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Reaction of SO_3 with $HONO_2$ and Implications for Sulfur Partitioning in the Atmosphere

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ABSTRACT: Sulfur trioxide is a critical intermediate for the sulfur cycle and the formation of sulfuric acid in the atmosphere. The traditional view is that sulfur trioxide is removed by water vapor in the troposphere. However, the concentration of water vapor decreases significantly with increasing altitude, leading to longer atmospheric lifetimes of sulfur trioxide. Here, we utilize a dual-level strategy that combines transition state theory calculated at the W2X//DF-CCSD(T)-F12b/jun′-cc-pVDZ level, with variational transition state theory with small-curvature tunneling from direct dynamics calculations at the M08-HX/MG3S level. We also report the pressure-dependent rate constants calculated by using system-specific quantum Rice-Ramsperger-Kassel (SS-QRRK) theory. The present findings show that falloff effects in the SO_3 + $HONO_2$ reaction are pronounced below 1 bar. The SO_3 + $HONO_2$ reaction can be a potential removal reaction for SO_3 in the stratosphere and for $HONO_2$ in the troposphere, and the reaction can potentially compete well with the $SO_3 + 2H_2O$ reaction between 25 and 35 km, as well as the OH + $HONO_2$ reaction. The present findings also suggest an unexpected new product from the SO_3 + $HONO_2$ reaction, which, although very short-lived, would have broad implications for understanding the partitioning of sulfur in the stratosphere, and the potential for the SO_3 reaction with organic acids to generate organosulfates without the need of heterogeneous chemistry.

1. INTRODUCTION

Atmospheric SO_3 is an important intermediate in the formation of H_2SO_4, which is a critical component of acid rain, the stratospheric aerosol layer, new particle formation, and secondary aerosol.[1-8] The formation of gaseous H_2SO_4 is initiated by the oxidation of SO_2 by the hydroxyl radical OH (R1), followed by the reaction of $HOSO_2$ with O_2 (R2).[9,10] The SO_3 produced by reactions (R1) and (R2) is expected to react with gaseous H_2O, leading to gas phase H_2SO_4. The kinetics and mechanism of this reaction has been the subject of several laboratory studies.[9-16] The overall underlying chemistry is now referred to as the traditional acid rain scheme, shown below.[17-20]

$$SO_2 + OH \rightarrow HOSO_2 \tag{R1}$$
$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{R2}$$
$$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O \tag{R3}$$

Results from a recent study[21] on the photochemistry of $HOSO_2$ suggest that the photolysis lifetime of the $HOSO_2$ radical is around 70 s, while the reactive lifetime of the $HOSO_2$ with O_2 is roughly 1 μs under Earth's stratospheric conditions.[22] Therefore, the photochemistry of the $HOSO_2$ radical will not compete with the O_2 reaction in the stratosphere. For SO_3, the photochemistry has been addressed experimentally and theoretically. However, an examination of the lowest-lying singlet excited states of SO_3 indicates that the system is photostable under stratospheric conditions.[21] Once the photochemical stability of SO_3 is ensured, the efficiency of H_2SO_4 generation from the association of SO_3 and H_2O is only conditioned by largely unknown SO_3 removal processes. The findings from Carmona-García et al.[21] clearly point to a long photolysis lifetime of this molecule in the Earth's stratosphere, being roughly 579 days ($J = 2 \times 10^{-8}\ s^{-1}$) at 16 km. Therefore, the only known reactive SO_3 sink is R3, which proceeds to form H_2SO_4 at a rate of $8.5 \times 10^{-41}\exp(+6540/T)\ [H_2O]^2\ s^{-1}$,[23,24] where there are two entrance channels $SO_3 + H_2O{\cdots}H_2O$ and $SO_3{\cdots}H_2O + H_2O$. Additional removal mechanisms of SO_3 are largely unknown and are the motivation of this work.

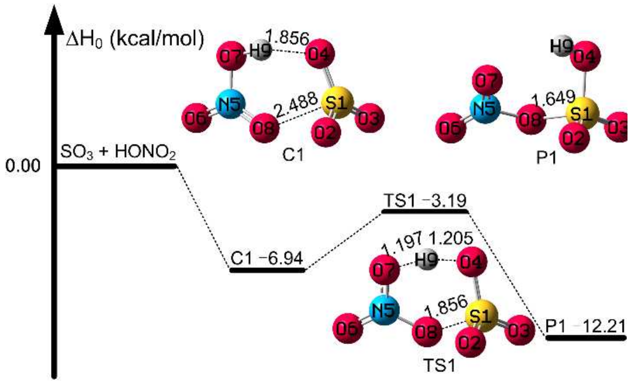

Figure. 1. The calculated enthalpy profile at 0 K for the SO_3 + $HONO_2$ Reaction and the values at the W2X//DF-CCSD(T)-F12b/ jun′-cc-pVDZ level.

