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SO_2 in the atmosphere: a wealth of monitoring data, but few reaction rate studies

Study of the reactions of SO_2—a vital clue to the chemistry of polluted atmospheres—is beset with difficulties

Sulfur dioxide, one of the more common air pollutants, has been implicated as one of the causative agents for damage to vegetation and materials, and for the respiratory difficulties encountered during air pollution episodes (U.S. Department of Health, Education, and Welfare). The complex nature of polluted atmospheres is such that it is extremely difficult to understand the chemical interactions of the residual and transient components known, or suspected, to be present in air. Laboratory attempts to reproduce the effects similar to those of a polluted atmosphere have not been entirely satisfactory. The types of physiologically active substances which may be present in an atmosphere heavily polluted with sulfur dioxide and other industrial and domestic emissions, and which has been in a stagnant state over a city or valley for a period of days, are a matter of conjecture and serious disagreement (Negherbon).

This article reviews the literature on atmospheric sulfur dioxide reactions, and was made possible by National Air Pollution Control Administration grant AP-00357.

Rohrman reviewed the sources of sulfur dioxide pollution, while Altshuller; Jensen and Nakai; Junge and Eriksson discuss the natural sources contributing to the presence of sulfurous compounds in the atmosphere. The U.S. Department of Health, Education, and Welfare reviewed in detail the literature pertinent to the establishment of air quality criteria for sulfur oxides. Exception to the interpretation of the air quality criteria evidence is expressed by the National Coal Association (Negherbon, 1967), and a comprehensive review of older literature on sulfur dioxide, sulfur trioxide, and sulfuric acid was published by the Edison Electric Institute (Negherbon, 1966). A recent book by Schroeter devotes several chapters to the inorganic and organic reactions of SO_2.

Reactions in the atmosphere

Although the presence of sulfur dioxide in air is measured on a routine basis by a large number of industries and municipalities, surprisingly few studies have been reported in which attempts have been made to measure the chemical reactions of sulfur dioxide in polluted atmospheres.

In 1950, Katz measured sulfur dioxide and total sulfur contaminants in a nickel smelting area (Sudbury, Ontario, Canada) where nitrogen oxides were not expected to play an important role. His data showed that sulfur dioxide comprised from 83–87% of the total sulfur-containing compounds in air. From his data, the conversion rate was determined at 2.1% per hour, and essentially independent of sulfur dioxide concentration (U.S. Department of Health, Education, and Welfare). Katz noted that oxidation of the sulfur dioxide may take place at night as well as in sunlight, and that fine particles of dust and metallic oxide help to catalyze the oxidation.

Meetham calculated that the overland life of sulfur dioxide in England was 8.75 hours but as little as 6 hours in the heavy London fog of 1952.

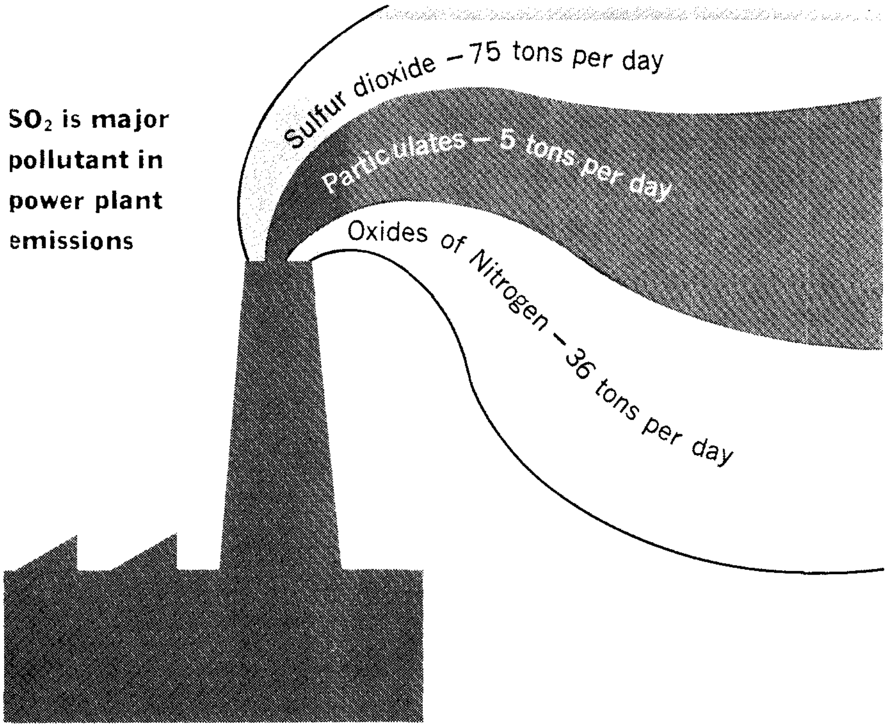
Junge reports the concentrations of trace gases such as ammonia, sulfur dioxide, and nitrogen oxides, along with the results of chemical analyses of natural aerosol particles in Florida and in the Boston area. His studies indicate that, over a wide variety of geographical locations, the concentration of these gaseous pollutants is considerably higher than that for the corresponding substances in the aerosols, a result which is in agreement with the data reported by Katz. Junge also found that either ammonium sulfate or ammonium bisulfate was the predominant soluble substance in the nuclei representative of polluted atmospheres.

Cholak, et al., found from data of a Cincinnati study that approximately 90% of the sulfurous material in air was gaseous in character. The sampling was done at two sites. Each site was equipped with recorders for continuous determination of NO_2 concentration, concentration of oxidant, and a sequential sampler for determining sulfur dioxide concentration in the air during each period of 2 hours, night and day.

