

FELLOWSHIP FINAL REPORT

Revisiting the gas-phase rate coefficient of the
 $\text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{HSO}_3 + \text{M}$ reactionMax R. McGillen,^{1,2} Hajar Elothmani,¹ Yangang Ren,¹ Zhou Li,¹ Mahmoud Idir¹, Souad El Hajjaji,³ Véronique Daële,¹ Akkihebbal R. Ravishankara,^{1,2,4,5} Wahid Mellouki¹¹Institut de Combustion Aérothermique Réactivité et Environnement, CNRS/OSUC, 45071 Orléans Cedex 2, France.²Le Studium Loire Valley Institute for Advanced Studies, Orléans, France.³Mohammed V University, Rabat, Morocco.⁴Departments of Chemistry and Atmospheric Science, Colorado State University, Fort Collins, CO 80253, USA.⁵NOAA Earth System Research Laboratory (ESRL) Chemical Sciences Division, 325 Broadway, Boulder, CO 80305, USA.

REPORT INFO

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ABSTRACT

Oxidation of SO₂ to sulfuric acid impacts acid precipitation and aerosol nucleation in Earth's atmosphere in remote and polluted environments. This oxidation can take place in both the liquid and gas phase. Only the gas-phase oxidation is expected to lead to new particles because of the clustering reactions of H₂SO₄. This aerosol nucleation has a major effect upon air quality and Earth's radiative balance, and is of crucial importance to the chemistry of the atmosphere.

The rate limiting step in this process is the reaction of OH radicals with SO₂ to form HSO₃. The pressure- and temperature-dependent reaction of OH + SO₂ has been studied many times previously – since its importance was first recognized in the 1970s. Notwithstanding, some of the most recent literature has cast doubt on much of this data, especially under conditions that are relevant to atmospheric chemistry.

Here, we present measurements of the rate coefficient using the pulsed laser photolysis–laser induced fluorescence technique as a function of temperature (249–373 K) and of pressure in helium, argon, nitrogen and oxygen bath gases (30–600 Torr). In addition, relative rate measurements using a chamber at 760 Torr (N₂, O₂ and air) were also performed to corroborate our absolute observations. By utilizing these new data, together with the available literature data, an updated pressure- and temperature-dependent parameterization will be provided. This allows the atmospheric impact of this reaction to be constrained with a new level of certainty.

1- Introduction

In the troposphere, sulphur dioxide represents the largest anthropogenic emission of sulphur

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into the atmosphere,¹ and its gas-phase oxidation by OH leads to the formation of H₂SO₄, a critical precursor to fine particulate matter,² whose deleterious effects on human health are only recently coming into perspective.³

In the stratosphere, volcanic eruptions can inject large volumes of SO₂ that result in long-lived stratospheric particulates that can cause global cooling events whose duration can extend over several years.⁴

The reaction of OH with SO₂ is pressure dependent and proceeds as follows:



The product HSO₃ is a weakly bound radical that may revert back to reactants unless it is collisionally stabilized through interaction with a third body, a bath gas molecule, M. Because of the thermal instability of HSO₃, the rate of this reaction changes with temperature, pressure and the identity of M.

Between the Earth's surface and the injection height of volcanic SO₂ (typically up to 25 km), the atmosphere experiences a range of temperatures (220–300 K) and pressures (25–760 Torr), and where M generally represents a mixture of nitrogen (78%) oxygen (21%) and argon (1%). Given its critical role in human health and global climate, it is therefore important that the OH + SO₂ reaction is well characterized under all conditions that are relevant throughout the troposphere and the lower half of the stratosphere. Despite this, previous studies have neglected to characterize this reaction under truly atmospherically relevant conditions (especially with respect to representative partial pressures of nitrogen and oxygen as a function of temperature).

This is likely to be a consequence of the difficulty with which such measurements can be made. A popular method for making temperature-dependent measurements of OH reactions is the pulsed-laser photolysis–laser-induced fluorescence (PLP–LIF) technique. However, both N₂ and O₂ are effective at quenching OH fluorescence signal, which leads

to a decrease in signal strength and an increase in technical difficulty for these experiments. Nevertheless, with a sufficiently stable and sensitive instrument and with a series of carefully designed experiments, we find that the PLP–LIF technique is capable of determining this crucial rate coefficient with a new degree of certainty.

