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The burden of the sulphate layer of the stratosphere during volcanic "quiescent" periods

By J. SERVANT, *Laboratoire d'Aérologie, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France*

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ABSTRACT

This paper deals with the origin of sulphates ($SO_4^=$) in the stratosphere during periods of volcanic quiescence. Based on measurements taken during the 1971-1981 Airstream Project, we determined that the oxidation of carbonyl sulphide molecules (COS) is sufficient to explain the distribution of $SO_4^=$ in the stratosphere. Oxidation by OH attack appears negligible, photodissociation is significant. The stratospheric life time of COS molecules is estimated at approximately 4 years. The mean oxidation rate of COS in the stratosphere is 1.0×10^7 molecules $cm^{-2} s^{-1}$.

1. Introduction

The thermal equilibrium of the troposphere and the stratosphere depends partly on the particulate content of the air. Following the Mount Agung eruption in March 1963, Newell and Weare (1976) observed a decrease of about 0.5 °C in the mean temperature of the tropical troposphere. At the same time, an increase of up to 5 °C was recorded at altitudes between 17 and 25 km over more than a quarter of the globe (Newell, 1970). At Mount Loa observatory, a 1.5% decrease in the apparent transmittance of the atmosphere was also noted after this same eruption (Ellis and Pueschel, 1971).

The particulate emitted during an eruption is a mix of super micron silicates and submicron aerosols formed by gas-particulate conversions. The silicates are eliminated from the atmosphere quite rapidly by gravity. The submicron aerosols remain in the atmosphere for one year or longer and are important for the physical properties of the atmosphere. One of the most abundant constituents of submicron aerosol is sulphate ($SO_4^=$). Junge et al. (1961) described the existence of an $SO_4^=$ layer at an altitude of about 20 km during a period of low volcanic activity. Crutzen (1976) suggested that this layer was created by the transfer of sulphur to the stratosphere by carbonyl sulphide (COS) and carbon disulphide (CS_2). This was explained by the fact that the other sulphur-bearing gases are water-soluble and reactive. As they can escape neither the rain nor reactions with OH, they do not diffuse into the stratosphere.

Since that time, new values for the rate constants have been established. They show that CS_2 cannot play a rôle in the stratosphere (Jones et al., 1983). Only COS has any significant value here, as shown through a one-dimensional aerosol model (Turco et al., 1981a).

Although COS and sulphur dioxide (SO_2) concentrations were measured in the stratosphere at latitudes higher than 30° N, no measurement has been made in either the intertropical zone or the southern hemisphere. This makes it difficult to establish the effects of the Brewer-Dobson circulation on COS by which the stratosphere is flushed by air entering through the tropical tropopause and leaving through the polar tropopauses and tropopause gaps. In this case, $SO_4^=$ would be created while the air was being transported in the atmosphere, with higher concentrations to be found at higher altitudes and in the polar regions. Recently, data on the $SO_4^=$ contents of the stratosphere have been published by Sedlacek et al. (1983), pertaining to both hemispheres for the decade 1971–1981. These data allow us to calculate the stratospheric $SO_4^=$ burden during a "quiescent" period.

This paper examines the modes of oxidation of COS and the rate of $SO_4^=$ formation during "quiescent" periods.

2. The sulphate of the stratosphere during the "quiescent" periods

2.1. Data

A nearly complete set of stratospheric sulphate data for the decade 1971 to 1981 have been given by Sedlacek et al. (1983). To illustrate the case of a "quiescent" period, five $SO_4^=$ distributions of this work are given in Figs. 1–5. They cover the period May 1973 to April 1974 and were taken at altitudes lower than 20 km in the two hemispheres. During this period, the sulphate mass mixing ratios are nearly constant with no seasonal variation. The mean concentrations in the air of the two hemispheres are comparable: 0.30 and 0.27 ppbm for the northern and the southern hemispheres, respectively. This value is about 20% of the sulphur burden of the stratosphere carried by the COS molecules. The distribution of the mixing ratio of $SO_4^=$ shows an increasing gradient with altitude at all latitudes and with latitude at all altitudes. Lines of isoconcentrations can be drawn. They parallel the tropopause configuration as previously shown for the dispersion of nuclear debris. These lines indicate that most of the oxidation of the COS molecules takes place at altitudes above 20 km and corresponds to a Brewer-Dobson circulation with

