

SO₂ oxidation in supercooled droplets in the presence of O₂

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(ricevuto il 21 Settembre 1998; approvato il 16 Dicembre 1998)

Summary. — Sulphur dioxide oxidation in supercooled monodisperse droplets at $T = -13$ °C was studied in the presence of oxygen. The SO₂ concentration was found to range from 0.08 to 7.1 ppmv and the contact time between gases and droplets was 210 s. The experimental results showed that sulphate concentration due to SO₂ oxidation is independent of temperature, *i.e.* the increase of SO₂ solubility in the liquid phase balances the rate constant decrease of the oxidation reaction. Following McKay's kinetics (*Atmos. Environ.*, 5 (1971) 7), we calculated the rate constant at $T = -13$ °C and the activation energy. A comparison was made between experimental S(VI) oxidation concentrations due to oxygen and theoretical oxidation values due to O₃, H₂O₂ and oxygen in the presence of catalyzers (Fe³⁺, Mn²⁺).

PACS 92.60.Hp – Chemical composition and chemical interactions.

1. – Introduction

The chemical composition of hydrometeors depends on physical mechanisms involving precipitation formation (water vapour condensation, coalescence of droplets, riming, etc.), chemical reactions in the liquid phase and scavenging processes of gases and aerosols. In the case of mixed precipitating clouds, supercooled droplets can sublimate, allowing the growth of ice crystals, or be captured by ice particles (riming).

Through the latter mechanism non-volatile compounds (*e.g.* SO₄²⁻), cations (Ca²⁺, Mg²⁺, Na⁺, etc.) and trace metals are transferred completely from liquid to solid phase, while in the case of S(IV) (*i.e.* SO₂·H₂O, HSO₃⁻, SO₃²⁻), the transfer is only partial [1, 2].

Oxidation of SO₂ in the atmosphere can occur through homogeneous gas-phase reactions or as a heterogeneous process taking place on the surface of solid particles or inside water (cloud or fog).

The aqueous chemistry of sulphur-containing species plays an important role in the phenomenon of acidic precipitation. Sulphur dioxide absorbed by cloud droplets

and raindrops can be converted to sulphate, with the hydrogen ions freed during this process contributing to the acidity of drops.

Laboratory studies of the aqueous-phase oxidation of S(IV) suggest that the major oxidants are H_2O_2 , O_3 or O_2 , sometimes with traces of catalyst (Fe^{2+} , Mn^{3+} , Cl^- , soot, etc.). The relative importance of each oxidant depends on its concentration in the liquid phase and pH of droplets.

Oxidation reaction rates have been studied in the laboratory at temperatures above 0°C , but in the atmosphere these reactions generally occur at $T < 0^\circ\text{C}$, *i.e.* in supercooled droplets, frequently present in the middle troposphere.

Thus, the problem is to transfer the results obtained in the laboratory to atmospheric conditions and this should be done with great caution. The effect of lowering the temperature is to decrease the reaction rate constant and to increase gases solubility. Such variations depend on the considered gases; consequently, the relative importance of various oxidation processes can also depend on the temperature.

The aim of these laboratory experiments is to study the oxidation reaction of SO_2 in supercooled droplets due to oxygen in the absence of catalyzers.

2. – Experimental part

The experimental configuration used in our experiments has already been presented in detail for other tests [2]. Monodisperse droplets $R = (3.9 \pm 0.2) \mu\text{m}$ were produced with a Sinclair LaMer generator located in a room at $T = 5^\circ\text{C}$. Droplets then passed through a pipe connected to a cylindrical chamber 200 cm in length and 11 cm in diameter located in a cold room at $T \cong -17^\circ\text{C}$. The pipe and chamber were lightly heated to reduce or prevent condensation on the walls.

SO_2 in nitrogen from a compressed gas cylinder entered the reaction chamber together with droplets in an air flux. Experimental and theoretical data show that the equilibrium of SO_2 with droplets can be expected in a time of the order of 10^{-2} s, *i.e.* a time scale which is short compared to the time necessary for chamber throughput ($\cong 210$ s). The temperature of gas at the end of the duct was measured by thermocouple and was $T = -(13.0 \pm 0.5)^\circ\text{C}$. At the outlet of the absorption section supercooled droplets were captured by an impactor and froze.

The impact velocity of droplets against the surface was about 6 m s^{-1} and the mass of the deposit was determined with a precision scale ($100 \mu\text{g}$ sensibility).

