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Importance of Photolysis of Nitrate in Oxidation of Atmospheric Sulfur Dioxide

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Photochemical oxidation of sulfite in concentrated solution of ammonium nitrate was studied with a mercury lamp and solar radiation as a chemical model system of the water-film on the atmospheric nitrate aerosol. Sulfite was found to be photo-oxidized with first-order reaction kinetics. Temperature and nitrate concentration dependences of the rate constant suggested that low temperature hardly decreased the atmospheric significance of this reaction and that the oxidation favored high conentration.

The formation of sulfuric acid from sulfur dioxide in the troposphere is an important process not only in acid precipitation occurrence but in the global sulfur cycle. The oxidation undergoes in both gaseous and aqueous phases[1)] and the chemistry of sulfate formation involves many reactions that vary in importance according to ambient conditions such as air-tempertaure and background air quality.

Meanwhile, Graedel, and Goldberg[2)] suggested the potentiality of photodecomposition of nitrate, which had been confirmed to occur with solar radiation by Petriconi and Papee,[3,4)] as a source of dissolved ozone in the case of the high initial nitrate concentration. Nonetheless, we regard this photochemical decomposition as a probable oxidant source for the oxidation of dissolved atmospheric sulfur dioxide, or sulfite and investigated its significance in the sulfite-to-sulfate conversion processes.

Ammonium nitrate is a substantial part of naturally and anthropogenically formed atmospheric aerosol.[5,6)] The nitrate solution is expected to be in the form of highly concentrated water-film on the aerosol surface exposed to the solar radiation. The residence time of aerosol is on the order of several days, which will assure a long exposure to solar radiation.[7)] In this work, the solution was simulated by a bulk solution of concentrated ammonium nitrate.

The oxidation was studied by dissolving sodium bisulfite, S(IV), in an ammonium nitrate solution, irradiating the solution with an ultra-high pressure mercury lamp (USHIO USH-500D), and following the S(IV) concentratrion.

The photolysis cell was a cylinder made all of Pyrex glass with a window on a side, which transmitted light of wavelength longer than about 300 nm. The vertical side of the body except the window was surrounded by a glass water-jacket within which thermostatted water was circulated. A quartz cylindrical cell was placed between the lamp and the window, and cooling water was permitted to flow inside the cell to absorb the heat of the radiation.

The S(IV) in the aliquots taken at various time intervals was quenched with tetrachloromercurate(II) and determined by the West-Gaeke spectrophotometry. All chemicals were of reagent grade and used without further purification. Expermients were performed at 25 °C unless otherwise stated.

A preliminary irradiation of 1.0 M nitrate (1 M = 1 mol dm^{-3}) with S(IV) showed a rapid decrease in S(IV) concentration. The concentrated solution probably contained various impurity metals even if the impurity level was on the order of sub ppm or less, and possible catalytic contribution of the impurity metal was involved. Then 1 ml of EDTA solution was added to 1.0 M nitrate solution during the course of the reaction so that the EDTA concentration became 1×10^{-4} M. EDTA suppressed the decrease of S(IV) to a small extent (Fig. 1), and we interpreted the decrease in the presence of EDTA was solely due to the photolysis of nitrate.

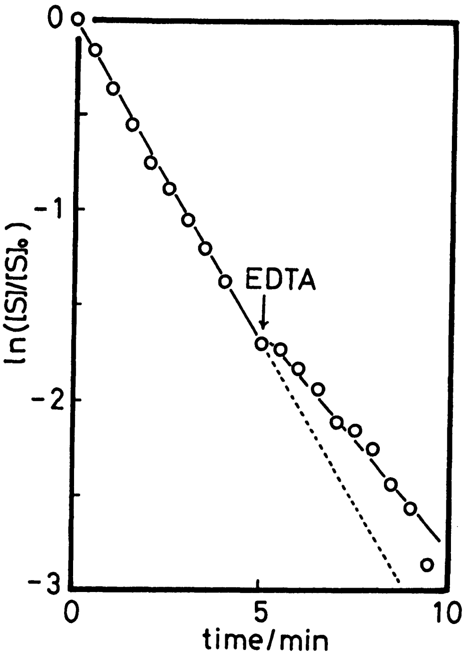

Fig. 1. A ln[S(IV)] vs. time plots for 1.0 M nitrate. EDTA was added at 5.0 min. [S(IV)]o denotes the initial S(IV) concentration.

