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# Rate Constants for the Reaction of SO with $NO_2$ over the Temperature Range 220–960 K

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**Abstract**

The kinetics of the reaction of SO radicals with $NO_2$ 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 $NO_2$ over SO using two different methods for generation of the SO radicals,: $k_1 = (6.7 \pm 0.2)\times10^{-12}$ exp(295 ± 10)/T) $cm^3$ $molecule^{-1}$ $s^{-1}$ (the uncertainties represent precision at the $2\sigma$ 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, $NO_2$, $SO_2$, kinetics, rate coefficient, temperature dependence.

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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,

$$SO + NO_2 \rightarrow SO_2 + NO \quad (1)$$

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 Macrobert[6] and by Black et al.[7] at T = 298 K and by Brunning and Stief[5] in the temperature range 210 − 363 K. The values of $k_1$ at room temperature (about $1.4\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) 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) $cm^3$ 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 $SO_2$/He mixtures. Monitoring of $SO_2$ by mass spectrometry showed that nearly 30% of $SO_2$ was dissociated in the microwave discharge. In the second method, SO radicals were formed in the fast reaction of oxygen atoms with thiirane:[12]

$$O + C_2H_4S \rightarrow SO + C_2H_4 \quad (2)$$

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

In this case, the oxygen atoms generated in the microwave discharge in $O_2$/He mixtures, were titrated with $C_2H_4S$ in the movable injector of SO radicals (Figure S1, SI). The title reaction carried out in an excess of $NO_2$ was used for the determination of the absolute concentrations of SO radicals by linking the concentration of SO radicals to those of $NO_2$ consumed and $SO_2$ formed: $[SO] = [SO_2] = \Delta[NO_2]$. The absolute concentrations of all stable species ($SO_2$, $C_2H_4S$, $NO_2$) 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 ($SO_2^+$), 60 ($C_2H_4S^+$), 46 ($NO_2^+$).

The purities of the gases used were as follows: He >99.9995% (Alphagaz), passed through liquid nitrogen trap; $O_2$ >99.7% (Alphagaz); $SO_2$ (> 99.9%, Alphagaz); $C_2H_4S$ (98% , Merck); $NO_2$ (> 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 $SO_2$ and kinetics of their consumption was monitored under pseudo-first order conditions in excess of $NO_2$. The main complication in this chemical system is the contribution of $SO_2$ (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 $SO_2$ 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 $SO_2$ 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)×$10^{11}$ 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 $k_1' = k_1 \times [NO_2] + k_w$ 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, $k_1' = k_1 \times [NO_2] + k_w$, on concentration of $NO_2$ at different temperatures are shown in Figure 2.

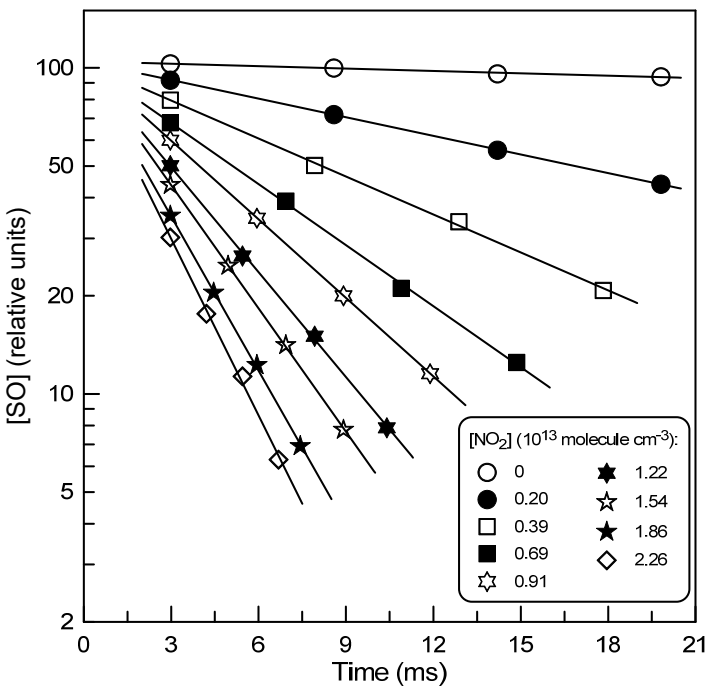


**Figure 1.** Typical decay profiles of SO in the presence of different concentrations of $NO_2$ observed at T = 270 K.

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 (≤ 2%) and those on the measurements of the absolute concentration of $NO_2$ (≤10%), flows (3%), pressure (2%) and temperature (1%).

