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Yuri Bedjanian. Rate constants for the reaction of SO with NO₂ over the temperature range 220–960 K. *International Journal of Chemical Kinetics*, 2022, 54 (9), pp.507-512. 10.1002/kin.21578 . hal-03671969

HAL Id: hal-03671969

<https://hal.science/hal-03671969v1>

Submitted on 19 Aug 2022

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Rate Constants for the Reaction of SO with NO₂ over the Temperature Range 220–960 K

Yuri Bedjanian*

*Institut de Combustion, Aérodynamique, Réactivité et Environnement (ICARE), CNRS 45071
Orléans Cedex 2, France*

Abstract

The kinetics of the reaction of SO radicals with NO₂ have been studied in a discharge flow reactor combined with an electron impact ionization quadrupole mass spectrometer at nearly 2 Torr total pressure of helium and in the temperature range 220 – 960 K. The reaction rate constant was determined under pseudo-first order conditions in excess of NO₂ over SO using two different methods for generation of the SO radicals, $k_1 = (6.7 \pm 0.2) \times 10^{-12} \exp(295 \pm 10)/T$ cm³ molecule⁻¹ s⁻¹ (the uncertainties represent precision at the 2σ level, the estimated total uncertainty on the rate constant being 15% at all temperatures). The present measurements indicate that the current recommendations for k_1 underestimate the rate constant at low stratospheric temperatures and overestimate it at the high temperatures characteristic of combustion.

Keywords: SO, NO₂, SO₂, kinetics, rate coefficient, temperature dependence.

Correspondence to: Yuri Bedjanian: Tel.: +33 238255474, e-mail: yuri.bedjanian@cnrs-orleans.fr
Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

1 INTRODUCTION

Reactions of SO radical, an intermediate in the oxidation of sulfur-containing compounds, are of considerable interest for both atmospheric and high temperature combustion chemistry. The title reaction,



is included in sulfur combustion submechanisms^{e.g.1} and in kinetic data evaluations for use in atmospheric modelling.^{2,3} Another potential implication of the reaction at high temperatures is its involvement in the hot near-source volcanic plume chemistry.⁴ Surprisingly, despite the potential practical interest in the reaction at high temperatures, there are no experimental data for the reaction rate constant at temperatures higher than 363 K.⁵ Previously the rate constant of reaction (1) has been measured in three studies: by Clyne and MacRobert⁶ and by Black et al.⁷ at $T = 298$ K and by Brunning and Stief⁵ in the temperature range 210 – 363 K. The values of k_1 at room temperature (about $1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) reported in the three studies are in good agreement, however more temperature dependence measurements over an extended temperature range are clearly needed.

In the present study, using the discharge flow technique combined with mass spectrometry the absolute rate constant of reaction (1) has been measured as a function of temperature in an extended temperature range, $T = 220 - 960$ K.

2 EXPERIMENTAL

Kinetic measurements have been conducted at nearly 2 Torr total pressure of Helium using a conventional fast-flow reactor combined with a molecular beam sampling electron-impact ionization mass spectrometer operated at 16–35 eV energy.⁸⁻¹⁰ Total flow rate of helium of (12 – 28) $\text{cm}^3 \text{ atm s}^{-1}$ gave linear flow velocities in the reactor of (1830 – 3200) cm s^{-1} at the temperatures used. Depending on the temperature range, two different flow reactors were used. The high temperature reactor, used at $T = 300 - 960$ K, consisted of a Quartz tube (45 cm length and 2.5 cm i.d.) with an electrical heater and water-cooled attachments (Figure S1, Supporting Information (SI)).¹¹ The low temperature reactor (Figure S2, SI), used at $T = 220 - 345$ K, consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) surrounded by a jacket through which a thermostated ethanol was circulated. The inner surface of the low temperature reactor was coated with Halocarbon wax.