During the course of an experimental run, a conic deposit of rime, about 1 cm in height, is formed on the collection surface of the impactor. The ice was scraped from the support and put in a plastic cylinder. Each run lasted about 40 min and two impactors were used in turn. Liquid water content (LWC), determined by the ratio between the mass of ice collected during each run ($\cong 300$ mg) and the flown gas volume ($\cong 200$ l), was 1.5 g m^{-3} .

The ice was then carefully mixed and put into two plastic cylinders, A and B.

A 5% H_2O_2 solution to convert S(IV) to S(VI) and a 0.1% formaldehyde solution, to prevent S(IV) oxidation were added to samples A and B, respectively. In this way total sulphur and S(VI) obtained in the reaction chamber due to oxidation of SO_2 could be determined. A 4500i Dionex ion chromatograph with conductivity detector was used for sulphate measurements. The separation was performed by a Dionex AS4A separator column followed by an electrochemical micro-membrane conductivity suppressor.

3. – Results and discussion

In fig. 1 we report total sulphur as S(VI) measured in samples A as a function of SO₂ in the gas phase. Total sulphur includes S(IV) in equilibrium with SO₂ in the gas phase and S(VI) due to the SO₂ oxidation process in supercooled droplets. Since SO₂ is only partially retained in the ice during droplet freezing, we recalculated S(IV) and then S(VI), using a previously measured interpolated SO₂ retention coefficient [2]. These data are also reported in fig. 1.

In fig. 2 we report S(VI) due to SO₂ oxidation in the supercooled droplets and also data obtained at $T = 25\text{ }^\circ\text{C}$ from the kinetics proposed by McKay [3], as a function of SO₂ in the gas phase. Since droplet condensation nuclei were obtained by bubbling filtered air from a compressed gas cylinder through a collision containing a NaCl solution of Milli-Q water, a Cl⁻ concentration of about $4 \times 10^{-5}\text{ M}$ was measured in the droplets. This low concentration rules out a catalytic activity on the part of Cl⁻.

As regards the uncatalyzed oxidation of SO₂ at $T > 0\text{ }^\circ\text{C}$, many authors agree that oxidation occurs due to a first-order reaction in SO₃²⁻, but no oxidation of HSO₃⁻ occurs directly, although the rate constant and activation energy proposed are very different [4].

Discrepancy among authors also exists as regards the relative importance of the uncatalyzed aqueous oxidation of SO₂ by dissolved oxygen in comparison with other oxidants.

In previous laboratory experiments with monodisperse droplets in the presence of SO₂ at $T = 25\text{ }^\circ\text{C}$ [5], we obtained results which agree with the values predicted by McKay's kinetics, *i.e.*

$$(1) \quad d[\text{S(VI)}]/dT = k[\text{SO}_3^{2-}],$$

where the rate constant value is $k = 0.013 + 59[\text{H}^+]\text{ s}^{-1}$ at $T = 298\text{ K}$.

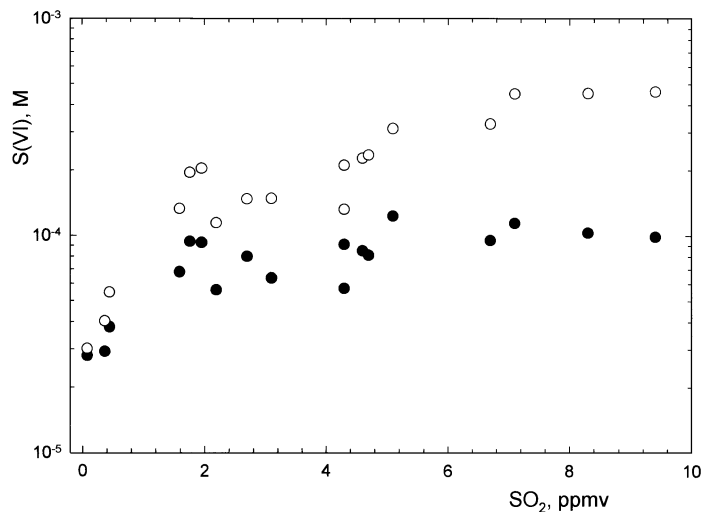


Fig. 1. – ● Total sulphur as S(VI) measured in samples A as a function of SO₂ in the gas phase. ○ Total sulphur as S(VI) calculated by considering SO₂ retention coefficient as a function of SO₂ in the gas phase (see text).

