3</sub><sup>-</sup>. Units are in angstrom.

atom	X	Y	Z
S	-1.018881	-0.000009	0.000016
O	-1.298949	-1.256781	0.633168
O	-1.298964	1.176750	0.771791
O	-1.299024	0.080039	-1.404952
Br	1.356503	0.000003	-0.000009

Table S14. Coordinates of BrSO<sub>3</sub>H. Units are in angstrom.

atom	X	Y	Z
S	-0.880751	0.120799	0.069210
O	-1.289144	-1.073702	-0.866719
H	-1.289927	-1.899639	-0.361576
O	-1.269048	-0.181821	1.397289
O	-1.259093	1.303032	-0.598161
Br	1.312006	-0.011806	-0.005859

Table S15. Coordinates of cis-H<sub>2</sub>SO<sub>4</sub>. Units are in angstrom.

atom	X	Y	Z
S	0.000000	0.091216	0.120238
O	-0.000020	1.494832	0.195960

O	0.000013	-0.758497	1.259994
O	-1.223808	-0.312199	-0.783942
H	-1.556128	-1.177623	-0.514162
O	1.223810	-0.312168	-0.783949
H	1.556168	-1.177575	-0.514159

Table S16. Coordinates of trans-H<sub>2</sub>SO<sub>4</sub>. Units are in angstrom.

atom	X	Y	Z
S	-0.000002	0.000001	-0.153840
O	0.641015	-1.068244	-0.819725
O	-0.641020	1.068270	-0.819690
O	1.029516	0.662937	0.836058
O	-1.029509	-0.662963	0.836045
H	1.691785	0.010654	1.099951
H	-1.691765	-0.010681	1.099974

Table S17. Coordinates of SO<sub>4</sub><sup>2-</sup>. Units are in angstrom.

atom	X	Y	Z
S	-0.000002	0.000017	-0.000050
O	0.374677	0.239450	1.421658
O	1.227987	-0.274813	-0.797412
O	-0.685196	1.206218	-0.542828
O	-0.917463	-1.170888	-0.081318

Table S18. Coordinates of H<sub>2</sub>O. Units are in angstrom.

atom	X	Y	Z
H	-0.000000	0.000000	0.116661
O	0.000000	0.760848	-0.466644
O	-0.000000	-0.760848	-0.466644

Table S19. Coordinates of OH<sup>-</sup>. Units are in angstrom.

atom	X	Y	Z
O	-0.000000	0.000000	0.106625
H	0.000000	0.000000	-0.853002

Table S20. Coordinates of HSO<sub>4</sub><sup>-</sup>. Units are in angstrom.

atom	X	Y	Z
S	-0.142029	-0.029869	-0.000006
O	-0.900566	1.193776	-0.000107
O	-0.232877	-0.817287	-1.211881
O	-0.233038	-0.817186	1.211922

O	1.405583	0.532161	0.000068
H	1.959652	-0.253800	0.000082

Table S21. Coordinates of reactant complex ( $R_{c1}$ ). Units are in angstrom.

atom	X	Y	Z
S	1.427633	-0.133204	0.040985
O	1.984175	1.296588	-0.572656
H	1.762363	2.010589	0.042141
O	2.052072	-0.212097	1.369052
O	2.014100	-1.067179	-0.926653
O	-3.151990	0.106632	0.025565
H	-3.440872	-0.543055	-0.625659
Br	-1.267156	-0.009366	0.021866

Table S22. Coordinates of transition state ( $P_{c2}$ ). Units are in angstrom.

atom	X	Y	Z
O	-1.144381	-1.843517	0.007509
H	-1.347257	-1.861750	0.947528
Br	1.441060	-0.591378	-0.024336
S	3.420095	0.327536	-0.019076
O	3.107250	1.842213	0.156205
H	2.966684	2.090686	1.088336
O	4.123158	-0.156613	1.120129
O	3.970510	0.189525	-1.321330
S	-3.870488	0.339355	-0.000272
O	-4.138490	1.790947	-0.057268
O	-5.113813	-0.415618	-0.262991
O	-3.334093	-0.024582	1.330302
O	-2.856848	-0.012079	-1.037890
H	-1.756586	-1.163181	-0.351873