Here, we report theoretical work on a new reaction between SO_3 and nitric acid, which is potentially important because nitric acid has a relatively high concentration (in the range 10^8-10^9 molecules cm^{-3}), in the stratosphere:[25]

$SO_3 + HONO_2 \rightarrow HOSO_2\text{-}NO_3$ (R4)

2. COMPUTATIONAL METHODS

We have investigated R4 using the dual-level rate strategy developed by our group[26] that combines transition state theory at the W2X[27]//DF-CCSD(T)-F12b[28,29]/jun′-cc-pVDZ level, with variational transition state theory including small-curvature tunneling[32,33] at the M08-HX/MG3S[34,35] level. The jun′-cc-pVDZ basis set is a revision of jun-cc-pVDZ,[30] which is similar to the jun′-cc-pVTZ basis set from jun-cc-pVTZ in our previous investigation.[31] The pressure-dependent rate constants are calculated using system-specific quantum Rice-Ramsperger-Kassel (SS-QRRK) theory;[36] the validity of this method was further shown by Master Equation (ME)[37] calculations in the SI (Supporting information). We have also computed the ultraviolet and visible (UV-Vis) absorption spectrum and cross sections of the final product of R4 by means of a well-established nuclear ensemble approach,[38-39] in conjunction with multi-state complete-active-space second-order perturbation theory (MS-CASPT2) method.[40-42] The resulting cross sections are then used to calculate the photodissociation rate (J/s^{-1}) and subsequent photolysis lifetime of this product under stratospheric conditions. Detailed information is provided in the SI.

3. RESULTS and DISSCUSION

3.1. Electronic structure of the SO_3 + $HONO_2$ reaction

We have found two different reaction pathways for reaction R4, as shown in Figure S1. We only consider the much lower reaction pathway due to the big difference (about 28 kcal/mol) in the enthalpies of activation at 0 K. The reaction in the SO_3 + $HONO_2$ potential energy surface for the lower reaction pathway begins with the formation of the pre-reactive C1 complex and proceeds to the transition state TS1 prior to the formation of product P1 (see Figure 1). Transition state TS1 corresponds to the transfer of the hydrogen atom (H9) from nitric acid to the oxygen atom (O4) of the sulfur trioxide, and simultaneous addition of the oxygen atom (O8) from nitric acid to the central sulfur atom (S1) of the sulfur trioxide, as shown in Figure 1. The O8-S1 bond length decreases from 2.488 Å in the pre-reactive complex C1 to 1.856 Å in the transition state, and the H9-O4 bond also shortens from 1.856 Å in C1 to 1.205 Å in TS1.

To provide further insight into the reaction mechanism, we also analyzed the natural orbitals of the transition state TS1. The results are provided in Figure S2, revealing that TS1 involves a hydrogen shift because the lone pair orbital of O8 in nitric acid is approximately perpendicular to the $HONO_2$ plane and cannot interact with the sulfur atom in SO_3.

The enthalpy of activation at 0 K of R4 is -3.19 kcal/mol calculated at W2X//DF-CCSD(T)-F12b/jun′-cc-pVDZ level (see Table S1). There is only 0.71 kcal/mol difference between the W2X//DF-CCSD(T)-F12b/jun′-cc-pVDZ and M08-HX/MG3S methods for the enthalpies of activation at 0 K. Therefore, M08-HX/MG3S has been used to do direct dynamics calculations.

3.2. Kinetics

The calculated high-pressure-limit (HPL) rate constants are listed in Table S2 and fitted to an analytic expression in SI. The calculated activation energies are provided in Table S3. They show a strong negative temperature dependence, increasing from -3.83 kcal/mol at 190 K to -2.97 kcal/mol at 350 K. This temperature dependence is also shown by the rate constant of R4, which decreases with increasing temperature from 6.18×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 190 K to 9.09×10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 350 K, as listed in Tables S2 and S3.