Corn and Demaio studied the sulfate composition of particulates in air and found that 35% of the weight of suspended sulfate was in particulate sizes of physiological importance. A large discrepancy was found between the average concentration of sulfate, determined by sampling for 24 hours, and the concentration resulting from the average of 24 one-hour samples collected during the same period. This phenomenon is further documented by Stalker, Dickerson, and Kramer, who made a comparison of results obtained from a great number of samples using several different methods of measuring both ambient sulfur dioxide and particulate matter. Their work indicates that two different concurrent standard methods of measuring a pollutant—the 24 hour standard bubbler method and the 2 hour sequential sampling technique—may give significantly different average results.

The findings of Lee and Wagman show that average particulate sulfate concentrations in ambient air, measured from serial short-term samples collected on glass fiber filters, were consistently and significantly higher than those from single long-term samples. During the investigation of this sampling anomaly, Lee and Wagman found that significant amounts of extraneous sulfate can be formed on glass fiber filters, presumably by oxidation of atmospheric sulfur dioxide, thus, leading to highly inflated values for particulate sulfate as determined by short-term samplers. They suggest that, in long-term sampling procedures, the formation of sulfate from sulfur dioxide is surface-limited and reaches a saturation level.

T. Shirai, et al., studied the photooxidation rates of sulfur dioxide in the vicinity of a smelter, and compared them to rates obtained in an industrial area near Tokyo, Japan. In comparison with values reported by others, the rates of disappearance of sulfur dioxide obtained at the smelter area were quite high, on the order of 12% per minute, and dependent upon the amount of moisture. This high rate was attributed to the fact that a greater amount of sunlight in the 3000 Å–3400 Å wavelength range was available in the smelter area than in the area near Tokyo. Also, the ratio of sulfur dioxide to total sulfur compounds was 0.15, compared with a ratio of 0.42–0.63 near Tokyo. A calculated quantum yield of 1.7—other cities show quantum yields of 10^{-2} to 10^{-3}—strongly suggested pronounced catalytic or complementary effects from other air pollutants.



SO_2 is major pollutant in power plant emissions

The above daily emissions are typical of a 350-megawatt power plant which burns coal with 10% ash, 1.5% sulfur, and 1.5% nitrogen

Gartrell, Thomas, and Carpenter studied sulfur dioxide oxidation rates in power plants plumes. They found reaction rates varying from 2–132% on a per hour basis, depending to a great extent upon the concentration (nearness to source) and relative humidity. During periods of low humidity, oxidation of sulfur dioxide was relatively slow, increasing from 2% at 1 mile (12 minutes) to 3% at 6 miles (60 minutes). With moderately high humidity, oxidation was initially rapid, 22% at 1 mile (12 minutes), increasing to 32% at 8 miles (96 minutes). The highest total oxidation, 55%, was observed in a slight mist at 9 miles (108 minutes).

Thomas (1962) discusses the relationship between sulfur dioxide, sulfuric acid, and visibility in Los Angeles, indicating that on days of high smog the sulfuric acid:sulfur dioxide ratio increased. He also reviews (1964) a number of studies of sulfur oxides as air pollutants, citing the literature on the various analytical methods used and how they compared to each other.

Photochemical reactions

Leighton reviews the photochemistry of air pollutants and the pertinent work on sulfur dioxide up to the time of his publication. In general, results are difficult to interpret because of the differences in reactants, reactant concentrations, types of irradiation sources, and types of reaction vessels or containers. The reported quantum yields for the photooxidation of sulfur dioxide at small concentrations in air, and at larger concentrations in oxygen, vary over approximately two orders of magnitude.

The bond dissociation energy of sulfur dioxide: $SO_2 \rightarrow SO + O - 135$ kcal. by photochemical or other reactions is much too high to be produced by solar radiation in air. Leighton proposed a primary mechanism based in part on the work of Hall and Dainton and Ivin:

Primary reactions

$$SO_2 + h\nu \rightarrow SO_2^-$$

$$\begin{tikzcd} SO_2^- \arrow[r] & SO_2^= \arrow[d, "+M"] \\ & SO_2 \end{tikzcd}$$

$$SO_2^- + M \rightarrow SO_2 + M$$

$$SO_2^- + O_2 \rightarrow SO_4$$

$$(M = N_2, O_2, \text{ and } SO_2)$$

The formation of an SO_4 molecule was postulated. This could lead to the formation of sulfur trioxide and ozone through secondary reactions:

Secondary reactions

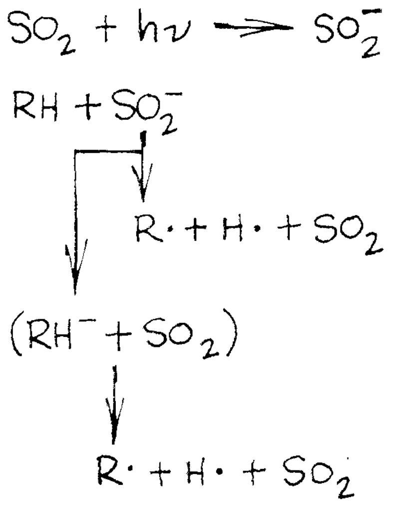
$$SO_4 + SO_2 \rightarrow 2SO_3$$

$$SO_4 + O_2 \rightarrow SO_3 + O_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

The SO_4 molecule was presumed to have a peroxy structure and, if the excited state of sulfur dioxide were a triplet, then the SO_4 molecule might exist as a biradical. But the SO_4 molecule has not been observed. In general, sulfur dioxide pollution is associated with reductive atmospheres where ozone, if produced in this manner, would react almost immediately and not be readily detected.

