INFLUENCE OF OXIDATION OF VOLCANIC SULFUR DIOXIDE ON SULFURIC ACID AEROSOL AND OZONE LEVELS IN THE STRATOSPHERE

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The kinetics of stratospheric accumulation of sulfuric-acid aerosols and the variation of the ozone content at altitudes from 27 to 32 km after a volcanic eruption are modelled. The chemical scheme includes the 10 main reactions of the oxygen cycle of ozone and SO_2 photooxidation. The peculiarity of this scheme is its account of SO_2 photooxidation by ozone. Satisfactory agreement between the calculated and experimental data on temporal variations of sulfuric acid aerosols concentration after a volcanic eruption was obtained.

1. Volcanic eruptions cause strong disturbances of the gaseous and aerosol composition of the stratosphere.[1–3] A sharp increase of the aerosol concentration at altitudes from 17 to 30 km was detected, in particular, after the eruption of the El Chichon volcano in September, 1982 (see, e.g., Refs. 3–9). The aerosol particles that were collected consisted mainly of sulfuric acid droplets or sulfate solutions.[5, 8] The measured concentration of stratospheric aerosols at low latitudes reached its maximum a few weeks after the volcanic eruption.[5, 9] During this period a conversion in the stratosphere of sulfur dioxide into aerosol[10, 11] evidently took place which had mainly a homogeneous (gaseous phase) character.[4] Heterogeneous SO_2 oxidation, in particular on the surface of volcanic ashes, is quite possible as well. Note that the largest measured concentration of formed Aitken nuclei was observed not within the Junge aerosol layer (17–19 km), but at the altitude of the maximum ozone concentration (24–27 km).[4,5,6,8] This fact allows one to suppose the participation of stratospheric ozone in aerosol-forming reaction with SO_2. Therefore one of the aims of the present paper is to calculate the H_2SO_4 accumulation in the stratosphere after a volcanic eruption taking account of ozone participation in SO_2 oxidation.

Volcanic eruptions have a strong effect on atmospheric ozone levels.[2, 13, 14] In addition to the various mechanisms for this effect that have been suggested, in particular, in Refs. 13 and 14, it is possible to add one more – the SO_2 photo-oxidation reaction. Indeed, ozone must be consumed in the reaction in Ref. 15 $^3SO_2(^3B_1) + O_3 \to SO_3 + O_2$. On the other hand, one can expect the reverse reaction – O_3 generation – as a result of the SO_2 photo-oxidation by atmospheric oxygen: in Refs. 16 and 17 $^3SO_2(^3B_1) + O_2 \to \to SO_3 + O(^3P)$. The possibility of ozone accumulation is also indicated by field observations, in particular those detailed in Refs. 18 and 19, in which a positive correlation is demonstrated between the ozone and sulfate concentrations in the atmosphere. Proceeding from this, the second aim of the present paper is to model the influence of gaseous-phase oxidation of volcanic SO_2 on stratospheric ozone levels.

2. The ozone balance and SO_2 conversion were examined for the stratospheric conditions from 27 to 32 km. The O_2, O_3, O, OH, and H_2O concentrations were taken from Refs. 20 and 21, the vertical temperature and air-density distributions from Ref. 21, the solar radiation intensity from Ref. 13, the value of the SO_2 absorption cross sections from Refs. 16 and 20, and those of O_2 and O_3 from Ref. 13. Dynamic factors were not included in the model, because at the examined altitudes they contribute less to the balance of the above-mentioned gaseous components than the chemical reactions do.[22] The main reactions of the oxygen ozone cycle and SO_2 photooxidation were included in the chemical scheme of the model (see Table I). The following simplifying assumptions were implemented:

a) The value of integral rate constant J_0 of $^3SO_2$ formation in reactions 2 and 3 is substantially influenced by the altitude and the composition of the atmosphere. For the examined range of altitudes J_0 is equal to $2.3 \cdot 10^{-4}\ s^{-1} \cdot cm^{-3}$, Ref. 20;

b) Since the relative SO_2 content in the atmosphere does not exceed a few per cent, and the ratio of the O_2 and N_2 concentrations varies hardly at all with altitude up to 80–90 km, one may take $K_B = 1.2 \cdot 10^{-13}\ cm^3 \cdot s^{-1}$ with M = air;

c) The constants K_{11} and K_{12} depend on altitude, but do not exceed the values given in the table;

