A kinetic study of the reaction of atomic oxygen with SO₂

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Abstract

The effective second-order rate constant for $\text{O} + \text{SO}_2 (+\text{Ar}) \rightarrow \text{SO}_3 (+\text{Ar})$ has been measured by pulsed laser-photolysis with resonance fluorescence detection of atomic oxygen under pseudo-first-order conditions. The pressure dependence was determined at five temperatures in the range 290–840 K. The results obtained at pressures up to 880 mbar reveal fall-off behavior. With an estimated broadening parameter F_c , Troe fits to the measurements yield the low-pressure limit $k_0 = 9.5 \times 10^{-23} T^{-3} \exp(-2400/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and the high-pressure limit $k_\infty = 6.1 \times 10^{-13} \exp(-850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. An RRKM extrapolation of the present k_0 values yields $k_0 = 6.7 \times 10^{-21} T^{-3.6} \exp(-2610/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, which is in good accord with several literature values over 220–2500 K. At low temperatures, k_0 shows a positive activation energy rationalized in terms of a barrier of 15.9 kJ mol^{-1} , and k_0 reaches a maximum at around 750 K. Our expression for k_∞ is in order-of-magnitude accord with values used to model a flow reactor and indicates a small pre-exponential factor. This may reflect the probability of triplet–singlet transitions in the spin-forbidden addition reaction and/or a tight transition state.

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1. Introduction

The second-order rate constant k for reaction of ground-state $\text{O } ^3\text{P}_J$ atoms with SO₂ is pressure-dependent, which suggests that the reaction may be written as

Previous studies with several different bath gases M have yielded low-pressure limiting values k_0 in the third-order regime, where $k = k_0[\text{M}]$, as summarized in [1] and references therein. Unlike most recombination reactions, k_0 shows a positive temperature dependence at low to moderate tem-

peratures $T = 220\text{--}440 \text{ K}$ [2–4]. Data from the reverse reaction at $T = 1700\text{--}2500 \text{ K}$ imply a negative temperature dependence there, and therefore that k_0 reaches a maximum at intermediate temperatures [5,6]. The present work describes the first experiments in this region. Also for the first time, sufficiently high pressures are reached to reveal fall-off behavior in k directly, which permits an assessment of the second-order high-pressure limit, where $k = k_\infty$. Previously, Atkinson et al. [7] expected that transition to the high-pressure range might occur at pressures “not too far” above 1 bar. Since then, Mueller et al. [8] have argued that k is in the fall-off regime at pressures above 1 bar around 1000 K, based on flow reactor modeling. Because atomic O has a triplet electronic ground state while SO₂ and SO₃ are singlet electronic states, k_0 and k_∞ are of theoretical

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interest because they describe a relatively rare, spin-forbidden association reaction. These rate parameters are of practical impact because they characterize a process important in combustion. Reaction (1) is the major path for formation of the significant pollutant SO_3 during the combustion of coal and other sulfur-containing fuels [9], and it propagates cycles for removal of atomic oxygen catalytically by SO_2 . These cycles involve $\text{O} + \text{SO}_3 \rightarrow \text{O}_2 + \text{SO}_2$, especially in lean flames [10,11], and/or reaction of H or HO_2 with SO_3 [8]. Such cycles are important because they provide mechanisms for sulfur to affect the overall radical pool in flames.

Here, we present new measurements of k over 290–840 K at pressures of up to 880 mbar Ar and rationalize the results in terms of RRKM theory [12]. The low-pressure limiting results are in agreement with several previous studies, and RRKM extrapolation over 220–2500 K is in excellent accord with measurements at those temperatures. The new high-pressure limiting information, obtained by RRKM extrapolation of the observed fall-off curves, is consistent with data needed to rationalize flow reactor studies.

2. Methodology

SO_2 (99.8%, MG Industries) was separated from high boiling point impurities by freeze-pump-thaw cycles with a liquid nitrogen/methanol slush at 175 K. Low-boiling point impurities were removed by distillation of the SO_2 from a slush at 263 K. Mixtures of SO_2 in Ar were prepared by filling a bulb with several mbar of gas evaporated from solid SO_2 at 223 K, which was made up to 1300 mbar with Ar (99.9999%, Air Liquide) and allowed to mix overnight.