Ogata, Izawa, and Tsuda suggested a free radical mechanism for the photochemical reaction of sulfur dioxide with hydrocarbons:



The primary photochemical process was postulated to involve two simultaneous reactions: the formation of alkyl radicals by abstraction of hydrogen with excited sulfur dioxide, and energy transfer by the excited sulfur dioxide. The excited sulfur dioxide molecule was said to undergo an $n \rightarrow \pi^*$ (90 kcal.; singlet to triplet) transition through which a free radical reaction mechanism is reasonable.

Hall exposed quartz tubes containing 56–230 mm. of sulfur dioxide and 5–200 mm. of oxygen to sunlight. The first-order reaction rate constant was 5×10^{-4} hr.$^{-1}$ corresponding to a rate of $8 \times 10^{-4}\%$ min.$^{-1}$, much lower than that expected on a theoretical basis. Jaffe and Klein studied the photolysis of NO_2 in the presence of sulfur dioxide at 3660 Å, obtaining a second order rate constant of 1×10^9 l./mole/sec. for the formation of SO_3 from SO_2 and atomic oxygen, produced by photodissociation of NO_2.

High reactant concentrations

Dainton and Ivin studied the reaction of sulfur dioxide with both saturated and unsaturated hydrocarbons. A low pressure mercury arc was used whose output was primarily in the region of 2400 Å–3340 Å, giving higher photon energies than those found in normal sunlight. Ratios of sulfur dioxide to hydrocarbon were varied from 0.085–24, and total pressures were varied from 140–600 mm. mercury. Chemical analysis of the reaction products showed the presence of sulfinic acids. No reaction rate for SO_2 oxidation was calculated from this study.

Ogata, Izawa, and Tsuda studied the photochemical sulfoxidation of *n*-hexane in which hexanesulfonic acid was formed. The yield was increased by raising the reaction temperature and by the addition of acetic anhydride. The reaction was sensitized by acetophenone and *p*-chloroacetophenone. It was inhibited by 2,3-dimethylbutane and 1-hexene, two compounds said to contain more easily extractable hydrogen atoms which preferentially reacted with the excited sulfur dioxide. Because of the formation of a small amount of hexanesulfonic acid from the photolysis of hexane and sulfur trioxide with no production of sulfur dioxide, the reaction of an excited sulfur trioxide molecule with the saturated hydrocarbon was postulated.

Johnston and Dev Jain exposed mixtures of 0–50 mm. sulfur dioxide, 0–50 mm. *n*-butane, and 0 or 400 mm. air (wet and dry) in 2-liter flasks to sunlight. They obtained light to heavy fogs depending upon the substances present. The heavy fogs were obtained when all three components—air, *n*-butane, and sulfur dioxide—were present. Gas chromatographic analysis of the reaction products showed eight major peaks. Chemical and elemental analysis showed a liquid having a pH of less than 2, an acid equivalent weight of 100–120 and a formula of $C_2H_5SO_5$. A highly oxidized strong organic acid was assumed to be at least one of the reaction products.

Kopczynski and Altshuller repeated and extended this work, and verified the formation of fogs at higher hydrocarbon concentrations, although they were not able to see any reaction products at concentrations of 50–100 p.p.m. Infrared analysis showed only carbonyl absorption bands. They concluded that saturated hydrocarbons did not contribute significantly to aerosol formation when compared to the more reactive olefin compounds.

Low reactant concentrations in air

Gerhard and Johnstone studied the photochemical reactions of sulfur dioxide in air at 5–30 p.p.m., using irradiation approximating the ultraviolet portion of normal sunlight (2950 Å–3650Å). They found that the reaction rate was first order with respect to sulfur dioxide, unaffected by the humidity and the presence or absence of salt nuclei, or by nitrogen dioxide up to 2 p.p.m. A few measurements in natural sunlight indicated the rate to be 0.1% per hr. The conclusion drawn was that the gas phase oxidation of sulfur dioxide in naturally polluted atmospheres would require 100 hours of intense sunlight to reduce visibility to 1 mile, and that other types of oxidation, such as liquid phase reactions, may be more effective in reducing visibility.

Probably the most concentrated series of studies of photochemical reactions in air were conducted by the Air Pollution Foundation at San Marino, Calif. Report No. 29 (Schuck and Doyle) describes in detail the many experimental studies undertaken. One of the summary paragraphs states that the ". . . photooxidation of sulfur dioxide in air proceeds at an appreciable rate and results in the production of a sulfuric acid aerosol. The rate of the photooxidation and the production of aerosol are greatly increased in the presence of an olefin-oxide of nitrogen mixture. In the absence of sulfur dioxide, however, the olefin-oxide of nitrogen photooxidation does not lead to the formation of appreciable aerosol, except when the olefin is cyclohexene. Saturated hydrocarbons photooxidized in the presence of both oxides of nitrogen and sulfur dioxide do not enhance aerosol formation." A number of publications resulted.

