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**Experimental Study of the Reaction of O(³P) with Carbonyl Sulfide
between 220 and 960 K**

Yuri Bedjanian*

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

* Corresponding author. E-mail: yuri.bedjanian@cnrs-orleans.fr

ABSTRACT

The reaction of ground-state O atom with carbonyl sulfide is of interest for atmospheric (stratosphere and hot near-source volcanic plume) and combustion chemistry. In the present work, we employed a discharge-flow system combined with modulated molecular beam mass spectrometry technique to measure the rate constant and products of the O+OCS reaction. The overall rate constant was determined either from kinetics of the reaction product, SO radical, formation or under pseudo-first order conditions from the decays of OCS in excess of oxygen atoms: $k_1 = 1.92 \times 10^{-12} \times (T/298)^{2.08} \times \exp(-1524/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at T= 220-960 K, with conservative uncertainty of 20 %. The yield of another reaction product, CO₂, was found to increase from 3.55 % at T = 455 K to 14.2 % at T = 960 K, resulting in the following Arrhenius expression for the rate constant of the minor (S + CO₂ forming) reaction channel: $k_{1b} = 4.19 \times 10^{-11} \times \exp(-4088/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at T= 455-960 K (with an uncertainty of 25 %). The kinetic and mechanistic data from the present work are discussed in comparison with previous experimental and computational studies.

1. INTRODUCTION

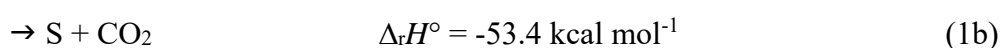
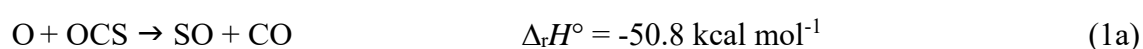
Carbonyl sulfide is the most abundant sulfur-containing gas phase compound in the troposphere due to its low reactivity and, as a consequence, reasonably long tropospheric lifetime.¹ OCS is transported from the troposphere or directly injected by volcanic eruptions to the stratosphere, where it undergoes photooxidation (through photolysis and reactions with O atoms and OH radicals) resulting in conversion to sulfate aerosol.¹ In this respect, the information on the kinetics and products of the title reaction



at low stratospheric temperatures is of importance. The high temperature data for O+OCS reaction is of interest for combustion chemistry, and also due to its potential involvement in the hot near-source volcanic plume chemistry.²

Reaction 1 has been extensively studied both experimentally³⁻¹⁵ and theoretically.¹⁶⁻¹⁷ Over a dozen available measurements of the reaction rate constant cover a wide temperature range between 239 and 1900 K.^{9,14} The previous kinetic data satisfactorily agree with each other (within a factor of 2, depending on temperature), and the general features of the temperature behaviour of the overall reaction rate constant (significant increase with temperature) can be considered as well known. However, the totality of the previous measurements performed by different methods and in different and limited temperature ranges does not allow to establish with precision the temperature dependence of the rate constant in the entire temperature range of the studies. One of the aims of this work was to reconcile previous disparate kinetic data by measuring k_1 within a single study and in an extended temperature range $T = 220\text{--}960$ K, which covers almost all previous measurements.

Reaction 1 has two exothermic channels:¹⁸



Currently, there is experimental evidence that SO + CO forming channel is the main reaction pathway. The second, S + CO₂ forming, channel of reaction 1 becomes important at high temperatures: with the branching ratio k_{1b}/k_1 up to 30% at T = 1500 K.¹⁵ Another task of this work was to determine the yield of CO₂, product of reaction 1b, as a function of temperature.

2. EXPERIMENTAL

Experiments have been carried out in a discharge-flow apparatus at total pressure of 2 Torr of Helium using an electron-impact ionization (25–30 eV energy) mass spectrometry to measure the concentrations of the species involved.¹⁹⁻²² The flow reactor used at low temperatures, T = 220 – 310 K, consisted of a halocarbon wax coated Pyrex tube (45 cm length and 2.4 cm i.d.). The temperature in the reactor was controlled by circulating thermostated ethanol. High temperature reactor, employed at T = 299 – 960 K, was an electrically heated Quartz tube (45 cm length and 2.5 cm i.d.) with water-cooled extremities (Figure S1, Supporting Information).²³

Oxygen atoms were produced by discharging a trace amounts of O₂ in He and were detected at their parent peak, m/z = 16 (O⁺): the contribution of O₂ at this mass due to fragmentation of the molecular oxygen in the ion source of the mass spectrometer was properly taken into account. In the procedure used for kinetic measurements, the uncertainty on the measurements of the absolute concentrations of oxygen atoms propagated directly to the uncertainty on the measurements of the reaction rate constant. For this reason, two independent methods were used to ensure the accurate measurements of the absolute concentrations of O atoms. In the first one, the O concentrations were determined from the decrease in the O₂ concentration upon initiation of the microwave discharge ($\Delta[\text{O}_2] = 2[\text{O}]$). In another method, oxygen atoms were titrated with an excess of NO₂,



$$k_2 = (6.1 \pm 0.4) \times 10^{-12} \exp((155 \pm 18)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (T = 220 – 950 K),}^{19}$$

and their absolute concentrations could be determined from the consumed fraction of NO₂ and concentrations of NO and O₂ formed: $[O] = \Delta[NO_2] = [NO] = [O_2]$. Both methods gave almost identical (within 10%) results.

All stable species (OCS, C₂H₄S, SO₂, O₂, CO₂, NO₂, NO and Br₂) were detected by mass spectrometry at their parent peaks. Their absolute concentrations were derived from measured flow rates of their manometrically prepared calibrated gas mixtures.

