

Investigation into the aerosol formation due to SO₂–H₂O–air photolysis at a reduced pressure

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The kinetics of nanoparticle formation due to SO₂ photolysis in air at a reduced pressure (100–400 Torr) has been investigated. The dependence of the aerosol formation rate and of the particle growth rate on SO₂ and water concentration, as well as on the total pressure, has been studied. The particle growth rate was found to be a linear function of the H₂SO₄ concentration and the SO₂ photolysis rate. This rate was a non-linear function of the water concentration, and at H₂O concentration in excess of 10¹⁷ cm⁻³, the growth rate saturates. The numerical simulation within a simplified Smoluchowski model of the gas kinetics has been performed. In this model, the particle formation and growth are considered to result from sulfuric acid condensation. Evaporation of clusters is neglected. The model also accounts for the cluster diffusion losses on the surface of the reactor and pipelines. The calculated results are in a good qualitative agreement with the experimental data obtained.

Introduction

The study of aerosol formation due to photolysis of sulfur dioxide in the presence of various compounds attracts attention of the researchers during the past four decades. The urgency of these studies is doubtless, because SO₂ is one of the most important anthropogenic pollutants and natural trace gases. Its concentration varies from tens of ppt in the background regions to several ppm in the polluted urban atmosphere. The global cycle of sulfur dioxide in the atmosphere and the photochemical processes with its participation are described thoroughly in Refs. 1 and 2. Owing to photooxidation and catalytic oxidation in droplets, a significant part of sulfur dioxide transforms into sulfuric acid, which then forms a sulfate component of the atmospheric aerosol.

Despite huge number of papers devoted to the investigation into the nucleation of sulfuric acid under laboratory and field conditions, as well as to theoretical modeling, many features of aerosol formation in this system remain poorly studied. In particular, there are no models describing quantitatively the kinetics of formation and growth of sulfuric acid nanoparticles. A typical discrepancy between theoretical calculations and experimental data amounts to several orders of magnitude.^{3,4} The aerosol formation initiated by photochemical processes has features associated, in the first turn, with the stages of formation of active intermediate particles (free radicals, excited molecules). Despite the large number of investigations in this field (see, for example, Refs. 2 and 5), many aspects of

photochemical aerosol formation remain unclear and call for further studies. The use of reduced pressure in combination with the photochemical initiation of aerosol formation allows the role of various excited states to be revealed and favors better understanding of the processes leading to the formation of fine sulfate aerosols due to photooxidation of sulfur dioxide in the upper troposphere and Junge layer.

1. Experimental technique

The kinetics of the photochemical aerosol formation was studied on an experimental setup, analogous to that described in Ref. 6. The setup comprised the following basic units: a flow-through cylindrical reactor, a source of UV radiation (DRSh-500 mercury lamp), and a DSA photoelectric counter,⁷ modernized for the operation at a reduced pressure.

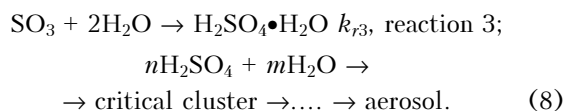
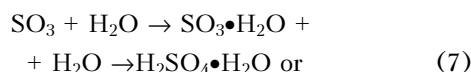
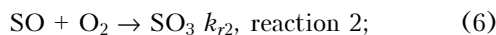
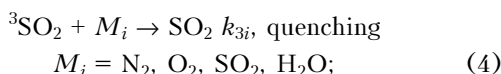
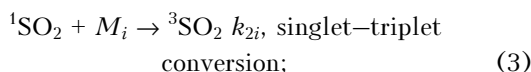
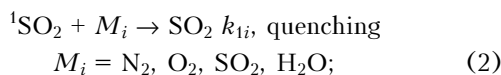
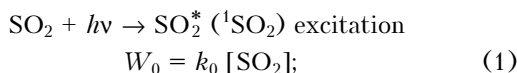
The performance characteristics of the setup were the following: the working pressure P from 100 to 400 Torr and the measurable number concentration from 10 to $2 \cdot 10^7$ cm⁻³ for the aerosol particles of 2 to 200 nm diameter. The mean diameter of nanoparticles was measured with a diffusion battery of the capillary type with the use of the Gormley–Kennedy equation.⁸ The exposure time of reagents varied from 0.1 to 20 s by changing the irradiated volume of the reactor. The reagent flow was prepared by mixing the flow of a mixture, containing 7.07% SO₂, 71.03% N₂, and 21.0% O₂, and two airflows: dry and humid air. The air was pre-purified from admixtures in passing through a set of columns with