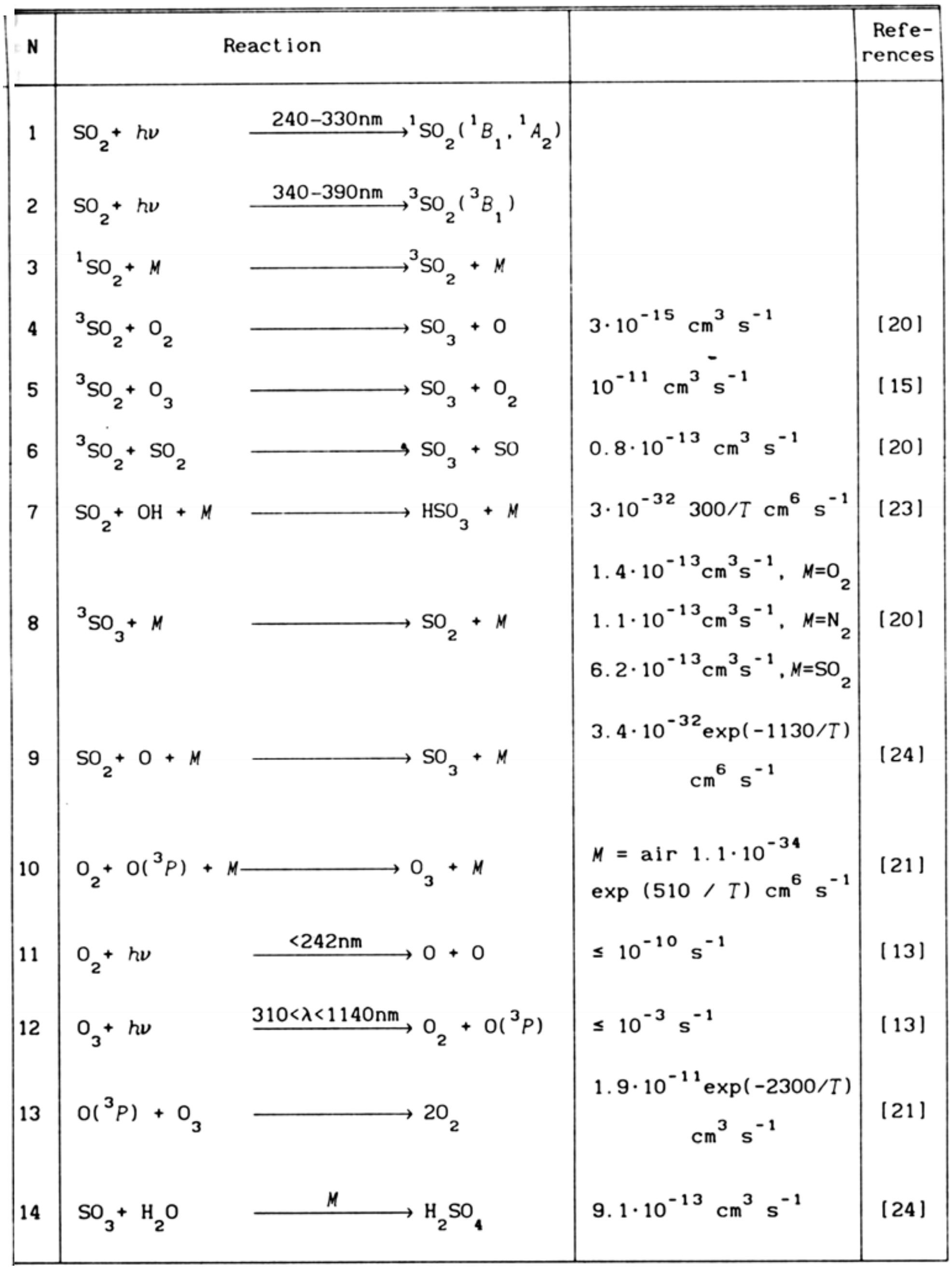
d) The reaction of SO_2 dissociation, proceeding under the action of the short-wave radiation ($\lambda \le 228$ nm),[20] is not taken into account in the present paper, because it is characteristic of altitudes greater than 40 km;

e) The temperature dependence of the $^3SO_2$ reactions rates in sifnificant,[20] therefore the value of K_4 obtained in Ref. 15 at room temperatures is used;

f) Photochemical reactions involving $^1SO_2$ are not considered, because the main role in atmospheric chemistry is played by the triplet excited state of the SO_2 molecule.[16, 25]

TABLE I

Reactions and rate constants used in the calculations.