Atomic oxygen was generated by pulsed excimer laser-photolysis of a small fraction of SO_2 at 193.3 nm. While the absolute concentration of O is not required for the pseudo-first-order kinetic analysis outlined below, [O] may be determined from the laser pulse energy I_0 , the beam area of 0.6 cm^2 , and the absorption cross-section σ of SO_2 . σ is defined by the Beer–Lambert relation

$$I_{\text{tr}} = I_0 \exp(-\sigma[\text{SO}_2]\ell). \quad (2)$$

We have carried out new measurements of σ at 295 K in a flowing gas cell ($\ell = 35 \text{ cm}$) using the excimer laser (MCB PSX-100) as the source of incident radiation. Three runs with various pressures of 1% SO_2 in Ar, with $I_0 \approx 45 \mu\text{J}$, and pulse repetition rates of 2–10 Hz gave consistent Beer–Lambert plots with maximum absorbances of 0.8. The mean σ is $(7.4 \pm 0.4) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$, where the error limit is one standard deviation and allows for uncertainty in $[\text{SO}_2]$. Our value lies between prior values of 6 and $8.2 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$

[13,14]. Fockenberg and Preses [13] report that the yield of O from 193 nm photolysis of SO_2 decreases by 40% from 345 to 925 K, while Vattulainen et al. examined UV spectra of SO_2 at wavelengths down to 200 nm at 873 and 1073 K [15]. On the assumption that the temperature dependence of σ is the same at 193 and 200 nm, we combine this information into $\sigma = (1.16 - T/1900) \times 7.4 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ for $T = 300$ –1070 K, with an uncertainty of around 15%. This expression was used to estimate the initial [O] in the kinetic experiments with the assumption that the photolysis quantum yield is 1 and independent of T and P .

Details of the kinetic apparatus have been given elsewhere [16–18]. Briefly, SO_2 diluted in Ar bath gas flowed through a stainless steel reaction cell. Actinic radiation at 193 nm entered through one side arm and probe radiation from a resonance lamp through a second side arm. This probe radiation at $\lambda \approx 130 \text{ nm}$ [$\text{O}(3s) \ ^3\text{S} \rightarrow \text{O}(2p) \ ^3\text{P}_j$] was generated from a microwave discharge through a flow of 0.9% O_2 in Ar at a pressure of 0.4 mbar and focused through calcium fluoride optics. The relative concentration of O atoms was measured by time-resolved resonance fluorescence observed through a third mutually perpendicular side arm. The fluorescence passed through a calcium fluoride window and detected with a solar-blind photomultiplier tube. Signals from up to 6000 decays were averaged via an amplifier/discriminator and multi-channel scaler to improve the signal-to-noise ratio. The temperature in the reaction zone, defined by the intersection of the three side arms, was measured with a retractable, sheathed, unshielded thermocouple corrected for radiation errors [19]. Reagent gas flows were set with calibrated mass-flow controllers, and experiments were carried out with a large excess of Ar bath gas. The photolysis rate was 1–2 Hz to allow fresh gas mixtures to enter the reaction zone between pulses.

O atoms are mainly consumed by reaction with SO_2

$$d[\text{O}]/dt = -(k[\text{SO}_2] + k')[\text{O}] = -k_{\text{ps1}}[\text{O}], \quad (3)$$

where k' accounts for losses other than through reaction (1), including diffusion out of the reaction zone and reaction with impurities, photolysis products (such as SO) or reaction products (such as SO_3). Under our conditions, $[\text{SO}_2] \gg [\text{O}]$, loss of O is pseudo-first-order with a decay coefficient $k_{\text{ps1}} = k[\text{SO}_2] + k'$. k_{ps1} is determined from non-linear least squares fitting of the fluorescence signals to exponential decays. A linear plot of k_{ps1} vs. $[\text{SO}_2]$ has a slope equal to the effective second-order rate constant k . Figure 1 shows an example. Experiments were carried out to determine the dependence of k on T and $[\text{Ar}]$ and to investigate the influence of experimental parameters such as the laser pulse energy I_0 and the aver-

Fig. 1. Plot of pseudo-first-order decay coefficient for loss of O vs. $[\text{SO}_2]$ at $T = 841$ K and $p = 748$ mbar. The inset shows the fluorescence decay corresponding to the open point.

age gas residence inside the heated cell before photolysis τ_{res} . These, in turn, impact $[\text{O}]_0$ and the extent of thermal decomposition of SO_2 .