activated carbon, silica gel, and Na–X zeolite. To humidify a part of the flow, it passed through a bubbler with bidistilled water. The temperature and water vapor concentration in the resultant flow were determined with a Center-310 flow-through hygrometer. The sulfur dioxide concentration in the flow was determined with a HP-8354 spectrophotometer from the absorption at the wavelength of 287 nm.

2. Results and discussion

2.1. Kinetics of photolysis in the SO₂–H₂O–air system

The photolysis of the SO₂–H₂O–air mixture was carried out in a static cylindrical quartz cell (diameter of 22 mm, length of 82 mm) under the same conditions as in the aerosol experiments (total pressure, concentration of SO₂ and H₂O, photolysis intensity). The dynamics of the sulfur dioxide concentration was monitored with a spectrophotometer. It was found that the decrease of the SO₂ concentration is well described by the first-order kinetics. The photolysis constant k_{phot} was independent of water vapor concentration in the [H₂O] range from $2 \cdot 10^{15}$ to $1.4 \cdot 10^{17}$ cm⁻³ and turned out to be equal to $(1.45 \pm 0.15) \cdot 10^{-5}$ s⁻¹ for the pressure of 170 Torr. The mechanism of SO₂ photooxidation has been thoroughly studied in Ref. 1 and can be described by the following equations:



The rate constants of the reactions (2)–(7) were taken from the literature.^{9,10} To determine the sulfuric dioxide generation rate W_{gen} , the kinetics of SO₂ photolysis was simulated numerically at different values of P and water vapor concentration. The obtained values of W_{gen} were then used to simulate the kinetics of the aerosol formation.

2.2. Kinetics of the aerosol formation in the SO₂–H₂O–air mixture

The dependence of the particle formation and growth rates on the sulfur dioxide concentration has been studied at constant P and [H₂O]. In Fig. 1, dots show the experimental data, and lines demonstrate the results obtained by numerical simulation. It can be seen that the 2.1 times increase in the SO₂ concentration (which is equivalent to the 2.1 times increase in the photolysis rate) leads to a more than 1000 times increase in the rate of aerosol formation (W_{aer}). The mean diameter of aerosol particles increases linearly with time from 2 to 4 nm. The particle growth rate (W_g) is proportional to the sulfur dioxide concentration (photolysis rate). Similarly, the 1.6 times increase in the photolysis rate leads to a 500 times increase in W_{aer} and the 1.8 times increase in W_g . Since the particle growth rate in this size range¹¹ is proportional to the concentration of the substances being condensed, these dependences of the growth rate indicate that this substance is the sulfuric acid, produced during the photooxidation of SO₂.