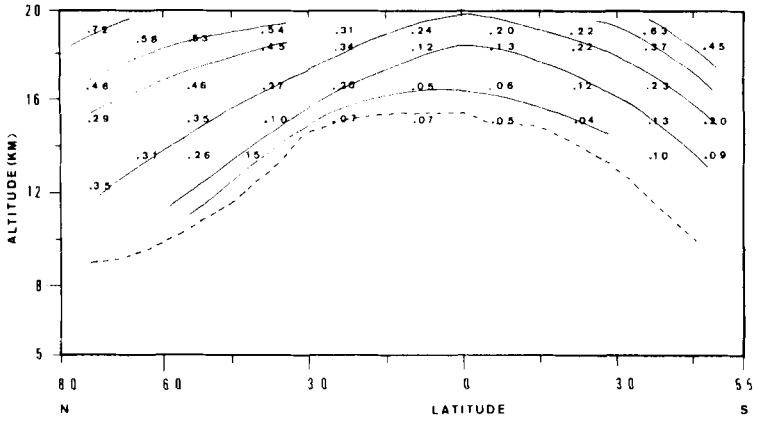

Fig. 1. Sulphate concentrations measured from May 29 to June 10, 1973. The average stratospheric concentrations are 0.27 and 0.21 ppbm in the northern and southern hemispheres, respectively.

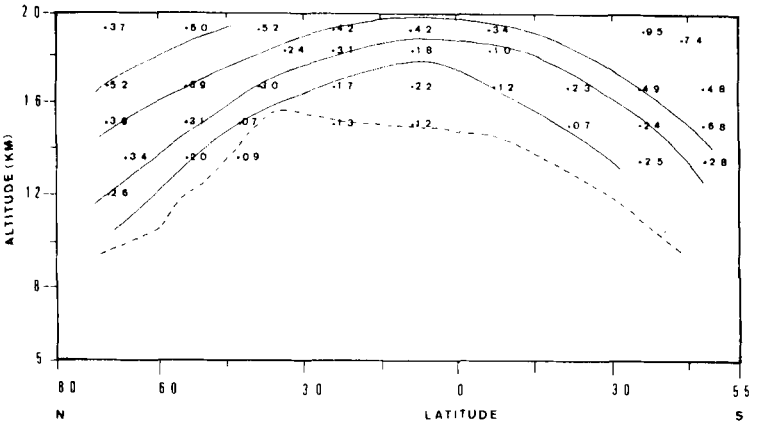

Fig. 2. Sulphate concentrations measured from September 5 to 25, 1973. The average stratospheric concentrations are 0.31 and 0.29 ppbm in the northern and the southern hemispheres, respectively.

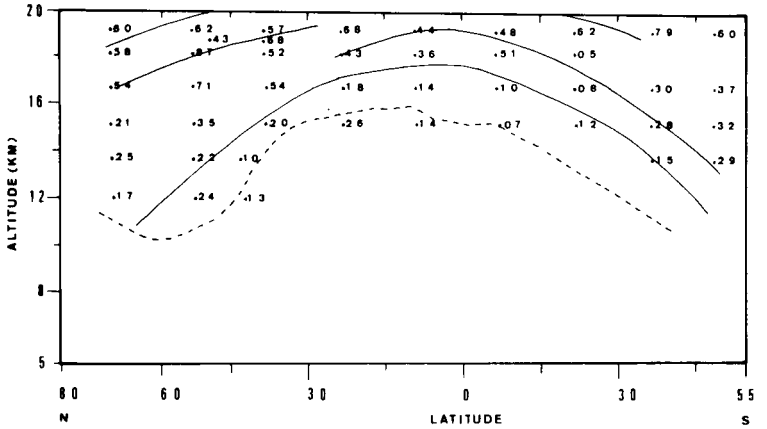

Fig. 3. Sulphate concentrations measured from October 30 to November 9, 1973. The average stratospheric concentrations are 0.36 and 0.28 ppbm in the northern and the southern hemispheres, respectively.