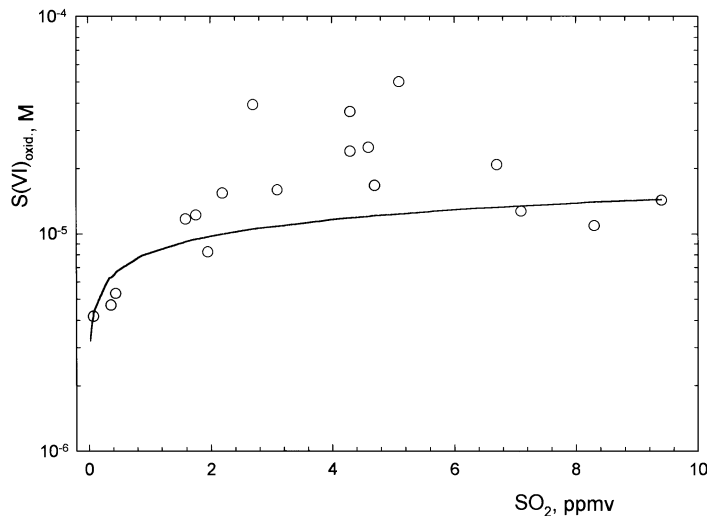


Fig. 2. — \circ Sulphate concentration in the supercooled droplets due to SO_2 oxidation, as a function of SO_2 in the gas phase ($T = -13^\circ\text{C}$). — Sulphate concentration in the liquid phase due to SO_2 oxidation following McKay kinetics ($T = 25^\circ\text{C}$).

The order of the reaction with respect to O_2 has been found to be zero over a wide range of concentrations [6-8].

From fig. 2 we observe that experimental runs at $T = -13^\circ\text{C}$ give S(VI) oxidation concentrations which can be considered, within experimental errors, equal to those calculated from McKay's kinetics at $T = 25^\circ\text{C}$. This is valid first of all for SO_2 concentrations lower than 2 ppm, *i.e.* for values including those of interest in the atmosphere. We can therefore conclude that a change of temperature from 25 to -13°C produces in the droplets an increase in SO_2 solubility which balances the decrease of the rate constant.

This statement agrees with Beilke *et al.* [9] and Larson *et al.* [10], who found that the oxidation rate has a weak temperature dependence in acidic solutions, while Penkett *et al.* [11], in an experiment on the aerobic oxidation of sodium sulphite solutions, found that the reaction proceeds about ten times faster at 42°C than at 23°C .

By supposing that McKay's kinetics for SO_2 oxidation due to oxygen is valid also at $T = 260\text{ K}$, we can calculate from (1) the value of the rate constant at $T = -13^\circ\text{C}$. In our model we presume an instantaneous equilibrium between the SO_2 in the gas and liquid phases ($\text{LWC} = 1.5\text{ g m}^{-3}$), *i.e.* the reaction velocity is governed only by the kinetic constant. In addition, we take into account the depletion of SO_2 in the gas phase due to its partition between the gas and liquid phases and the oxidation process, which influences pH and SO_2 solubility in the liquid phase.

The solubility, which depends on pH and temperature, can be calculated by

$$[\text{S(IV)}] = K_{\text{hs}} p_{\text{SO}_2} (1 + K_{\text{s1}} / [\text{H}^+] + K_{\text{s1}} K_{\text{s2}} / [\text{H}^2]),$$

where K_{hs} , K_{s1} and K_{s2} are Henry's coefficient and the first- and second-ionization constants for SO_2 . K_{hs} , K_{s1} and K_{s2} can be calculated by Maahs' equation [12].

For example, at $T = -13\text{ }^{\circ}\text{C}$, K_{hs} , K_{s1} and K_{s2} are 5.91 M atm^{-1} , $3.47 \times 10^{-2}\text{ M}$ and $1.3 \times 10^{-7}\text{ M}$, respectively, while at $T = 25\text{ }^{\circ}\text{C}$, the values are 1.24, 1.29×10^{-2} and 6.01×10^{-8} . The solubility of SO₂ in water increases with decreasing temperature. For example, in an unbuffered solution, $\text{SO}_2 = 10^{-2}\text{ ppm}$ and the ratio $[\text{S(IV)}]_{260\text{K}}/[\text{S(IV)}]_{298\text{K}}$ is about 3.4. As regards O₂, the solubility ratio is 2.4.