Some special precautions were taken in these experiments. SO_2 flowed through the reactor for at least an hour before experiments to passivate the surfaces with respect to adsorption. The photolysis beam was attenuated to reach a region where the measured k did not vary with changes in I_0 . At room temperature, where k is the smallest, $I_0 = 12\text{--}34\ \mu\text{J}$ was employed. At higher temperatures, up to $120\ \mu\text{J}$ were used. Under these conditions of low $[\text{O}]_0$, interference by secondary chemistry involving SO and SO_3 was minimized. SO_2 is itself a potential third-body M in reaction (1), about nine times more efficient than Ar [3]. Accordingly, experiments were conducted at Ar pressures typically above 100 mbar to ensure that $\text{M} = \text{Ar}$ is the dominant collisional stabilization partner. Diffusional loss of O dominates the intercept of plots such as Fig. 1 and is separated from reactive loss of O by variation of $[\text{SO}_2]$. At lower pressures, a difficulty is that diffusional contributions to k_{ps1} via k' become large (as indicated in tabulated measurements in the electronic supplementary material) while the $[\text{M}]$ -dependent k drops, so that the overall variation in k_{ps1} with $[\text{SO}_2]$ becomes small. The abstraction process $\text{O} + \text{SO}_2 \rightarrow \text{O}_2 + \text{SO}$ is negligibly slow under our conditions, with a rate constant below $10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ [1].

3. Results

Tables summarizing 53 individual k measurements and their conditions are provided in the electronic supplementary material. Data were obtained at 5 temperatures over 290–840 K. Each k value is based on at least 5 values of k_{ps1} . Typical minimum $[\text{SO}_2]$ values were of the order of $(0.02\text{--}$

$0.1) \times 10^{16}\ \text{molecule cm}^{-3}$, and typical maximum $[\text{SO}_2]$ values were of the order of $(0.5\text{--}5) \times 10^{16}\ \text{molecule cm}^{-3}$. $[\text{O}]_0$ is proportional to $[\text{SO}_2]$ and varied over $(0.2\text{--}70) \times 10^{12}\ \text{molecule cm}^{-3}$. The k results are shown in Fig. 2 as a function of $[\text{Ar}]$. Within the scatter of the data at each temperature, the results do not vary significantly with I_0 or τ_{res} . This indicates that mixing was attained, that thermal decomposition was negligible, and that reaction (1) was isolated from secondary chemistry. The error bars shown in Fig. 2 represent the statistical uncertainty in the plot of k_{ps1} vs. $[\text{SO}_2]$ (one standard deviation) and do not include systematic errors.

Figure 2 indicates that results were obtained in the fall-off region. The k data are rationalized in terms of unimolecular RRKM rate theory by application of the approximate master equation solutions of Troe [12] for the general scheme

Within this framework, the pressure-dependent k at a given T can be expressed as

$$k = \left(\frac{k_0[\text{M}]}{1 + k_0[\text{M}]/k_\infty} \right) \times F_c^{\left\{ 1 + [\log_{10}(k_0[\text{M}]/k_\infty)] / (0.75 - 1.27 \log_{10} F_c) \right\}^{-1}} \quad (5)$$

The broadening parameter F_c was estimated as outlined by Troe [20] and then the parameters k_0 and k_∞ were varied to obtain the best fit with our measurements.

Several mechanisms have been proposed for reaction (1), which differ as to the location of inter-system crossing and potential barriers [2,5,21]. Here, we implement the assumptions of Astholtz et al. [5] that a barrier arises at the intersection of a repulsive triplet $\text{O} + \text{SO}_2$ surface with a singlet SO_3 Morse potential, and that the SO_3^* intermediate is an energized singlet SO_3 molecule. Astholtz et al. [5] estimated that the critical geometry for the formation of SO_3^* occurs at $r(\text{S}\text{--}\text{O}) = 2.05\ \text{\AA}$ for the newly forming bond, with the structure of SO_2 unchanged. We use this value here together with the vibrational frequencies of SO_3 [22], an exponential correlation of ν and r [23], and a standard loosening parameter $\alpha = 1\ \text{\AA}^{-1}$ [12], to estimate frequencies in the transition state of 266, 285, 524, 1106, and $1378\ \text{cm}^{-1}$. These values are used to evaluate the vibrational partition function $Q^\ddagger$. The enthalpy at 0 K of SO_3^* above $\text{O} + \text{SO}_2$ is V_0 , previously estimated to be $13.8 \pm 4\ \text{kJ mol}^{-1}$ [5]. The enthalpy above SO_3 is $E_0 = V_0 + \Delta H_0$, where ΔH_0 is the bond dissociation enthalpy of SO_3 , $342.5 \pm 0.7\ \text{kJ mol}^{-1}$ [22].

