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Sulfuric acid decomposition chemistry above Junge layer in Earth's atmosphere concerning ozone depletion and healing

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Sulfuric acid (H_2SO_4) is the seed molecule for formation of stratospheric sulfate aerosol layer that assists ozone depletion by activation of halogen species. The impact of increased stratospheric sulfate aerosols due to large volcanic eruptions and possible side effect claimed in the geoengineering scheme of global climate using man-made injected stratospheric sulfate aerosols is ozone depletion. Given that both volcanic eruptions and geoengineering scheme are ultimately connected with increased upper stratospheric concentrations of H_2SO_4 , here we show by theoretical approach that the pressure-independent $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions via barrierless formation of peroxydisulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$) or $\text{HSO}_4 + \text{OH}$ radicals or sulfur trioxide (SO_3) + hydrogen peroxide (H_2O_2) molecules are the potential routes towards H_2SO_4 loss above the stratospheric sulfate aerosol layer, and for the regeneration or transportation of consumed lower-middle stratospheric OH radical in the upper stratosphere at the cost of $\text{O}(^1\text{D})$ /ozone.

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The highly dispersed microscopic particles in stratospheric aerosol layer play an important role in the stratospheric ozone depletion, and affect the Earth's climate by absorbing and scattering the solar-radiation^{1–7}. It is believed that this layer (Junge layer) is composed of mainly the sulfuric acid (H_2SO_4) and water (H_2O) molecules to form the sulfate aerosols or droplets. Similarly, the sulfate aerosols and other atmospheric aerosols resulting from various inorganic and organic species in troposphere also play an important role in degrading visibility, promoting heterogeneous chemistry through atmospheric chemical reactions, as well as negatively impacting human health^{8–12}. It is seen from the chemical composition of aerosol particles in the Earth's atmosphere that the H_2SO_4 among various species is the most important precursor for the formation of aerosol particles at a wide range of altitudes including both the troposphere and stratosphere^{1,8–12}. Indeed, the nucleated aerosol particles from trace atmospheric vapors are expected to provide ~45% or more of global cloud condensation nuclei (CCN)^{11–13}. Consequently, the H_2SO_4 molecule becomes of major importance in atmospheric chemistry—which has led to many studies investigating its formation, decomposition and its crucial role as a nucleating species for aerosols and cloud formation^{8–22}.

The most abundant sulfur molecules in the Earth's atmosphere at altitudes above 35 km or above the stratospheric sulfate aerosol layer or ozone layer are H_2SO_4 and sulfur dioxide (SO_2)^{23–25}. Moreover, the seed molecule for the formation of stratospheric sulfate aerosols, which assist ozone depletion through activation of halogen species, especially after volcanic eruptions, is H_2SO_4 ^{26–29}. The H_2SO_4 above 35 km altitude is formed from the surface of stratospheric sulfate aerosol layer via evaporation^{1,4,23–25}. Hence, the decomposition mechanisms of H_2SO_4 in upper stratosphere or above 35 km altitude are the potential routes towards the degradation of enhanced stratospheric sulfate aerosols that assist ozone depletion after volcanic eruptions.

In the quest for an answer to the question about the decomposition of H_2SO_4 molecule in the Earth's upper stratosphere, the visible solar radiation ($h\nu$) pumping photolysis of H_2SO_4 vapor ($\text{H}_2\text{SO}_4 + h\nu \rightarrow \text{SO}_3 + \text{H}_2\text{O}$) is the potential mechanism. This mechanism has been proposed by Vaida et al.¹⁷ in 2003, and absorption of visible sunlight by the H_2SO_4 molecule is the prerequisite step for the occurrence of its unimolecular decomposition^{17–19}. This visible photolysis mechanism via direct formation of sulfur trioxide (SO_3), an important molecule in atmospheric sulfur cycle, explains not only the decomposition of H_2SO_4 in the upper stratosphere; but also satisfy model requirements that explains the field observations of the SO_2 vertical profiles at higher altitudes¹⁹. Similarly, the dominant photo-dissociation mechanism of H_2SO_4 above 70 km altitude is the absorption of Lyman- α radiation by high energy Rydberg excited states³⁰. Hence, these two mechanisms are two important pathways towards the upper atmospheric loss of H_2SO_4 molecule.

Here we show that the barrierless fast $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions are the potential mechanism that also interprets the upper stratospheric loss of H_2SO_4 molecule via formation of, especially, the peroxy-sulfuric acid (H_2SO_5) or $\text{HSO}_4 + \text{OH}$ radicals or $\text{SO}_3 + \text{H}_2\text{O}_2$ (hydrogen peroxide) molecules. We also find that the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions are involved in affecting the upper stratospheric ozone chemistry. In addition, this mechanism via direct involvement of $\text{O}(^1\text{D})$ provides physical insight towards the claim or sensitivity of the ozone depletion in geoengineering scheme of climate using injected stratospheric sulfate aerosols^{2–7}.

Results

Potential energy diagrams. The detailed theoretical methodologies for geometries, energetics, kinetics and direct dynamics of the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions in the ground potential energy surface have been given below (Methods Section). In H_2SO_4 , there are six chemical bonds wherein the insertions or additions of the $\text{O}(^1\text{D})$ are possible. However, among these six bonds, two equivalent O–H, S=O and S–O bonds are there. Therefore, the study of insertion/addition reactions of $\text{O}(^1\text{D})$ into the O–H, S=O and S–O bonds are effectively important, and each reaction pathway can be considered with reaction degeneracy (σ) = 2³¹. To keep our presentation simple, we label the insertions or additions of $\text{O}(^1\text{D})$ into the O–H, S=O and S–O bonds as the *Channel-I*, *Channel-II* and *Channel-III*, respectively.

It is seen from our calculations that the insertions/additions of $\text{O}(^1\text{D})$ through *Channel-I* to *III* produce directly either the adduct intermediates ($\text{H}_2\text{SO}_4 + \text{O}(^1\text{D}) \equiv \text{Ad}$) or H_2SO_5 in the first step. Moreover, the reactions are highly exothermic, and because of the large exothermicities, the adducts or H_2SO_5 formed in the first steps of *Channel-I* to *III* are expected to undergo further unimolecular isomerizations or decompositions followed by isomerizations to form various other product molecules. It is also seen from our calculations that the H_2SO_5 is the most stable product molecule and the formations of H_2SO_5 or $\text{SO}_3 + \text{H}_2\text{O}_2$ are energetically the most favorable pathways.