Renzetti and Doyle found that, of the hydrocarbons studied, olefins were the only important aerosol-forming hydrocarbons. They also noted that the rate of photolysis of sulfur dioxide at low concentrations in purified air was 0.45% min.$^{-1}$—250 times the rate observed by Gerhard and Johnstone—and that this rate gave significant conversions of sulfur dioxide. Consequently, a catalyst mechanism was not necessarily required to account for the oxidation of sulfur dioxide in the atmosphere. The oxidation of sulfur dioxide in the presence of olefins and nitrogen oxides was called a cooxidative process. Doyle, Endow, and Jones found that the addition of sulfur dioxide to olefin-nitrogen dioxide mixtures resulted in a slight decrease in eye irritation accompanied by the appearance of an aerosol.

Endow, Doyle, and Jones found that irradiated mixtures of 3 p.p.m. olefin, 1 p.p.m. nitrogen dioxide, and 0.5 p.p.m. sulfur dioxide at 50% relative humidity formed aerosols which had aqueous sulfuric acid as a major component. Moreover, their data indicated that aerosols formed in slightly humid atmospheres (10–20% R.H.) differ considerably in physical and chemical properties from those formed at 50% relative humidity. Sulfuric acid still was present in the collected materials formed under conditions of low humidity, but infrared spectral absorption attributable to inorganic nitrogen and, particularly, to unidentified components was much stronger than in conditions of high humidity. A test for nitrate, nitrite, or peroxide was positive for an aerosol sample derived from propylene. No conclusions were drawn as to the relative contributions of inorganic and organic components. Doyle and Jones reviewed the studies conducted at Stanford Research Institute for the Air Pollution Foundation, and summarized the principal contributions.

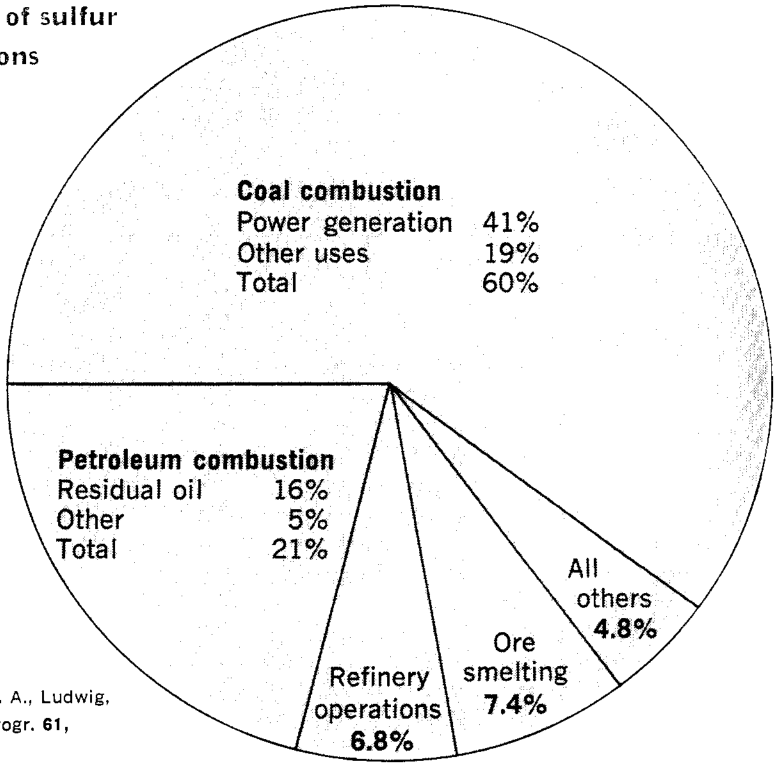
Prager, Stephens, and Scott summarized studies conducted at Franklin Institute, and found that, in nitrogen dioxide-olefin photo-chemical reactions at parts-per-million concentrations carried out in a long-path infrared absorption cell, only highly substituted or cyclic olefins and diolefins formed aerosols. When sulfur dioxide was added, all types of olefins produced particulates. The greatest amounts of particulates were formed when sulfur dioxide was present at the start of the photolysis. The longer the reaction had proceeded before sulfur dioxide was introduced, the less aerosol was formed. This and other experimental evidence led Prager and his colleagues to believe that "aerosol is therefore produced by reaction of sulfur dioxide with an intermediate in the nitrogen dioxide-olefin photolysis." Ozone plus mono-olefins at low concentrations in the dark gave little or no aerosol. The infrared spectra of the reaction products from the cyclohexene-NO$_2$-SO$_2$ photolysis showed the possible presence of a nitrate ester. An olefin-sulfur dioxide copolymer also was postulated to be produced.

Stevenson, Sanderson, and Altshuller observed increased aerosol production when sulfur dioxide at less than 1 p.p.m. was present, as compared to when it was not present, in irradiated air mixtures containing nitrogen dioxide at 3 p.p.m., and various unsaturated hydrocarbons at 10–20 p.p.m. carbon content. They also found that the participation of sulfur dioxide in the photooxidation of unsaturated hydrocarbon-nitrogen dioxide mixtures in air was not increased when a greater fraction of the incident light was centered at the lower wavelength of 3100 Å.

Goetz and his coworkers have studied pollutant aerosols in some detail. In 1967, Goetz and Pueschel investigated the effect of sulfur dioxide, humidity, and order of mixing on the photochemical production of aerosol from 1-octene and nitrogen dioxide in air. They found that, in the absence of particulates, the sequence of adding reactants is negligible, but becomes quite significant when particulates are present. The presence of small SO$_2$:NO$_2$ fractional concentrations reduces aerosol formation sharply when stable centers are absent. Humidity increases this effect. Greater sulfur dioxide concentrations gradually reverse the inhibition.