We apply the standard Troe formalism [12] with a similar notation in this work, and unless noted use the same input data as Astholtz et al. [5]. The variation of $Q^\ddagger$ with temperature yields

Fig. 2. Measurements of the effective second-order rate constant for $\text{O} + \text{SO}_2 (+\text{Ar}) \rightarrow \text{SO}_3 (+\text{Ar})$ at 289, 399, 581, 699, and 840 K as function of $[\text{Ar}]$. The solid curves are fits to a fall-off expression (see text).

the S_K parameter, an effective number of oscillators, via the relation $S_K = 1 - \frac{1}{T} \frac{d \ln Q^\ddagger}{d(1/T)}$ [20], from which F_c is derived (see Table 1). F_c incorporates strong and weak collision broadening effects. Figure 2 shows the fits obtained, and each k value was weighted inversely to the square of its statistical uncertainty. The resulting k_0 and k_∞ values are given in Table 1 and plotted in Figs. 3 and 4. They may be summarized as:

$$k_0 = 9.5 \times 10^{-23} T^{-3} \times \exp(-2400/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}, \quad (6)$$

$$k_\infty = 6.1 \times 10^{-13} \times \exp(-850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (7)$$

4. Discussion

4.1. Low-pressure limit

It may be seen that k_0 levels off at around 750 K, which is the region where a maximum was predicted by Astholtz et al. [5]. This behavior reflects two competing factors: as the temperature is raised, surmounting the energy barrier V_0 becomes easier, but eventually the efficiency of collisional stabilization of SO_3^* decreases more rapidly. There are differing measurements of the relative efficiency of different bath gases. For example, Timmons et al. [24] reported that $k_0(\text{Ar})/k_0(\text{He}) = 1.25$, whereas Davis found 1.93 for the same ratio [2], so here we compare our k_0 only with prior work where Ar was directly

Table 1

Fall-off parameters for the reaction $\text{O} + \text{SO}_2 (+\text{Ar}) \rightarrow \text{SO}_3 (+\text{Ar})$

T (K)	F_c	k_0 ($10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$)	k_∞ ($10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
289	0.65	1.0	0.33
399	0.58	3.7	0.70
581	0.50	7.6	1.3
699	0.47	9.1	1.6
840	0.44	9.1	2.6

employed. Figure 5 summarizes several studies made close to the low-pressure limit. It may be seen that at room temperature there is good accord with the flash-photolysis resonance fluorescence study of Davis [2] and the flash-photolysis O/NO chemiluminescence experiments of Atkinson and Pitts [3]. The earlier determinations of Halstead and Thrush [25], and Mulcahy et al. [26] appear somewhat high. We obtain a slightly steeper temperature dependence than Atkinson and Pitts, but the greatest difference between our k_0 values is only a factor of 1.5. Given the challenges of measuring such a slow, pressure-dependent process, we consider this to be good accord. Propagation of potential systematic errors and consideration of the scatter in the plots of Fig. 2 suggest likely error limits for k values, fitted via Eq. (5), of about $\pm 15\%$.

Similar to Astholtz et al. [5], we have computed k_0 via RRKM theory by application of the relation

$$k_0 = \beta_c Z_{\text{LJ}} F_E F_{\text{anh}} F_{\text{rot}} \frac{\rho_{\text{vib}}(E_0) RT}{Q_{\text{vib}}(\text{SO}_3)} \times \frac{Q(\text{SO}_3)}{Q(\text{O})Q(\text{SO}_2)} \exp\left(\frac{-V_0}{RT}\right). \quad (8)$$

We used the same input parameters as they did. The barrier V_0 was adjusted to 15.9 kJ mol^{-1} to match our $k_0(298 \text{ K})$, with the same $-\langle\Delta E\rangle$ of

Fig. 3. Arrhenius plot of the interpolated low-pressure limit k_0 for $\text{O} + \text{SO}_2 (+\text{Ar}) \rightarrow \text{SO}_3 (+\text{Ar})$. The curve is a fit to the modified Arrhenius expression $A T^n \exp(-B/T)$ (see text).