In Fig. 1, we present the CCSD(T)/aug-cc-pVTZ level predicted potential energy diagrams of energetically the most favorable paths of three channels that produce either the H_2SO_5 or $\text{SO}_3 + \text{H}_2\text{O}_2$ molecules, especially, to understand the potential atmospheric impact of $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions with respect to visible solar radiation pumping photolysis of H_2SO_4 . The M06-2X/aug-cc-pVTZ level optimized geometries of various species, especially the adducts, transition states (TSs) and product molecules, involved in the potential energy diagrams have also been shown in the Fig. 1. The potential energy diagrams with various interconnectivities between the above-mentioned insertion/addition reactions via the *Channel-I* to *III* and the optimized geometries of the species involved in potential energy diagrams have been shown in the Supplementary Figs. 1 and 2. Importantly, it is worth noting here that our main focus is on the upper stratospheric loss of H_2SO_4 molecule through its decomposition into all possible products, while H_2SO_4 is the perpetrator for the formation stratospheric sulfate aerosol layer involved in ozone loss. From Fig. 1, it is seen that the formation of H_2SO_5 and $\text{SO}_3 + \text{H}_2\text{O}_2$ in *Channel-I* occurs through the formation of a common adduct intermediate (Ad-I). Moreover, energetically the most favorable path is the formation of $\text{SO}_3 + \text{H}_2\text{O}_2$ via TS-IA, as the barrier heights for the unimolecular $\text{Ad-I} \rightarrow \text{H}_2\text{SO}_5\text{-I}$ and $\text{Ad-I} \rightarrow \text{SO}_3 + \text{H}_2\text{O}_2$ conversion steps via TS-I and TS-IA are only ~3.2 and ~1.0 kcal mol^{–1}, respectively. It is seen from the T_1 diagnostic calculations at the CCSD(T)/aug-cc-pVTZ level that the TS-I might have slight multi-reference character (Supplementary Note-1 and Supplementary Table 3). Because of this prediction, we further perform the CASPT2/CASSCF calculations (Supplementary Note-1), and the predicted unimolecular barrier heights for the $\text{Ad-I} \rightarrow \text{H}_2\text{SO}_5\text{-I}$ conversion at the CASPT2(12,12)/aug-cc-pVDZ and CASPT2(12,12)/aug-cc-pVTZ levels are respectively ~2.7 and ~2.1 kcal mol^{–1} (Supplementary Fig. 3 and Supplementary Table 4). Therefore, when we consider both the CCSD(T) and CASPT2 levels of calculations, energetically the most favorable path in the *Channel-I* is the formation of $\text{SO}_3 + \text{H}_2\text{O}_2$ via TS-IA, as mentioned above.

Similarly, we also note that while the formation of H_2SO_5 in *Channel-II* occurs via the formation of another adduct intermediate (Ad-II), the formation of H_2SO_5 in *Channel-III* occurs

Fig. 1 The potential energy diagrams of energetically the most favorable reaction pathways. The potential energy (kcal mol⁻¹) diagrams of energetically the most favorable reaction pathways (*Channel-I* to *III*) have been predicted at the CCSD(T)/aug-cc-pVTZ level based upon the M06-2X/aug-cc-pVTZ level optimized geometries including zero point vibrational energy (ZPE) corrections at the M06-2X/aug-cc-pVTZ level. The M06-2X/aug-cc-pVTZ level optimized geometries of various species involved in the potential energy diagrams have also been shown in the Figure. **a** *Channel-I* (black color) is corresponding to the insertions/additions of O(¹D) into the O–H bond of H₂SO₄. **b** *Channel-II* (blue color) is corresponding to the insertions/additions of O(¹D) into the S=O bond of H₂SO₄. **c** *Channel-III* (red color) is corresponding to the insertions/additions of O(¹D) into the S–O bond of H₂SO₄. The atoms with yellow, red and whitish-gray colors of various species represent respectively sulfur, oxygen, and hydrogen

directly without formation of any adduct compound. It is to be noted here that Ad-I and Ad-II are different with respect to their geometries (Fig. 1). Moreover, the H₂SO₅ formed via *Channel-III* is a different conformer with respect to the identical H₂SO₅ conformers formed in *Channel-I* and *II* (Fig. 1). For our convenience, the identical H₂SO₅ conformers that are formed via *Channel-I* or *II* are labeled as H₂SO₅-I and for *Channel-III*, it is H₂SO₅-II. The barrier height for the unimolecular Ad-II → H₂SO₅-I conversion step via TS-II in the *Channel-II* is only ~4 kcal mol⁻¹. Therefore, the effective barriers, defined as the relative energies of TSs with respect to the total energy of isolated starting H₂SO₄ + O(¹D) reactants, for reaction pathways via TS-IA, TS-I and TS-II are negative and the values are ~ -24.5, -22.3 (or -21.1 kcal mol⁻¹ at the CASPT2(12,12)/aug-cc-pVTZ level, Supplementary Fig. 3) and -42.6 kcal mol⁻¹, respectively.

In contrast, as mentioned above that the formation of H₂SO₅-II in the *Channel-III* is a direct process, and H₂SO₅-II is ~ 82.6 kcal mol⁻¹ more stable than the isolated H₂SO₄ + O(¹D) reactants. Also, the barrier height for the direct unimolecular H₂SO₅-II → SO₃ + H₂O₂ decomposition is ~ 35.3 kcal mol⁻¹, and hence, the effective barrier, as defined above, for the H₂SO₄ + O(¹D) → SO₃ + H₂O₂ reaction via *Channel-III* is also negative, and the value is ~ -47.3 kcal mol⁻¹. It should be noted here that unlike H₂SO₅-II, the H₂SO₅-I formed in the *Channel-I* or *II* is not directly decomposed into the SO₃ + H₂O₂ molecules. This follows as the H₂SO₅-I requires a H₂SO₅-I → H₂SO₅-II conversion via internal rotation of the O–OH functional group before its decomposition starts from the H₂SO₅-II (Supplementary Fig. 2). However, while the unimolecular barrier height for the H₂SO₅-I → H₂SO₅-II conversion via TS-VII is only ~ 3.1 kcal mol⁻¹ and the energy of H₂SO₅-I with respect to the H₂SO₄ + O(¹D) reactants is ~ -80 kcal mol⁻¹, the *Channel-II* in particular via the formation of H₂SO₅-I can also equally contribute to the formation of SO₃ + H₂O₂ molecules similar to that occurs in *Channel-III* (Supplementary Fig. 1). It should also be noted here that energetically the most favorable path in the *Channel-I* is the formation of SO₃ + H₂O₂ via TS-IA, as mentioned above. Indeed, because of such energetics in the *Channel-I* to *III*, the kinetic analysis at standard pressure of 1 bar (see below, and Supplementary Note-1 and 2) shows that the first steps in the H₂SO₄ + O(¹D) insertion/addition reactions control the overall reactions for the formation of various stable product molecules. In other words, at standard pressure of 1 bar, the overall rate constants of the insertion/addition reactions (*k*) are basically the rate constants associated with the first steps of the insertion/addition reactions (*k*₁) or (*k* = *k*₁). Moreover, we also point out here that the populations of various product species in H₂SO₄ + O(¹D) reactions depends upon the potential depths of those species in the potential energy diagrams and certainly on the surrounding environments. For example, if these reactions occur in supersonic jet environments with a carrier/buffer gas expansion, the population of H₂SO₅-II is expected to be highest, especially, for the *Channel-II* and *III*. This follows as the H₂SO₅-II is not only the most stable product molecule in the reactions but also prevented by large (~ 35.3 kcal mol⁻¹) activation barrier associated with its unimolecular H₂SO₅-II → SO₃ + H₂O₂ decomposition. However, in upper atmosphere, where the collisional rates are less, and where the temperatures are not like cold supersonic jet environment, the formation of SO₃ + H₂O₂ molecule from the H₂SO₄ + O(¹D) reactants can occur not only via the *Channel-I* but also through the *Channel-II* and *III*, especially, while the energy of TS-III associated with the H₂SO₅-II → SO₃ + H₂O₂ unimolecular decomposition is ~ 47.3 kcal mol⁻¹ lower than the total energy of the isolated H₂SO₄ + O(¹D) reactants. More importantly, the H₂SO₅-II formed via *Channel-III* may further decompose into the HSO₄ + OH radicals in the presence of sunlight similar to other peroxyacids^{32,33}. Indeed, as the energy of HSO₄ + OH radicals with respect to H₂SO₅-II formed via *Channel-III* is ~ 41.5 kcal mol⁻¹ (~ 688 nm light, Supplementary Fig. 1) and this value is higher than the ~ 35.3 kcal mol⁻¹ (~ 809 nm light) barrier height associated with the H₂SO₅-II → SO₃ + H₂O₂ unimolecular decomposition, it is expected that the sunlight-initiated H₂SO₅ photolysis should produce SO₃ + H₂O₂ molecule (H₂SO₅ + *hν* → SO₃ + H₂O₂), similar to the H₂SO₄ + *hν* → SO₃ + H₂O reaction¹⁷, along with the HSO₄ + OH radicals.