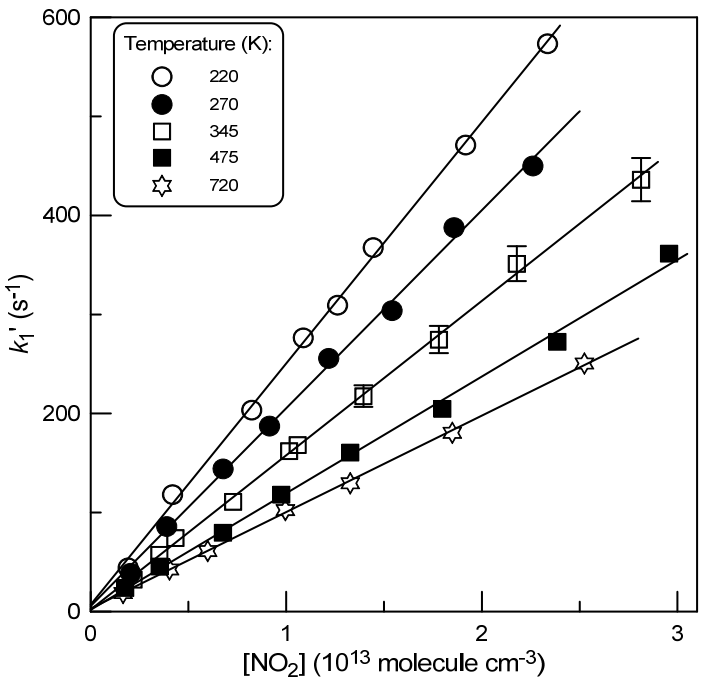


**Figure 2.** Pseudo-first-order rate constant $k_1' = k_1 \times [NO_2] + k_w$ as a function of $NO_2$ concentration at selected temperatures. Partially shown error bars represent typical uncertainties (≤5%) on the determination of $k_1'$.

**Table 1** Reaction SO + $NO_2$: summary of the measurements of the rate constant

| $T$ (K) [a] | [$NO_2$] ($10^{12}$ molecule cm$^{-3}$) | $k_1$ (± 2σ) [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 | O+$C_2H_4S$ |
| 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 | O+$C_2H_4S$ |
| 270 | 2.04-22.6 | 1.99±0.04 | HW | $SO_2$ discharge |
| 285 | 0.77-24.1 | 1.89±0.05 | HW | O+$C_2H_4S$ |
| 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 | O+$C_2H_4S$ |
| 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 | O+$C_2H_4S$ |
| 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 $SO_2$ can be accompanied by the formation of oxygen and sulfur atoms. We have analyzed the products of $SO_2$ discharge for the presence of O and S. $Br_2$ was added into the main reactor in order to scavenge any O and S atoms present,

$$O + Br_2 \rightarrow BrO + Br \quad (3)$$

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

$$S + Br_2 \rightarrow SBr + Br \quad (4)$$

$k_4 = (9.5 \pm 1.7) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (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 $NO_2$,

$$O + NO_2 \rightarrow NO + O_2 \quad (5)$$

$k_5 = 6.1 \times 10^{-12} \exp(155/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (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 $NO_2$:[16]

$$S + NO_2 \rightarrow SO + NO \quad (6)$$

$k_6 = 4.9 \times 10^{-11} \exp(84/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (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 $SO_2$ 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 $C_2H_4S$ (reaction 2). In addition, to avoid the problem of the contribution of $SO_2$ (reaction product) to the SO signal, in these experiments, the kinetics of $SO_2$ 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.