He (carrier gas) and O₂ were taken directly from high-pressure tanks and had stated purities better than 99.99% (Alphagaz). SO₂, NO₂, NO were Alphagaz products (> 99.9%). The purities of OCS (15% in He, Messer), C₂H₄S (Merck) and Br₂ (Aldrich) were 99.99, 98 and 99.99%, respectively.

3. RESULTS AND DISCUSSION

3.1. Rate constant of reaction 1. The rate constant of the title reaction was determined using two different methods. At low temperatures, under conditions where reaction 1 is relatively slow and consumption of the reactants is insignificant, the rate constant was determined by monitoring the kinetics of the reaction product, SO radical. The second approach used at higher temperatures, consisted in a direct monitoring of the OCS decays in excess of oxygen atoms.

3.1.1. Kinetics of SO production in reaction 1. In this series of experiments, the rate constant of reaction 1 was determined in the temperature range 220 - 410 K from the kinetics of the reaction product, SO, formation under conditions where consumption of the reactants (OCS and O-atom) was insignificant (less than 10 % at all temperatures of the study). Under such experimental conditions where the concentrations of O-atom and OCS can be considered as constant, the [SO] buildup is governed by zeroth order kinetics, $d[SO]/dt = k_{1a} \times [O] \times [OCS] = \text{constant}$, and linear increase of the concentration of the SO radicals with reaction time is

expected. Experiments were carried out in the presence of NO_2 which was added in the end of the reactor, 5 cm upstream of the sampling cone of the mass spectrometer ($[\text{NO}_2] = (5 - 8) \times 10^{13}$ molecule cm^{-3}), which led to a rapid conversion of the SO radicals, formed in reaction 1a, to SO_2 through reaction 3:



$$k_3 = (6.7 \pm 0.2) \times 10^{-12} \exp((295 \pm 10)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (T = 220 - 960 \text{ K}).^{24}$$

The chemical conversion of SO to stable species SO_2 allowed the determination of the absolute concentrations of the SO radicals. Thus, the Figures and expressions showing [SO] in this section actually mean the measured $[\text{SO}_2]$, which is equal to [SO]. Examples of the SO kinetics are shown in Figure 1.

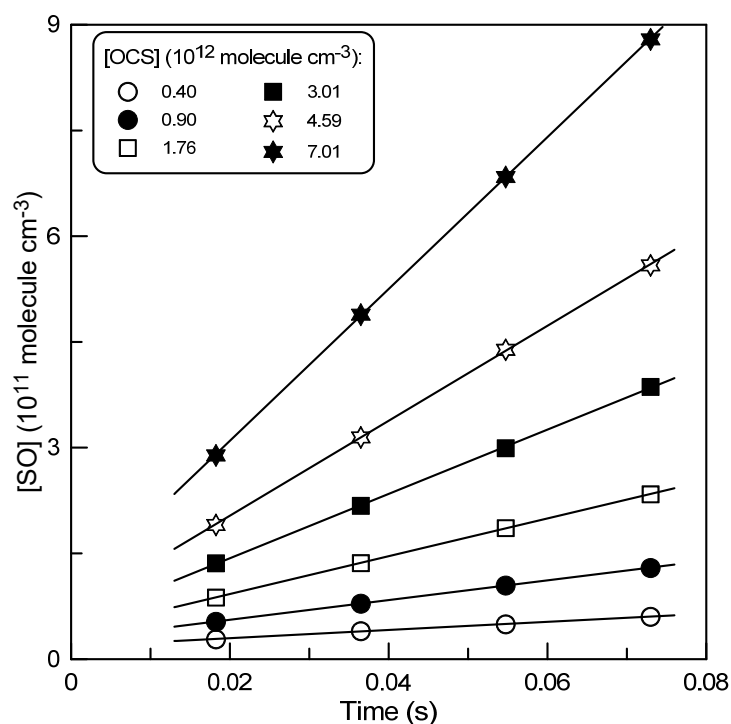


Figure 1. Kinetics of SO radical production in reaction 1 observed at $T = 310 \text{ K}$ with $[\text{O}] = 1.0 \times 10^{14}$ molecule cm^{-3} and different initial concentrations of OCS. Continuous lines represent linear fit to the experimental data.

The slopes of the straight lines in Figure 1 provide the rate of the SO production, $d[\text{SO}]/dt$ (in molecule $\text{cm}^{-3} \text{ s}^{-1}$). The rate of SO production measured as a function of product of the O-atom and OCS concentrations at different temperatures is shown in Figures 2 and S2 (Supporting

Information). Most of the experiments were carried out with fixed oxygen atom and varied OCS concentrations (Table 1). Figure S2 displays the experimental data demonstrating that variation of [O] had no impact on the results of the measurements. The slopes of the observed linear dependences of $d[\text{SO}]/dt$ on $[\text{O}]\times[\text{OCS}]$ provide the values of k_{1a} at respective temperatures. All the data obtained in this way, as well as initial concentrations of the reactants used in these experiments, are given in Table 1. The combined uncertainty on the measurements of k_{1a} was estimated to be of nearly 20 %, including statistical error and those on the measurements of the flows, pressure, temperature and absolute concentrations of the three species involved.