2- Experimental details

Measurements were conducted over the temperature range 219–373 K, with pressures (in Torr) ranging from 27–605 (He), 31–599 (Ar) 21–601 (N₂), 30–601 (O₂) using a PLP–LIF instrument (see Figure 1).

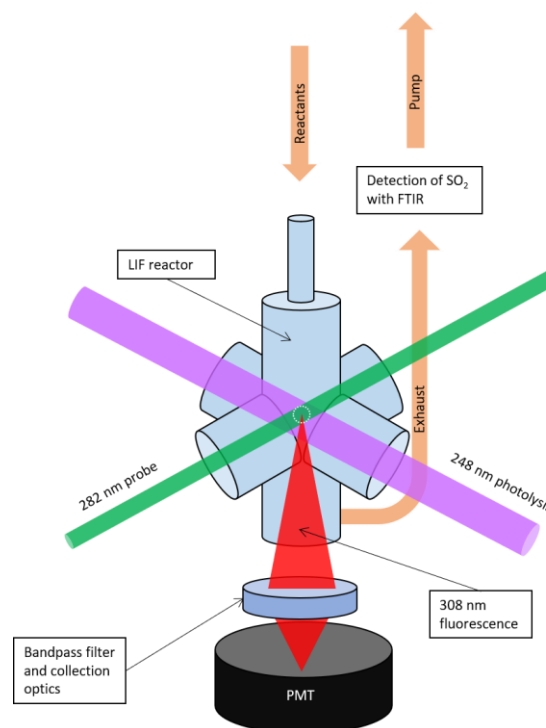
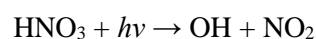
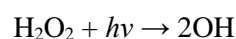


Figure 1: Diagram of the PLP–LIF apparatus used for determining rate coefficients in this work.

Rate coefficients were determined under pseudo-first-order conditions where [SO₂] >> [OH]. OH radicals were produced from the 248 nm photolysis of H₂O₂ or HNO₃ using a KrF excimer laser in the following reactions:



HNO₃ was found to perform better at the lowest temperatures of this study, whereas H₂O₂ was observed to condense out leading to experimental difficulties.

OH radicals were probed using OH fluorescence, induced following excitation of the A²Σ⁺ ← X²Π (ν = 0) transition using a frequency-doubled Nd:YAG pumped dye laser centred near 282 nm.

Photolysis and probe beams were introduced orthogonally through quartz windows and intersected in the centre of a 5-way cross-shaped reactor, with the resultant fluorescence measured using a photomultiplier tube (PMT) located out-of-plane of these laser beams. A 308 nm bandpass filter was employed to selectively detect the OH fluorescence.

Temporal profiles of OH signal were generated by changing the delay time between the lasers. This delay time is equivalent to the reaction time between OH and its various loss processes.

OH temporal profiles were found to be exponential, and obeyed pseudo-first-order behaviour such that:

$$\ln\left(\frac{[\text{OH}]_t}{[\text{OH}]_0}\right) = \ln\left(\frac{S_t}{S_0}\right) = -(k[\text{SO}_2] + k_d)t = -k't$$

where [OH]_t and [OH]₀ are the concentrations of OH at time *t* and time = 0 respectively, *S_t* and *S₀* are the OH signal at those same times, *k* is the rate coefficient, [SO₂] is the sulphur dioxide concentration, *k_d* are the loss processes of OH besides reaction with SO₂ and *k'* is the pseudo-first-order decay rate.

The rate coefficient, *k*, was obtained from the gradient of the weighted linear least-squares fit of *k'* against [SO₂]. Where [SO₂] was quantified on-line using a Fourier transform infrared spectrometer coupled with a multipass cell (pathlength = 1000 cm) and an integrated band strength for SO₂ of 2.96 × 10⁻¹⁷ cm² molecule⁻¹ cm⁻¹ between 1283.3 and 1418.6 cm⁻¹.