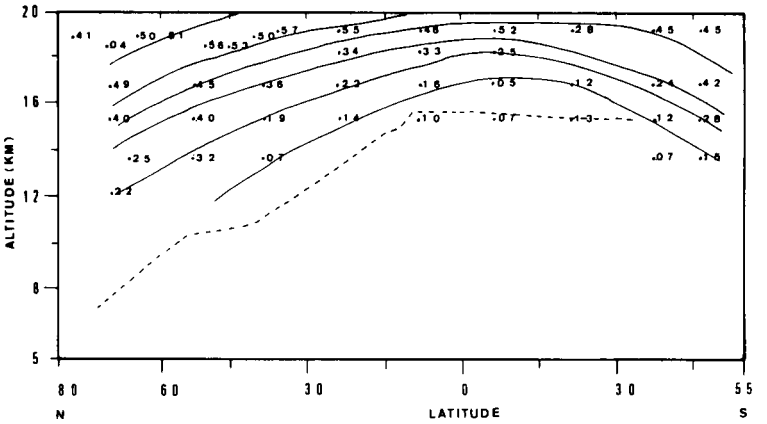

Fig. 4. Sulphate concentrations measured from January 22 to February 2, 1974. The average stratospheric concentrations are 0.30 and 0.24 ppbm in the northern and the southern hemispheres, respectively.

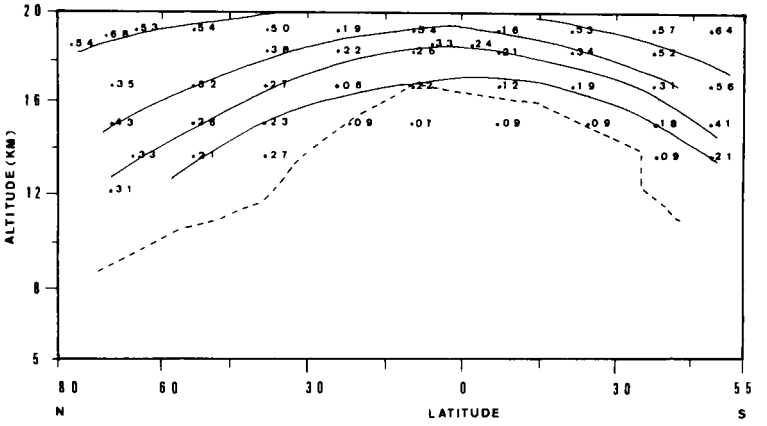

Fig. 5. Sulphate concentrations measured from April 12 to 29, 1974. The average stratospheric concentrations are 0.27 and 0.27 ppbm in the northern and the southern hemispheres, respectively.

the flow of air through the tropical tropopause and the return to the troposphere through the polar tropopause. The entry of tropospheric air was visible between 0 and 30° S of latitude in May–June 1973 and September–October 1973.

2.2. Discussion

The ability to estimate the stratospheric burden of $SO_4^=$–S is essential. First during the "quiescent" period (May 1973–October 1974), no documented or undocumented stratospheric volcanic injection has been reported. However, in the northern and southern hemispheres, the mixing ratio of $SO_4^=$ prior to this period (January 1973) was 0.63 and 0.41 ppbm respectively—twice the values of the "quiescent" period. It seems that these values (January 1973) were already too high because 4 months later at the beginning of the "quiescent" period, the mixing ratio attained the value which would be that of the next year. A decrease following a volcanic injection is associated with a residence time of 14 months, as shown later in the discussion. Therefore such a decrease being not apparent, the values of January 1973 were too high for an unknown reason.