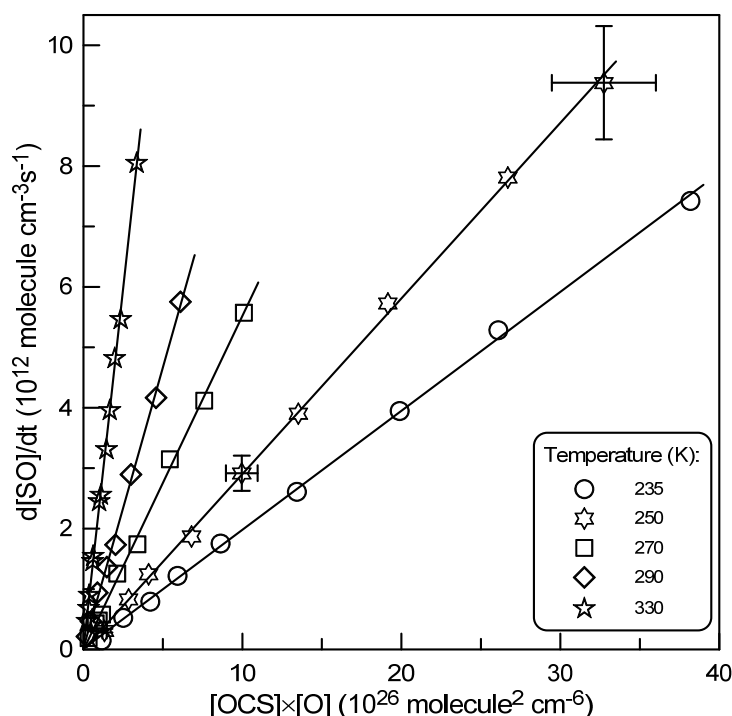


Figure 2. Examples of the dependence of the rate of SO production in reaction 1 on the product of the concentrations of OCS and O-atom. Partially shown error bars represent the typical 10% uncertainties on the measurements of the respective parameters.

Table 1. Experimental Conditions and Results of the Measurements of the Rate Constant of Reaction 1

T (K) ^a	[O] ^b	[OCS] ^b	k^c	Reactor surface ^d	method ^e
220	15.9	0.343-7.53	0.00974	HW	SO kinetics
235	4.87	0.236-7.80	0.0197	HW	SO kinetics
250	7.69	0.173-4.24	0.0290	HW	SO kinetics

270	4.56	0.072-2.21	0.0553	HW	SO kinetics
290	4.36	0.050-1.39	0.0929	HW	SO kinetics
299	4.55	0.188-2.44	0.116	Q	SO kinetics
310	2.38-10.1	0.040-2.00	0.150	HW	SO kinetics
330	2.10-3.59	0.090-0.93	0.239	Q	SO kinetics
360	1.74	0.201-3.29	0.436	Q	SO kinetics
385	3.01-27.5	0.02	0.636	Q	OCS kinetics
410	1.74	0.164-2.81	0.870	Q	SO kinetics
430	2.63-27.4	0.02	1.17	Q	OCS kinetics
500	1.21-13.0	0.04	2.72	Q	OCS kinetics
595	0.93-10.2	0.03	6.38	Q	OCS kinetics
735	0.69-8.66	0.02	15.9	Q	OCS kinetics
960	0.37-5.76	0.02	44.5	Q	OCS kinetics

^a 8-12 kinetic runs at each temperature. ^b Units of 10^{13} molecule cm^{-3} . ^c k_{1a} in case of SO kinetics, k_1 in case of OCS kinetics; units of 10^{-13} $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$; statistical 2σ uncertainty is $\leq 2\%$; total estimated uncertainty is 15-20%. ^d HW: halocarbon wax; Q: quartz. ^e k_1 derived from kinetics of SO formation (SO kinetics) or OCS consumption (OCS kinetics).

3.1.2. Kinetics of OCS consumption in excess of O atoms. The measurements were carried out under pseudo-first order conditions with $[\text{O}] \gg [\text{OCS}]$ (see Table 1). The concentrations of both reactants, OCS and oxygen atoms, at various reaction times were monitored by mass spectrometry. Examples of the observed exponential decays of $[\text{OCS}]$, in accordance with $d[\text{OCS}]/dt = -k_1[\text{O}][\text{OCS}]$, are shown in Figure S3 (Supporting Information). These concentration-time profiles yield $k_1' = k_1[\text{O}]$, the pseudo-first-order rate constant. It is worth noting that consumption of oxygen atom was negligible (no more than a few percent) in all the experiments due to its high excess over OCS and relatively low rate of heterogeneous loss on the wall of the flow reactor ($k_w = (0.8 - 2.0) \text{ s}^{-1}$, increasing with temperature). Figure 3 shows the pseudo-first order rate constants, $k_1' = k_1[\text{O}]$, plotted against the concentration of oxygen atoms. The slopes of the straight lines in Figure 3 (linear fit to the experimental data) provide the values of k_1 at respective temperatures, shown in Table 1.