SO radicals were generated using two methods. The first one employed the microwave discharge in SO₂/He mixtures. Monitoring of SO₂ by mass spectrometry showed that nearly 30% of SO₂ was dissociated in the microwave discharge. In the second method, SO radicals were formed in the fast reaction of oxygen atoms with thiirane:¹²



$$k_2 = 1.34 \times 10^{-11} \exp(-4/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (T = 268 - 424 \text{ K}).$$

In this case, the oxygen atoms generated in the microwave discharge in O₂/He mixtures, were titrated with C₂H₄S in the movable injector of SO radicals (Figure S1, SI). The title reaction carried out in an excess of NO₂ was used for the determination of the absolute concentrations of SO radicals by linking the concentration of SO radicals to those of NO₂ consumed and SO₂ formed: [SO] = [SO₂] = Δ[NO₂]. The absolute concentrations of all stable species (SO₂, C₂H₄S, NO₂) in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of their mixtures in He stored in calibrated volume flasks. All species were detected by mass spectrometry at their parent peaks: *m/z* = 48 (SO⁺), 64 (SO₂⁺), 60 (C₂H₄S⁺), 46 (NO₂⁺).

The purities of the gases used were as follows: He >99.9995% (Alphagaz), passed through liquid nitrogen trap; O₂ >99.7% (Alphagaz); SO₂ (> 99.9%, Alphagaz); C₂H₄S (98% , Merck); NO₂ (> 99%, Alphagaz).

3 RESULTS AND DISCUSSION

3.1 Rate Constant of Reaction (1)

Two methods were employed for the absolute measurements of *k*₁. In the first one, SO radicals were generated in the microwave discharge of SO₂ and kinetics of their consumption was monitored under pseudo-first order conditions in excess of NO₂. The main complication in this chemical system is the contribution of SO₂ (from the source of SO and produced in reaction (1)) to the mass spectrometric signal of SO at *m/z* = 48 due to the dissociative ionization of SO₂ in the ion source of the mass spectrometer. In order to minimize this interference, the electron energies were lowered to approximately 16 eV, which reduced the SO₂ contribution at *m/z* = 48 to a few percent of the SO signal, obviously with some loss of detection sensitivity.

The temporal profiles of SO ($[SO]_0 = (1.5 - 4.0) \times 10^{11}$ molecule cm^{-3}) monitored in excess of NO_2 (see Table 1 for the range of the NO_2 concentrations used) followed exponential decay, $[SO] = [SO]_0 \times \exp(-k_1' \times t)$, where $k_1' = k_1 \times [\text{NO}_2] + k_w$ is the pseudo-first-order rate constant and k_w corresponds to the loss rate of SO radicals in the absence of NO_2 in the reactor. Examples of first order plots observed at $T = 270$ K are shown in Figure 1. Examples of the dependencies of the pseudo-first order rate constant, $k_1' = k_1 \times [\text{NO}_2] + k_w$, on concentration of NO_2 at different temperatures are shown in Figure 2.

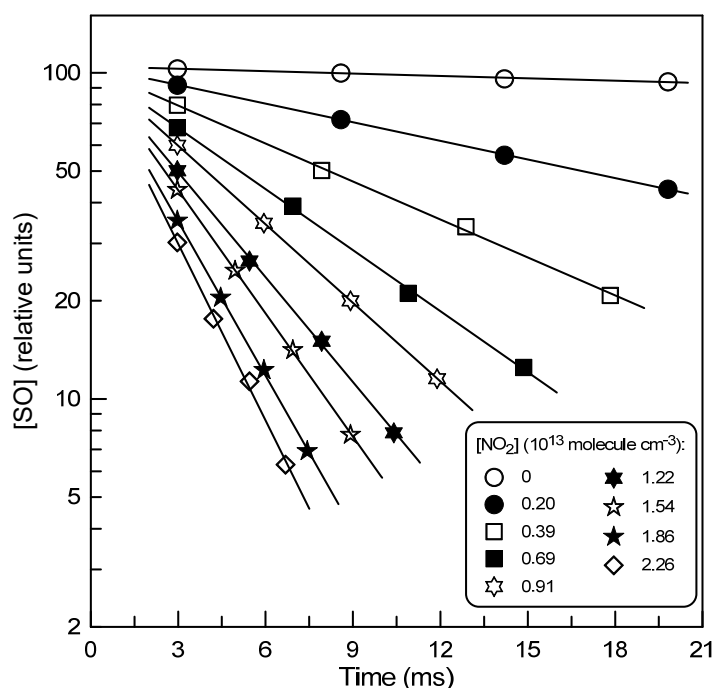


Figure 1. Typical decay profiles of SO in the presence of different concentrations of NO_2 observed at $T = 270$ K.