Table S23. Coordinates of product complex ( $R_{c3}$ ). Units are in angstrom.

atom	X	Y	Z
S	0.342745	0.690269	0.003442
O	0.941680	0.406782	1.282483
O	1.088154	0.183042	-1.128057
O	-0.168271	2.024963	-0.160272
O	3.413365	-1.184098	-0.062709
H	2.642865	-0.745384	-0.450686
H	3.355970	-0.974361	0.874341
Br	-1.533776	-0.593430	0.001992

Table S24. Coordinates of reactant complex ( $TS_3$ ). Units are in angstrom.

atom	X	Y	Z
S	0.716046	-0.160474	0.024768
O	0.828803	-0.877085	-1.212304
O	0.834227	1.389566	-0.020218
O	0.798791	-0.790021	1.307656
O	2.762989	0.191429	0.053070
H	1.890476	1.354598	-0.027653
H	3.085191	-0.041956	-0.822830
Br	-1.663740	0.055538	-0.016327

Table S25. Coordinates of transition state ( $P_{c3}$ ). Units are in angstrom.

atom	X	Y	Z
S	1.566238	0.110840	0.041666
O	1.435473	0.195213	1.462515
O	0.529932	-0.850525	-0.536860
O	1.611906	1.328763	-0.698770
O	2.891271	-0.637893	-0.313916
H	-0.466335	-0.543199	-0.330771
H	3.040588	-1.409501	0.258348
Br	-2.268078	-0.003006	0.002915

Table S26. Coordinates of product complex ( $R_{c4}$ ). Units are in angstrom.

atom	X	Y	Z
S	-0.007458	-0.439482	0.316425
O	0.581178	0.674236	1.025632
O	0.615932	-0.738344	-0.951016
O	-0.312041	-1.582439	1.134257
O	3.133176	1.680571	0.232594
H	3.061303	2.250234	-0.539509
H	2.220600	1.434724	0.449935
O	3.532374	-0.981495	-0.673097
H	2.599736	-1.130289	-0.872705
H	3.545202	-0.057229	-0.374920
Br	-2.048927	0.346115	-0.282073

Table S27. Coordinates of reactant complex ( $TS_4$ ). Units are in angstrom.

atom	X	Y	Z
S	0.549142	0.449643	-0.010165
O	0.723513	-0.368873	-1.157271
O	0.676697	-0.116827	1.286406
O	0.163766	1.807765	-0.153016
O	3.575070	-1.535051	-0.013867

H	3.332726	-1.898494	0.845035
H	2.970702	-1.956567	-0.635498
O	2.677961	0.990897	-0.088258
H	2.917195	1.471972	0.713745
H	3.114746	0.107844	-0.019547
Br	-2.390220	-0.318353	0.007627

Table S28. Coordinates of transition state ( $P_{c4}$ ). Units are in angstrom.

atom	X	Y	Z
S	-1.615124	-0.594010	-0.012610
O	-1.237412	0.699913	-0.521949
O	-1.288087	-0.833345	1.371653
O	-1.332044	-1.702429	-0.889505
O	-4.285826	1.834307	0.062815
H	-3.659131	2.469530	0.449969
H	-4.489010	2.119938	-0.843837
O	-3.255946	-0.460310	-0.031933
H	-3.675133	-1.138295	0.519892
H	-3.852918	0.894894	0.039745
Br	3.791791	0.252943	0.003067

Table S29. Coordinates of product complex ( $R_{c5}$ ). Units are in angstrom.

atom	X	Y	Z
S	-1.663798	-0.064638	0.000002
O	-2.830060	1.106089	-0.000001
H	-3.702334	0.678324	-0.000009
O	-1.969735	-0.850822	-1.214745
O	-1.969751	-0.850827	1.214738
O	1.230612	1.376371	0.000001
H	0.291344	1.101905	0.000006
Br	2.124092	-0.199786	0.000001

Table S30. Coordinates of reactant complex ( $TS_5$ ). Units are in angstrom.

