

KINETICS OF THE ASSOCIATION REACTION OF SO₂ WITH THE HYDROXYL RADICAL

A. W. CASTLEMAN, Jr.*

Department of Chemistry, University of Colorado and Cooperative Institute for Research in Environmental Sciences, University of Colorado/NOAA, Boulder, Colorado 80309 (U.S.A.)

I. N. TANG

Brookhaven National Laboratory, Upton, N. Y. 11973 (U.S.A.)

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Summary

Utilizing a steady-state photolysis technique, the rates of the (associative) oxidation of SO₂ via the hydroxyl free radical were measured over the pressure range 20 to 1000 Torr. With nitrogen as a third body, the third-order rate constant is found to be $1.6 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ at 297 °K. At the same temperature and a total pressure of 760 Torr, the effective second-order rate constant is $6.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The third-order rate constant increases with decreasing temperature; the activation energy for the reaction is — 2.8 kcal/mol.

Introduction

Sulfur compounds are known to be an important constituent of both stratospheric and tropospheric aerosols, but the basic mechanisms by which SO₂ is chemically oxidized and subsequently nucleated to aerosol particles are not well understood. Earlier work [1 - 3] suggested that reaction of SO₂ with the hydroxyl free radical was likely to be an important step in the formation of sulfate aerosols, and the present study was undertaken to elucidate the kinetics of the reaction.

Preliminary data by Castleman [4] indicated that the effective second-order rate constant at atmospheric pressure, with a mixture of Ar, H₂O, and SO₂ as third body, was greater than $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Utilizing data from a study undertaken to measure the rate constant for the reaction of SO₂ with HO₂, Payne *et al.* [5] deduced a value for the OH-SO₂ reaction at a water (vapor) pressure of 20 Torr and a nitrogen pressure of 18 Torr; the data yielded a rate constant of $1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. (Apparently, however, the authors inadvertently deduced their rate constant from an

*To whom correspondence and requests for reprints should be directed.

inverse of the proper ratio for the competitive CO_2 production.) More recently, Davis *et al.* [6] used a flash photolysis-resonance fluorescence method to remeasure the rate constants in helium over the pressure range 50 to 500 Torr. In the more recent study, the effective second-order rate constant was found to range from $(8.7 \pm 0.6) \times 10^{-14}$ to $(2.8 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Limited data were obtained in nitrogen at 5, 10, and 20 Torr; the rate constants for the reaction were (0.80 ± 0.08) , (1.43 ± 0.14) , and $(2.44 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively.

Wayne and coworkers [7] used a discharge flow system with resonance fluorescence detection to study the reaction at total pressures up to 10 Torr. They reported third order rate constants of 4.5×10^{-31} and $7.2 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ in Ar and N_2 , respectively. Gordon and Mulac [8] have reported a value of $1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the effective second-order rate constant at 435 K and 1 atm. of water vapor. Finally, Cox [9] deduced a value of $5.6 \pm 0.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for a system composed of N_2 and O_2 at 1 atm. pressure, and at a temperature of 294 K.

Because of the potential atmospheric importance of this association reaction, and due to the fact that no systematic investigation of the pressure dependence of this reaction has been undertaken over a wide range of atmospherically important pressures with N_2 as third body, we undertook such a study. The data are reported herein.

Experimental

A steady-state competitive rate technique was used to make the rate measurements. Specifically, appropriate mixtures of CO and SO_2 were prepared, and the rate of CO_2 generation was monitored in order to determine the relative competition between CO and SO_2 for the OH free radical. Nitrogen was used for the make-up gas in order to control the total pressure at which the reaction was being studied. The competitive photolysis experiments were carried out in a cylindrical quartz cell, 1.4 cm diameter and 44 cm long, equipped with a 1 mm thick Suprasil window. The choice of this window effectively prevented the transmission of light below 1650 Å. The reaction cell was thermally jacketed so that its temperature could be controlled during the course of an experiment.

Hydroxyl radicals were produced by photochemically dissociating water vapor with a nitrogen atom resonance lamp. The microwave discharge lamp contained 20% N_2 in helium; the total lamp pressure was 1 Torr. In order to eliminate sources of impurity lines other than the resonance lines of atomic nitrogen at 1743 - 1745 Å, the lamp was equipped with a side-arm tube containing barium as a getter material. The side arm was immersed in liquid nitrogen during operation.