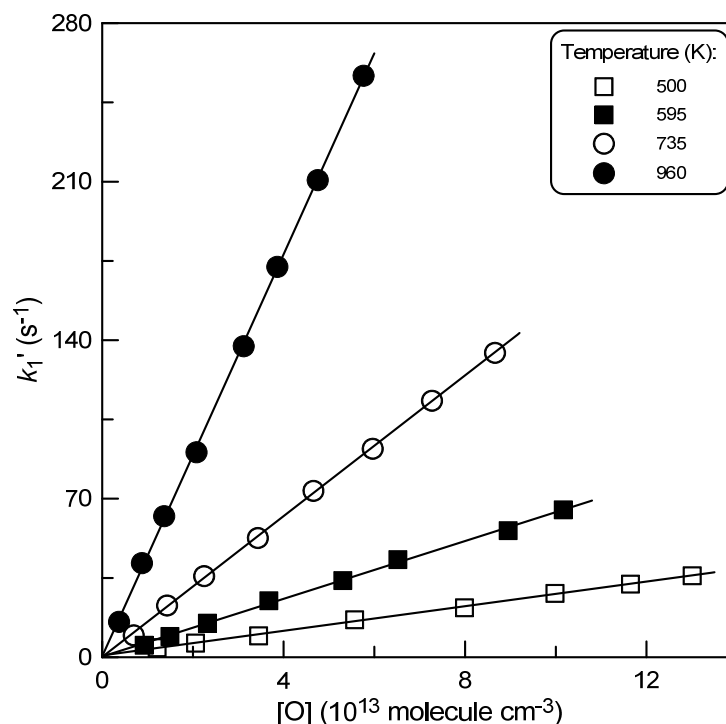


Figure 3. Pseudo-first order rate constant, $k_1' = k_1[\text{O}]$, as a function of the O-atom concentration at different temperatures.

3.1.3 Temperature dependence of k_1 . All the kinetic data from the present work are shown in Figure 4 in line with previous temperature dependent measurements. Before discussing the temperature dependence of the rate constant of reaction 1, it should be noted that the data of the present study obtained from the OCS and SO kinetics correspond to the total rate constant and to that of channel 1a, respectively. However, as will be shown below, at $T < 410$ K (highest temperature of the k_{1a} measurements) the contribution of the second reaction channel (1b) to the overall rate constant is less than 2.5 %, and k_1 , in this temperature range, can be considered identical to k_{1a} .

The present value of the rate constant at $T = 299$ K, $k_1 = (1.16 \pm 0.23) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is in good agreement with previous room temperature measurements ($T = 296$ - 300 K, not shown in Figure 4) of Sullivan and Warneck, $(0.91 \pm 0.14) \times 10^{-14}$,³ Manning et al., $(1.39 \pm 0.14) \times 10^{-14}$,¹⁰ and Yoshida and Saito, $(1.18 \pm 0.12) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹¹ Somewhat higher value, $k_1 = (1.7 \pm 0.2) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 296$, was reported by Robertshaw and

Smith.¹³ The use of two different approaches in k_1 measurements in the present work allowed to determine the absolute values of the rate constant varying by a factor of ~ 5000 . The combination of the relatively precise measurements (within 15-20%) and a wide temperature range (220 – 960 K) allowed to discern a weak curvature of the Arrhenius plot at $T > 600$ K. This has been difficult to do in previous disparate studies conducted over limited temperature ranges. The three-parameter fit to the present data for k_1 (solid line in Figure 4) yields the following modified Arrhenius expression:

$$k_1 = 1.92 \times 10^{-12} \times (T/298)^{2.08} \times \exp(-1524/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

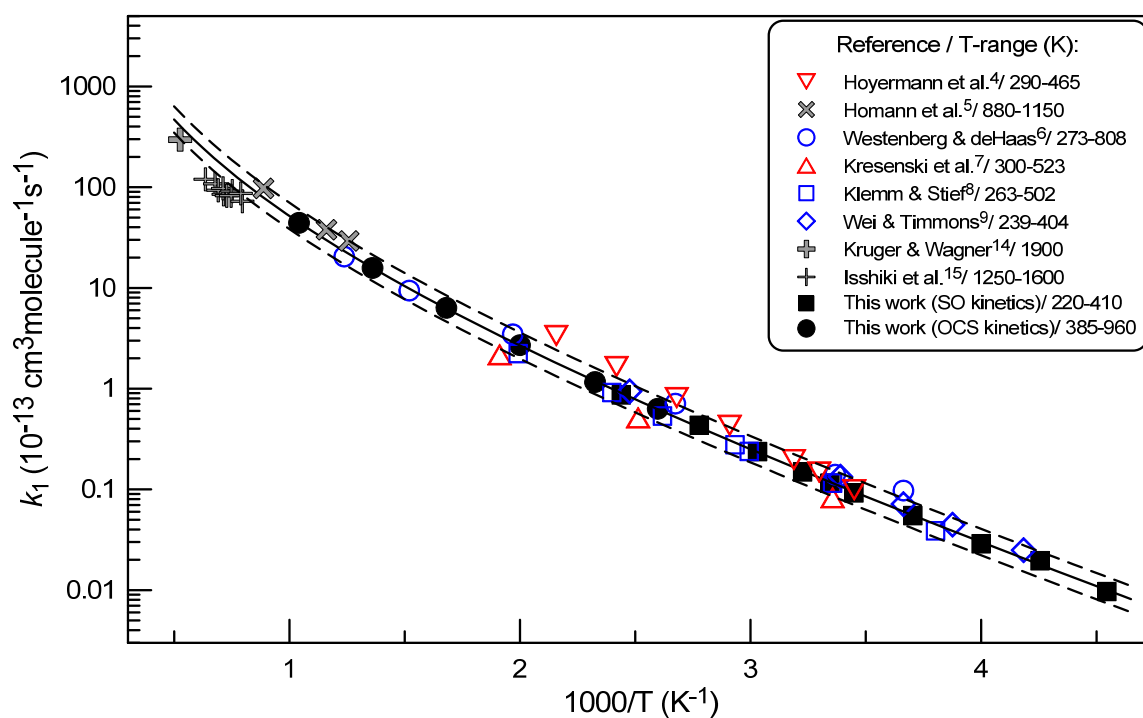


Figure 4. Summary of the temperature dependent measurements of the rate constant of the reaction O+OCS. Uncertainty on the values of k_1 from the present study (nearly 15-20 %) corresponds to the size of the symbols. Solid line: three-parameter fit to the present data; dashed lines: deviation from the three-parameter fit by a factor of 1.35.