Using radiochemical tracer techniques, Urone, et al., verified the photochemical reaction rate of sulfur dioxide in purified air obtained by Gerhard and Johnstone. They also confirmed that moisture and salt particles did not affect the reaction. In addition, they reported the photochemical reaction rate of sulfur dioxide at 10–20 p.p.m. was increased by one to two orders of magnitude in the presence of equal amounts of nitrogen dioxide and *n*-hexane. Some evidence indicates that NO$_2$-*n*-hexane photochemical products reacted slowly in aqueous solution to oxidize the residual sulfur dioxide. With 1-hexene, sulfur dioxide tended to condense on the flask walls with the

Major sources of sulfur dioxide emissions



Source: Rohrman, F. A., Ludwig, J. H., Chem. Eng. Progr. **61**, 59-63 (1965)

Summary of sulfur dioxide reaction rate studies

Reference	Rel. Hum.	Source of Irradiation	Other Experimental Conditions	Initial concentration of reactants	Rate of SO consumption % Min.
Hall	0	Sunlight between 10 A.M.–3 P.M.	Quartz tubes	$SO_2 = 56–230$ mm. Hg $O_2 = 5–200$ mm. Hg	8×10^{-4}
Gerhard and Johnstone	32–91%	G.E. Type RS, 275-Watt sunlamp	64 cu. ft. chamber for tests in sunlight and a 7.94 l. lucite cell in artificial light. H_2SO_4 collected on indicator film and determined colorimetrically with photocell and microscope.	5–30 p.p.m. SO_2 in moist air	0.011 [(1.7–3.3) × 10^{-3}]
Renzetti and Doyle; Schuck and Doyle	50%	Four G.E. H 400-E1 Medium-Pressure Mercury Arc Lamps	50-l. Pyrex stirred-flow reactor; effluent analyzed by aerosol counter, light scattering photometers, nuclei counter, and continuous colorimetric analyzer.	0.2–0.6 p.p.m. SO_2 in purified air	0.45 ± 0.1 (50% conf.) [0.11 ± 0.03]
			Same conditions as above were used to investigate SO_2 consumption during photolysis of mixtures of nitric oxide and 2-methyl-2-butene in air.	NO (pphm) RH (pphm) SO_2 (pphm)	
				98 49 11	4.9
				96 290 52	0.9
				100 100 10	1.8
				100 300 10	1.8
				100 300 100	0.8
Urone, Lutsep, Noyes, and Parcher	50%	Bank of 16,30 cm. × 1.5 cm. UV lamps with 90% output at 3500 Å., flux of 5.39 × 10^{15} photons $sec.^{-1}$ $cm.^{-3}$	Radiochemical tracer techniques and West-Gaeke method employed. Mixtures prepared in 20 l. Mylar bags and irradiated in 2-l. borosilicate glass flasks.	SO_2 (p.p.m.) NO_2 (p.p.m.) n-hexane (p.p.m.)	
				21 15 16	0.2[0.03]
				15 410 11	2[0.2]
			Dark reactions in presence of particulates	Type of particulate	
				14 NaCl	~0
				14 $CaCO_3$	~0
				18 Fe_2O_3	>75
				14 Al_2O_3	~2.5
				14 Cr_2O_3	>0.01
Ripperton, Decker, and Page	44%	Seven 30-watt daylight fluorescent lamps plus two 400-watt mercury vapor lamps.	Blends in a Mylar bag held in a temperature-controlled cabinet; SO_2 by West-Gaeke analysis.	1.0 p.p.m. SO_2 4.46 p.p.m. 1-hexene 1 p.p.m. NO_2	0.25
Katz		Daylight	Air samples taken from the Sudbury, Ont., nickel smelting area, to determine SO_2, SO_3, and H_2SO_4 by iodometric and conductivity measurements.	0.2–1.0 p.p.m. SO_2	0.035

irradiation products, but gave the usual pararosaniline color reaction for sulfur dioxide when analyzed.

Roddy studied the formation of condensation nuclei in city air by irradiation with ultraviolet light of greater than 2900 Å wavelength. He found that nuclei production was proportional to the ambient sulfur dioxide concentration. No nuclei were produced when the sulfur dioxide concentration was less than 2 p.p.h.m.; many nuclei were formed when the air containing the sulfur dioxide was filtered through either cotton, wool, or Millipore filter; no nuclei were formed when sulfur dioxide was added to mixtures of tanked oxygen and nitrogen plus water vapor. Roddy postulated a homogeneous nucleation due to a photochemical reaction product between sulfur dioxide and a trace gas such as ammonia, or a mixture of nitrogen oxides, or olefins, or alternatively a catalyzed reaction of sulfur dioxide.

Harkins and Nicksic did an interesting series of experiments with radiochemically tagged propylene and ethylene. Air mixtures of these substances were irradiated with and without sulfur dioxide. Aerosols were formed when sulfur dioxide was not present; however, when sulfur dioxide was present, light scattering measurements indicated an increase in aerosol. When the air was filtered through a Millipore filter, increased acidity was found on the filters, but no radioactive products were obtained. A considerable amount of sulfur dioxide was adsorbed by the walls of the experimental equipment.

Ripperton, Decker, and Page studied the effect of sulfur dioxide at 1 p.p.m.

