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Reaction of $O(^3P)$ with Carbon Disulfide: Kinetics and Products

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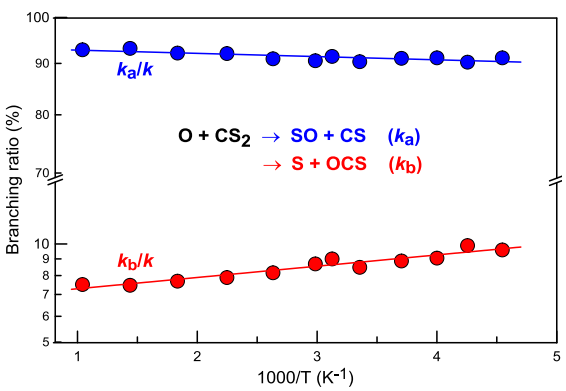
ABSTRACT

The kinetics and products of the reaction of ground-state O atom with carbon disulfide, of interest for atmospheric and combustion chemistry, were studied using a discharge-flow system combined with modulated molecular beam mass spectrometry. The total reaction rate constant was determined either in an absolute way from kinetics of CS_2 consumption and reaction product, SO radical, formation and employing a relative rate method with two reference reactions: k_1 = (3.35±0.10)×10^{-11}exp(-(665±15)/T) $cm^3molecule^{-1}s^{-1}$ at T= 220-960 K, with estimated independent of temperature uncertainty of 15 %. The yields of two reaction products, SO and OCS, were determined at T = 220 – 960 K, resulting in the following expressions for the branching ratio of the corresponding (SO + CS and OCS + S forming) reaction pathways: k_{1a}/k_1 = (0.935±0.005)×exp(-(7.4±0.2)/T) and k_{1b}/k_1 = (0.067±0.002)×exp(80±8/T), where the uncertainties reflect the statistical 2σ precision. The reaction rate constant and product data from the present work are discussed in comparison with previous experimental and theoretical studies.

Keywords: carbon disulfide, oxygen atom, OCS, kinetics, atmospheric chemistry

TOC Graphic



1. INTRODUCTION

Oxidation of reduced sulfur species such as H_2S, OCS and carbon disulfide (CS_2) is of great interest for atmospheric chemistry,[1] combustion[2] and a number of industrial processes.[3] In the present work, we report the results of an experimental kinetics and product study of the reaction of ground-state oxygen atom with carbon disulfide. CS_2 is one of the principal sulfur compounds in the atmosphere. Emitted by biomass burning, oceans and industrial processes, CS_2 is relatively rapidly oxidized in the troposphere (mainly, in reaction with OH radicals, lifetime of ~ 1 week) leading to production of OCS.[4] Tropospheric oxidation of CS_2 is an important source of OCS, the further photooxidation of which in the stratosphere leads to the formation of sulphate aerosols impacting the concentration of stratospheric ozone and the radiative properties of the atmosphere.[4] O-atom initiated oxidation of CS_2 is negligible in the troposphere due to low concentrations of oxygen atoms; however, the title reaction can be an important removal process of CS_2 in the stratosphere upon direct injection of carbon disulfide into the stratosphere during volcanic eruptions. The estimated global volcanic input of CS_2 into the stratosphere is comparable with that of OCS: (1.3×10^{7}-4.4×10^{10}) and (9.4×10^{7}-3.2×10^{11}) g/yr, respectively.[5] In this respect, the information on the kinetics of the title reaction

$$O + CS_2 \rightarrow \text{products} \qquad (1)$$

at low stratospheric temperatures as well as at high near-source volcanic plume temperatures is of importance.

In the past, the kinetics of the title reaction has been extensively studied.[6-15] The interest in this reaction was mainly due to its importance for the development of a chemical laser based on the emission of the vibrationally excited carbon monoxide formed in the sequence of the reactions:

$$O + CS_2 \rightarrow CS + SO \qquad (1a)$$

$$O + CS \rightarrow S + CO^* \quad (2)$$

The previous kinetic data obtained for k_1 in different and limited temperature ranges (between 218 and 500 K) are generally consistent within a factor of 1.5. However, only one measurement is available for k_1 at T > 500K.[6]

Reaction 1 has three exothermic channels:[16]

$$O + CS_2 \rightarrow SO + CS \qquad \Delta_r H° = -19.4 \text{ kcal mol}^{-1} \quad (1a)$$

$$\rightarrow S + OCS \qquad \Delta_r H° = -55.1 \text{ kcal mol}^{-1} \quad (1b)$$

$$\rightarrow CO + S_2 \qquad \Delta_r H° = -83.1 \text{ kcal mol}^{-1} \quad (1c)$$

Information on the branching ratios of different reaction pathways as a function of temperature is important for atmospheric chemistry and combustion, CS_2 based laser performance and is of great fundamental interest for the theory of elementary reactions. Despite this, the current quantitative data on the products of $O+CS_2$ reaction are extremely scarce and are limited to two determinations of k_{1b}/k_1[10,14] and k_{1c}/k_1.[13-14]

The aim of this work was to fill the gaps in the available data on the kinetics and products of reaction 1 by measuring the total reaction rate constant and determining the branching ratios for the possible reaction pathways over an extended temperature range, T = 220 – 960 K.