This expression, with conservative temperature-independent uncertainty on k_1 of 20%, can be recommended from the present work in the temperature range 220 – 960 K. The dashed lines in Figure 4 represent deviations from the above expression for k_1 by a factor of 1.35, showing

that almost all the previous data fall into this range. This also applies to the previous measurements at $T > 1000$ K (temperatures not covered by the present study), which makes it possible to recommend k_1 defined by the above expression (with the uncertainty factor of 1.35) for use at temperatures up to 2000 K.

Figure 5 demonstrates the available experimental temperature dependent k_1 data in comparison with current recommendations and theoretical calculations of the rate constant. Current recommendation of the NASA Panel for data evaluation, $k_1 = 2.1 \times 10^{-11} \exp(-2200/T)$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at $T = (239 - 808)$ K,¹⁸ adequately represents the experimental data at low temperatures, however underestimates k_1 at $T > 600$ K. Similar expression for k_1 is recommended by the IUPAC Subcommittee on kinetic data evaluation: $k_1 = 1.6 \times 10^{-11} \exp(-2150/T)$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at $T = (230 - 500)$ K.²⁵

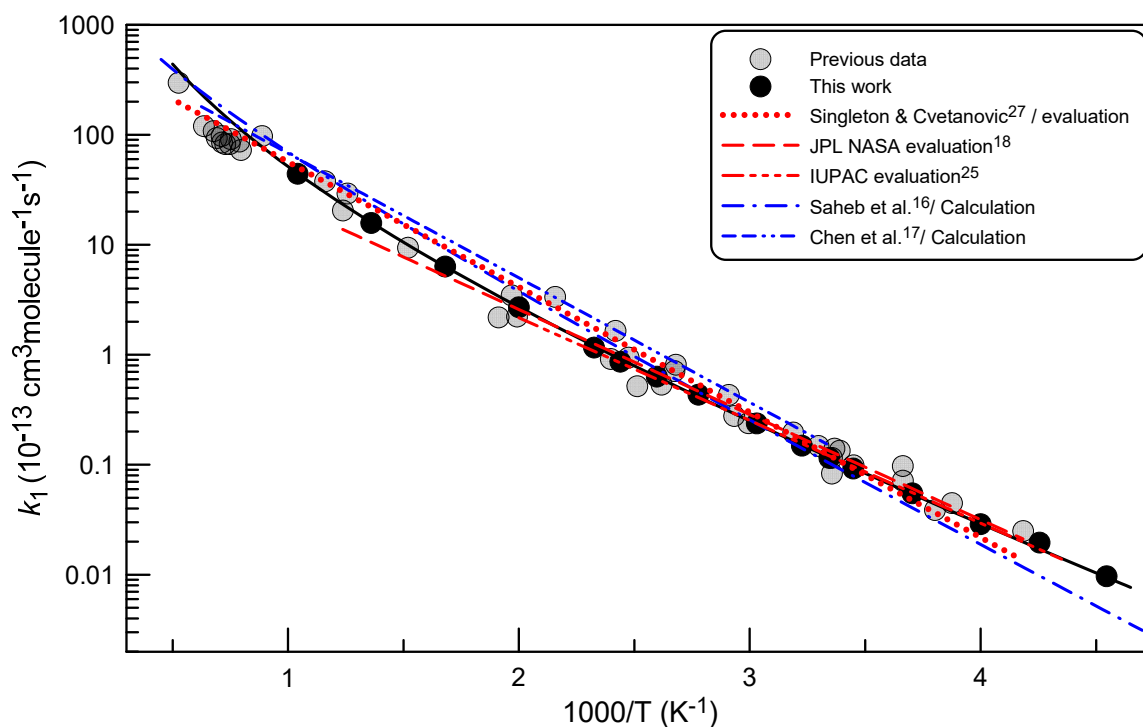


Figure 5. Available experimental temperature dependent data for k_1 in comparison with current recommendations and computational studies.

In a theoretical study of the $\text{O} + \text{OCS}$ reaction, Saheb et al.¹⁶ calculated the following non-Arrhenius expressions for two reaction channels: $k_{1a} = 1.14 \times 10^{-12} \times T^{0.6} \times \exp(-2430/T)$ and $k_{1b} =$

$5.83 \times 10^{-14} \times T^{0.87} \times \exp(-3600/T)$ cm³molecule⁻¹s⁻¹ at T = (200 – 2500) K. In another, more recent theoretical study, Chen et al.¹⁷ predicted $k_{1a} = 6.37 \times 10^{-11} \exp(-2461/T)$, $k_{1b} = 1.08 \times 10^{-10} \exp(-4615/T)$ and $k_1 = k_{1a} + k_{1b} = 9.2 \times 10^{-11} \exp(-2607/T)$ cm³molecule⁻¹s⁻¹ at T = (300 – 1600) K. The resulting total rate constants, $k_1 = k_{1a} + k_{1b}$, from both computational studies are shown in Figure 5. The calculated values of k_1 are fairly close to the experiment; however, do not adequately reflect the curvature of the Arrhenius plot.