atom	X	Y	Z
S	1.858352	-0.165624	0.008480
O	1.791103	1.453275	-0.086653
H	2.694794	1.811313	-0.068148
O	2.584834	-0.441692	1.252171
O	2.593166	-0.589871	-1.187213
O	-0.311657	-0.186245	0.008596
H	-0.342084	-1.155452	0.010163
Br	-2.438454	0.003154	0.000774



Table S31. Coordinates of transition state (P<sub>c5</sub>). Units are in angstrom.

atom	X	Y	Z
S	-1.646423	-0.066252	0.071228
O	-1.474783	1.280283	-0.719095
H	-1.870957	2.026630	-0.240316
O	-2.892207	-0.663925	-0.287792
O	-1.416258	0.195703	1.457212
O	-0.535877	-0.889315	-0.553785
H	0.446609	-0.544225	-0.324029
Br	2.237717	0.005590	0.007211

Table S32. Coordinates of product complex (R<sub>c6</sub>). Units are in angstrom.

atom	X	Y	Z
S	1.689482	-0.562651	-0.043972
O	2.509761	0.820847	-0.413508
H	1.919010	1.569443	-0.179470
O	1.691389	-0.578780	1.435606
O	2.618258	-1.568023	-0.596455
O	-1.127050	0.566290	-0.976709
H	-0.270441	0.094833	-0.874743
O	0.553102	2.671870	0.214998
H	0.441513	2.710033	1.170763
H	-0.228160	2.205248	-0.112441
Br	-2.253066	-0.367850	0.096799

Table S33. Coordinates of reactant complex (TS<sub>6</sub>). Units are in angstrom.

atom	X	Y	Z
S	1.922238	-0.395002	0.056415
O	1.898289	0.923038	-0.870401
H	1.156423	1.510337	-0.566685
O	2.373114	0.061716	1.378490
O	2.909066	-1.230674	-0.637011
O	-0.320428	-0.547812	-0.001948
H	-0.303256	-1.246435	0.670306
O	-0.186343	2.383894	-0.058873
H	-0.002392	2.865784	0.754916
H	-0.793121	1.675779	0.198362
Br	-2.405801	-0.320192	-0.012617

Table S34. Coordinates of transition state (P<sub>c6</sub>). Units are in angstrom.

atom	X	Y	Z
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S	1.728078	-0.216876	0.065513
O	1.430815	0.949666	-0.879776
H	0.648574	1.572122	-0.528750
O	1.471728	0.189932	1.415420
O	3.022655	-0.726752	-0.252612
O	0.724141	-1.323632	-0.337102
H	-0.241275	-1.031739	-0.189258
O	-0.460709	2.343385	-0.096662
H	-0.277743	2.756432	0.756309
H	-1.143845	1.656424	0.064091
Br	-2.175543	-0.369829	0.001579

#### 4.2 Cartesian coordinates of the structures involving in the reaction of HOBr with $\text{SO}_3^{2-}$ .

Table S35. Coordinates of  $\text{SO}_3^{2-}$ . Units are in angstrom.

atom	X	Y	Z
S	-0.000055	-0.000023	0.332061
O	-0.171848	1.409296	-0.221366
O	-1.134796	-0.853445	-0.221340
O	1.306754	-0.555805	-0.221415

Table S36. Coordinates of monomer ( $\text{M}_7$ ). Units are in angstrom.

atom	X	Y	Z
S	-1.05978900	0.00994400	-0.02952400
O	-1.74023800	1.37383200	0.08497500
O	-1.44002600	-0.74724400	1.24208400
O	-1.77860300	-0.71314900	-1.16886200
O	3.28879445	0.93178316	-1.76698883
H	3.81448122	1.05680239	-0.96306569
Br	1.60237850	0.67795094	-1.19116728

Table S37. Coordinates of product complex ( $\text{P}_{c7}$ ). Units are in angstrom.

atom	X	Y	Z
S	-1.517619	-0.063942	0.004340
O	-1.798264	-0.498979	1.348972
O	-1.763046	-1.047084	-1.019481
O	-1.962285	1.269939	-0.310948
O	4.757766	-0.149211	0.034197
H	3.866296	-0.399166	-0.218029
Br	0.758350	0.137855	-0.007809

Table S38. Coordinates of reactant complex ( $R_{c8}$ ). Units are in angstrom.