The temperature of the measurement was adjusted by passing heated (water) or cooled (ethanol) through the outer jacket of the reactor.

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Pressure was determined using a calibrated capacitance manometer and was regulated through the adjustment of a throttling valve located on the inlet of the vacuum pump attached to the exhaust of the reactor and also through the adjustment of bath gas mass flow rate.

3- Results and discussion

The reaction of OH + SO₂ + M → HSO₃ + M where M = He, Ar, N₂ and O₂ was found to be measurably pressure- and temperature-dependent over the range of conditions that were studied. The experimental results of this work are shown in Figures 2–5, together with literature data and temperature- and pressure-dependent parameterizations. Where direct comparisons could be made, our results compared well with the literature. Importantly, we were able to access higher pressures and a greater range of temperature for the atmospherically critical cases where M = N₂ and O₂ (see Figures 4 and 5). In these important cases, we find good general consistency with the current recommendations of IUPAC,⁵ whose parameterizations are based largely on results for M = He and theoretical work.

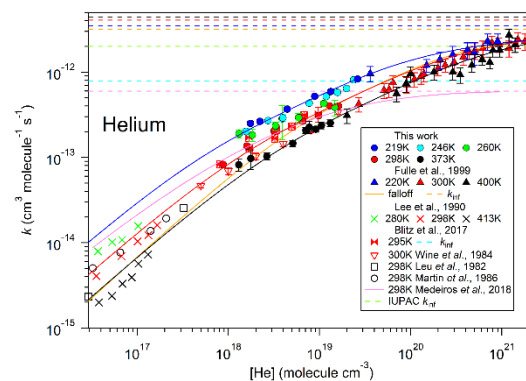


Figure 2: kinetic data from this work, the literature and parameterizations for M = He.

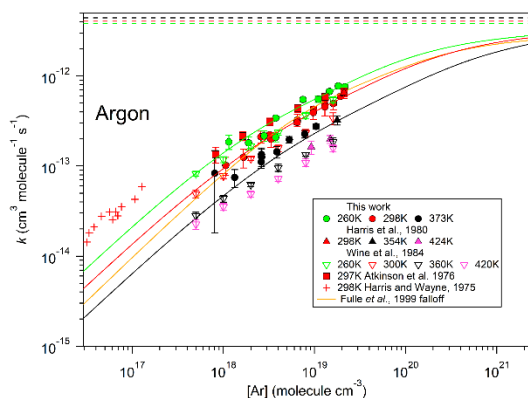


Figure 3: kinetic data from this work, the literature and parameterizations for $M = \text{Ar}$.

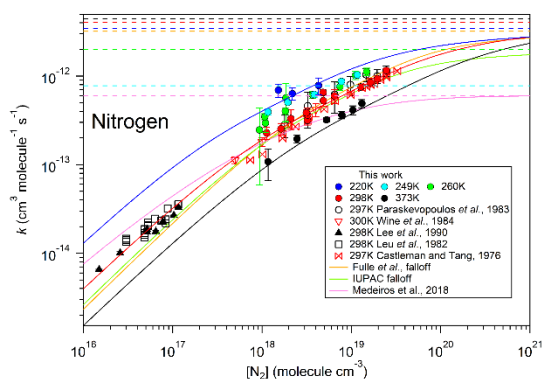


Figure 4: kinetic data from this work, the literature and parameterizations for $M = \text{N}_2$.

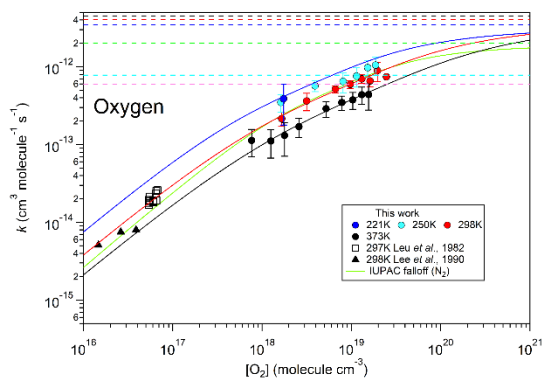


Figure 5: kinetic data from this work, the literature and parameterizations for $M = \text{O}_2$.

