

Significance of Oxide-Induced Sulphate Formation Improving Air-Aqueous Interface

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Perspective

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DESCRIPTION

The heterogeneous oxidation of Sulfur-dioxide (SO_2) by Nitrogen-dioxide (NO_2) on aerosol particles has recently been identified as one of the major sulphate formation pathways in the polluted troposphere, but the underlying chemical mechanisms and kinetics remain unknown. Sulfate is a major component of fine particulate matter in the atmosphere, with significant consequences for climate, human health and the environment. Many parts of the world particularly developed and developing countries have experienced severe haze pollution with high levels of sulphate, owing primarily to the massive amount of Sulfur-dioxide emissions from coal combustion. Sulfur-dioxide is a by-product of the Sulfuric acid (H_2SO_4) production process, first being converted to Sulfur-trioxide (SO_3) and then to oleum, which is then converted to Sulfuric acid.

Because of its antimicrobial properties and ability to prevent oxidation, Sulfur-dioxide is sometimes used as a preservative for dried apricots, dried figs and other dried fruits and it is also an effective reductant. Sulfur-dioxide has the ability to decolorize substances in the presence of Water (H_2O). It is particularly useful as reducing bleach for papers and delicate materials such as clothing. Normally, the bleaching effect does not last long but the reduced dyes are reoxidized by oxygen in the atmosphere, restoring the colour. Sulfur-dioxide is used in municipal wastewater treatment to treat chlorinated wastewater before it is released. Free and combined Chlorine (Cl) are reduced to chloride by Sulfur-dioxide. Sulfur-dioxide is an inert solvent that is widely used to dissolve highly oxidising salts and it is also used as a sulfonyl group source in organic synthesis. When aryl diazonium salts are treated with Sulfur-dioxide and Cuprous chloride (CuCl), the corresponding aryl sulfonyl chloride is formed.

Sulfate in the troposphere is considered to be formed primarily through heterogeneous reactions of Sulfur-dioxide with oxidants like Ozone (O_3) and Hydrogen peroxide (H_2O_2) catalysed by transition metal ions in aerosols and cloud droplets. However, numerical models frequently underestimate the rapid formation of sulfate during haze periods,

implying some unknown sulfate formation mechanisms. Few studies have proposed that heterogeneous oxidation of Sulfur-dioxide by Nitrogen-dioxide with neutralisation by Ammonia (NH_3) under humid conditions is a major pathway of sulfate formation during winter haze periods, but the role of Nitrogen-dioxide in the Sulfur-dioxide oxidation process is controversial. According to some researchers, the oxidation of Sulfur-dioxide by Nitrogen-dioxide in the aerosol aqueous phase produces sulfate and gas-phase Nitrous acid (HNO_2), which then evaporates into the gas phase.

On the other hand, some believe that dissolved Sulfur-dioxide is oxidised into sulfate not only by Nitrogen-dioxide but also by nitrogen oxides, which are reduced into nitrogen oxide and then evaporate into the gas phase. These findings imply that some fundamental processes governing the heterogeneous reaction of Sulfur-dioxide with nitrogen oxide in the troposphere remain unknown because Sulfur-dioxide, nitrogen oxide and their secondary products sulfate and nitrate are the major pollutants in the troposphere by revealing the potential mechanisms and kinetics are critical. Studies on the heterogeneous formation of sulfate *via* Sulfur-dioxide oxidation in aerosols and clouds have only focused on reaction processes in the bulk phase, concluding that bulk phase acidity is a critical factor controlling Sulfur-dioxide oxidation pathways and sulfate production in the atmosphere. Several studies over the last decade have discovered that the ion distribution at the air-water interface of an electrolyte solution differs from that in the bulk phase. Some polarizable anions such as Chlorine (Cl) and Bromine (Br) prefer to remain near the surface, whereas some cations such as Sodium (Na), Calcium (Ca) and anions such as sulfate and carbonate prefer to remain near the bulk phase.

Due to this difference in ion distribution, some anions may be enriched at the air-aqueous interface, which may have a significant impact on the heterogeneous reactions of gaseous pollutants with atmospheric aerosols and cloud droplets. However, there is no direct field evidence of such interfacial effect and thus the atmospheric reactions involved are unknown because of the air-aqueous interfacial changes cannot be measured directly. According to field observations, laboratory chamber experiments and molecular dynamics simulations, the charges at the air-aqueous interface of atmospheric aerosols around the world are dominated by negative ones, which promote the uptake of Nitrogen-dioxide by haze particles.