3.2. Products of reaction 1. In accordance with available experimental and theoretical data for the reaction products (although very scarce), one would expect that in the temperature range of this work, channel 1a of the O+OCS reaction would be the dominant one with the branching ratio more than 80 %. We have verified this point by measuring the yield of SO, product of reaction 1a, at T = 700 K. To avoid measuring absolute concentrations and thus improve the precision of the measurements, we used a relative method to determine the k_{1a}/k_1 ratio. Experiments consisted in a consecutive titration of the initial concentration of O-atoms with OCS and thirane accompanied with a direct detection of the reaction product, SO. Thereby the yield of SO in reaction 1 was measured relatively to that in the reaction of oxygen atoms with C₂H₄S, where the yield of SO is 100%:



$$k_4 = 1.34 \times 10^{-11} \exp(-4/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (T = 268 – 424 K).}^{26}$$

The observed data are shown in Figure 6. The slope of the line in Figure 6 corresponds to the branching ratio for the SO forming channel of reaction 1: $k_{1a}/k_1 = 0.922 \pm 0.008$ (2 σ).

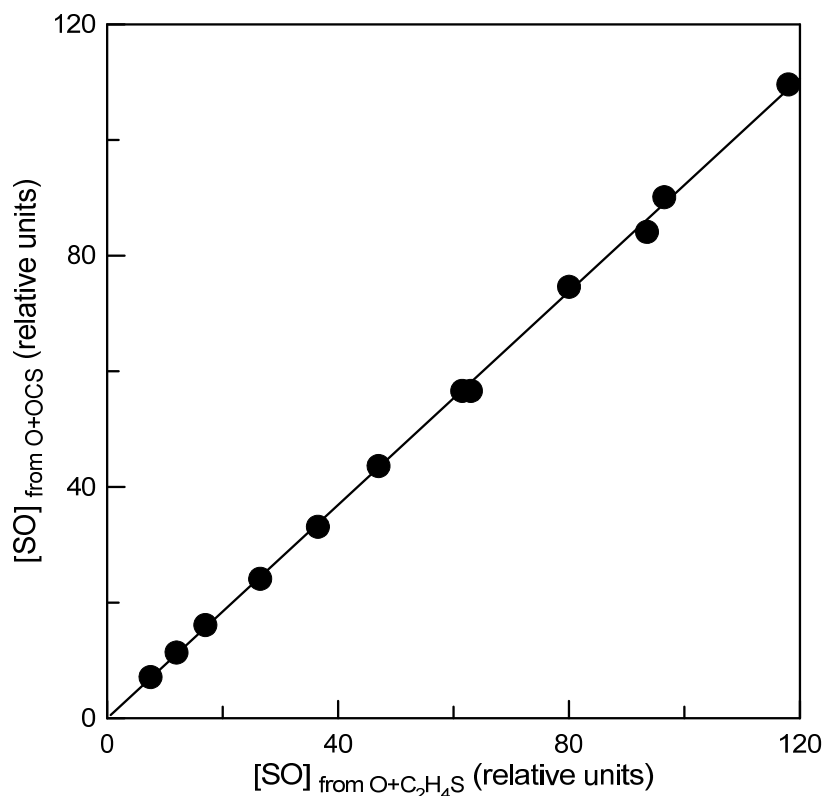


Figure 6. Concentration of SO radicals formed in reaction of O atoms with OCS as a function of the concentration of SO formed in reaction O+C₂H₄ upon consumption of the same concentration of oxygen atoms.

The main part of the experiments on the measurements of the reaction products in the present study was focused on the determination of the branching ratio for the minor channel of reaction 1, forming S and CO₂, and consisted in the determination of the CO₂ yield. Experiments were conducted in an excess of oxygen atoms ($[O] = (0.35 - 1.25) \times 10^{14}$ molecule cm⁻³) over OCS in order, among other things, to minimize the contribution of OCS to the mass spectrometric signal of CO₂ due to dissociative ionization of OCS in the ion source of the mass spectrometer ($m/z = 44$, CS⁺). Reaction time was in the range (0.025-0.070) s and consumption of OCS was between 65 and 97 %, depending on concentration of oxygen atoms and temperature in the reactor. The concentration of CO₂ was measured as a function of [OCS] consumed. Some typical experimental data are shown in Figure 7. All the results obtained for the yield of CO₂ (corresponding to k_{1b}/k_1 ratio) from slopes of the straight lines like those in Figure 7 are presented in Table S1 and in Figure 8 in comparison with existing experimental

and computational data. The estimated combined uncertainty of about 10 % on the branching ratio is mainly due to the precision of the measurements of the absolute concentrations of OCS and CO₂.