Atom	X	Y	Z
S	0.478604	-0.144418	0.000202
O	0.960060	1.211467	-0.095560
O	0.730443	-0.792814	1.261157
O	0.712723	-0.957736	-1.165307
O	4.076786	0.228760	0.000537
H	3.194267	0.605716	-0.005628
Br	-1.791200	0.119645	-0.000121

Table S39. Coordinates of transition state ( $TS_8$ ). Units are in angstrom.

Atom	X	Y	Z
S	-0.805044	0.020026	0.001853
O	-0.908701	-0.770179	-1.185880
O	-0.904517	-0.617157	1.278226
O	-0.889124	1.444709	-0.086122
O	-3.236596	0.066687	-0.004440
H	-3.354624	-0.886284	-0.000933
Br	1.821338	-0.012189	-0.001228

Table S40. Coordinates of product complex ( $P_{c8}$ ). Units are in angstrom.

Atom	X	Y	Z
S	2.214578	-0.003426	0.002085
O	1.937760	-0.718536	1.232736
O	1.919999	-0.781246	-1.185951
O	1.701369	1.347694	-0.028589
O	3.800961	0.241372	-0.017181
H	4.266137	-0.607657	-0.025444
Br	-3.273717	-0.001480	-0.000458

Table S41. Coordinates of product complex ( $R_{c9}$ ). Units are in angstrom.

Atom	X	Y	Z
S	0.099989	0.193893	-0.122658
O	0.178015	1.484651	-0.756089
O	0.576831	0.149098	1.235996
O	0.509025	-0.916889	-0.948145
O	3.565197	1.050631	0.152463
H	2.708483	1.355295	0.461188
O	3.298822	-1.455676	0.067919
H	3.399915	-0.419514	0.104905
H	2.393865	-1.584610	-0.234120

Br	-2.146435	-0.141371	0.103240
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Table S42. Coordinates of product complex (TS<sub>9</sub>). Units are in angstrom.

Atom	X	Y	Z
S	-0.416334	0.372256	0.013357
O	-0.141088	1.767413	-0.128730
O	-0.708500	-0.408842	-1.149640
O	-0.630845	-0.186859	1.310827
O	-2.712679	0.948934	0.084185
H	-2.823758	1.306087	-0.800649
O	-3.356177	-1.496017	0.014534
H	-3.094648	-0.496893	0.022570
H	-2.547212	-1.949180	-0.237139
Br	2.157751	-0.280375	-0.007083

Table S43. Coordinates of product complex (P<sub>c9</sub>). Units are in angstrom.

Atom	X	Y	Z
S	1.803550	-0.621420	0.029320
O	1.183605	-1.817192	-0.498729
O	1.519515	0.562813	-0.770030
O	1.627225	-0.423605	1.448062
O	3.386406	-0.844040	-0.087539
H	3.632852	-1.003432	-1.010836
O	3.358252	2.593792	-0.006868
H	4.139951	2.093188	0.244675
H	2.715140	1.920713	-0.281804
Br	-3.655565	0.181660	-0.002866

Table S44. Coordinates of reactant complex (R<sub>c10</sub>). Units are in angstrom.

Atom	X	Y	Z
S	-1.762919	0.004596	-0.006057
O	-2.791349	1.056405	-0.368336
O	-1.953122	-1.149073	-0.967020
O	-2.115418	-0.505624	1.374949
O	1.014734	1.244662	-0.019949
H	0.097153	0.820882	-0.026365
Br	2.139165	-0.173297	-0.000968

Table S45. Coordinates of reactant complex (TS<sub>10</sub>). Units are in angstrom.

Atom	X	Y	Z
S	1.978718	0.024790	-0.008049
O	2.399176	-1.033901	-0.991108

O	2.745377	1.285385	-0.320605
O	2.374501	-0.430605	1.370218
O	-0.469252	-0.024219	-0.007909
H	-0.307053	0.909569	-0.196009
Br	-2.507167	0.009157	-0.002285

Table S46. Coordinates of reactant complex ( $P_{c10}$ ). Units are in angstrom.