Kinetics and relative rates. Given that the above-mentioned insertion/addition reactions finally form either the H₂SO₅ or SO₃ + H₂O₂ or HSO₄ + OH radicals depending upon the surrounding

environments and sunlight, we note here, however, that the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions represent certainly the loss of H_2SO_4 into various product molecules. Therefore, we calculate further the atmospheric pressures and temperatures dependent overall rate constants (k) for each effectively barrierless $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ reactions in *Channel-I* to *III* to understand the potential atmospheric impact of these reactions towards the loss of H_2SO_4 molecule, especially, with respect to the steady-state $\text{O}(^1\text{D})$ concentrations in the upper atmosphere^{34–36}. It has been mentioned above that the first steps in the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions control the overall reactions for the formation of various stable product molecules at standard pressure of 1 bar. The detailed kinetics analysis of energetically the most favorable pathways according to potential energy profile predicted at 0 K and the equations used for the kinetic analysis at standard pressure of 1 bar have been given in the Supplementary Note-1. The rate constants for the first steps of insertion/addition reactions (k_1), which are barrierless, have been calculated using the multifaceted variable reaction coordinate–variational transition state theory (VRC-VTST)^{37–39} in the temperature from 100 to 400 K (Supplementary Note-2 and Supplementary Tables 5–8) and these rate constants have been used as initial guesses in the master equation solver for multi-energy well reactions (MESMER) program⁴⁰ to understand the pressure dependency of rate constants (Supplementary Note-3, Supplementary Tables 10–15) predicted by VRC-VTST. It is seen from our calculations that the VRC-VTST predicted rate constants are pressure independent in atmospheric pressures (Supplementary Note-3 and Supplementary Tables 13–15) and here, we only focus upon the overall rate constants ($k = k_1$) of *Channel-I* to *III* relevant to 35 to 65 km altitude of the Earth's atmosphere (Table 1), as our main aim is to understand the potential impact of $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ reaction in upper stratosphere and lower mesosphere. The data relevant to the 30 to 110 km altitude at 5 km interval and corresponding potential atmospheric impact of the insertion/addition reactions have been presented in the Supplementary Note-4 and Supplementary Table 16. The potential impact of the insertion/addition reactions has been explored with respect to simple relative rate analysis. In the case of solar-pumping photolysis of H_2SO_4 , the loss or decomposition of H_2SO_4 molecule can be written as: $v_{\text{Photolysis}} = J^*[\text{H}_2\text{SO}_4]$, where J is the photolysis rate coefficient (sec^{-1}). Similarly, the loss of H_2SO_4 molecule via the insertion/addition reactions with reaction degeneracy (σ) can be written as: $v_{\text{Insertion}} = \sigma[k_{(\text{Channel-I})} + k_{(\text{Channel-II})} + k_{(\text{Channel-III})}]^*[\text{H}_2\text{SO}_4]^*[\text{O}(^1\text{D})] = \sigma k_{(\text{Total})}^*[\text{H}_2\text{SO}_4]^*[\text{O}(^1\text{D})]$, where $k_{(\text{Total})} = k_{(\text{Channel-I})} + k_{(\text{Channel-II})} + k_{(\text{Channel-III})}$. Moreover, the five $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ potential energy surfaces in the asymptotic region corresponding

to the fivefold degeneracy of $\text{O}(^1\text{D})$ might contribute an important role in estimating the effective rate of the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ bimolecular reaction, although we have taken into account the electronic degeneracy of $\text{O}(^1\text{D}) = 5$ in our VRC-VTST calculations to predict the rate constants for the first step of barrierless insertion/addition reactions. Similarly, we also note that the experimental results of the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ reaction system are yet to be reported in the literature. Hence, we only consider here the statistically distributed minimum 20% (one-fifth) steady-state atmospheric concentration of $\text{O}(^1\text{D})$ for the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions. In addition, it is worth noting here that numerous bimolecular reactions involving $\text{O}(^1\text{D})$ also occur simultaneously in the Earth's upper atmosphere^{34–36}. We also point out here that it is not the goal of present work to evaluate the absolute reaction rate but to only examine the potential atmospheric impact of $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions over the visible photolysis mechanism of H_2SO_4 . Therefore, here we use $v_{\text{Insertion}}/v_{\text{Photolysis}} = \sigma[k_{(\text{Total})}/J]^*[\text{O}(^1\text{D})/5]$ as the final equation to evaluate the potential atmospheric impact of $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions, where the " $\text{O}(^1\text{D})/5$ " represents 20% steady-state atmospheric concentration of $\text{O}(^1\text{D})$. For an example, by taking $J = 2.2 \times 10^{-8} \text{ sec}^{-1}$ at the 45 km altitude and $k_{(\text{Total})} = 6.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, we find that the $v_{\text{Insertion}}/v_{\text{Photolysis}} = \sim 3.6$ (Table 1), when we take the steady-state atmospheric concentration of $\text{O}(^1\text{D}) \sim 3 \times 10^2 \text{ molecules cm}^{-3}$ [here atoms $\equiv$ molecules].