Fig. 4. Arrhenius plot of the extrapolated high-pressure limit k_∞ for $\text{O} + \text{SO}_2 (+\text{Ar}) \rightarrow \text{SO}_3 (+\text{Ar})$.

3000 J at 298 K. We allowed for temperature variation of the energy transferred upon collisional stabilization via the relation $-\langle\Delta E\rangle \propto T^n$, and determined $n = -0.42$ by matching the calculated k_0 with our measurements at 800 K. Over 220–2500 K our computed F_c can be summarized as $0.558 \exp(-T/316) + 0.442 \exp(-T/7442)$. The full RRKM calculation over 220–2500 K is shown in Fig. 5. This calculation, which rationalizes our measurements, is seen to extrapolate very well over a wide range of temperatures and may be represented to within ca. 15% as $k_0 = 6.7 \times 10^{-21} T^{-3.6} \exp(-2610/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. The agreement with several sets of measurements does not prove that the underlying mechanistic assumptions are correct, but the RRKM treatment does provide a physically based model to summarize the results. Together with our expression for k_∞ (Eq. (7)), it enables k to be predicted over a wide range of conditions.

4.2. High-pressure limit

There are no prior measurements of k_∞ for comparison. Kinetic studies of quenching of vibrationally excited SO_2 by atomic oxygen and isotopic exchange between O and SO_2 yield rate constants of $(1\text{--}2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [27,28]. In general such experiments can give information about the high-pressure limit for recombination,

Fig. 5. Plot of measured low-pressure limits k_0 for $\text{O} + \text{SO}_2 (+\text{Ar}) \rightarrow \text{SO}_3 (+\text{Ar})$. Solid line, this work; dashes, Astholtz et al. [5]; short dashes, Atkinson and Pitts [3]; dash-dot, Davis [2]; square, Mulcahy et al. [26]; and circle, Halstead and Thrush [25]. The dotted curve is an RRKM calculation (see text).

but in the case of the $\text{O} + \text{SO}_2$ interaction Astholtz et al. [5] note that they may proceed in a spin-allowed manner entirely on a triplet surface, without intersystem crossing to a single state.

Mueller et al. [8] have developed an expression for k_∞ in part by analogy with that for the spin-forbidden $\text{O} + \text{CO}$ recombination, and in part by matching observed concentration profiles when moist CO was oxidized in the presence of traces of NO and SO_2 at around 1000 K. They assumed $F_c = 1$, i.e., the Lindemann model, so our RRKM model should be more realistic. Their proposed $k_\infty(1000 \text{ K})$ is a factor of 5.7 smaller than that from Eq. (7). This is reasonable agreement, considering that our own k_∞ values reflect considerable pressure extrapolation, that Mueller et al. suggest a factor of 2 uncertainty in their k_∞ , and that a factor 5.7 increase in k_∞ would have only a modest impact on their CO and SO_2 profiles.

k_∞ is of the order of $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, some two orders of magnitude below typical values for spin-allowed reactions [6]. As Astholtz et al. point out, within the context of their mechanism, k_∞ incorporates the probability of intersystem crossing (unlike k_0 , where at the low-pressure limit equilibrium is maintained between reactants and singlet SO_3 [5]). Presumably probabilities below 1 account in part for the small pre-exponential factor. The transition state may also be unusually tight. This aspect is being investigated in our laboratory via ab initio methods. A potential difficulty with the Astholtz et al. mechanism is that the derived activation energy E_a for k_∞ of 7 kJ mol^{-1} is smaller than the barrier V_0 . We may speculate that the intersystem crossing probability decreases with temperature, which would tend to lower E_a .

5. Conclusions

Direct measurements of the effective second-order rate constant for $\text{O} + \text{SO}_2 (+\text{Ar}) \rightarrow \text{SO}_3 (+\text{Ar})$ over 290–840 K reveal pressure fall-off behavior. Troe fits yield low- and high-pressure limiting rate constants. The former exhibit a maximum near 750 K, and are rationalized in terms of an energy barrier to the spin-forbidden addition. The high-pressure limit exhibits a modest positive temperature dependence and has a small pre-exponential factor, suggesting that triplet–singlet crossing has a low probability and/or that the reaction passes through a tight transition state. The high-pressure limit is compatible with a recent flow reactor model.

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