At $T = 298\text{ K}$, with an initial concentration in the gas phase of $\text{SO}_{2,\text{i}} = 10^{-2}\text{ ppm}$ comparable to atmospheric values (the “i” subscript stands for initial), McKay’s kinetics gives, after 210 s (the contact time in our runs), $\text{S(VI)} \cong 2.5 \times 10^{-6}\text{ M}$, with a $\text{LWC} = 1.5\text{ g m}^{-3}$. To obtain the same S(VI) values at $T = 260\text{ K}$, the calculated rate constant of McKay’s kinetics must be

$$k_{260} = 3.1 \times 10^{-3} + 14.2[\text{H}^+].$$

From $k_{260} = k_{298} \exp[(E_a/R) \times (1/298 - 1/260)]$, where E_a is the activation energy for the oxidation and R is the universal gas constant, we obtain for McKay’s rate constant $E_a = 24\text{ kJ/mole}$. Beilke *et al.* [9] (buffered solutions, pH 3–6), report 58.6 kJ mol^{-1} ; Larson *et al.* [10] (buffered solutions, pH 7–9) report 89 kJ mol^{-1} and (in acidic solutions) 7.1 kJ mol^{-1} ; Penkett *et al.* [11] (unbuffered distilled water) report 109.6 kJ mol^{-1} . In rainwater Clarke and Radojevic [13] obtained 104 kJ mol^{-1} , at temperatures in the 17–40 °C range.

It is important to note that the SO₂ conversion obtained during this short time (3.5 min) cannot be extrapolated to much longer time periods, as aqueous-phase sulphate production can be self-limiting, due to the strong pH dependence of several of the mechanisms proposed for sulphate production in clouds.

To evaluate the relative importance of various pathways for the production of sulphates in the liquid phase, we compared the previous values obtained with oxygen with those calculated in the presence of catalyzers such as Fe^{2+} , Mn^{3+} or oxidants such as H_2O_2 and O_3 .

With $\text{O}_3 = 50\text{ ppb}$, assuming its concentration in the gas-phase to remain constant due to its low solubility, Hoffmann’s kinetics [14] gives, $\text{S(VI)} = 4.7 \times 10^{-6}\text{ M}$ at $T = 260\text{ K}$, and $\text{S(VI)} = 5.8 \times 10^{-6}\text{ M}$ at $T = 298\text{ K}$, with $\text{SO}_{2,\text{i}} = 10^{-2}\text{ ppm}$ and after 210 s.

Theoretical final pH values are 4.2 and 4.7, respectively. Thus, at lower temperatures the relative importance of SO₂ oxidation due to O₂ increases with respect to O₃. The O₃-S(IV) reaction becomes more important as the pH increases, for example, in water associated with sea-salt particles present in the marine boundary layer [15, 16].

With regard to SO₂-catalyzed oxidation, the rate law of Ibusuki and Takeuchi [17], with $\text{SO}_{2,\text{i}} = 10^{-2}\text{ ppm}$ and $\text{Mn(II)} = \text{Fe(III)} = 10^{-6}\text{ M}$, gives $\text{S(VI)} = 4.7 \times 10^{-6}\text{ M}$ and $3.8 \times 10^{-5}\text{ M}$, at $T = 260\text{ K}$ and 298 K , respectively. The value at $T = 260\text{ K}$ is about double with respect to our experimental results and about equal to the value obtained with O₃.

Concerning the influence of H₂O₂, it can be considered the primary oxidant involved in the production of sulphuric acid in atmospheric cloud water when the pH is less than 4–5. Since the solubility of this gas is very high, on entering cloud it will tend to transfer predominantly to the cloud water. For example, if the concentration of H₂O₂ in the atmosphere is 1 ppb and $\text{LWC} = 1.5\text{ g m}^{-3}$, the fraction theoretically incorporated is about 0.71 at $T = 298\text{ K}$, while at $T = 260\text{ K}$, the incorporation in the liquid phase is total.

Over the temperature range between 25 and $-13\text{ }^{\circ}\text{C}$, the increase in solubility for H₂O₂ is about 26 times, while for O₃ it is 3.5.

Khwaja *et al.* [18] also measured very low H₂O₂ interstitial concentrations in cloud, while O₃ concentrations (13–83 ppb) were comparable to those in clean air. Similarly, Mohnen and Kadlecck [19] observed that gaseous H₂O₂ concentration drops below the detection limit of the instrument whenever clouds appear at the summit of Whiteface Mountain.

Following Hoffmann and Calvert kinetics [20], computations give at $T = 298$ K, $S(\text{VI}) = 2.2 \times 10^{-5}$ M, while at $T = 260$ K, with the same H₂O₂ concentration, $S(\text{VI}) = 2.5 \times 10^{-5}$ M (H₂O_{2, i} = 1 ppb; SO_{2, i} = 10⁻² ppm; $t = 210$ s).

These computations show that the relative importance of SO₂ oxidation due to H₂O₂ with respect to O₂ and O₃ decreases at lower temperatures.