The microwave discharge lamp was equipped with Suprasil windows on both ends, and a separate reaction cell was located adjacent to each window. This enabled the CO_2 in a CO- H_2O - N_2 system to be determined simulta-

neously with that in the $\text{SO}_2\text{-CO-H}_2\text{O-N}_2$ reaction system. Earlier data from preliminary experiments in which CO_2 was determined in two successive experiments, one with SO_2 present and the other under similar conditions without SO_2 , were found to be rather scattered. The difficulty was found to be attributable to a fluctuation with time in the output of the u.v. lamp and the technique of making simultaneous measurements in the reference cell substantially reduced the scatter in the data; only the latter data are reported herein.

The quantity of CO_2 produced during the course of an experiment was measured using gas chromatography. A Penning ionization detector was developed for the quantitative measurement of the CO_2 at p.p.m. levels. Briefly, the principle of the detector is as follows: it contains a tritium foil β -emitter which causes excitation of a He carrier gas flowing through the analytical system. Excited He then reacts with the species of interest (CO_2 in the present experiments), causing ionization. Downstream, a set of charged electrodes are used to measure the amount of ionized material produced. For the case of CO_2 , the detector has a sensitivity of $0.2 \mu\text{g}$ with a precision of $\pm 2\%$; extensive calibrations established a proportionality to concentration.

Results and Discussion

Experiments were carried out over the pressure range 20 to 1000 Torr and temperatures ranging from -20° to 24°C . In order to ensure that the dimensions of the reaction cell were properly chosen so that the data were not influenced by OH recombination on the walls, a series of CO_2 production experiments were made for the $\text{CO-H}_2\text{O}$ system alone. The nitrogen pressure was varied systematically; the data are shown in Fig. 1.

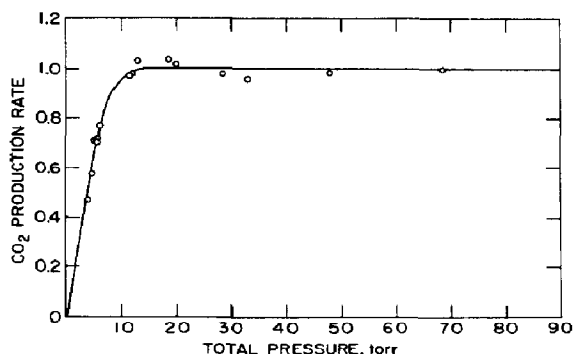


Fig. 1. Study of the rate of CO_2 production as a function of pressure for the reaction $\text{OH} + \text{CO}$.

The homogeneous gas phase reactions being monitored were as follows:





Clearly, at constant water vapor concentration, CO_2 production should be independent of total pressure, and this is in fact observed at pressures above 12 Torr. In making the measurements for the reaction system involving SO_2 , no data were taken below 20 Torr in order to eliminate wall recombination as a potential source of error.

With SO_2 present, there are additional reactions leading to a competition for the OH free radical. The data are well represented by the Lindemann mechanism:



The overall reaction of SO_2 can be represented by:



where at low SO_2 , CO , and H_2O pressures, N_2 serves as the third body.

Based on the above mechanism, the following relationship was derived for the ratio of the rate of CO_2 production in the absence of SO_2 , $R_0(\text{CO}_2)$, to that in the presence of SO_2 , $R(\text{CO}_2)$,

$$\frac{R_0(\text{CO}_2)}{R(\text{CO}_2)} = 1 + \frac{1}{k_2} \left(\frac{k_3 k_4}{k_{3r} + k_4 [\text{N}_2]} \right) \frac{[\text{N}_2] [\text{SO}_2]}{[\text{CO}]} \quad (6)$$

The square brackets denote concentration of the individual species, and the entity contained in the parentheses on the right-hand side of eqn. (6) can be identified as the third-order rate constant, k_5 . Therefore, from an experimental determination of the ratio $R_0(\text{CO}_2)/R(\text{CO}_2)$ and knowledge of k_2 , the overall rate constant, k_5 , may be obtained as a function of pressure.

Reaction (2) has been studied extensively, and a critical review given in ref. [10]. A value of $1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was used in evaluating the rate constants for the present experiments. This rate constant was assumed independent of temperature over the range -20 to $+25$ °C.