Furthermore, it is found with this experimental setup and protocol, that high precision and high accuracy rate coefficient measurements can be obtained.

Larger disagreements are found when we compare our measurements with recent work,^{6–8} which has indicated that the high-pressure limit for this reaction is significantly lower than previous determinations would suggest. The present work adds to a substantial body of measurements that are found to be in excess of these revised high-pressure limiting rate coefficients. Although it is premature to ascribe a reason for this, the variety of techniques and datasets that demonstrate these values to be unfeasibly small is sufficient to give us confidence that either some experimental or computational error is likely to be responsible for this discrepancy.

4- Conclusion

An extensive series of experiments for the pressure- and temperature-dependent reaction of $\text{OH} + \text{SO}_2$ are presented. This dataset makes important progress in covering the full range of atmospheric conditions that are necessary for producing an accurate, precise parameterization of this crucial reaction, which should lead to improved representations of SO_2 within chemistry and climate models.

5- Perspectives of future collaborations with the host laboratory

The study that is described in this report is one of several that have been performed during my stay at ICARE, CNRS-Orléans. It is anticipated that this, along with several other interesting projects will result in a suite of journal articles in the near future. These will, of course, be the product of many exchanges between myself and the host laboratory in the future, and I therefore expect that my communication with the host laboratory will be extensive in this regard.

Furthermore, I have been sufficiently impressed by the resources and collegial atmosphere of the host laboratory that I have taken the opportunity to apply for a long-term CNRS appointment at ICARE. If successful, I will bring my international expertise to the labs in Orléans, which I hope is very much in accordance with Le Studium's goal of improving the international presence of the facilities in Orléans.

6- Articles published in the framework of the fellowship

McGillen, M. R.; Carter, W. P. L.; Mellouki, A.; Orlando, J. J.; Picquet-Varrault, B. Database for the Kinetics of the Gas-Phase Atmospheric Reactions of Organic Compounds. *Earth Syst. Sci. Data* **2020**, *12*, 1203–1216.

Ren, Y.; McGillen, M. R.; Ouchen, I.; Daële, V.; Mellouki, A. Kinetic and Product Studies of the Reactions of NO₃ with a Series of Unsaturated Organic Compounds. *J. Environ. Sci.* **2020**, *in press*.

Ren, Y.; McGillen, M. R.; Daële, V.; Casas, J.; Mellouki, A. The Fate of Methyl Salicylate in the Environment and its Role as Signal in Multitrophic Interactions. *Sci. Total Environ.* *under review*.

McGillen, M. R.; Elothmani, H.; Ren, Y.; Zhou, L.; Idir, M.; El Hajjaji, S.; Daële, V.; Ravishankara, A. R.; Mellouki, A. Revisiting the gas-phase rate coefficient of the OH + SO₂ + M → HSO₃ + M reaction. *in preparation*.

Foulal, S.; McGillen, M. R.; Daële, V.; Mellouki, A. An Assessment of the Atmospheric Implications of Jettisoning Aviation Fuel. *in preparation*.

Elothmani, H.; McGillen, M. R.; Bedjanian, Y.; Daële, V.; Mellouki, A. Gas-Phase Rate Coefficients for the OH + 1,2-Epoxybutane Reaction Over an Extended Temperature Range. *in preparation*.

Aggelaki, M.; Elothmani, H.; Ren, Y.; McGillen, M. R.; Daële, V.; Ravishankara, A. R.; Mellouki, A.; Papadimitriou, V. C. Atmospheric Chemistry of CHF₂CH=CF₂: OH Radicals, Cl-Atoms and O₃ Kinetics, Infrared Spectra and Products. *in preparation*.

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continue long into the future. I thank the Le Studium fellows that I got to know during this time. Finally, I thank the PIVOTS programme (ARD 2020, Région Centre-Val de Loire) for financial support.

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