Direct dynamics trajectory surface hopping. Our results show that the average value of the $v_{\text{Insertion}}/v_{\text{Photolysis}}$ in upper stratosphere (35–50 km altitude) is ~ 3 (Table 1), especially; with respect to the corrected J values reported by Miller et al. from the different photolysis quantum yields at different altitudes¹⁹. Importantly, it is worth noting here that the above-mentioned average value of $v_{\text{Insertion}}/v_{\text{Photolysis}}$ becomes ~ 3 when all the collisions between H_2SO_4 and $\text{O}(^1\text{D})$ are considered to be involved mostly in the insertion/addition reactions or when the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ encounters result in minor $\text{O}(^1\text{D}) \rightarrow \text{O}(^3\text{P})$ quenching or $\text{O}(^1\text{D}) \rightarrow \text{O}(^1\text{D})$ nonreactive scattering. It is seen from our direct dynamics trajectory surface hopping (TSH) calculations (Supplementary Note-5) with 390 trajectories that the $\sim 85\%$ $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ encounters resulting in the reactions and $\sim 14\%$ are involved in the $\text{O}(^1\text{D}) \rightarrow \text{O}(^1\text{D})$ [singlet to singlet surface] non-reactive scattering and minor $\sim 1\%$ $\text{O}(^1\text{D}) \rightarrow \text{O}(^3\text{P})$ [singlet to triplet surface] collisional quenching. Moreover, among the 85% reactive $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ encounters, 85% encounters are involved in the insertion and/or addition reactions for the formation of

Table 1 The calculated rate constants and relative rates

Altitude (km)	$[\text{O}(^1\text{D})]^a \text{ atoms cm}^{-3}$	<i>Channel-I</i> $k_1 = k$ ($1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	<i>Channel-II</i> $k_1 = k$	<i>Channel-III</i> $k_1 = k$	J values (s^{-1})	$\frac{v_{\text{Insertion}}}{v_{\text{Photolysis}}}$
					Overtone (corrected)	Overtone (corrected)
35	$(1.0 \times 10^2)^b$	2.36	2.25	2.00	9.1×10^{-9}	2.9
40	$(2.0 \times 10^2)^b$	2.36	2.26	2.01	1.4×10^{-8}	3.7
45	$(3.0 \times 10^2)^b$	2.37	2.26	2.01	2.2×10^{-8}	3.6
50	$(3.2 \times 10^2)^b$	2.37	2.27	2.02	3.0×10^{-8}	2.8
55	1.5×10^2	2.37	2.26	2.01	3.8×10^{-8}	1
60	1.1×10^2	2.36	2.25	2.01	4.7×10^{-8}	0.6
65	7.5×10^1	2.36	2.25	2.00	5.4×10^{-8}	0.4

The VRC-VTST predicted rate constants ($k_1 = k$) for the reactions via *Channel-I* to *III* and the $v_{\text{Insertion}}/v_{\text{Photolysis}}$ (relative rates) with respect to the corrected J values for visible solar pumping (overtone) photolysis of H_2SO_4 reported by Miller et al.¹⁹ from the different photolysis quantum yields at different altitudes (Supplementary Note-4)

^aThe concentrations of $\text{O}(^1\text{D})$ have been taken from refs. ^{34, 35}, and we consider 20% of these concentration in estimating the relative rates

^bReference³⁴

either the H_2SO_5 or $\text{SO}_3 + \text{H}_2\text{O}_2$ or $\text{HSO}_4 + \text{OH}$ radicals, as mentioned above. We understand that much more trajectories are required to get statistics that are more accurate particularly for the branching ratios of different products; but we defer these works for future. It should be noted here that we have considered the spin orbit coupling (SOC) in our TSH calculation (Supplementary Note-5).

Impact in the Earth's upper stratosphere. It has been mentioned above that the average value of the $v_{\text{Insertion}}/v_{\text{Photolysis}}$ in upper stratosphere (35–50 km altitude) is ~ 3 (Table 1), especially, with respect to corrected J values for visible solar pumping (overtone) photolysis of H_2SO_4 ¹⁹. Hence, the results reported here provide clearly that the insertion/addition reactions compete equally with the photolysis mechanism, especially, towards H_2SO_4 decomposition or loss in the upper stratosphere.

In addition, the possible geoengineering scheme to ease the global warming aspect of climate change is believed through the deliberate injection of stratospheric sulfate aerosol particles of right size^{2–7}. This follows as the injected aerosol particles would reduce the Earth's radiative balance through scattering of solar-radiation back into the space. However, a number of studies have also addressed the question of possible side effect on stratospheric ozone loss^{2,3,5–7}. Similarly, the volcanic eruptions also accelerate the stratospheric ozone destruction^{2,26–29,41}. We find that excess stratospheric sulfate aerosol particles due to both the volcanic eruptions and geoengineering scheme (if applied) are connected with the increase of H_2SO_4 concentrations in the upper stratosphere, as the stratospheric sulfate aerosol particles/droplets evaporate to their seed H_2SO_4 molecule and H_2O at ~ 35 km altitude^{1,4,23–25}. Basically, both these two mechanisms/processes depending upon the seasons will gradually and eventually produce an excess amount of H_2SO_4 molecules in the upper stratosphere; considering the fact that the most abundant sulfur molecules through atmospheric sulfur cycle at altitudes above ~ 35 km are H_2SO_4 and SO_2 ^{23–25}. Consequently, the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertions/additions mechanism along with H_2SO_4 photolysis will play an important role towards the removal of excess upper stratospheric H_2SO_4 molecules resulting from stratospheric sulfate aerosols formed either via volcanic eruptions or any other sources.

Moreover, the insertions/additions mechanism is involved not only in the loss of H_2SO_4 but also in the reaction with steady-state concentration of $\text{O}(^1\text{D})$ —which is the key atomic species required to cause numerous chemical reactions of potential atmospheric significance^{34–36}. The maximum background atmospheric concentrations of H_2SO_4 in upper stratosphere are within the 30–40 km altitude, and the average concentration of H_2SO_4 within the ~ 30 –40 km altitude is $\sim 3.4 \times 10^7$ molecules cm^{-3} ^{17,24,25}. Similarly, the average steady-state concentration of $\text{O}(^1\text{D})$ within the ~ 30 –40 km altitude is 1.1×10^2 atoms cm^{-3} ³⁴. By taking the average value of $k_{(\text{Total})} = \sim 6.6 \times 10^{-10}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and only 20% of the average steady-state concentration of $\text{O}(^1\text{D})$ in the same altitude range (Table 1), the loss rate of $\text{O}(^1\text{D}) = v_{\text{O}(^1\text{D})} = \sigma k_{(\text{Total})} [\text{H}_2\text{SO}_4] [\text{O}(^1\text{D})/5] = \sim 1$ atoms $\text{s}^{-1} \text{ cm}^{-3}$ [here atoms $\equiv$ molecules]. It is well known that the loaded stratospheric sulfuric acid aerosols are enhanced by a few orders of magnitude due to a significantly large volcanic eruption^{26,42,43}. In this scenario, or due to the geoengineering scheme by extension in future and other natural sources⁴² including some other man-made activities, if we suppose one to two orders of magnitude enhancement of H_2SO_4 concentration within the 30–40 km altitude of Earth's atmosphere, the $v_{\text{O}(^1\text{D})}$ in the same altitude range becomes either ~ 10 atoms $\text{s}^{-1} \text{ cm}^{-3}$ (for one order of increase) or ~ 98 atoms $\text{s}^{-1} \text{ cm}^{-3}$ (for two orders of increase),