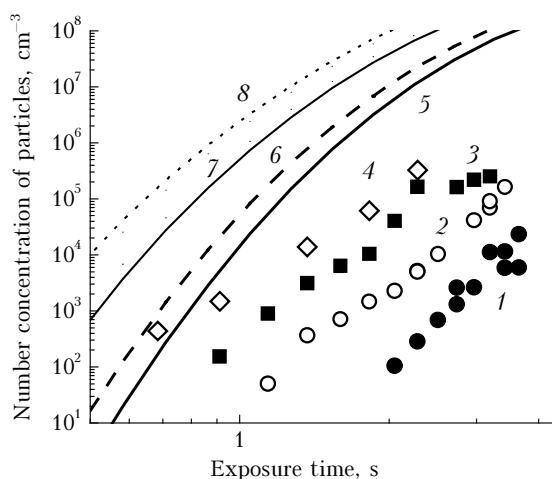


Fig. 1. Dependence of the rate of aerosol formation at the photolysis of SO₂–H₂O–air mixture on the sulfur dioxide concentration; the total pressure in the reactor is 170 Torr, the water vapor concentration is $2.35 \cdot 10^{15}$ cm⁻³. Symbols stand for the experimental data, and lines show the results obtained by numerical simulation; [SO₂] = $2.11 \cdot 10^{17}$ (1, 5), $2.45 \cdot 10^{17}$ (2, 6), $3.36 \cdot 10^{17}$ cm⁻³ (3, 7), and $4.42 \cdot 10^{17}$ cm⁻³ (4, 8).

The dependence of the aerosol formation rate on the water vapor concentration at a constant pressure, SO₂ concentration, and photolysis rate has been studied as well. Figure 2 shows the dependences of the particle formation rate due to the photolysis of the SO₂–H₂O–air mixture on the water vapor concentration at the total pressure of 240 Torr and a constant sulfur dioxide concentration of $1.15 \cdot 10^{17}$ cm⁻³.

As can be seen from Fig. 2, approximately tenfold increase of [H₂O] leads to an increase in W_{aer} by 20 to 50 times. The particle growth rate also

increases, as water vapor concentration increases up to 10^{17} cm^{-3} , and then it saturates at a constant level (Fig. 3).

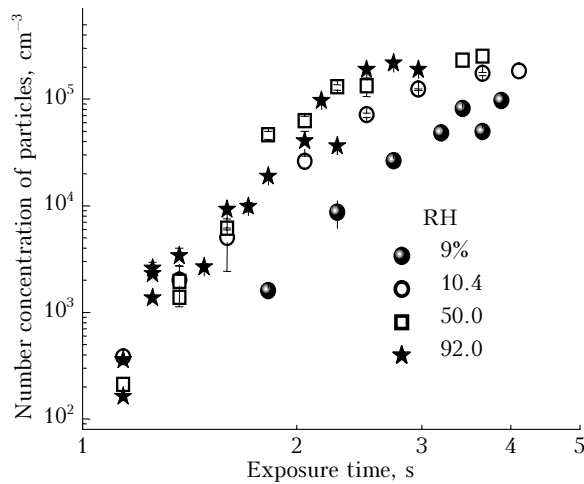


Fig. 2. Dependence of the aerosol formation rate on the water vapor concentration at the constant sulfur dioxide concentration of $1.15 \cdot 10^{17} \text{ cm}^{-3}$ and the total pressure of 240 Torr.

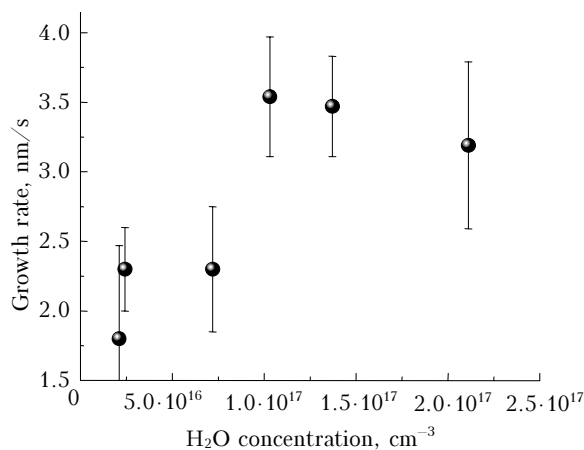


Fig. 3. Dependence of the aerosol particle growth rate on the water vapor concentration at a constant sulfur dioxide concentration of $1.15 \cdot 10^{17} \text{ cm}^{-3}$ and total pressure of 240 Torr.

Since the rate of sulfuric acid generation under our experimental conditions depends only on the SO_2 photolysis rate and is almost independent of $[\text{H}_2\text{O}]$, the change of the aerosol formation rate is connected with the stages of formation of critical clusters. Since sulfuric acid has strong hydrophilic properties, the increase of the H_2O concentration should accelerate the aerosol formation. The nonlinear dependence of the particle growth rate on the humidity is also indicative of the active role of water in the particle formation and growth. The increase of water vapor concentration up to a certain threshold likely leads to the moistening of particles and to the acceleration of the particle growth. At a high water vapor concentration (above 10^{17} cm^{-3}), the rate of water condensation on particles becomes equal to the

evaporation rate, and the particle growth rate saturates.