The pressure-dependent rate constants $k_4(T, p)$ of reaction R4 are given in Table S4. The details of the determination of these values and the equations used[43] are described in the SI. The low-pressure limit rate constant $k_{04}(T)$ is defined as the limit of $k_4(T, p)/[N2]$ when the pressure goes to zero. The calculated $k_0(T)$ of R4 is 9.34×10^{-32} cm^6 $molecule^{-2}$ s^{-1} at 298 K. The falloff effect, defined as the ratio $k_{\infty4}(T)/k_4(T,p)$ significantly increases with temperature as shown in Table S4 and Figure 2. For example, $k_{\infty4}(T)/k_4(T,p)$ at 1 bar increases from 1.02 at 200 K to 1.73 at 350 K. Figure 2 shows that the rate constant of R4 increases with increasing pressure below 1 bar. Table S5 shows that the ratio $k_{\infty4}(T)/k_{04}(T)$ is 4.2×10^{17} at 200 K and this ratio increases to 5.4×10^{18} at 350 K. The temperature dependence is more pronounced in the low-pressure limit rate constants than in the high-pressure limit ones. For example, between 200 and 350 K the calculated $k_{04}(T)$ decreases by a factor of 528, compared with a factor of only 40 for $k_{\infty4}(T)$. Of particular note is that falloff effects are very large under stratospheric conditions: the pressure-dependent rate constant is predicted to be 96-458 times lower than the high-pressure limit rate constant between 40-50 km altitude (Table S7).

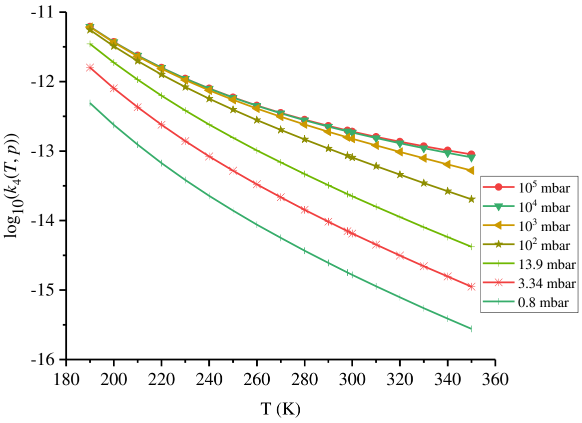

Figure 2. The rate constant of the SO_3 + $HONO_2$ reaction at different temperatures and pressures (bath gas: N2).

The transition pressure $p_{1/2}$ is defined as the pressure where the pressure-dependent rate constant is half of the high-pressure limit rate constant. The transition pressure of reaction R4 as a function of temperature is plotted in Figure S3, showing positive correlation with temperature. In addition, $p_{1/2}$ increases from 0.0136 bar at 200 K to 0.6596 bar at 350 K, which indicates that the pressure effect must be considered for reaction R4 (see Table S5).

Table 1. Atmosphere lifetimes (s) of the bimolecular reactions SO_3 + $HONO_2$ and SO_3 + $(H_2O)_2$ and the concentration of $HONO_2$ and $(H_2O)_2$ as functions of altitude.

H[a] (km)	T[a] (K)	p[a] (mbar)	$k_4(T,p)$[b] (cm^3 $molecule^{-1}$ s^{-1})	$k_3(T)$[c] (cm^6 $molecule^{-2}$ s^{-1})	[$HONO_2$][a] (molecules cm^{-3})	[H_2O][a] (molecules cm^{-3})	τ_{HONO_2}[d] (s)	τ_{H_2O}[d] (s)
0	290.2	1013	1.89×10^{-13}	4.69×10^{-31}	3.80×10^{8}	4.40×10^{17}	1.39×10^{4}	1.10×10^{-5}
5	250.5	495.9	5.05×10^{-13}	1.44×10^{-29}	1.50×10^{8}	1.70×10^{16}	1.32×10^{4}	2.40×10^{-4}
10	215.6	242.8	1.68×10^{-12}	8.52×10^{-28}	1.90×10^{9}	3.00×10^{14}	3.13×10^{2}	1.30×10^{-2}
15	198	118.8	3.59×10^{-12}	1.16×10^{-26}	1.30×10^{9}	1.50×10^{13}	2.14×10^{2}	3.82×10^{-1}
20	208	58.18	1.92×10^{-12}	2.49×10^{-27}	5.50×10^{9}	4.20×10^{12}	9.48×10^{1}	2.27×10^{1}
25	216.1	28.48	1.05×10^{-12}	7.96×10^{-28}	4.60×10^{9}	2.50×10^{12}	2.08×10^{2}	2.01×10^{2}
30	221.5	13.94	5.82×10^{-13}	3.90×10^{-28}	2.30×10^{9}	1.50×10^{12}	7.47×10^{2}	1.14×10^{3}
35	228.1	6.826	2.65×10^{-13}	1.71×10^{-28}	5.80×10^{8}	8.90×10^{11}	6.50×10^{3}	7.39×10^{3}
40	240.5	3.341	8.17×10^{-14}	4.10×10^{-29}	5.70×10^{7}	4.80×10^{11}	2.15×10^{5}	1.06×10^{5}
45	251.9	1.636	2.50×10^{-14}	1.25×10^{-29}	2.50×10^{6}	2.50×10^{11}	1.60×10^{7}	1.28×10^{6}
50	253.7	0.801	1.17×10^{-14}	1.05×10^{-29}	1.60×10^{5}	1.20×10^{11}	5.34×10^{8}	6.61×10^{6}