while the average steady-state concentration of $\text{O}(^1\text{D})$ is ~ 110 atoms cm^{-3} . Hence, the timescale required to consume the steady-state concentration of $\text{O}(^1\text{D})$, resulting from the background atmospheric concentration of ozone, becomes significantly shorter when H_2SO_4 concentrations are enhanced by one to two orders of magnitude with respect to its background atmospheric concentration. Also, at the same time, the production rates of $\text{O}(^1\text{D})$ resulting from the background atmospheric concentrations of ozone in the same altitude range via photolysis is very much constant. It is to be noted here that the solar photon intensity for the photolysis of O_3 can assume to be constant at any particular daytime and over the wavelengths regions at which photolysis of O_3 occurs to produce fresh $\text{O}(^1\text{D})$, although some solar light will definitely be scattered because of excess concentrations of H_2SO_4 . Hence, the overall effect due to enhancement of H_2SO_4 concentrations is the consumption of a significant portion of steady-state concentrations of $\text{O}(^1\text{D})$ in the above-mentioned altitude range, particularly, if there is no additional source of $\text{O}(^1\text{D})$ or ozone that can produce additional $\text{O}(^1\text{D})$ via photolysis. In other words, a supply or production of excess ozone with respect to its background atmospheric concentration are required further for formation and reestablish the steady-state concentrations of $\text{O}(^1\text{D})$ when upper stratospheric H_2SO_4 concentrations are enhanced by one to two orders of magnitude due to a significantly large volcanic eruption or other process, as mentioned above. Considering the $\text{O}(^1\text{D})$ loss via our mechanism and formation of fresh $\text{O}(^1\text{D})$ from ozone photolysis are two separate processes that interfere each other, we also note here that the fresh $\text{O}(^1\text{D})$ produced by the photolysis of excess ozone in the upper stratosphere will further and mostly be quenched by N_2 and O_2 . Hence, not only the supply of excess ozone molecules; but the supply of large number of excess ozone molecules in comparison to $\text{O}(^1\text{D})$ atoms per cm^3 are required to produce and maintain the steady-state concentrations of $\text{O}(^1\text{D})$ in the above-mentioned altitude range. Also, as the additional important source of ozone formation except the most important $\text{O}_2 + \text{O}(^3\text{P}) \rightarrow \text{O}_3$ reaction (Chapman Mechanism) is not known yet in the upper stratosphere, the ozone loss is expected to occur at the upper edge of ozone layer (~ 30 km altitude), as the transportations of ozone (Product) and $\text{O}_2 + \text{O}(^3\text{P})$ (Reactants) of the $\text{O}_2 + \text{O}(^3\text{P}) \rightarrow \text{O}_3$ reaction from the upper edge of ozone layer to higher altitudes is expected to be the effective mechanism by which the concentrations of $\text{O}(^1\text{D})$ in upper stratosphere will be maintained at their steady-state/equilibrium values. In addition, we also note that similar to the above-mentioned mechanism, the simultaneous occurrence of $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ addition/insertion reactions and other similar $\text{O}(^1\text{D})$ —insertion/addition reactions involving molecules like CH_4 , HCl , etc.^{34,35,44,45} are expected to play vital role in ozone depletion, particularly, if the upper stratospheric concentrations of these species increase significantly from their equilibrium background atmospheric concentrations.

It should also be noted here, while the loss of excess H_2SO_4 molecule formed from the surface of stratospheric sulfate aerosols at ~ 35 km altitude is essential in healing the ozone depletion, the loss of same H_2SO_4 , resulting from the same stratospheric sulfate aerosol layer, also occurs in presence of $\text{O}(^1\text{D})$ produced from the ozone. Therefore, as the H_2SO_4 is the most abundant sulfur molecule in upper stratosphere (35–50 km)^{23–25}, the present $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertions/additions are expected to be an important mechanism in altering the upper stratospheric ozone chemistry both with respect to ozone depletion and healing, especially, after a significantly large volcanic eruption. It is worth noting here that the reactions involving $\text{O}(^1\text{D})$ are indispensable in the stratospheric loss processes for various ozone depleting substances^{34–36,46} and the primary source of $\text{O}(^1\text{D})$ in upper

stratosphere is ozone that coexists with the H_2SO_4 and sulfate aerosols, and decompositions or loss of H_2SO_4 are the potential routes towards the degradation of stratospheric sulfate aerosol layer. It should also be noted here that the industrial chlorofluorocarbons and other halogenated compounds that cause ozone depletion are expected to be reduced under the Montreal Protocol, and volcanic eruptions that enhance the formation of stratospheric sulfate aerosols are interfering with the ozone healing process episodically^{28,41}.

It has been mentioned earlier that the reactions between upper stratospheric H_2SO_4 and $\text{O}(^1\text{D})$ form finally the H_2SO_5 or $\text{SO}_3 + \text{H}_2\text{O}_2$ or $\text{HSO}_4 + \text{OH}$ radicals. In addition, we also note here that while the background atmospheric OH radical and huge excess SO_2 , resulting from a significantly large volcanic eruptions, are consumed in the lower-middle stratosphere in presence of O_2 ($\text{SO}_2 \rightarrow \text{SO}_3$ conversion) and $\text{H}_2\text{O}/\text{acids}$ to form excess H_2SO_4 responsible for the excess stratospheric sulfate aerosol burden^{20,21,25,35,47–50}, the decomposition or loss of same excess H_2SO_4 above the stratospheric sulfate aerosol layer is expected to regenerate both the aforementioned consumed SO_2 and OH radical in the upper stratosphere, especially, to bring back the equilibrium background atmospheric condition in prolonged timescale after a significantly large volcanic eruptions. In this circumstance, we also note that the present $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ reactions through barrierless formation and subsequent photolysis of H_2SO_5 and $\text{H}_2\text{O}_2 + \text{SO}_3$ molecules have the potential to regenerate both the OH radical^{51–54} and SO_2 finally above the stratospheric sulfate aerosol layer. It should be noted here that the HO_x also catalyzes the ozone loss, and a significant amount of OH radical (involved in HO_x) is expected to be transported from the lower-middle stratosphere to upper stratosphere because a significantly large volcanic eruption injects huge amount of SO_2 in the Earth's stratosphere^{25,29,42,43}. Thus, this new mechanism involving H_2SO_4 and $\text{O}(^1\text{D})$ can definitely impact our understanding of H_2SO_4 decomposition or loss chemistry beyond the facts that have been thought before through its photolysis in upper stratosphere or above the ozone layer in the Earth's atmosphere.