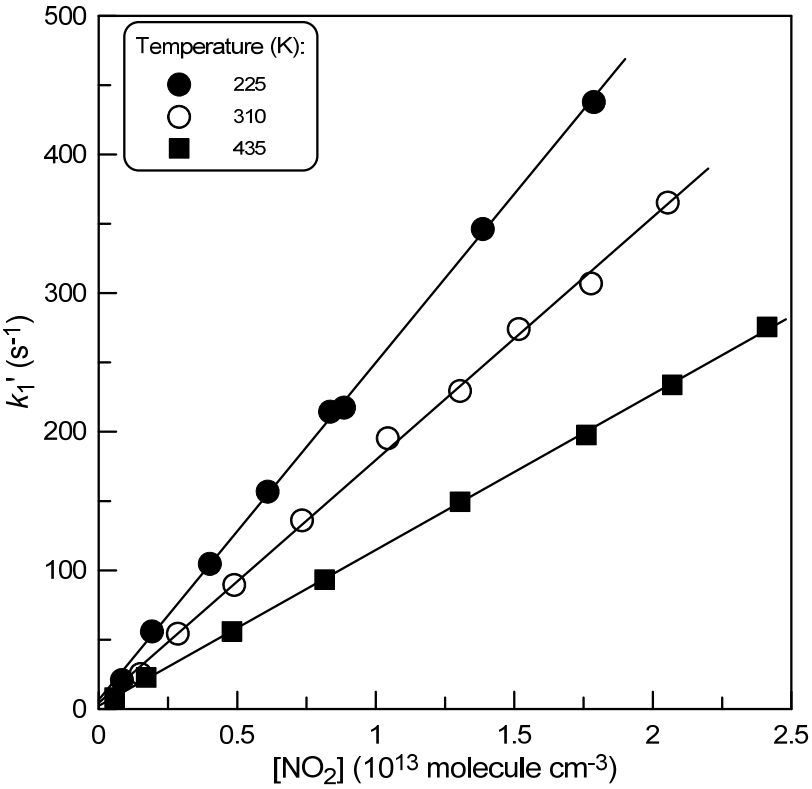


**Figure 3.** Pseudo-first-order rate constant, $k_1'$, obtained from the kinetics of $SO_2$ formation at selected temperatures as a function of $NO_2$ concentration.

### 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:

$k_1 = (6.7 \pm 0.2)\times10^{-12} \exp(295 \pm 10)/T)$ cm$^3$ molecule$^{-1}$ 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 Macrobert[6] and Brunning and Stief[5] using an experimental approach and apparatus similar to that of the present study reported $k_1 = (1.36 \pm 0.1)\times10^{-11}$ at T = 295 K and $(1.37 \pm 0.07)\times10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at T = 298 K, respectively. Black et al.[7] determined $k_1 = (1.48 \pm 0.2)\times10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at T = 298 K using laser photolysis of $SO_2$ to generate SO and chemiluminescence from the SO + $O_3$ reaction to monitor the SO radicals. The agreement between these data and somewhat higher value of $k_1 = (1.80 \pm 0.27)\times10^{-11}$ cm$^3$ molecule$^{-1}$ 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.

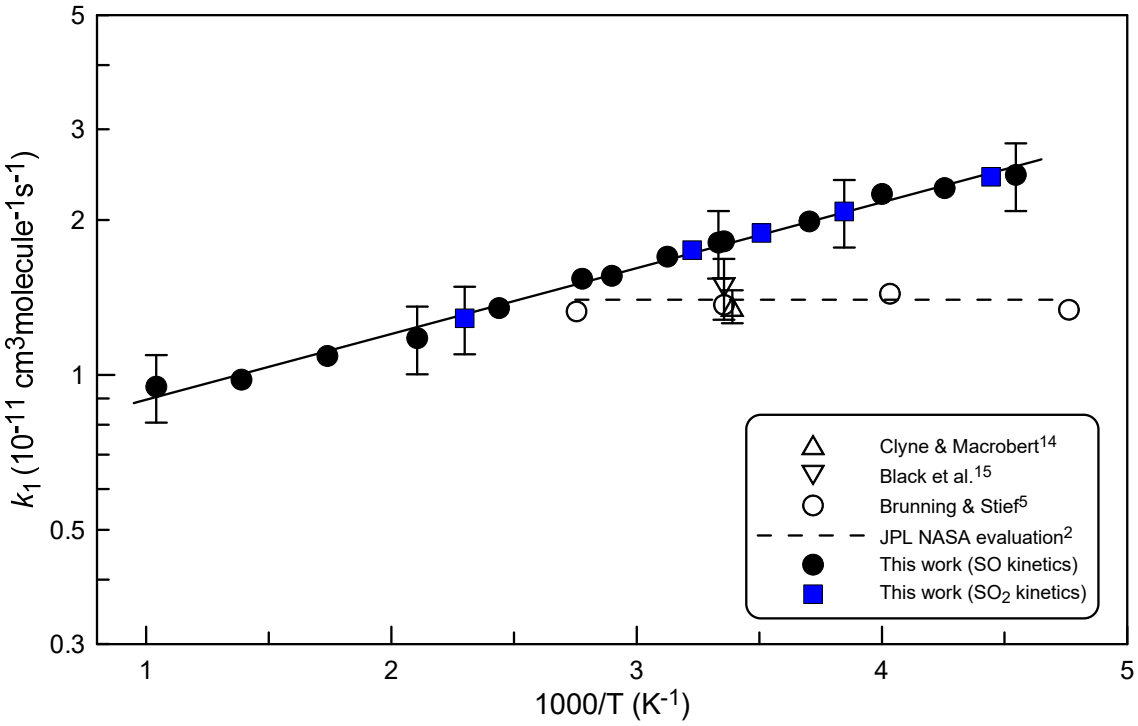


**Figure 4.** Summary of the data on the rate constant of the SO+$NO_2$ reaction. Partially shown representative error bars for $k_1$ values from this study correspond to the estimated systematic uncertainty of 15 %.

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 $k_1 = (1.37 \pm 0.10)\times10^{-11}$ cm$^3$ molecule$^{-1}$ 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; [$NO_2$] 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, $k_1 = (1.4 \pm 0.2)\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at T = (210 – 360) 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.

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## SUPPORTING INFORMATION

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

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