The small, statistically non-significant intercepts in Figure 2 indicate a negligible rate of the heterogeneous loss of SO. All the pseudo-first order rate constants, k_1' , were corrected for axial and radial diffusion of SO.¹³ The corrections typically did not exceed 10%. The results of the measurements of k_1 are shown in Table 1. The combined uncertainty on k_1 was estimated to be about 15% by adding in quadrature statistical error ($\leq 2\%$) and those on the measurements of the absolute concentration of NO_2 ($\leq 10\%$), flows (3%), pressure (2%) and temperature (1%).

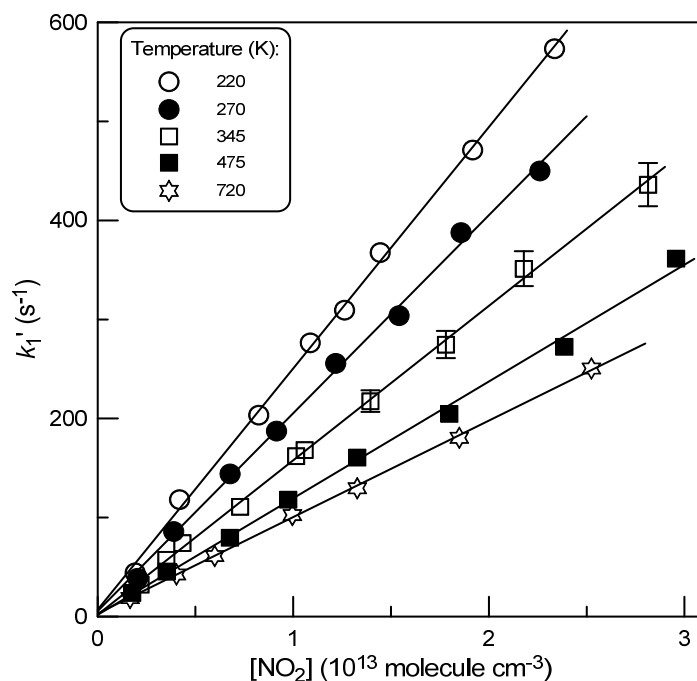


Figure 2. Pseudo-first-order rate constant $k_1' = k_1 \times [\text{NO}_2] + k_w$ as a function of NO_2 concentration at selected temperatures. Partially shown error bars represent typical uncertainties ($\leq 5\%$) on the determination of k_1' .

Table 1 Reaction $\text{SO} + \text{NO}_2$: summary of the measurements of the rate constant

T (K) ^a	$[\text{NO}_2]$ (10^{12} molecule cm^{-3})	$k_1 (\pm 2\sigma)$ ^b (10^{-11} cm^3 molecule ⁻¹ s ⁻¹)	Reactor surface ^c	Source of SO
220	1.92-23.4	2.45 ± 0.04	HW	SO_2 discharge
225	0.84-17.9	2.43 ± 0.03	HW	$\text{O} + \text{C}_2\text{H}_4\text{S}$
235	2.33-25.1	2.31 ± 0.03	HW	SO_2 discharge
250	2.38-24.1	2.25 ± 0.05	HW	SO_2 discharge
260	0.68-17.9	2.08 ± 0.03	HW	$\text{O} + \text{C}_2\text{H}_4\text{S}$
270	2.04-22.6	1.99 ± 0.04	HW	SO_2 discharge
285	0.77-24.1	1.89 ± 0.05	HW	$\text{O} + \text{C}_2\text{H}_4\text{S}$
298	0.80-26.3	1.82 ± 0.02	HW	SO_2 discharge
300	1.07-20.8	1.81 ± 0.03	Q	SO_2 discharge
310	1.51-17.8	1.75 ± 0.03	HW	$\text{O} + \text{C}_2\text{H}_4\text{S}$
320	2.17-32.5	1.70 ± 0.02	HW	SO_2 discharge
345	2.19-28.1	1.56 ± 0.03	HW	SO_2 discharge
360	0.98-17.5	1.54 ± 0.03	Q	SO_2 discharge
410	2.29-31.9	1.35 ± 0.03	Q	SO_2 discharge
435	0.50-20.9	1.29 ± 0.02	Q	$\text{O} + \text{C}_2\text{H}_4\text{S}$
475	1.76-29.6	1.18 ± 0.03	Q	SO_2 discharge