[a] Data is from ref. 27.

[b] Rate constant of the SO_3 + $HONO_2$ reaction (R4) at different temperature and pressure.

[c] Rate constant of the SO_3 + $2H_2O$ reaction (R3) from ref. 27.

[d] τ_{HNO_3} and τ_{H_2O} are atmosphere lifetimes of SO_3 for reaction with $HONO_2$ and H_2O, respectively.

3.3. Atmospheric implications

Our estimated atmospheric lifetimes for SO_3 with respect to R4 from 0 km to 50 km are listed in Table 1. While the lifetime of SO_3 with respect to R4 increases from 208 s at 25 km to 6500 s at 35 km (SO_3 peaks in the atmosphere in this altitude range),[44] the lifetime with respect to R3 increases from 201 s at 25 km to 7390 s at 35 km. Hence, our calculations indicate that the SO_3 + $HONO_2$ reaction should compete with the SO_3 + $2H_2O$ reaction over the altitude range between 25 km and 35 km. Outside this range, however, the atmospheric lifetime of SO_3 with respect to R4 becomes significantly longer than that with respect to R3, because of the large falloff effects mentioned above. It should be noted that the atmospheric lifetime of SO_3 in the troposphere is only 10^{-5} s; nevertheless, field measurements still observe detectable SO_3 concentrations.[45] In addition, we note that the rate constant for the SO_3 + $HONO_2$ reaction is about 2 times faster than that of the OH + $HONO_2$ reaction in Table S8. Typically, the concentration of OH is 10^4 to 10^6 molecules cm^{-3} and the concentration of SO_3 can also reach 10^6 molecules cm^{-3} in the troposphere.[45-50] Therefore, the SO_3 + $HONO_2$ reaction should be competitive with OH + $HONO_2$. Although these similar reactions such as SO_3 with organic acids have been reported in the literature,[51-56] their quantitative kinetics are still unknown; this leads to that these reactions have not been put forward and identified as an important sink for organic acids in the atmosphere.

The product of reaction R4, $HOSO_2$-NO_3, is shown in Figure 1 as P1. Based on its computed UV-Vis absorption spectrum, displayed in Figure 3, the system only exhibits significant absorption at wavelengths shorter than 260 nm. Thus, the photolysis lifetime of P1 ranges from ~30 hours at 20 km to 12 minutes at 40 km, indicating that it should be relatively photostable under the stratospheric conditions considered. However, the thermal dissociation lifetime with respect to the reactants is around 10^{-3}-10^{-4} s in the stratosphere as shown in Table S9, which result in very low concentrations under current-day stratospheric conditions (Figure S4). The lifetime of any reaction of P1 with OH in the stratosphere at the collision number ([OH]= 0.75 pptv) would be on the order of 1500 s. These results suggest that the SO_3 + $HONO_2$ reaction will introduce a new $HOSO_2$-NO_3 product in the stratosphere that would potentially partitions sulfur in a high SO_3 geoengineering scenario. The concentration of P1, from the SO_3 + $HONO_2$ reaction, is distributed between 10-35 km as shown in Figure S4 (See SI). An increased SO_3 represents a sensitivity exercise assuming the injection of large amounts of SO_2, e.g. 5 and 25 Tg(S) yr^{-1} to the stratosphere as proposed in some geoengineering scenarios.[57] Increasing SO_3 in the stratosphere would increase the concentration of P1, suggesting that new partitioning of sulfur can occur because of the SO_3 + $HONO_2$ reaction. Intriguingly, experimental balloon-borne observations between 30 and 40 km detect a $NO_3SO_3^-$ ion.[58-59] This ion has been previously attributed to a fragment of the $HSO_4HNO_3^-$ atmospheric ion,[58-59] but it may be also an atmospheric ion linked to other processes, including the formation of P1 via R4.