Atom	X	Y	Z
S	-1.754022	-0.059252	-0.000000
O	-2.971243	0.732127	-0.000063
O	-1.578224	-0.846523	-1.210208
O	-1.578296	-0.846432	1.210276
O	-0.616661	1.038607	-0.000005
H	0.299226	0.625160	-0.000007
Br	2.334872	-0.008553	0.000000

Table S47. Coordinates of product complex ( $R_{c11}$ ). Units are in angstrom.

Atom	X	Y	Z
S	-2.634408	-0.347818	0.028644
O	-2.403512	1.183851	0.017230
O	-3.512993	-0.615614	-1.180143
O	-3.495360	-0.599065	1.253707
O	1.308934	-0.597938	-0.311710
H	0.831738	0.285631	-0.235772
Br	3.030841	-0.192045	0.063369
O	0.081799	1.674644	-0.155736
H	-0.918114	1.475923	-0.066061
H	0.326529	2.158114	0.638836

Table S48. Coordinates of product complex ( $TS_{11}$ ). Units are in angstrom.

Atom	X	Y	Z
S	-1.932451	-0.343078	0.006494
O	-2.497382	1.063223	-0.129999
O	-2.429340	-1.148983	-1.156352
O	-2.481078	-0.935078	1.270459
O	0.480756	-0.347346	0.012370
H	0.346078	0.619160	-0.026424
Br	2.542389	-0.249425	0.001074
O	-0.224743	2.462798	-0.099816
H	-1.124119	2.055332	-0.080650
H	-0.072078	2.787701	0.792293

Table S49. Coordinates of product complex ( $P_{c11}$ ). Units are in angstrom.

Atom	X	Y	Z
S	1.818543	-0.144016	0.025328
O	1.598060	0.941193	-0.925433
O	1.566247	0.266097	1.394594
O	3.085081	-0.819185	-0.165699
O	0.758178	-1.266085	-0.318662
H	-0.175847	-0.933869	-0.194309
Br	-2.259173	-0.384878	0.002879
O	-0.614029	2.490254	0.005977
H	0.214372	2.086389	-0.296635
H	-1.212452	1.724289	0.058735

### 4.3 Cartesian coordinates of the structures involving in the reaction of OBr<sup>-</sup> with SO<sub>3</sub><sup>2-</sup>.

Table S50. Coordinates of OBr<sup>-</sup>. Units are in angstrom.

atom	X	Y	Z
O	0.000000	0.000000	-1.461728
Br	0.000000	0.000000	0.334109

Table S51. Coordinates of reactant complex (R<sub>c12</sub>). Units are in angstrom.

Atom	X	Y	Z
S	2.853608	-0.024325	-0.027034
O	3.340422	-0.209897	1.409439
O	3.741249	-0.926377	-0.883550
O	3.238968	1.405373	-0.407701
O	-4.355405	0.494444	0.058548
Br	-2.667988	-0.163404	-0.028039

Table S52. Coordinates of transition state (TS<sub>12</sub>). Units are in angstrom.

Atom	X	Y	Z
S	-1.297174	-0.022195	-0.000003
O	-1.686205	-0.759764	1.214203
O	-1.860775	1.338720	-0.000603
O	-1.686046	-0.760764	-1.213654
O	3.429158	-0.147585	-0.000029
Br	1.005306	0.085436	0.000020

Table S53. Coordinates of reactant complex (R<sub>c13</sub>). Units are in angstrom.

Atom	X	Y	Z
	2.225526	0.168093	-0.001913

2.766911	1.553194	-0.361704
2.838207	-0.163935	1.360741
2.883470	-0.795551	-0.991087
-2.941489	-0.811399	0.002889
-4.032427	1.431459	-0.001775
-3.549279	0.500573	0.000055
-3.324858	2.080082	-0.000989
-1.167190	-0.428008	-0.001170

Table S54. Coordinates of transition state (TS<sub>13</sub>). Units are in angstrom.