575	2.30-23.7	1.09±0.03	Q	SO ₂ discharge
720	1.66-25.2	0.98±0.02	Q	SO ₂ discharge
960	2.25-23.4	0.95±0.02	Q	SO ₂ discharge

^a 7-11 kinetic runs at each temperature.

^b The quoted errors represent the statistical 2σ fit precision, the estimated total uncertainty on k_1 is nearly 15 %.

^c HW: halocarbon wax; Q: quartz.

The generation of SO in the microwave discharge of SO₂ can be accompanied by the formation of oxygen and sulfur atoms. We have analyzed the products of SO₂ discharge for the presence of O and S. Br₂ was added into the main reactor in order to scavenge any O and S atoms present,



$$k_3 = 9.85 \times 10^{-16} T^{1.41} \exp(543/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (T = 220 – 950 K)},^{14}$$



$$k_4 = (9.5 \pm 1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (T = 298 K)},^{15}$$

with their subsequent detection at $m/z = 95/97$ (BrO⁺) and $111/113$ (SBr⁺), respectively. The signal of BrO was found to be an order of magnitude smaller than that of SO indicating a rather low concentration of the oxygen atoms. In the reactive system, the small concentrations of O atoms, even if present, are removed with NO₂,



$$k_5 = 6.1 \times 10^{-12} \exp(155/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (T = 220 – 950 K)},^{14}$$

and, in any case, do not interfere with the kinetics of SO. In contrast, S atoms can lead to the production of SO in reaction with NO₂.¹⁶



$$k_6 = 4.9 \times 10^{-11} \exp(84/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (T = 296 – 410 K)}.$$

However, no observable signal was found at $m/z = 111/113$ (SBr⁺), which indicates a negligible concentration of S atoms entering the main reactor from the microwave discharge of SO₂ under experimental conditions and in the configuration of the flow system used.

To be more confident that the source of SO radicals does not affect the measurements of k_1 , we conducted a series of experiments with the generation of SO in the reaction of oxygen atoms with an excess C₂H₄S (reaction 2). In addition, to avoid the problem of the contribution of SO₂ (reaction product) to the SO signal, in these experiments, the kinetics of SO₂ formation was monitored. The kinetics of the reaction product follows the following

expression: $[SO_2] = [SO]_0 - [SO]_0 \times \exp(-k_1't)$. Rearrangement of this expression results in $[SO_2]_\infty - [SO_2] = [SO_2]_\infty \times \exp(-k_1't)$, where $[SO_2]_\infty = [SO]_0$ and $k_1' \approx k_1 \times [NO_2]$, considering negligible heterogeneous loss of SO radicals. In experiments, the kinetics of SO_2 growth was monitored and $[SO_2]_\infty$ was determined upon total consumption of SO. Typical first-order plots are shown in Figure S3 (SI). Examples of the plots of the pseudo-first-order rate constants versus NO_2 concentration observed at different temperatures are shown in Figure 3. The values of k_1 determined in this series of experiments from the slopes of the straight lines like those in Figure 3 are given in Table 1.