N	Reaction		References
1	$SO_2 + h\nu \xrightarrow{240-330nm} {}^1SO_2(^1B_1, {}^1A_2)$		
2	$SO_2 + h\nu \xrightarrow{340-390nm} {}^3SO_2(^3B_1)$		
3	$^1SO_2 + M \longrightarrow {}^3SO_2 + M$		
4	$^3SO_2 + O_2 \longrightarrow SO_3 + O$	$3 \cdot 10^{-15}$ cm^3 s^{-1}	[20]
5	$^3SO_2 + O_3 \longrightarrow SO_3 + O_2$	10^{-11} cm^3 s^{-1}	[15]
6	$^3SO_2 + SO_2 \longrightarrow SO_3 + SO$	$0.8 \cdot 10^{-13}$ cm^3 s^{-1}	[20]
7	$SO_2 + OH + M \longrightarrow HSO_3 + M$	$3 \cdot 10^{-32}$ $300/T$ cm^6 s^{-1}	[23]
8	$^3SO_3 + M \longrightarrow SO_2 + M$	$1.4 \cdot 10^{-13}$cm^{3}s^{-1}, $M=O_2$ $1.1 \cdot 10^{-13}$cm^{3}s^{-1}, $M=N_2$ $6.2 \cdot 10^{-13}$cm^{3}s^{-1}, $M=SO_2$	[20]
9	$SO_2 + O + M \longrightarrow SO_3 + M$	$3.4 \cdot 10^{-32}\exp(-1130/T)$ cm^6 s^{-1}	[24]
10	$O_2 + O(^3P) + M \longrightarrow O_3 + M$	M = air $1.1 \cdot 10^{-34}$ exp $(510 / T)$ cm^6 s^{-1}	[21]
11	$O_2 + h\nu \xrightarrow{<242nm} O + O$	$\leq 10^{-10}$ s^{-1}	[13]
12	$O_3 + h\nu \xrightarrow{310<\lambda<1140nm} O_2 + O(^3P)$	$\leq 10^{-3}$ s^{-1}	[13]
13	$O(^3P) + O_3 \longrightarrow 2O_2$	$1.9 \cdot 10^{-11}\exp(-2300/T)$ cm^3 s^{-1}	[21]
14	$SO_3 + H_2O \xrightarrow{M} H_2SO_4$	$9.1 \cdot 10^{-13}$ cm^3 s^{-1}	[24]

The set of differential equations for $[SO_2]$, $[^3SO_2]$, $[O_2]$, $[O]$, and $[O_3]$, based on reactions (1)–(13), might be substantially simplified if one takes into account that the times τ of forming a stationary concentration of each of the examined components are quite diverse. Estimates show that $\tau_{SO_2} \simeq 10^3$ s, $\tau_{^3SO_2} \simeq 10^{-5}$ s, $\tau_{O_2} \simeq 10^{-8}$ s, $\tau_O \simeq 10^{-2}$ s, and $\tau_{O_3} \simeq 10^4$ s for the examined altitude range. The times $\tau_{^3SO_2}$ and τ_O are extremely small; therefore one can assume that $\frac{d[^3SO_2]}{dt} \simeq 0$ and $\frac{d[O]}{dt} \simeq 0$. Besides, since $\tau_{O_2} \gg \tau_{SO_2}$ and τ_{SO_3}, the molecular concentration of oxygen during the period of SO2 conversion can be considered to be unchanged, i.e., $[O_2] \simeq [O_2]_0$. Taking these simplifications into account (assuming $10^{12} \leq [SO_2] \leq 10^{14}$ cm^{-3}) for altitudes of 27—32 km, we obtain

$$\frac{d}{dt}[SO_2] = -[SO_2]\{\alpha K_4[O_2] + \alpha K_5[O_3]\};$$

$$\frac{d}{dt}[O_3] = \alpha K_4[O_2][SO_2] + 2K_{11}[O_2] - \alpha K_5[SO_2][O_3], \qquad (1)$$

where $\alpha = \frac{J_0}{K_8[M]}$.

3. The time dependence of $[SO_2]$ and $[O_3]$ calculated from Eqs. (1) are shown in Fig. 1. A decrease of $[SO_2]$ with time takes place, obeying a law close to an exponential one, and over the entire range of [SO2]0 values the time constant of the SO_2 conversion process lies within the limits of $(\alpha K_4[O_2])^{-1} > \tau_{SO_2} > (2\alpha K_4[O_2])^{-1}$.