Discussion

In the hunt of atmospheric sinks of H_2SO_4 , the present study suggests that the $\text{O}(^1\text{D})$ –insertion/addition reaction mechanism is competitive with the H_2SO_4 visible photolysis in the upper stratosphere. Consequently, we conclude that the barrierless fast $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions as the potential routes for upper stratospheric loss of H_2SO_4 molecule. In addition, we also find that the barrierless fast $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertion/addition reactions are the important mechanism in altering the upper stratospheric ozone chemistry both with respect to ozone depletion and healing, especially, after a significantly strong volcanic eruptions, as ozone that produces $\text{O}(^1\text{D})$ in presence of sunlight coexists with H_2SO_4 resulting from sulfate aerosols. It is worth noting here that our conclusion, particularly, about the involvement of $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ insertions/additions mechanism with ozone depletion is not only based upon the reasonable assumption that a few orders of magnitude enhancement of loaded stratospheric sulfuric acid aerosols due to a significantly large volcanic eruption^{26,42,43} may enhance one to two orders of magnitude H_2SO_4 concentration within the 30–40 km altitude; but also because a significant amount of OH radical, involved in the HO_x radical family that catalyzes ozone depletion, is expected to be transported from the lower middle stratosphere to upper stratosphere. We also point out here that the above-mentioned insertion/addition reactions might be an important route for the formations of various sulfur

containing molecules and H_2O_2 in outer space, especially, in the Venus with respect to existence of both the ozone and large amount of H_2SO_4 ^{55–57}.

Methods

Computational methods. Quantum chemistry calculations at the M06-2X level of theory in conjunction with the aug-cc-pVDZ and aug-cc-pVTZ basis sets have been performed using Gaussian-09 suite of program⁵⁸. Both the geometry optimizations and frequency calculations of the monomers and adducts or complexes associated with the insertion/addition reactions between H_2SO_4 and $\text{O}(^1\text{D})$ have been carried out. It should be noted here that the H_2SO_4 , which we have taken into consideration, is the most stable conformer of H_2SO_4 ⁵⁹. It is seen from the literature that various reactions involving $\text{O}(^1\text{D})$ predominantly occur in the ground electronic (Singlet potential energy surface) state^{44,45,60–62}, especially, when the low translation energy of $\text{O}(^1\text{D})$ is considered, relevant to our present study. Hence, the calculations in the ground electronic state for the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ reaction system have been performed with closed-shell or open-shell approximations depending upon the spin multiplicities of both the reactants and products involved in the reactions. Moreover, the geometry optimizations are performed at the M06-2X level of theory using Schlegel's method⁶³ with a self consistent field convergence of at least 10^{-9} of the density matrix. The residual root-mean-square (rms) forces were $< 1 \times 10^{-4}$ au, and TSs have been located using the QST2/QST3 and OPT = TS routines. Intrinsic reaction coordinate (IRC) calculations are performed at the M06-2X/aug-cc-pVDZ level of theory to explicitly verify that the reactants and products are connected with located TSs. In order to improve the estimates of reaction energetics for all the reactions, we also carry out single point energy calculations at the CCSD(T)/aug-cc-pVTZ level using the M06-2X/aug-cc-pVTZ level optimized geometries. We also calculate the T_1 diagnostic^{64,65} for each stationary points and transitions states in the potential energy diagram to understand whether the species involved in the reaction mechanism are of single or multi-reference in characters (Supplementary Note-1, Supplementary Table 4 and Supplementary Figures 3–4). For the closed-shell systems, the T_1 diagnostic value larger than 0.020 implies that the single reference methods may not give reliable predictions. Similarly, the T_1 diagnostic cut off value for an open-shell system is ~ 0.045 . It is seen from our calculations that two TSs and SO_2 (possible product molecule in the exit channel) in the potential energy diagrams of insertion/addition reactions are multi-reference in characters according to the T_1 diagnostic values at CCSD(T)/aug-cc-pVTZ level of calculations (Supplementary Note-1). Therefore, we also perform CASPT2//CASSCF calculations for the TSs of multi-reference character and stationary points of single reference character, especially, which are directly connected with the above-said TSs of multi-reference character (Supplementary Note-1). The CASPT2//CASSCF calculations have been performed using MOLCAS@UU package^{66,67}. Normal mode vibrational frequencies have been used to estimate the zero point vibration energy (ZPE) corrections for the reactants, products and TSs. The computed total electronic energies (E_{total}), ZPE corrected electronic energies [$E_{\text{total}}(\text{ZPE})$] for the monomeric species, dimeric complexes, adducts and the TSs at the M06-2X and CCSD(T) levels of theory are given in Supplementary Table 1. Normal mode vibrational frequency analyses have been performed for all the stationary points to verify that the stable minima have all positive vibrational frequencies and that the TSs have only one imaginary frequency (Supplementary Table 2). In addition, we also perform various calculations at UCIS, CASSCF and TDDFT levels of theories in conjunction with the cc-pVDZ and aug-cc-pVDZ basis sets to understand to stability of ground state optimized H_2SO_4 – $\text{O}(^1\text{D})$ adducts and peroxy-sulfuric acid (H_2SO_5) in the first two low-lying excited states of the $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$ reaction (Supplementary Note-1). Finally, we also perform temperature and pressure dependent kinetics analysis (Supplementary Notes 2 and 3, Supplementary Tables 5–15 and Supplementary Figure 5) and direct dynamics trajectory surface hopping (TSH) calculations to estimate the contribution of collisional quenching or nonreactive scattering [$\text{H}_2\text{SO}_4 + \text{O}(^1\text{D}) \rightarrow \text{H}_2\text{SO}_4 + \text{O}(^3\text{P})$ or $\text{H}_2\text{SO}_4 + \text{O}(^1\text{D})$] associated in the present study (Supplementary Note-5).

Data availability

All data supporting the findings of this study are available in the paper and its Supplementary Information. Additional data related to this paper may be requested from the corresponding author upon reasonable request.

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References

1. Toon, O. B. & Turco, R. P. Polar stratospheric clouds and ozone depletion. *Sci. Am.* **264**, 68–74 (1991).
2. Tilmes, S., Müller, R. & Salawitch, R. The sensitivity of polar ozone depletion to proposed geoengineering schemes. *Science* **320**, 1201–1204 (2008).