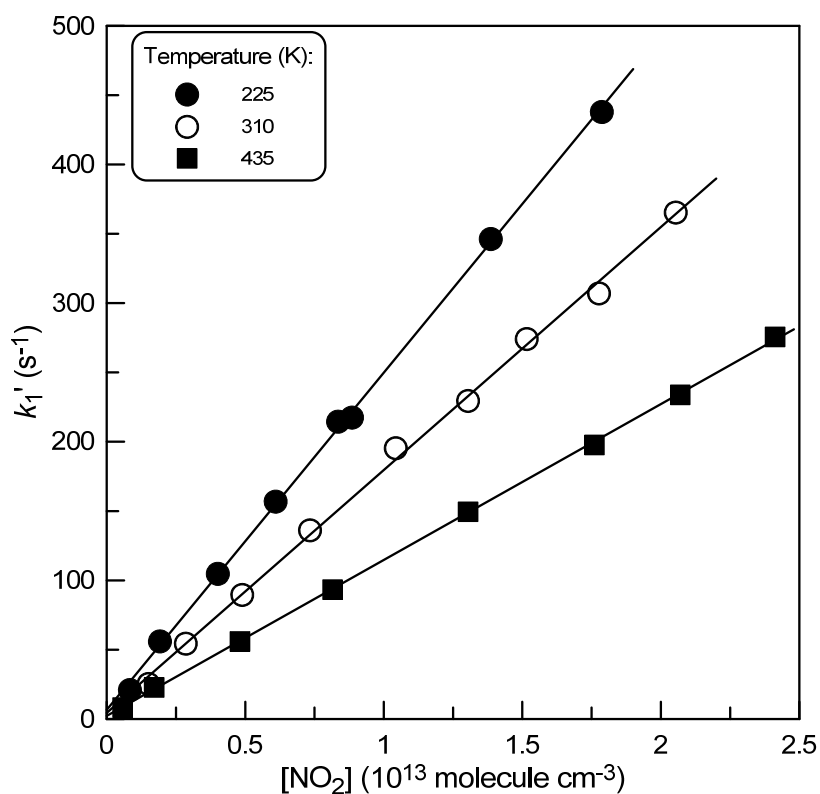


Figure 3. Pseudo-first-order rate constant, k_1' , obtained from the kinetics of SO_2 formation at selected temperatures as a function of NO_2 concentration.

3.2. Comparison with Previous Data

Figure 4 summarizes the results of the current measurements of the rate constant of reaction (1) in comparison with those from previous studies. Concerning the results from this study, one can note an excellent agreement between the measurements of the rate constant carried out with two different sources of SO. Least-squares analysis of the present temperature dependent data for k_1 yields the following Arrhenius expression in the temperature range $T = 220-960$ K:

$$k_1 = (6.7 \pm 0.2) \times 10^{-12} \exp(295 \pm 10)/T \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with 2σ uncertainties representing the precision of the fit. Three absolute measurements of the reaction rate constant at near room temperature are available in the literature. Clyne and Macrobert⁶ and Brunning and Stief⁵ using an experimental approach and apparatus similar to that of the present study reported $k_1 = (1.36 \pm 0.1) \times 10^{-11}$ at $T = 295$ K and $(1.37 \pm 0.07) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 298$ K, respectively. Black et al.⁷ determined $k_1 = (1.48 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 298$ K using laser photolysis of SO_2 to generate SO and chemiluminescence from the $\text{SO} + \text{O}_3$ reaction to monitor the SO radicals. The agreement between these data and somewhat higher value of $k_1 = (1.80 \pm 0.27) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 298$ K from the present work can be considered as satisfactory, especially taking into account that the uncertainties reported in the previous studies represent only statistical (1 or 2σ) errors.