Note that the value $\alpha K_4[O_2]$ varies hardly at all with altitude within the interval 27–32 km, and τ_{SO_2} depends only on $[SO_2]_0$ at the given altitude. At night time $\alpha = 0$ and $K_{11} = 0$, and thus $\frac{d}{dt}[SO_2] \simeq 0$ and $\frac{d[O_3]}{dt} \simeq 0$. In view of this, the value of τ_{SO_2} under the examined conditions varies from 1.3 to 2.6 weeks depending on $[SO_2]_0$. The lower bound of the τ_{SO_2} values (~ 1.3 weeks) is obtained when reaction (5) is taken into account in the calculation. Neglecting this reaction yields the upper bound of $\tau_{SO_2} \simeq 2.6$ weeks. Experimental estimates of τ give values close to 1 week.[8] Thus, reaction 5 (see Table I) probably plays an important role under the considered conditions. Note that the "dark" SO_2 conversion in the reaction with OH, which plays the main role at small altitudes, is not essential in the examined altitude range in comparison with photochemical conversion (the rate constant of the reaction of SO_2 with OH was taken from Ref. 20).

Unlike the time dependence of $[SO_2]$, the ozone concentration increases with time, approaching a value determined by the relationship $[O_3] \simeq \frac{K_{2a}}{K_{2b}}[O_2]$ (Fig. 1). This result does not agree well with the experimental data on decreasing [OCOl after volcanic eruptions.[3] On the one hand, the disagreement may be associated with the fact that the given scheme, for example, does not allow for a heterogeneous sink of stratospheric ozone. On the other hand. It is possible to admit the reality of the obtained increase in $[O_3]$ in the given altitude interval during the first weeks after the eruption with the simultaneous decrease of [OCO].

The conversion of volcanic sulfur dioxide in the stratosphere causes the formation of aerosols which are 80% sulfuric acid.[8] Reaction set (1)–(14) enables one to calculate the time dependence of the concentration of H_2SO_4 – the final product of SO_2 conversion. It turns out that the SO_2 decrease is followed almost instantaneously by am increase in H_2SO_4 (the lifetime of the intermediate product SO_3 is equal to ~ 1 s). Taking into account the first order character of reaction (14), it is clear that the following relationship is satisfied:

$$1 - \frac{[SO_2]}{[SO_2]_0} = \frac{[H_2SO_4]}{[H_2SO_4]_0}. \qquad (2)$$

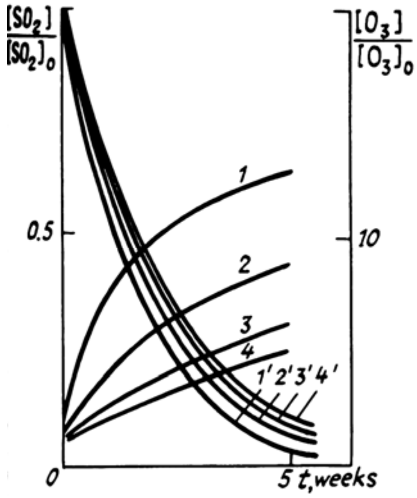


FIG. 1. Time dependence of the relative concentration of ozone (curves 1, 2. 3, and 4) and sulphur dioxide (curves 1', 2', 3', and 4') with different $[SO_2]_0$. $[SO_2]_0 = 10^{14}$ cm^{-3} (1 and 1'); $[SO_2]_0 = 3 \cdot 10$ cm^{-3} (2 and 2'); $[SO_2]_0 = 10^{13}$ cm^{-3} (3 and 3') $[SO_2]_0 = 3 \cdot 10^{12}$ cm^{-3} (4 and 4').

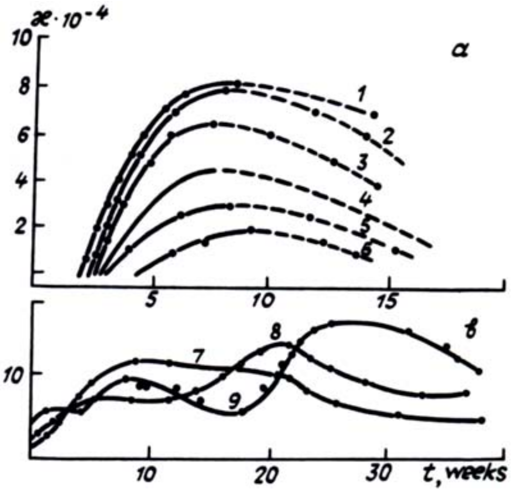


FIG. 2. Time dependence of the aerosol absorption coefficient: calculated curves (solid lines.) and experimental data (dashed lines) (a):[9] 27 km (1), 26 km (2). 29 km (3), 30 km (4), 31 km (5), 32 km (5); experimental data (b):[9] 25 km (7), 22 km (6), 20 km (9).