3. Heckendorn, P. et al. The impact of geoengineering aerosols on stratospheric temperature and ozone. *Environ. Res. Lett.* **4**, 045108 (2009).
4. Solomon, S. et al. The persistently variable “background” stratospheric aerosol layer and global climate change. *Science* **333**, 866–870 (2011).
5. Pope, F. D. et al. Stratospheric aerosol particles and solar-radiation management. *Nat. Clim. Change* **2**, 713–719 (2012).
6. Rasch, P. J. et al. An overview of geoengineering of climate using stratospheric sulphate aerosols. *Philos. Trans. R. Soc. A* **366**, 4007–4037 (2008).
7. Keith, D. W., Weisenstein, D. K., Dykema, J. A. & Keutsch, F. N. Stratospheric solar geoengineering without ozone loss. *Proc. Natl Acad. Sci. USA* **113**, 14910–14914 (2016).
8. Kulmala, M., Pirjola, L. & Mäkelä, J. M. Stable sulphate clusters as a source of new atmospheric particles. *Nature* **404**, 66–69 (2000).
9. Zhang, R. et al. Atmospheric new particle formation enhanced by organic acids. *Science* **304**, 1487–1490 (2004).
10. Pöschl, U. Atmospheric aerosols: composition, transformation, climate and health effects. *Angew. Chem. Int. Ed.* **44**, 7520–7540 (2005).
11. Kirkby, J. et al. Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature* **476**, 429–433 (2011).
12. Dunne, E. M. et al. Global atmospheric particle formation from CERN CLOUD measurements. *Science* **354**, 1119–1124 (2016).
13. Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J. & Carslaw, K. S. Impact of nucleation on global CCN. *Atmos. Chem. Phys.* **9**, 8601–8616 (2009).
14. Kolb, C. E. et al. Gas phase reaction of sulfur trioxide with water vapor. *J. Am. Chem. Soc.* **116**, 10314–10315 (1994).
15. Morokuma, K. & Murguruma, C. Ab initio molecular orbital study of the mechanism of the gas phase reaction $\text{SO}_3 + \text{H}_2\text{O}$: importance of the second water molecule. *J. Am. Chem. Soc.* **116**, 10316–10317 (1994).
16. Loerting, T. & Liedl, K. R. Toward elimination of discrepancies between theory and experiment: the rate constant of the atmospheric conversion of SO_3 to H_2SO_4 . *Proc. Natl Acad. Sci. USA* **97**, 8874–8878 (2000).
17. Vaida, V., Kjaergaard, H. G., Hintze, P. E. & Donaldson, D. J. Photolysis of sulfuric acid vapor by visible solar radiation. *Science* **299**, 1566–1568 (2003).
18. Miller, Y. & Gerber, R. B. Dynamics of vibrational overtone excitations of H_2SO_4 , $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$:hydrogen-hopping and photodissociation processes. *J. Am. Chem. Soc.* **128**, 9594–9595 (2006).
19. Miller, Y., Gerber, R. B. & Vaida, V. Photodissociation yields for vibrationally excited states of sulfuric acid under atmospheric conditions. *Geophys. Res. Lett.* **34**, L16820 (2007).
20. Hazra, M. K. & Sinha, A. Formic acid catalyzed hydrolysis of SO_3 in the gas phase: a barrierless mechanism for sulfuric acid production of potential atmospheric importance. *J. Am. Chem. Soc.* **133**, 17444–17453 (2011).
21. Torrent-Sucarrat, M., Francisco, J. S. & Anglada, J. M. Sulfuric acid as autocatalyst in the formation of sulfuric acid. *J. Am. Chem. Soc.* **134**, 20632–20644 (2012).
22. Mackenzie, R. B., Dewberry, C. T. & Leopold, K. R. Gas phase observation and microwave spectroscopic characterization of formic sulfuric anhydride. *Science* **349**, 58–61 (2015).
23. Burkholder, J. B., Mills, M. & McKeen, S. Upper limit for the UV absorption cross sections of H_2SO_4 . *Geophys. Res. Lett.* **27**, 2493–2496 (2000).
24. Turco, R. P., Hamill, P., Toon, O. B., Whitten, R. C. & King, C. S. A. One-dimensional model describing aerosol formation and evolution in the stratosphere: I. physical processes and mathematical analogs. *J. Atmos. Sci.* **36**, 699–717 (1979).
25. Weisenstein, D. K. et al. A two-dimensional model of sulfur species and aerosol. *J. Geophys. Res.* **102**, 13019–13035 (1997).
26. Hanson, D. R., Ravishankara, A. R. & Solomon, S. Heterogeneous reactions in sulfuric acid aerosols: a framework for model calculations. *J. Geophys. Res.* **99**, 3615–3629 (1994).
27. Solomon, S. Stratospheric ozone depletion: a review of concepts and history. *Rev. Geophys.* **37**, 275–316 (1999).
28. Zuev, V. V., Zueva, N. E., Savelieva, E. S. & Gerasimov, V. V. The Antarctic ozone depletion caused by Erebus volcano gas emissions. *Atmos. Environ.* **122**, 393–399 (2015).
29. Klobas, J. E., Wilmouth, D. M., Weisenstein, D. K., Anderson, J. G. & Salawitch, R. J. Ozone depletion following future volcanic eruptions. *Geophys. Res. Lett.* **44**, 7490–7499 (2017).
30. Lane, J. R. & Kjaergaard, H. G. Calculated electronic transitions in sulfuric acid and implications for its photodissociation in the atmosphere. *J. Phys. Chem. A* **112**, 4958–4964 (2008).
31. Fernández-Ramos, A., Ellingson, B. A., Meana-Pañeda, R., Marques, J. M. C. & Truhlar, D. G. Symmetry numbers and chemical reaction rates. *Theor. Chem. Acc.* **118**, 813–826 (2007).
32. Roehl, C. M., Nizkorodov, S. A., Zhang, H., Blake, G. A. & Wennberg, P. O. photodissociation of peroxyxynitric acid in the near-IR. *J. Phys. Chem. A* **106**, 3766–3772 (2002).
33. Indulkar, Y. N., Louie, M. K. & Sinha, A. UV photochemistry of peroxyformic Acid ($\text{HC}(\text{O})\text{OOH}$): an experimental and computational study investigating 355 nm photolysis. *J. Phys. Chem. A* **118**, 5939–5949 (2014).
34. DeMore, W. B. et al. Chemical kinetics and photochemical data for use in stratospheric modeling. *JPL Publ. No. 97-4, Evaluation Number 12*, (1997).
35. Brasseur, G. P. & Solomon, S. *Aeronomy of the Middle Atmosphere*. (Springer, Netherlands, 2005).
36. Burkholder, J. B., Cox, R. A. & Ravishankara, A. R. Atmospheric degradation of ozone depleting substances, their substitutes, and related species. *Chem. Rev.* **115**, 3704–3759 (2015).
37. Georgievskii, Y. & Klippenstein, S. J. Variable reaction coordinate transition state theory: analytic results and application to the $\text{C}_2\text{H}_3 + \text{H} \rightarrow \text{C}_2\text{H}_4$ reaction. *J. Chem. Phys.* **118**, 5442–5455 (2003).
38. Georgievskii, Y. & Klippenstein, S. J. Transition state theory for multichannel addition reactions: multifaceted dividing surfaces. *J. Phys. Chem. A* **107**, 9776–9781 (2003).
39. Bao, J. L., Zhang, X. & Truhlar, D. G. Barrierless association of CF_2 and dissociation of C_2F_4 by variational transition-state theory and system-specific quantum rice-rampersperger-kassel theory. *Proc. Natl Acad. Sci. USA* **113**, 13606–13611 (2016).
40. Glowacki, D. R., Liang, C.-H., Morley, C., Pilling, M. J. & Robertson, S. H. MESMER: an open-source master equation solver for multi-energy well reactions. *J. Phys. Chem. A* **116**, 9545–9560 (2012).
41. Solomon, S. et al. Emergence of healing in the Antarctic ozone layer. *Science* **353**, 269–274 (2016).
42. Vernier, J.-P. et al. Major influence of tropical volcanic eruptions on the stratospheric aerosol layer during the last decade. *Geophys. Res. Lett.* **38**, L12807 (2011).
43. English, J. M., Toon, O. B. & Mills, M. J. Microphysical simulations of large volcanic eruptions: Pinatubo and Toba. *J. Geophys. Res. Atmos.* **118**, 1880–1895 (2013).
44. Kohguchi, H. et al. Collision energy dependence of the $\text{O}(^1\text{D}) + \text{HCl} \rightarrow \text{OH} + \text{Cl}(^2\text{P})$ reaction studied by crossed beam scattering and quasiclassical trajectory calculations on ab initio potential energy surfaces. *J. Phys. Chem. A* **112**, 818–825 (2008).
45. Lin, J. J., Shu, J., Lee, Y. T. & Yang, X. Multiple dynamical pathways in the $\text{O}(^1\text{D}) + \text{CH}_4$ reaction: a comprehensive crossed beam study. *J. Chem. Phys.* **113**, 5287–5301 (2000).
46. Baasandorj, M., Fleming, E. L., Jackman, C. H. & Burkholder, J. B. $\text{O}(^1\text{D})$ kinetic study of key ozone depleting substances and greenhouse gases. *J. Phys. Chem. A* **117**, 2434–2445 (2013).
47. Turco, R. P., Whitten, R. C., Toon, O. B., Inn, E. C. Y. & Hamill, P. Stratospheric hydroxyl radical concentrations: New limitations suggested by observations of gaseous and particulate sulfur. *J. Geophys. Res.* **86**, 1129–1139 (1981).
48. Stockwell, W. R. & Calvert, J. G. The mechanism of the $\text{HO}-\text{SO}_2$ reaction. *Atmos. Environ.* **17**, 2231–2235 (1983).
49. McKeen, S. A., Liu, S. C. & Kiang, C. S. On the chemistry of stratospheric SO_2 from volcanic eruption. *J. Geophys. Res.* **89**, 4873–4881 (1984).
50. Margitan, J. J. Mechanism of the atmospheric oxidation of sulfur dioxide. catalysis by hydroxyl radicals. *J. Phys. Chem.* **88**, 3314–3318 (1984).
51. Suto, M. & Lee, L. C. $\text{OH} (\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi)$ yield from photodissociation of H_2O_2 at 106–193 nm. *Chem. Phys. Lett.* **98**, 152–156 (1983).
52. Vaghjiani, G. L., Turnipseed, A. A., Warren, R. F. & Ravishankara, A. R. photodissociation of H_2O_2 at 193 and 222 nm: Products and quantum yields. *J. Chem. Phys.* **96**, 5878–5886 (1992).
53. Thiebaud, J., Aluculesei, A. & Christa, F. Formation of HO_2 radicals from the photodissociation of H_2O_2 at 248 nm. *J. Chem. Phys.* **126**, 186101 (2007).
54. Hazra, M. K., Matthews, J. & Sinha, A. Influence of initial parent vibrational excitation in promoting two-photon absorption in HOOH and CH_3OOH . *Chem. Phys. Lett.* **512**, 25–29 (2011).
55. Montmessin, F. et al. A layer of ozone detected in the nightside upper atmosphere of venus. *Icarus* **216**, 82–85 (2011).
56. Zhang, X. et al. Photolysis of sulphuric acid as the source of sulphur oxides in the mesosphere of venus. *Nat. Geosci.* **3**, 834–837 (2010).
57. Krasnopolsky, V. A. Vertical profiles of H_2O , H_2SO_4 , and sulfuric acid concentration at 45–75 km on Venus. *Icarus* **252**, 327–333 (2015).
58. Frisch, M. J. et al. *Gaussian 09, Revision B.01*, (Gaussian, Inc., 2010).
59. Demaison, J., Herman, M., Liévin, J. & Rudolph, H. D. Equilibrium structure of sulfuric acid. *J. Phys. Chem. A* **111**, 2602–2609 (2007).
60. Aoiz, F. J. et al. The $\text{O}(^1\text{D}) + \text{H}_2$ reaction at 56 meV collision energy: a comparison between quantum mechanical, quasiclassical trajectory, and crossed beam results. *J. Chem. Phys.* **116**, 10692–10703 (2002).
61. Sayós, R., Oliva, C. & González, M. A theoretical approach to the $\text{O}(^1\text{D}) + \text{H}_2\text{O}(\text{X}^1\text{A}_1)$ reaction: Ab initio potential energy surface and quasiclassical trajectory dynamics study. *J. Chem. Phys.* **113**, 6736–6747 (2000).