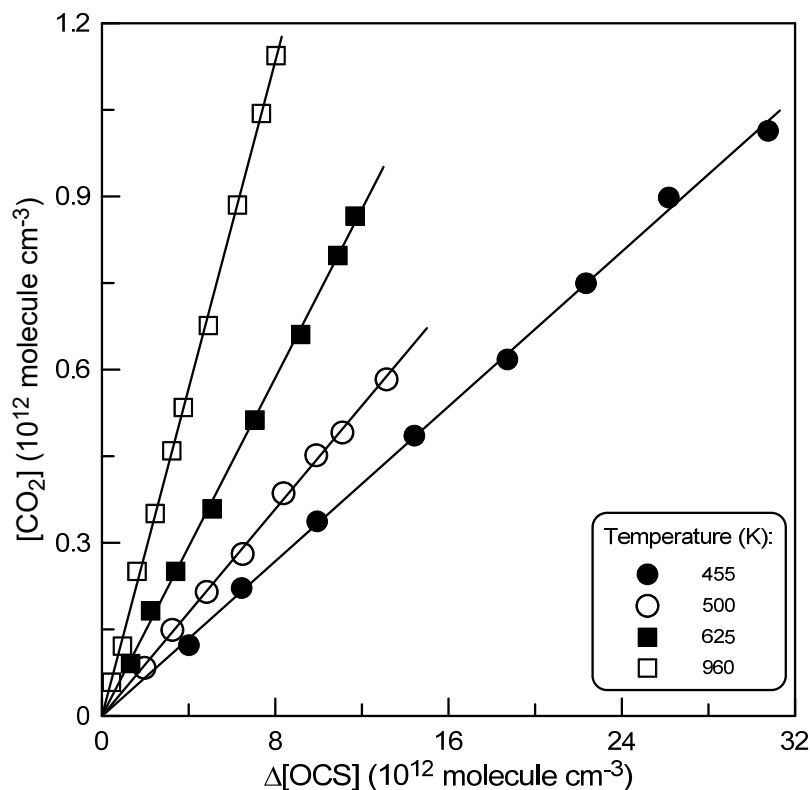


Figure 7. Concentration of CO₂ formed in reaction of O atoms with OCS as a function of the consumed concentration of OCS.

It can be noted that the CO₂ yield (k_{1b}/k_1) at $T = 700$ K is in good agreement with the results for the SO yield (k_{1a}/k_1) discussed above. Isshiki et al.¹⁵ have determined the k_{1b} to k_1 ratio by analysis of time profiles of the S atom upon photolysis of COS and SO₂ mixtures diluted in Ar behind reflected shock waves. Their results are quite consistent with the extrapolation (which is, of course, conditional) of our data to the corresponding temperatures. As for the theoretical calculations of k_{1b}/k_1 presented in Figure 8, one can note that those of Saheb et al.¹⁶ describe quite well the temperature behavior observed for k_{1b}/k_1 in the present work, although in absolute value they are shifted down by a factor of ≈ 1.6 .

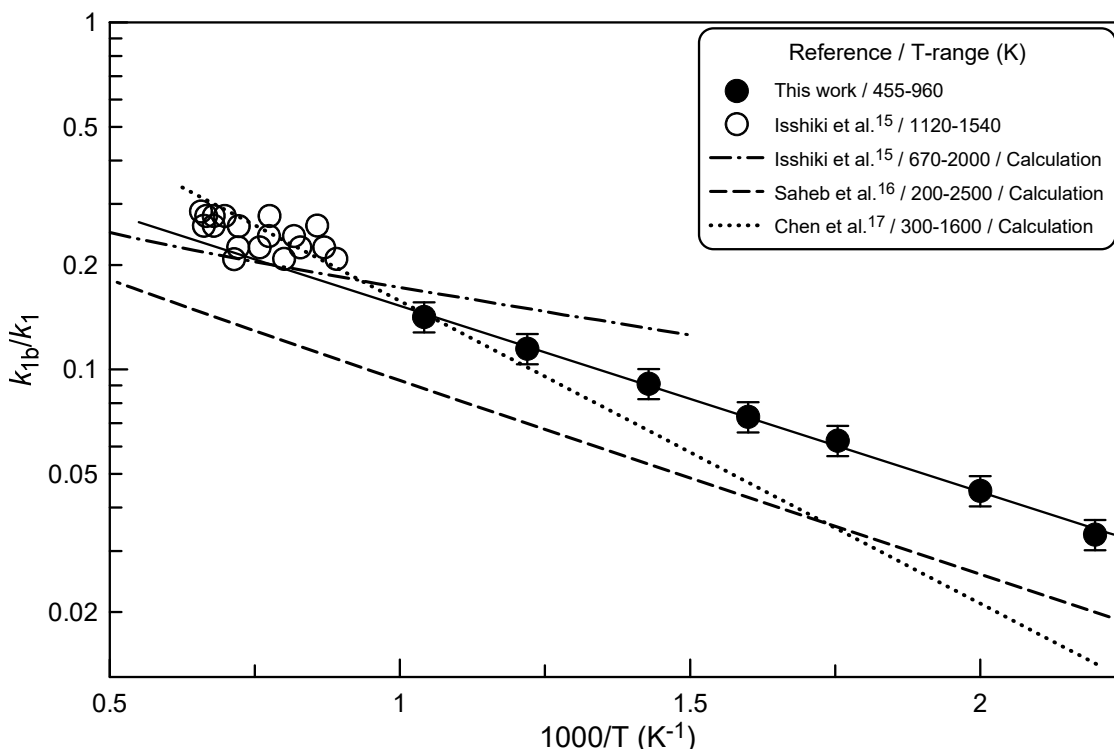


Figure 8. Branching ratio for the S+CO₂ forming channel 1b of the reaction O+OCS as a function of temperature.