Figure 2 shows time dependences of the aerosol absorption for different altitudes in the 27–32 km interval according to the data from Ref. 9 and the calculated results of system (1) and relationship (2). Note that we have calculated the time dependence of $[H_2SO_4]$, not that of the absorption coefficient κ. However, the $[H_2SO_4]$ and κ time dependences may be considered as symbatic, assuming that the radius of photochemical sulfuric acid aerosols $r \approx \lambda$ (here $\kappa \sim [H_2SO_4]$). As can be seen from Fig. 2a, satisfactory agreement between the experimental and calculated dependences is observed. Comparison of the experimental data with the results of the calculation based on the above scheme is possible only on the initial part of the curve (up to the maximum), because the processes causing aerosol removal (and decrease of the aerosol absorption coefficient) are not taken into account in the scheme. For the same reason the calculation of the time dependences of $[SO_2]$ and $[O_3]$ quantities (see Fig. 1) was carried out for the initial stage of SO_2 conversion (5–7 weeks). Note that the characteristic time of aerosol removal may be estimated from the data of Ref. 9 to be $\simeq 40$ weeks.

The initial segments of the curves in Fig. 2a are shifted relative to each other in time by 2–3 weeks, i.e., there is observed a delay of the startup of SO_2 conversion (and aerosol formation) in comparison with the start of the volcanic eruption. In other words, the best coincidence of the calculated and experimental curves is obtained if one takes into account the delay of the startup of SO_2 conversion (and formation of aerosol) relative to the start of the eruption and one shifts the calculated curves relative to the origin of coordinates in such a way that their behavior would be in coincidence with the behavior of the experimental curves. At the same time for altitudes less than ≈ 25 km, the startup of SO_2 conversion and eruption coincide (Fig. 2b). The delay obtained for altitudes ≥ 27 km can be associated with SO_2 diffusion In the vertical direction. For the same reason probably, the deviation of the experimental points from the calculated ones in the starting part of the curves is observed. As is seen from Fig. 2, the startup of conversion at the altitude of 32 km has a 1.9 week delay relative to that at the altitude of 27 km. From these data the value of the diffusion coefficient $D \simeq \frac{(\Delta h)^2}{\Delta t} = \frac{(5 \cdot 10^5)^2}{1.9 \cdot 6 \cdot 10^5} = 2.2 \cdot 10^5\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$ can be estimated. The obtained value D is close to the value assumed for the vertical turbulent diffusion coefficient at these altitudes ($\sim 10^5\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$ for the altitudes of 30–50 km Refs. 26 and 27), which confirms the reasonability of these assumptions. Turbulent vertical diffusion can also explain the fact that the particle concentration reaches its maximum value later at large altitudes, rather than at small ones (Fig. 2a). A different picture is observed at altitudes lower than 27 km (Fig. 2b) the formation of aerosol (and the growth of κ) begins as soon as the eruption starts but soon stops and starts up again 10–15 weeks later. The end of growth of the particle concentration is observed from the start at low altitudes (20 and 22 km) and only later at high altitudes (25 km). Such a time dependence can be attributed to the fact that the SO_2 that penetrates Into the higher layers (≥ 27 km) strongly attenuates the solar radiation within the limits of the SO_2 absorption bands. Simple estimates show that the total absorption in this spectral, range enters with $[SO_2] \simeq 3 \cdot 10^{13}\ \mathrm{cm}^{-3}$ at an altitude of 27 km. This value of $[SO_2]$ warn used in the calculation of the theoretical curves that are shown In Fig. 2a. After the conversion of SO_2 in the higher layers and SO_2 photo-oxidation the latter clear out recommences at altitudes below 25 km. According to this assumption the second wave of photo-chemical generation of particles at the altitudes of 22 and 20 km (Fig. 2b) begins during the decay of the particle concentration in the higher layers.

Thus, the suggested approach enables us to qualitatively explain the mutual influence between the photoformation process and the subsequent evolution of sulfuric-acid aerosol in different layers of the stratosphere.

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