2.3. Numerical simulation of the kinetics of aerosol formation

There are many theoretical models of aerosol formation in the sulfuric acid–water system that can be found in the literature.^{2,4,5} The majority of them use the thermodynamic approach. The kinetic approach, based on Smoluchowski coagulation equations,^{12,14} is used much rarely. In this work we use, for numerical simulation of the aerosol formation, the Smoluchowski model, analogous to that described in Refs. 6 and 12. The basic assumptions made in this model are the following:

1. The generation rate of the substances involved in condensation ("monomers," sulfuric acid molecules) is constant in time.

2. The evaporation of clusters is insignificant.

3. The water vapor concentration is so high that the sulfuric acid clusters balance it, and therefore the factor determining the aerosol formation rate is the sulfuric acid concentration.

In this case, the dynamics of clusters will be described by the following equations:

$$\frac{dN_1}{dt} = -N_1 \sum_{i=1}^{\infty} \beta_{1i} N_i + F(t) - \gamma_1 N_1, \quad (9)$$

$$\frac{dN_k}{dt} = \beta_{1,k-1} N_1 N_{k-1} - \beta_{1k} N_1 N_k - \gamma_k N_k. \quad (10)$$

The rate of sulfuric acid generation is $F(t) = F = \text{const}$ at $0 < t \leq t_0$, $F(t) = 0$ at $t_0 \leq t \leq t_0 + t_1$ (the generation of monomers ceases once the reagents leave the exposure zone), where t_0 is the exposure time, t_1 is the period between the time of termination of reagents photolysis and the time of particle recording, N_1 and N_k are the concentrations of monomers and clusters, consisting of k monomers, β_{1i} is the gas-kinetic constant of monomer collision with a cluster consisting of j monomers,¹³ γ_i is a constant of deposition of the i th cluster on the reactor surface.⁸ Since the particle number concentrations are not too high, we can neglect the coagulation of particles and take into account only the condensation. The algorithm of solving Smoluchowski equations is described in detail in Ref. 13.

Figure 1 shows the results of numerical simulation of the aerosol formation kinetics. In this case, the sulfuric acid generation rate was calculated from the experimentally measured photolysis rate of sulfur dioxide and it was believed that the efficiency of dimer formation upon the collision of two sulfuric acid molecules is equal to 0.1.

As can be seen from Fig. 1, the calculated rate of aerosol formation is 4 to 5 orders of magnitude higher than the experimental values. Such a discrepancy is typical of the most thermodynamic models.^{4,5,14} However, even such a simple model gives a qualitatively correct description of the dependence

of the aerosol formation rate on the sulfuric acid concentration. Since this model ignores the participation of H₂O in the aerosol formation, it fails to describe the dependence of the aerosol formation rate on the water vapor concentration. The fact that calculations give higher values of the aerosol formation rate indicates that the evaporation plays an important role in the formation of particles.

Conclusions

The experimental technique has been developed for studying the initial stages of photochemically induced aerosol formation in the SO₂–H₂O–air mixture at a reduced pressure. The dependence of the rate of nanoparticle formation on the concentration of reagents, the irradiation intensity, and the total pressure in the mixture has been studied. It has been shown that a small (roughly twice) increase of the H₂SO₄ concentration leads to approximately thousandfold increase in the aerosol formation rate, while the particle growth rate increases by only 3 to 4 times. The increase of the H₂O concentration does not lead to such acceleration of the aerosol formation. The particle growth rate is a nonlinear function of the water vapor concentration.

A simple numerical model based on the Smoluchowski equations has been proposed. The kinetics of aerosol formation in the studied mixture has been simulated numerically. A qualitative agreement has been obtained between the experimental data and the numerical calculations.

Acknowledgments

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