Reference	Rel. Hum.	Source of Irradiation	Other Experimental conditions	Initial concentration of reactants	Rate of SO_2 consumption % Min.$^{-1}$
Shirai, et al.	65–70%	Daylight	Comparative atmospheric study of area near Zao mine smelter and Keihin industrial area (near Tokyo).	0.010–20.3 p.p.m. SO_2	11.7
Gartrell, Thomas, and Carpenter	70–100%	Daylight	Air-borne (helicopter) study of atmospheric oxidation of SO_2 emissions from coal-burning power plant.	2200 p.p.m. SO_2; 70% R.H. 2200 p.p.m. SO_2; 100% R.H.	0.1 0.5
Matteson	≥96%		Humid air stream containing $MnSO_4$ aerosols reacted in 260 cm. × 30 cm. Plexiglas tube.	70 p.p.m. SO_2 30 mg./m.^{3} $MnSO_4$	0.56
Johnstone and Coughanowr	100%		Single drop of catalyst exposed to humid air containing SO_2; resulting acid content analyzed in a 0.1 ml. microconductivity cell.	20–200 p.p.m. SO_2; 4.0–14.0 p.p.m. $MnSO_4$	Estimated conversion of 1 p.p.m. SO_2 to sulfuric acid in a fog nucleated by 1 micron $MnSO_4$ particles may be 1% per minute.
Johnstone and Moll	77–96%		Artificial fogs formed in 4.2 cu. ft. lucite chamber. Sulfuric and sulfurous acids titrated with 0.02N NaOH.	SO_2 (ppm) · $MnSO_4$ · $FeSO_4$ (mg./m.^{3}) · NaCl · % R.H. 250 · 2 · — · — · 77 250 · 2 · — · — · 95 250 · — · 2 · — · 96 250 · — · — · 0.8 · 95	 0.01 2.1 0.48 0.04
Junge and Ryan			SO_2 oxidation studied in dilute catalyst solutions. SO_4^{-2} analysis of solutions by $BaCl_2$ nephelometric method.	15 p.p.m. SO_2; $FeCl_2 = 1\ \gamma/cm.^3$	1.8 × 10^{-4}
van den Heuval and Mason	100%		Measured rate of formation of $(NH_4)_2SO_4$ in water drops exposed to air containing gaseous SO_2 and NH_3. Approximately 100 drops of H_2O supported on quartz fiber grid in 5 l. glass flask.	2.5–10 p.p.m. SO_2 2.5–10 p.p.m. NH_2	Extrapolation of data to conditions in an industrial atmosphere containing 100 μg m.$^{-3}$ SO_2 and 10 μg m.$^{-3}$ NH_3 yields a value of 2.5.

on the photochemical production of oxidant from irradiated 1-hexene (1.5 p.p.m.), NO_2 (1 p.p.m.), air mixtures. Less oxidant was produced when sulfur dioxide was present. Rates of reaction of sulfur dioxide in the irradiated mixtures varied from 0.5–15% per hour of intense ultraviolet irradiation. Little to no reaction occurred in the dark.

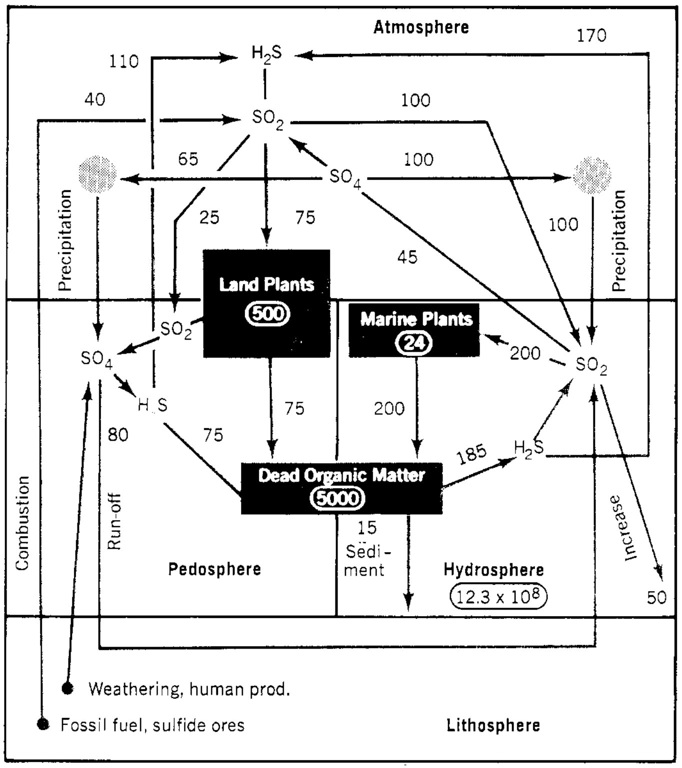
Cadle and Robbins discussed the application of chemical kinetic theory to heterogeneous atmospheric chemical reactions involving aerosols, and compared the derived rate equations with experimental results for model systems. They stated that, in heterogeneous atmospheric chemical reactions involving aerosols, the reaction rate may be controlled by one of several factors—namely, gas-phase diffusion, chemical reaction, or diffusion in the liquid or solid phase—and that readily obtainable rate and equilibria data can supply important information concerning the relative importance and mechanisms of atmospheric reactions involving aerosols.

Haagen-Smit (1963) reviewed the subject of photochemistry and smog. He devotes most of his discussion to the photochemical reactions of nitrogen oxides and hydrocarbons. However, he does state that the reaction of sulfur dioxide with oxygen was slow, and that heavy metals catalyzed the reaction. Nitrogen oxides, olefins, and sunlight substantially increased the reaction rate.

Reactions in solution

Some investigators have been concerned with the rate of oxidation of sulfur dioxide in aqueous solutions containing metal ions and ammonia.