Hereafter, EDTA was added in this proportion to nitrate solutions of different concentrations prior to the reaction. The decrease in S(IV) obeyed first-order kinetics as shown in Fig. 1 to provide a rate constant, k_1 of 2.25×10^{-3} s^{-1}, which was equivalent to a half-life of 5.1 min.

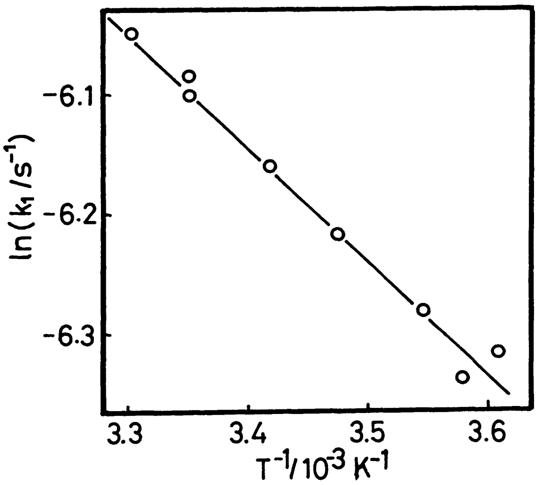

Fig. 2. Arrhenius plots of k_1 for 1.0 M nitrate.

The rate constants were determined at temperatures, 4 - 30 °C for 1.0 M ammonium nitrate solution. The temperature dependence of k_1 was rather slight. For a decrease in temperature from 25 to 4 °C, k_1 decreased only by 20%. This supports the view that low temperatures at high altitudes or in wintertime hardly decreases the importance of this photochemical process. A linear relation was obtained between ln k_1 and 1/T, and led to an activation energy for the oxidation reaction of 7.9 kJ mol^{-1} (Fig. 2). This is rather a small value and suggests a radical reaction mechanism.

The water-film is expected to be a saturated solution. The solubility of ammonium nitrate in water is about 15 and 25 M at 0 and 25 °C, respectively. Rate constants were determined at 4 °C for different nitrate concentrations. The increasing concentration of nitrate increased the rate constant: seven folds increase in nitrate concentration increased the rate constant for 1.0 M nitrate by three folds or more (Fig. 3). Atmospheric nitrate aerosol would oxidize sulfur dioxide more rapidly through this reaction.

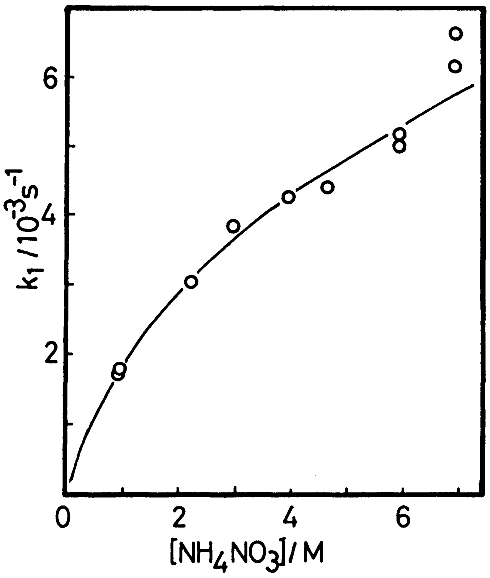

Fig. 3. Concentration dependence of k_1. temp : 4 °C.