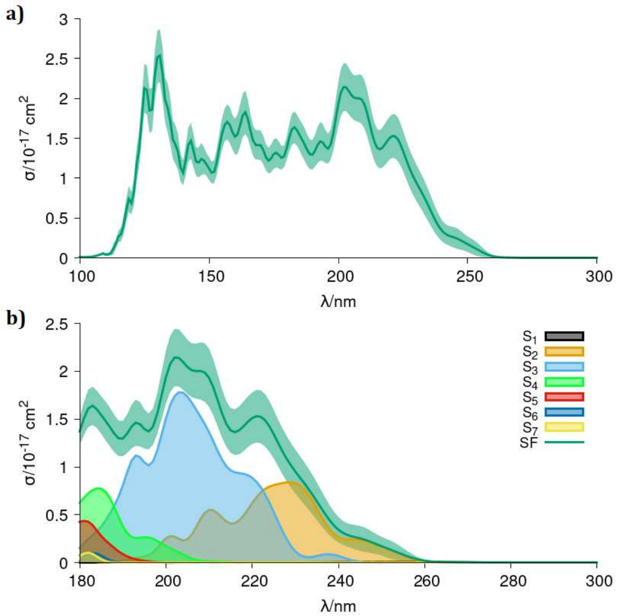

Figure 3. UV-Vis absorption spectrum and cross sections (σ/cm^2) of the P1 product (a) and contributions to the spectrum of the lowest-energy singlet excited states S1-S7 (b) of the system. The light green areas correspond to the uncertainty of the cross section due to statistical sampling.

4. CONCLUSIONS

In summary, we find a new reaction for sulfur trioxide, namely, SO_3 + $HONO_2$, which brings new insights into our understanding of atmospheric sulfur chemistry. We also find that the falloff effect is an important parameter for controlling the atmospheric lifetimes of SO_3 in the upper stratosphere by the SO_3 + $HONO_2$ reaction. Experimental verification using chemical ionization mass spectrometry could be used to monitor the relative concentrations of the SO_3 and $HONO_2$ reactants to determine the kinetics of the reaction as well as probe for the $HOSO_2$-NO_3 product. A final point is that this type of reaction may extend to other atmospheric acids such as carboxylic acids, potentially leading to the formation of organosulfates, previously considered to form via heterogeneous chemistry.[60]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

In the supporting information are contained: the computational methods, fitting of high-pressure-limit rate constant and calculated activation energies, fitting the pressure-dependent rate constant, the concentration of P1, the calculated k(T, p) under different methods, the equilibrium constant, activation enthalpy and barrier height, tunneling transmission coefficients, high-pressure-limit rate constants (k_∞(T) and activation energies (E_a), Pressure-dependent k_4(T, p), the fitted k_4(T, p) at different temperatures, the rate constant, atmospheric lifetimes, Cartesian coordinates, vibrational frequencies, the calculated enthalpy profile, the natural orbitals, and the transition pressure (PDF)

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Notes

The authors declare no competing financial interests.

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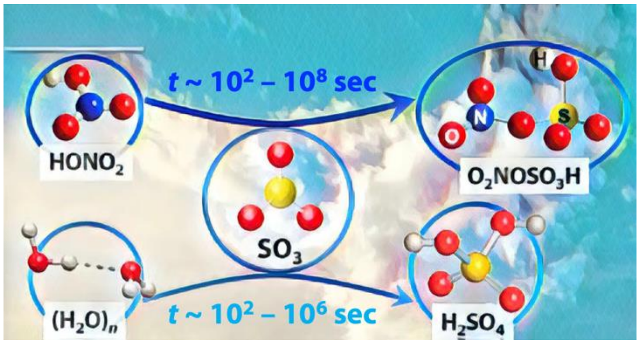
HONO$_2$
$t \sim 10^2 - 10^8$ sec
O$_2$NOSO$_3$H
H
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SO$_3$
(H$_2$O)$_n$
$t \sim 10^2 - 10^6$ sec
H$_2$SO$_4$

TOC Graphic