Concentrations of COS and SO_2, procursors of the $SO_4^=$, have been measured in the stratosphere. The punctual chemical analyses by aircraft and ballon sampling were made between 35° N and 70° N (Inn et al., 1979a, b, 1981; Jaeschke et al., 1976; Georgii and Meixner, 1979). Between 12 and 20 km of altitude, the SO_2 concentration was about 50 pptv, COS concentration was 281–405 pptv at 15 km, 170–199 pptv at 21 km and 16 pptv at 31 km. These measurements show a progressive oxidation of the COS molecules with altitude in the stratosphere and a constant SO_2 concentration at the different levels. These experimental results have been explained by the use of a one-dimensional aerosol model (Turco et al., 1981a). The two key reactions are:

$$OH + COS \xrightarrow{k_1} \text{products}, \quad (1)$$

$$OH + SO_2 + M \xrightarrow{k_2} HSO_3 + M \quad (2)$$

with $k_1 = 8.4 \times 10^{-12} \exp(-2040/T)$ cm^3 molecule^{-1} s^{-1} (Ravishankara et al., 1980) and $k_2 = 5.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Moortgat and Junge, 1977).

Tests have been conducted with these rate constants in combination with different values of the diffusion coefficients. Calculated height distribution profiles of COS and SO_2 show rather good agreement with observational data. From the more recent work of Leu and Smith (1981), rate constant given by an Arrhenius expression $1.3 \times 10^{-12} \exp(-2300/T)$ cm^3 molecule^{-1} s^{-1} is one order of magnitude lower than that of Ravishankara et al. (1980). If this rate is accepted with broad uncertainties (De More et al., 1983), it shows even more convincingly that OH attack is probably of minor importance.

The lowering of chemical rates and OH radical concentrations, however, aggravated the problem of matching calculated and observed SO_2 concentrations. To overcome this difficulty, photodissociation was soon considered by Turco et al. (1981a). The effect at long wavelength (between 270 and 350 nm) was discussed, based on the data obtained by Rudolph and Inn (1981). UV absorption cross sections from 185 to 300 nm have also been measured by Molina et al. (1981). These authors have concluded that photodissociation at longer wavelengths was negligible and solar photolysis in the 200 nm "window" was expected to be considerably greater.

The total rate of the mechanisms involved in the dissociation and oxidation of COS molecules can be appreciated considering the annual rate of $SO_4^=$–S formation. This rate is the ratio of the total burden of $SO_4^=$–S in the stratosphere, to the residence time of this particulate matter.

The zone where the photodissociation is active is shown by the altitude profile of COS concentrations (Fig. 6). This profile is comparable to that of the CH_3Cl concentrations (Fig. 7). In the troposphere, these concentrations are between 500 and 600 pptv and at 31 and 32 km of altitude, between 20 and 30 pptv. The CH_3Cl molecules are oxidized below 30 km of altitude mainly by the OH radicals at a rate coefficient given by an Arrhenius expression, $1.8 \times 10^{-12} \exp(-1112/T)$ cm^3 molecule^{-1} s^{-1} (De More et al., 1983). The meridional cross-section of CH_3Cl calculated by a two-dimensional model of photochemistry (Cariolle, 1982) coincides quite well with the observations at mid-latitudes in the northern hemisphere (Fig. 7). The meridional cross-section of COS has recently been calculated with a two-dimensional model for equinox conditions (Crutzen and Schmailzl, 1983). From these data, it has been calculated that the total $SO_4^=$–S burden in the stratosphere would be

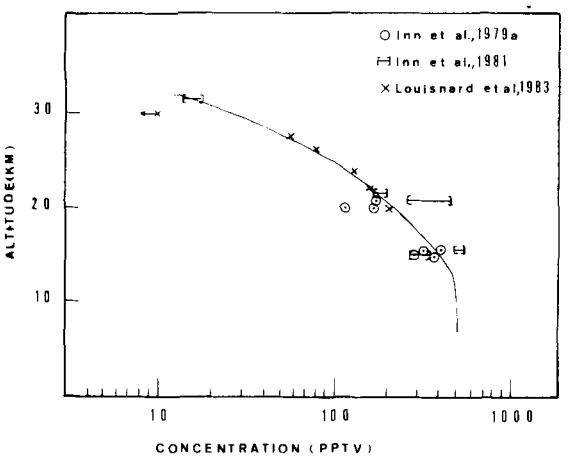

Fig. 6. Vertical distribution of COS concentrations at mid-latitudes in the northern hemisphere.