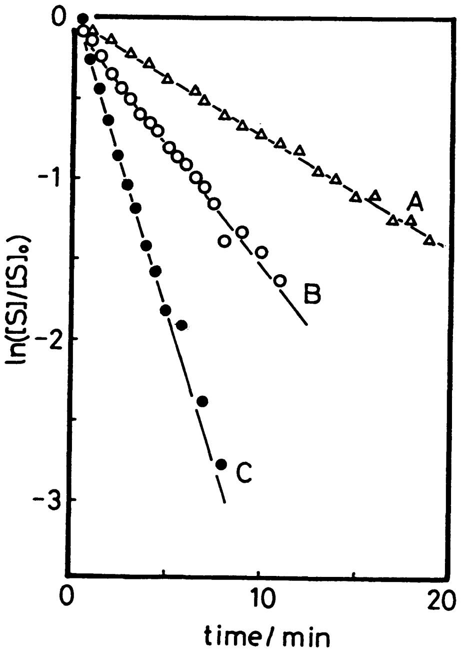

Fig. 4. Runs with solar radiation.

Oxidation experiments with solar radiation is indispensable for the evaluation of the role that this photochemical reaction will play in the atmospheric processes. The solution in a spherical cell of Pyrex glass was exposed to the solar radiation with little cloud coverage (A: Dec. 27, 1985, 12:09, 1.0 M nitrate, B: Feb. 26, 1986, 12:27, 1.0 M nitrate, and C : Feb. 25, 1986, 12:08, 6.0 M nitrate). First-order decreases of S(IV) were also observed as depicted in Fig. 4. The rate constants were 1.18×10^{-3}, 2.47×10^{-3}, and 6.22×10^{-3} s^{-1} for cases A, B, and C, respectively. Values of the constant for 1.0 M nitrate were similar to that obtained with mercury-lamp as irradiating source. A high nitrate concentration favored this reaction. Summertime solar radiation will increase this rate constant.

The oxidation rate of sulfur dioxide dissolved in 6.0 M nitrate solution (pH 4.4) is compared with those by dissolved hydrogen peroxide8) and ozone9) which are currently accepted as the dominant oxidants in the aqueous phase. Under the condition that the nitrate is saturated with 10 ppb sulfur dioxide at 25 °C, the rate of photochemical oxidation is 3.4×10^{-8} M s^{-1} while those by hydrogen peroxide(1.0 and 0.1 ppb) and ozone (30 ppb) are 8.0×10^{-7}, 8.0×10^{-8}, and 6.9×10^{-9} M s^{-1}, respectively. The photo-oxidation rate is comparable to those by hydrogen peroxide and ozone, whichi indicates that this photochemical reaction should be considered in the discussion of the sulfur dioxide oxidation in the troposphere.

Nitrate is also found in those aerosols which can act as condensation nuclei.10) After cloud droplets are formed by condensation of water vapor on the aerosols, most cloud will evaporate again leaving aerosol particles behind. The cycle aerosol-cloud droplet-aerosol will be repeated at least ten times before the aerosol is deposited.10) This cycle results in concentration of nitrate solution in the in-cloud process. Light scattering by cloud droplets scarecely decreases the total intensity of solar radiation for the photochemical reaction. The cloud life time is around half an hour but long enough for this reaction to be completed.

A conversion rate of atmospheric sulfur dioxide through this photolysis was tentatively evaluated under the following conditions : nitrate concentration; 16 $\mu g\ m^{-3}$ (observed during Nov. 17-22, 1980 in Tokyo11)) SO_2; 10 ppb, k_1; 6.22×10^{-3} s^{-1}, Temp; 25 °C. If all the nitrate is assumed to form a 6.0 M solution, the rate is 1.3×10^{-3} % h^{-1}, which is two or three orders of magnitude lower than the rates obtained in field studies.12)

For the current discussion, it suffices to note that the photochemical oxidation of sulfur dioxide in concentrated nitrate solution is a novel feature of atmospheric chemistry and that it should be involved in the evaluation of the fate of sulfur and nitrogen species. A more definite conclusion must await a more detailed examination of the kinetics of this reaction at high concentrations of nitrate with solar radiation.

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