Using the branching ratio data and the modified Arrhenius expression for the total rate constant from the present study, the absolute value of k_{1b} at respective temperatures can be calculated. The values of k_{1b} determined in this way are shown in Figure 9 along with previous measurements and theoretical calculations. The estimated combined uncertainty on the present k_{1b} data is 20-25 %. The temperature dependence of k_{1b} is well described by the following Arrhenius expression:

$$k_{1b} = (4.19 \pm 0.34) \times 10^{-11} \exp(-4088 \pm 46/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at $T = 455 - 960$ K and with 2σ statistical uncertainties. This expression can be used to derive k_{1a} by subtracting k_{1b} from the experimental data for k_1 (Table 1). The fit of three-parameter modified Arrhenius expression to obtained in this way ($k_1 - k_{1b}$) results in

$$k_{1a} = 2.35 \times 10^{-12} \times (T/298)^{1.84} \times \exp(-1585/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

It can be noted that in the temperature range of the study, the sum of the two partial rate constants, $k_1 = k_{1a} + k_{1b}$, provides the values of k_1 similar (within 0.6 %) to those calculated

using the modified Arrhenius expression derived for k_1 above. The present experimental data for k_1 and k_{1b} support the statement of Isshiki et al., that "the increase of the activation energy with increasing temperature for the calculated overall rate constants is mainly due to the thermal nature of partition functions, rather than the increasing contribution of the substitution channel."¹⁵

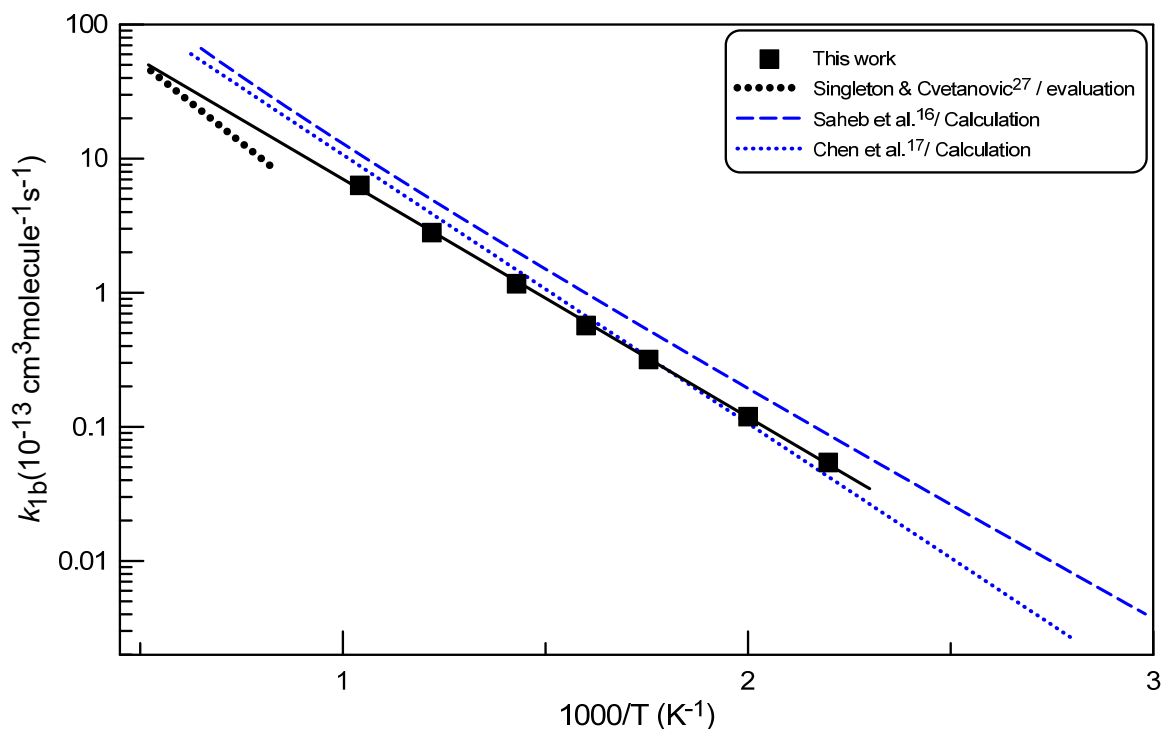


Figure 9. Temperature dependence of k_{1b} observed in the present work and in previous studies.

The k_{1b} data at $T = 1200 - 1900$ K from the review of Singleton and Cvetanovic,²⁷ shown in Figure 9, correspond, in fact, to unpublished, to our knowledge, experimental results from the dissertation of T. Topaloglu. Extrapolation of the current Arrhenius curve of k_{1b} to this temperature range shows that the results of two studies are in satisfactory agreement with a maximum deviation of a factor of 1.5 at the lowest temperature $T = 1200$ K. Computational data of Chen et al.¹⁷ reproduce quite well the experimental values of k_{1b} , at least, in the temperature range of the present study, while the calculations of Saheb et al.¹⁶ describe well the observed temperature behavior of the rate constant.

CONCLUSIONS

In this study, a discharge flow reactor combined with an electron impact ionization mass spectrometer is employed to measure the total rate constant of the reaction of O(³P) atoms with carbonyl sulfide as well as the branching ratio for the minor, S+CO₂ forming, channel of the reaction. Analysis of the previous data shows that the modified Arrhenius expression $k_1 = 1.92 \times 10^{-12} \times (T/298)^{2.08} \times \exp(-1524/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained at $T = 220 - 960 \text{ K}$ can be recommended to calculate k_1 at temperatures up to 2000 K. The measurements of CO₂ yield resulted in a first determination of the rate constant of the corresponding reaction pathway, $k_{1b} = 4.19 \times 10^{-11} \times \exp(-4088/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 455-960 \text{ K}$. Comparison of the current data with computational studies shows that the latter describe the reaction quite adequately. The present kinetic data for k_1 and k_{1b} provide an experimental dataset for use in atmospheric chemistry and combustion modelling and in refining theoretical models.

Supporting Information. Diagram of the flow reactor (Figure S1); rate of SO production in reaction 1 as a function of the product of the concentrations of OCS and O (Figure S2); example of concentration-time profiles of OCS in reaction with excess O (Figure S3); branching ratio for the S + CO₂ forming channel of reaction 1 (Table S1).

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TOC Graphic