Atom	X	Y	Z
S	2.200092	0.160574	0.000273
O	2.638973	1.558353	-0.384433
O	2.758057	-0.146772	1.374266
O	2.812254	-0.812874	-0.985825
O	-2.802225	-0.849052	-0.001615
O	-4.593387	1.073930	0.008946
H	-3.425683	-0.027806	0.005266
H	-4.026542	1.846462	-0.057585
Br	-0.978818	-0.313614	-0.001222

Table S55. Coordinates of product complex (P<sub>c13</sub>). Units are in angstrom.

Atom	X	Y	Z
S	1.680182	0.294937	0.002518
O	1.247056	1.664175	-0.109322
O	2.262447	-0.060844	1.271474
O	2.366513	-0.226120	-1.152215
O	-4.702118	-0.480589	0.008649
O	-2.525596	2.110024	-0.006312
H	-4.011289	0.188924	0.006819
H	-1.921365	1.363421	-0.004143
Br	-0.289619	-0.866415	-0.004033

Table S56. Coordinates of reactant complex (R<sub>c14</sub>). Units are in angstrom.

Atom	X	Y	Z
S	-2.700801	-0.009142	-0.007471
O	-3.426318	-1.004225	-0.911704
O	-3.267196	-0.247406	1.391073
O	-3.209200	1.369546	-0.428942
O	1.386490	-0.230448	-0.065239
Br	3.181217	0.029901	0.006801

Table S57. Coordinates of transition state (TS<sub>14</sub>). Units are in angstrom.

Atom	X	Y	Z
S	-1.965569	-0.001749	0.004910
O	-2.581893	-0.972745	1.001481
O	-2.540862	1.368806	0.331517
O	-2.518632	-0.382531	-1.360782
O	0.401586	-0.010089	0.011996
Br	2.553358	0.000013	0.001364

Table S58. Coordinates of product complex ( $P_{c14}$ ). Units are in angstrom.

Atom	X	Y	Z
S	-2.737586	-0.000020	-0.000480
O	-3.236137	-0.991822	-0.982126
O	-3.269488	-0.328038	1.344195
O	-3.189840	1.356420	-0.392233
O	-1.255369	-0.036244	0.030762
Br	3.754516	-0.000063	0.000083

Table S59. Coordinates of reactant complex ( $R_{c15}$ ). Units are in angstrom.

atom	X	Y	Z
S	-2.670341	-0.299962	0.054776
O	-3.459629	-0.995073	-1.048382
O	-3.581805	-0.288517	1.277370
O	-2.561983	1.167557	-0.385797
O	1.318766	-0.535554	0.086303
O	0.128712	1.765063	-0.059203
H	0.621165	0.885025	-0.006872
H	-0.814677	1.531032	-0.167580
Br	3.090471	-0.186413	0.009592

Table S60. Coordinates of transition state ( $TS_{15}$ ). Units are in angstrom.

atom	X	Y	Z
S	-1.923184	-0.260883	0.005550
O	-2.393834	-1.179550	-1.103496
O	-2.493103	-0.806138	1.299634
O	-2.592694	1.088458	-0.232432
O	0.402517	-0.244062	0.021135
O	-0.006298	2.291460	0.009184
H	0.271889	1.304286	0.016765
H	-0.967399	2.188663	-0.060632
Br	2.518107	-0.243433	0.000082

Table S61. Coordinates of reactant complex ( $P_{c15}$ ). Units are in angstrom.



atom	X	Y	Z
S	-2.469126	-0.171390	-0.000000
O	-3.276439	-0.441475	-1.209997
O	-3.276486	-0.441413	1.209979
O	-2.049808	1.256881	-0.000028
O	-1.261647	-1.027580	0.000046
O	0.647233	1.859217	0.000001
H	1.306647	1.141179	0.000006
H	-0.239866	1.454381	-0.000010
Br	3.205040	-0.271382	-0.000000

## 6 Note and References

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- 2 W. F. McCoy, E. R. B. III and R. W. Johnson, Hypohalous Acid and haloamine flashoff in industrial evaporative cooling systems, Cooling Tower Institute Annual Meeting, 1990.