Circulation pattern of sulfur in nature



The circulation pattern of sulfur in nature and estimated fluxes. Circled numbers are amounts present in different reservoirs; other numbers are yearly fluxes, all in million tons sulfur units

Source: Eriksson, E., J. Geophys. Res. 68, 4001-08 (1963)

The implication is that these substances may be present in a polluted fog or smog. An extensive investigation of the oxidation of concentrated sulfurous acid by oxides of manganese, by ferric and cupric salts, and by molecular oxygen in the presence of various dissolved salts was reported by Bassett and Parker.

Johnstone and Coughanowr studied the rate of oxidation of sulfur dioxide in drops of metal salt solutions suspended in air. Solutions studied included the sulfates of manganese, ferrous and ferric iron, nickel, and copper. Manganese showed the greatest effect, increasing the rate of oxidation to within one tenth that of an hydrogen peroxide solution. Assuming a 1 μ $MnSO_4$ crystal as the nucleus for a 20 μ aerosol droplet in air having 0.2 gram water moisture/m^3, or 4.8 $\times 10^7$ droplets/m^3, 1 p.p.m. sulfur dioxide oxidized at the rate of 1% per minute, or 500 times the photochemical reaction rate previously measured by Gerhard and Johnstone.

Johnstone and Moll studied the rate of reaction in artificially produced fogs without ultraviolet irradiation. The results essentially were the same as those found earlier by Johnstone and Coughanowr when manganese sulfate and ferric sulfate nuclei were present. When only water and sodium chloride nuclei were present, no significant conversions of sulfur dioxide to sulfuric acid were found.

Matteson investigated the oxidation of trace amounts of sulfur dioxide in a flowing humid air stream containing aerosols of manganese sulfate. He measured the rates of formation of sulfuric acid as well as the absorption of sulfur dioxide in the aerosol droplets. Matteson proposed a three-step reversible reaction model involving an intermediate of sulfur dioxide with the manganese sulfate to explain the rate-controlling mechanism, and evaluated the rate constants. Results indicated that the rate-controlling mechanism was found within the liquid phase.

Junge and Ryan studied the rate of sulfur dioxide oxidation by bubbling air-SO_2 mixtures of approximately 20 p.p.m. through solutions containing metal ion salts and ammonia, and then determining the amount of sulfate formed by a nephelometric method. The solutions contained the chlorides of manganese, copper, iron (II), cobalt, and sodium as well as ammonium hydroxide. Oxidation occurred most rapidly in solutions containing manganese followed by those containing copper and iron (II). The reaction stopped when a pH of 2.2 was reached, but continued when ammonia was added. The system SO_2-NH_3-catalyst solution can explain the main features of sulfate formation in the atmosphere, according to this reference.

Van den Heuval and Mason measured the rate of formation of ammonium sulfate in water droplets exposed to air containing known concentrations of gaseous sulfur dioxide and ammonia. They found that the mass of sulfate formed was proportional to the product of the surface area of the drops and the time of exposure. When the sulfur dioxide alone was in air, the amount of sulfate formed was at least two orders of magnitude smaller than when ammonia was present with the sulfur dioxide. The authors concluded that the amounts of sulfate found by Junge to be abundant in polluted atmospheres were formed by the absorption of sulfur dioxide and ammonia in cloud and fog droplets.

Scott and Hobbs studied theoretically the formation of sulfate in water droplets using the data of Junge and Ryan and van den Heuval and Mason. They found that their theoretical curves, although similar to Junge and Ryan's experimental curves, did not show a limiting value for sulfate or a direct proportionality between sulfate and sulfur dioxide concentrations. The theory did provide a satisfactory explanation of the SO_2-NH_3-liquid H_2O system.

Terraglio and Manganelli studied the absorption of sulfur dioxide by water solutions, and found that the rate of solution of atmospheric sulfur dioxide in distilled water over a concentration range of 0.8–8.7 mg. SO_2/m^3 (0.3–3 p.p.m.) was a function of sulfur dioxide concentration. The pH of exposed water samples was found to reach about 4.0 or less, comparable to values observed in fog and cloud droplets over large industrial areas. The overall solubility of sulfur dioxide, however, did not follow the law of partial pressures in the sulfur dioxide concentration ranges studied.

Applying a quasi-thermodynamic approach, Doyle (1961) determined theoretically the minimum amount of dispersed sulfuric acid vapor required to initiate nucleation in humid air. A numerical calculation carried out for the typical case of 50% relative humidity at 25°C., showed that rapid self-nucleation for the sulfuric acid-water system would take place at sulfuric acid partial pressures in the range 10^{-8}–10^{-10} mm. of mercury. Doyle concluded that, in the vicinity of a heavily populated area, there is no lack of a source of acidic nuclei.

Reactions on solid particulates

Interest in the possible atmospheric reaction of sulfur dioxide with suspended solids has been limited because of a more direct interest in the absorption, catalytic oxidation at elevated temperatures, and removal of sulfur from stack plumes as reviewed by Bienstock and his coworkers. Corn and his coworkers, however, were concerned with sulfate in particulates. Urone, et al. did some preliminary studies with powdered metal oxides, sodium chloride, and calcium carbonate, reporting rapid oxidation rates when air containing 20 p.p.m. sulfur dioxide was exposed to hydrous ferric oxide, alkaline alumina, and calcium oxide. Sodium chloride and calcium carbonate particles showed little to no effects. Surprisingly, particles of vanadium and chromium oxides reacted but little with sulfur dioxide at room temperature. The amount of surface area for these oxides, however, may have been a factor. In Urone's studies, the weight of the powdered solids was about 100 times the weight of the sulfur dioxide taken. In polluted atmospheres, the opposite is generally true, and the amount of solid particles available for adsorption, reaction, or catalysis usually is quite limited, according to Schuck, Stephens, et al.