62. Sayós, R., Hernando, J., Puyuelo, M. P., Enríquez, P. A. & González, M. Influence of collision energy on the dynamics of the reaction. $\text{O}(^1\text{D}) + \text{CH}_4(X^1A_1) \rightarrow \text{OH}(X^2II) + \text{CH}_3(X^1A_2)$. *Phys. Chem. Chem. Phys.* **4**, 288–294 (2002).
63. Schlegel, H. B. Optimization of equilibrium geometries and transition structures. *J. Comput. Chem.* **3**, 214–218 (1982).
64. Lee, T. J. & Taylor, P. R. A diagnostic for determining the quality of single-reference electron correlation methods. *Int. J. Quantum Chem.* **23**, 199–207 (1989).
65. Rienstra-Kiracofe, J. C., Allen, W. D. & Schaefer, H. F. III The $\text{C}_2\text{H}_5 + \text{O}_2$ reaction mechanism: high-level ab Initio characterizations. *J. Phys. Chem. A* **104**, 9823–9840 (2000).
66. Karlström, G. et al. MOLCAS: a program package for computational chemistry. *Comput. Mater. Sci.* **28**, 222–239 (2003).
67. Aquilante, F. et al. Molcas 8: new capabilities for multiconfigurational quantum chemical calculations across the periodic table. *J. Comput. Chem.* **37**, 506–541 (2016).

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Author contributions

M.K.H. defined the scientific problem. S.G. performed the calculations related to energetics and kinetics, and prepared all the Figures and Tables. Both S.G. and M.K.H. analyzed the data for energetics and kinetics, MKH performed excited state calculations.

B.M. and P.M. performed the TSH calculations and analyzed the data. M.K.H. wrote the Manuscript and Supplementary Information.

Additional information

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