For the experiments reported herein, the initial concentrations of the reactants were established at 0.5 Torr water vapor, and a partial pressure ratio of SO_2 to CO of approximately 0.3. In all experiments, the conversion of CO to CO_2 never exceeded 1%. Therefore, the concentration ratio $[\text{N}_2] \times [\text{SO}_2] / [\text{CO}]$, was essentially constant throughout each photolysis experiment with the total H_2O , CO , and SO_2 concentration generally being less than 2 Torr. The use of the Suprasil windows on the reaction cell, and a nitrogen atom resonance lamp, ensured that the excitation of SO_2 would be minimal [11]. It was established in separate experiments that the production of CO_2 from the photolysis of CO and SO_2 was negligible in the absence of water vapor, a fact also reported by other investigators [5, 9].

The results of the experiments show a strong pressure dependence for $R_0(\text{CO}_2)/R(\text{CO}_2)$ below 250 Torr, with only a weak dependence above 500 Torr. A plot of k_5^{-1} against pressure over the pressure range 20 to 1000 Torr at 297 K is given in Fig. 2. The data show amazing linearity, confirming the validity of a Lindemann-type mechanism for the conditions of the experiments.

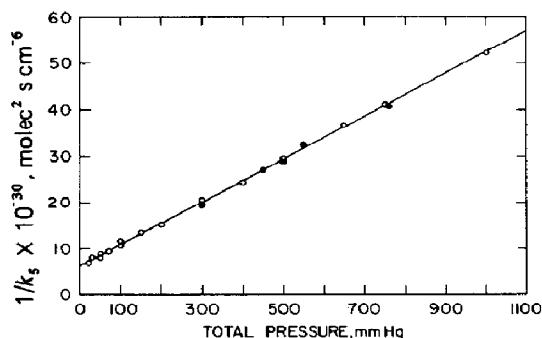


Fig. 2. Pressure dependence of the third-order rate constant k_5 , for the reaction $\text{SO}_2 + \text{OH}$.

A least-squares analysis of the data obtained at 297 K gives a value of $7.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for k_3 . At low pressures, the third-order rate constant approaches the limiting ratio $k_3 k_4 / k_{3r}$. Because of the extreme linearity of the data, a precise value of $k_3 k_4 / k_{3r}$ can, therefore, be deduced by an extrapolation of the line to zero pressure. A value of $2.3 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is thereby deduced for the ratio k_4 / k_{3r} .

The limiting (low pressure) value for the third-order rate constant becomes $1.6 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ which is in reasonably good agreement (better than a factor of 2) with the value of Davis *et al.* [6] and fair agreement with the less extensive data reported by Wayne [7]. The effective second-order rate constant at 760 Torr is $6.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; this is seen to be in excellent agreement with the single atmospheric pressure value given by Cox [9].

A rather limited number of experiments were done at temperatures below 24 °C, extending down to -20 °C. These experiments yielded an activation energy of -2.8 kcal/mol for the termolecular reaction (5) at low pressures. The sign of the activation energy is in accordance with that expected for a third order association reaction. If the data are expressed in a power notation, $k_5 = 7.0 \times 10^{-19} T^{-5.1}$.

Conclusions

Using a steady-state photolysis competitive reaction technique, the rate of reaction of OH with SO_2 has been determined over the pressure range 20 to 1000 Torr. The reciprocal of the overall third-order rate constant is found to be linear with pressure over the entire range leading to values for k_3 and k_4 / k_{3r} of 7.1×10^{-13} and $2.3 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.

Clearly, the reaction of SO₂ with the OH free radical represents a rapid reaction at both tropospheric pressures, and under stratospheric conditions. The effective second-order rate constant $k_5[M]$ is $1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 15 km elevation and a temperature of 220 K. The OH-SO₂ reaction is almost certainly a primary mechanism in the overall formation of the stratospheric sulfate layer [2, 12]. Furthermore, it is probably important in the conversion of SO₂ in the troposphere as well, although due consideration must be given to the OH concentration and possible heterogeneous reactions in the case of the latter [13].

Following completion of this paper, recent measurements of the reaction of OH with SO₂, with argon as third-body, were published by Atkinson *et al.* [14]. The results, which were obtained at 298 K over the pressure range 25 to 648 Torr are in remarkably good agreement with our N₂ results. A value of $(1.64 \pm 0.33) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ was reported at 25 Torr and $(6.7 \pm 0.7) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as the effective second-order rate constant at 760 Torr; these values are to be compared with our results of 1.4×10^{-31} and $6.0 \times 10^{-13} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, respectively.

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