Usually in winter time H₂O₂ concentration in cloud water is very low due to lower solar ultraviolet radiation and this reduces its contribution to SO₂ oxidation. Oxidation of S(IV) may proceed via other reactions, such as oxidation by O₃ and O₂, sometimes catalyzed by traces of metal catalysts. Low concentrations of H₂O₂ are generally present in supercooled clouds [21, 22].

In addition it is important to note that, by way of comparison, we considered different SO₂ oxidation processes separately, while in real clouds there is a very complex situation, as a variety of gases (O₂, O₃, SO₂, H₂O₂, NH₃, etc.) and ions are simultaneously present; the contribution of different oxidants depends on temperature and pH of droplets. Moreover, some organic (*e.g.* HCHO) and inorganic compounds may also form complexes with S(IV) [23, 24], thus influencing gas-liquid equilibrium concentration and oxidation reaction rates.

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The assistance of M. TERCON and the cooperation of D. SANTACHIARA in carrying out the computations are gratefully acknowledged.

REFERENCES

- [1] IRIBARNE J. V., PYSHNOV T. and NAIK B., *Atmos. Environ. A*, **24** (1990) 389.
- [2] SANTACHIARA G., VIVARELLI F. and PRODI F., *11th International Conference on Clouds and Precipitation, Montreal, 1992*, p. 916.
- [3] MCKAY H. A. C., *Atmos. Environ.*, **5** (1971) 7.
- [4] HEGG D. A. and HOBBS P. V., *Atmos. Environ.*, **12** (1978) 241.
- [5] SANTACHIARA G. and PRODI F., *Nuovo Cimento C*, **20** (1997) 111.
- [6] RICCOBONI L., FOFFANI A. and VECCHI E., *Gazz. Chim. Ital.*, **79** (1949) 418.
- [7] WINKELMANN D., *Z. Elektrochem.*, **59** (1955) 891.
- [8] BARRON C. H. and O'HERN H. A., *Chem. Engin. Sci.*, **21** (1966) 397.
- [9] BEILKE S., LAMB D. and MULLER J., *Atmos. Environ.*, **9** (1975) 1083.
- [10] LARSON T. V., HORIKE N. R. and HARRISON H., *Atmos. Environ.*, **12** (1978) 1597.
- [11] PENKETT S. A., JONES B. M. R., BRICE K. A. and EGGLETON A. E. J., *Atmos. Environ.*, **13** (1979) 123.
- [12] MAAHS H. G., in *Heterogeneous Atmospheric Chemistry*, edited by D. R. SCHRYER (American Geophysical Union) 1982, p. 187.
- [13] CLARKE A. G. and RADOJEVIC M., *Atmos. Environ.*, **21** (1987) 1115.
- [14] HOFFMANN M. R., *Atmos. Environ.*, **20** (1986) 1145.
- [15] CHAMEIDES W. L. and STELSON A. W., *J. Geophys. Res.*, **97** (1992) 20565.
- [16] SIEVERING H., GORMAN E., LEY T., PSZENNY A., SPRINGER-YOUNG M., BOATMAN J., KIM Y., NAGAMOTO C. and WELLMAN D., *J. Geophys. Res.*, **100** (1995) 23075.

- [17] IBUSUKI T. and TAKEUCHI K., *Atmos. Environ.*, **21** (1987) 1555.
- [18] KHWAJA H., BRUDNOY S. and HUSAIN L., *Chemosphere*, **31** (1995) 3357.
- [19] MOHNEN V. A. and KADLECEK J. A., *Tellus B*, **41** (1989) 79.
- [20] HOFFMANN M. R. and CALVERT J. G., *Chemical Transformation Modules for Eulerian Acid Deposition Models*, Vol. II. *The aqueous-phase chemistry* (National Center for Atmospheric Research, Boulder, Co.) 1985.
- [21] ISAAC G. A. and DAUM P. H., *Atmos. Environ.*, **21** (1987) 1587.
- [22] DAUM P. H. and KELLY T. J., *J. Geophys. Res.*, **92** (1987) 8426.
- [23] GRAEDEL T. E., WESCHLER C. J. and MANDLICH M. L., *Nature*, **317** (1985) 240.
- [24] HOFFMANN M. R., WALDMAN J. M., MUNGER W. J. and JACOB D. J., in *Aerosols*, edited by S. D. LEE, T. SCHNEIDER, L. D. GRANT and P. J. VERKERK (Lewis Publishers, Chelsea, MI) 1986, p. 121.