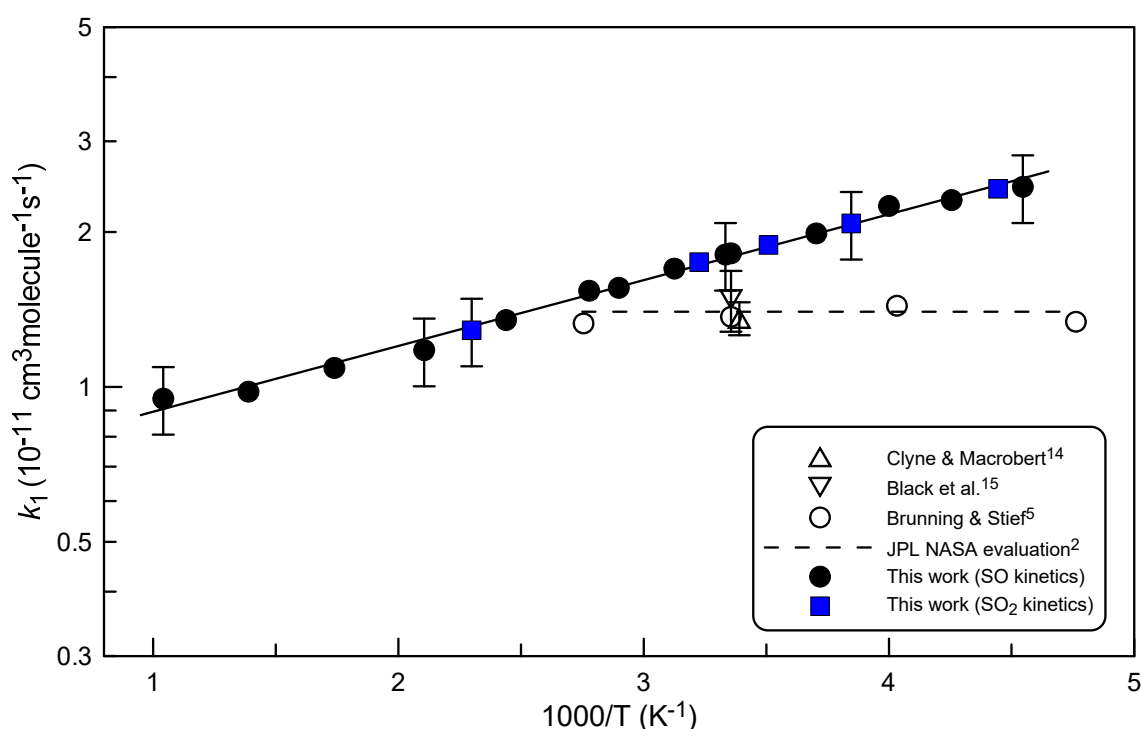


Figure 4. Summary of the data on the rate constant of the $\text{SO} + \text{NO}_2$ reaction. Partially shown representative error bars for k_1 values from this study correspond to the estimated systematic uncertainty of 15 %.

A negative temperature dependence of k_1 is clearly observed in the whole temperature range of the present work in a disagreement with the temperature invariant value of $k_1 = (1.37 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = (210 - 363)$ K reported in the only previous

temperature dependent study.⁵ The difference between absolute values of k_1 from the two studies increases at low temperatures reaching a factor of ≈ 1.8 at $T = 220$ K, the lowest temperature of the present work. It is difficult to establish the reason for the discrepancy between these two studies, conducted under similar experimental conditions and using the same methodology. One of the possible reasons could be the contribution of SO_2 to SO signal at $m/z = 48$ due to its dissociative ionization. As noted in the study of Brunning and Stief,⁵ to prevent the contribution all the measurements were made at electron energies less than or equal to 16 eV. Unfortunately, it was not indicated whether this was sufficient for complete elimination of the SO_2 signal at $m/z=48$, and if not, whether it was taken into account in the calculations. It can also be noted that in the study of Brunning and Stief,⁵ a relatively narrow range of concentrations of the excess reagent, NO_2 , was used at low temperatures; $[\text{NO}_2]$ was varied only by a factor of 3.2 and 2.6 at $T = 248$ and 210 K, respectively.

Current recommendation of the NASA Panel for data evaluation, $k_1 = (1.4 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = (210 - 360) \text{ K}$,² shown as dashed line in Figure 4, is based on the only temperature dependent study of Brunning and Stief.⁵ A similar expression is recommended by the IUPAC subcommittee on kinetic data evaluation.³ Furthermore, the temperature invariant value of k_1 , obtained at relatively low temperatures (210-363 K)⁵ is used also in the sulfur oxidation submechanisms for the modelling of the combustion processes at high temperatures.^{e.g.1} The present new measurements indicate that the currently recommended values of k_1 are underestimated at low stratospheric temperatures and overestimated at high temperatures relevant to combustion.

ACKNOWLEDGEMENT

Support from the VOLTAIRE project (ANR-10-LABX-100-01) funded by ANR through the PIA (Programme d'Investissement d'Avenir) is gratefully acknowledged.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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