Summary

The study of the reactions of sulfur dioxide in polluted atmospheres is beset with many difficulties. The atmospheric matrix is highly variable in composition, degree of humidity, temperature, and angle and intensity of sunlight. Analytical techniques for measuring sulfur dioxide, sulfuric acid, and sulfate compounds leave much to be desired (Thomas, 1964), and, in some cases, have led to high sulfate measurements (Stalker, Dickerson, and Kramer; Corn and Demaio; Lee and Wagman).

Those experiments which readily gave data usable for calculating sulfur dioxide rates of reactions are summarized. The first three entries give conditions and results for the photochemical oxidation of sulfur dioxide at high concentration and in the presence of oxygen, or in clean air at low concentrations. The reaction rates differ by several orders of magnitude (the figures in brackets indicate the values adjusted to noon-day-sunlight equivalents). The next three table entries give the photochemical reaction rates of sulfur dioxide in air when nitrogen dioxide and olefins also were present. These rates are within one order of magnitude of each other. Renzetti and Doyle's results may be high because of possible analytical difficulties with the small concentrations of sulfur dioxide used and because of possible wall effects.

The seventh, eight, and ninth experiments compare the reaction rates present under actual atmospheric conditions (Katz; Shirai et al.; Gartrell, Thomas, and Carpenter). The reaction rates were obtained by comparing changes in total sulfate to sulfur dioxide ratios with distance or time. Gartrell's data were obtained from power plant stack plumes while Katz and Shirai obtained data from ambient air measurements. The results may be compared to the 0.2–0.3% min.^{-1} rates calculated by Meetham for sulfur dioxide over England.

The last five experiments described give the reaction rates found for sulfur dioxide in aqueous solutions or aerosols containing either metal ions or ammonia. In general, the reaction rate of sulfur dioxide is considerably more rapid in solutions containing metal ions (or on particulates containing heavy metal oxides) than it is in air. Ammonia helps increase the rate of reaction by neutralizing the sulfuric acid produced (Junge; Junge and Ryan; van den Heuval and Mason).

The photochemical reaction rate for sulfur dioxide in clean air in the presence of sunlight is quite slow (Hall; Gerhard and Johnston; Urone, et al.). In the presence of nitrogen oxides, hydrocarbons, and ultraviolet irradiation, the rate is increased considerably (Renzetti and Doyle). The mechanisms for these latter reactions would have to include both the oxidative mechanisms of the nitrogen oxide photochemical reactions (Schuck and Doyle) and the free radical photochemical mechanisms of sulfur dioxide (Ogata, Izawa, and Tsuda).

The chemical oxidation of sulfur dioxide in aqueous and solid aerosols containing heavy metal ions is quite rapid. However, the weights of suspended particulates in polluted atmospheres are of the order of 100–200 $\mu\text{g./m.}^3$ (Schuck, et al., 1966) whereas the combined weight of gaseous pollutants may amount to several thousand $\mu\text{g./m.}^3$; that is, 1 p.p.m. C_6H_{10} = 3300 $\mu\text{g./m.}^3$; 0.1 p.p.m. SO_2 = 260 $\mu\text{g./m.}^3$; 0.1 p.p.m. NO_2 = 190 $\mu\text{g./m.}^3$, and so forth. The extent of the chemical reaction of sulfur dioxide, consequently, is limited to the capacity of the aerosols including the amount of ammonia present (Junge [1956]; Junge and Ryan; van den Heuval and Mason). This may explain why sulfur dioxide frequently is found to be 60–90% of the total sulfur compounds present in polluted atmospheres (Katz; Cholak, et al.; Thomas [1964]).

Because of the wide variations in atmospheric conditions and experimental studies, it is difficult to make any direct comparisons without first carefully considering all factors involved. Laboratory experiments, however, have consistently shown that aerosol formation as measured by light scatter is increased by the presence of sulfur dioxide in irradiated hydrocarbon-nitrogen oxide-air mixtures. However, the composition as well as the rate of formation of the aerosols seem to be highly dependent upon the types and amounts of substances present, as well as on the order of mixing (Endow, Doyle, and Jones; Prager, Stephens, and Scott; Goetz and Pueschel; Roddy). The work of Harkins and Nicksic is interesting in that the enhanced amount of aerosol formed by irradiated C^{14} tagged propylene and ethylene in the presence of sulfur dioxide did not show radioactivity when filtered with a Millipore filter. The implication is that no organic matter was found in the aerosol. The questions that remained unanswered are: What constituted the aerosol? And why was not at least some of it observed in the presence of sulfur dioxide?

Inasmuch as sulfur dioxide is constantly present in polluted atmospheres on an approximate steady-state basis, a large number of reactions of sulfur dioxide other than oxidation to sulfuric acid are possible during stagnant periods of severe temperature inversions. At such times, a mass of air can be subjected to many hours of solar irradiation and thermal catalysis. The photochemical reaction products observed by Dainton and Ivin, Johnston and Dev Jain, Prager, Stephens, and Scott, and Stevenson, Sanderson, and Altshuller, plus those suggested by Schroeter, should be especially considered for reaction products of possible physiological importance.

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