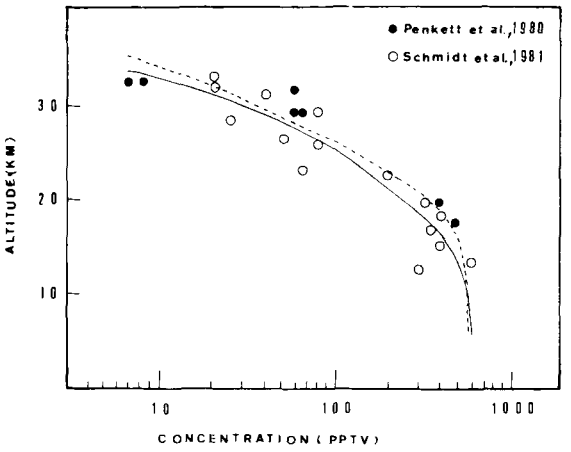

Fig. 7. Vertical distribution of CH_3Cl concentrations at mid-latitudes in the northern hemisphere (the dashed line is the theoretical profile for January and the solid line the experimental profile).

2.7 times larger than that below 20 km of altitude. According to the $SO_4^=$ measurements of Sedlacek et al. (1983) the total stratospheric $SO_4^=$–S burden could be equal to 0.15×10^6 *t*.

The residence-time of air molecules in the stratosphere can be estimated from that of gases or particulates with very low gravitational settling velocities. Decreases of the stratospheric burden of ^{90}Sr and ^{54}Mn-introduced in the stratosphere near or below 20 km of altitude at polar and tropical latitudes in 1961 and 1962 by the Russian and American nuclear tests, give a residence time of 14.6 months (Feely et al., 1966). For ^{95}Zr and HTO (tritiated water), introduced in the stratosphere above 20 km of altitude and 40° N of latitude in 1976 by the Chinese nuclear tests, there was a residence-time of 14 months (Mason et al., 1982). These values are both close to 14 months, and they represent stratospheric injections at different latitudes, from the pole to the equator. One can hypothesize that this value of the residence-time is quite general and can be applied also for $SO_4^=$. For the 1974 Fuego eruption, the $\frac{1}{2}$-fold removal time of $SO_4^=$ has been estimated at 11.2 ± 1.2 months (Sedlacek et al., 1983). This is close to the value given by the analysis of the nuclear debris removal. Assuming a value of 14 months for the removal time from the stratosphere of $SO_4^=$ and a burden equal to 0.13×10^6 *t* $SO_4^=$–S, the intensity of the oxidation of the COS molecules in the stratosphere for equinox conditions would be 0.13 *t* $SO_4^=$–S year^{-1} or 1.3×10^7 molecules cm^{-2} s^{-1}. The influx of COS from the troposphere in the model of Crutzen and Schmailzl is about equal to 0.5×10^7 molecules cm^{-2} s^{-1}; this flux is just sufficient to explain the production of the $SO_4^=$ layer observed below 20 km of latitude. Therefore the upward flow of COS through the tropopause must be at least two times larger. A $SO_4^=$–S burden in the stratosphere equal to 0.15×10^6 *t* $SO_4^=$–S seems reasonable and the measurements of $SO_4^=$ reported by Sedlacek et al. (1983) representative of the reality.

3. Conclusions

During the volcanic "quiescent" period considered in this study, the oxidation of COS could explain the formation of the stratospheric sulphate layer. Two working mechanisms have been suggested: the oxidation by OH radicals on one hand and, on the other hand, photodissociation. The photodissociation appears to be the main mechanism but its rate at different wavelengths is still to be determined.

In the present study, the intensity of the sulphate formation has been estimated from the calculated burden of $SO_4^=$–S in the stratosphere and the residence time of this particulate matter. It is equal to 0.09×10^6 *t* S per year or 1.0×10^7 molecules cm^{-2} s^{-1}, a value close to Crutzen and Schmailzl's estimate of 5×10^6 molecules cm^{-2} s^{-1}.

It is shown that the data collected during the Department of Energy's High Altitude Sampling Program for sulphate mixing ratio in stratospheric air are consistent with the COS distribution with altitude measured at mid-latitudes.

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