2. EXPERIMENTAL

Experiments have been carried out in a discharge-flow apparatus at total pressure of 2 Torr of Helium using electron-impact ionization (25–30 eV energy) mass spectrometry to measure the concentrations of the species involved.[17-20] The flow reactor used at low temperatures, T = 220 – 320 K, consisted of a halocarbon wax coated Pyrex tube (45 cm length and 2.4 cm i.d.) (Figure S1, Supporting Information (SI)). The temperature in the reactor was controlled by circulating thermostated ethanol. The high temperature reactor, employed at T = 300 – 960 K,

was an electrically heated Quartz tube (45 cm length and 2.5 cm i.d.) with water-cooled extremities (Figure S2, SI).[17]

Oxygen atoms detected by mass spectrometry at their parent peak, m/z = 16 (O^+), were produced using two different methods: discharging of trace amounts of O_2 in He and through rapid reaction of N atoms (produced in a microwave discharge of N_2/He mixtures) with NO,

$$N + NO \rightarrow O + N_2 \quad (2)$$

$k_2 = 2.1 \times 10^{-11} \exp(100/T)$ cm^3 molecule^{-1} s^{-1} (T = 196 – 370 K),[16]

To ensure accurate measurements of the absolute concentrations of O atoms, three independent methods were used, all of which gave consistent results with an accuracy of 10%. In the first one, the O concentrations were determined from the decrease in the O_2 concentration upon initiation of the microwave discharge ($\Delta[O_2] = 2[O]$). In another method, oxygen atoms were titrated with an excess of NO_2,

$$O + NO_2 \rightarrow NO + O_2 \quad (3)$$

$k_3 = (6.1 \pm 0.4) \times 10^{-12} \exp((155 \pm 18)/T)$ cm^3 molecule^{-1} s^{-1} (T = 220 – 950 K),[18]

and their absolute concentrations could be determined from the consumed fraction of NO_2: $[O] = \Delta[NO_2]$. Finally, the absolute concentrations of oxygen atoms could also be determined using their titration by C_2H_4S ($[O] = [SO] = \Delta[C_2H_4S]$):

$$O + C_2H_4S \rightarrow SO + C_2H_4 \quad (4)$$

$k_4 = 1.13\times10^{-12} (T/298)^{2.18} \exp(733/T)$ cm^{3}molecule^{-1}s^{-1} (T = 220 – 950 K)[20]

This procedure was also employed for the measurements of the absolute concentrations of SO.

All stable species (CS_2, OCS, C_2H_4S, O_2, NO_2, NO and Br_2) were detected by mass spectrometry at their parent peaks. Their absolute concentrations were derived from measured flow rates of their manometrically prepared gas mixtures.

He (carrier gas) and O_2 were taken directly from high-pressure tanks and had stated purities better than 99.99% (Alphagaz). NO_2, NO were Alphagaz products (> 99.9%). The purities of CS_2 (Aldrich), OCS (15% in He, Messer), C_2H_4S (Merck) and Br_2 (Aldrich) were ≥ 99.9, 99.99, 98 and 99.99%, respectively.

3. RESULTS AND DISCUSSION

3.1. Absolute measurements of k_1. In most experiments, the rate constant of the title reaction was determined from decays of CS_2 ($[CS_2]_0$ = (4-7)×10^{10} molecule cm^{-3}) monitored under pseudo-first order conditions in excess of oxygen atoms (see Table 1 for concentrations of O). Under the employed pseudo-first-order conditions, the concentration of CS_2 may be expressed as $[CS_2] = [CS_2]_0 \times \exp(-k_1' \times t)$ with the pseudo-first-order rate constant given by $k_1' = k_1[O]$. The consumption of oxygen atom was observed to be negligible (no more than a few percent) in all the experiments due to its high enough excess over CS_2 and relatively low rate of heterogeneous loss on the wall of the flow reactor (k_w < 2 s^{-1}). Examples of the observed concentration-time profiles of CS_2 are shown in Figure S3 (SI). Figure 1 shows the pseudo-first order rate constants, $k_1' = k_1[O]$, as a function of the concentration of oxygen atoms. The slopes of the straight lines in Figure 1 (linear through origin fit to the experimental data) provide the values of k_1 at respective temperatures, shown in Table 1.

For more confidence in the above measurements carried out in an excess of oxygen atoms, we conducted additional experiments (at T = 815 K), where k_1 was determined under pseudo-first order conditions, however, this time in an excess of CS_2 over the oxygen atoms. Due to the difficulty of controlling low concentrations of oxygen atoms with mass spectrometry, in these experiments, the kinetics of SO formation was monitored. The kinetics of the reaction product follows the following expression: $[SO] = \alpha \times ([O]_0 - [O]_0 \times \exp(-k_1't))$, where α is the branching ratio for SO forming channel of reaction (1) (≈ 0.93 at T = 815 K,

see below). Rearrangement of this expression results in $[SO]_\infty$ - [SO] = $[SO]_\infty \times \exp(-k_1't)$, where $[SO]_\infty = \alpha \times [O]_0$ and $k_1' \approx k_1 \times [CS_2]$, considering negligible heterogeneous loss of O atoms.

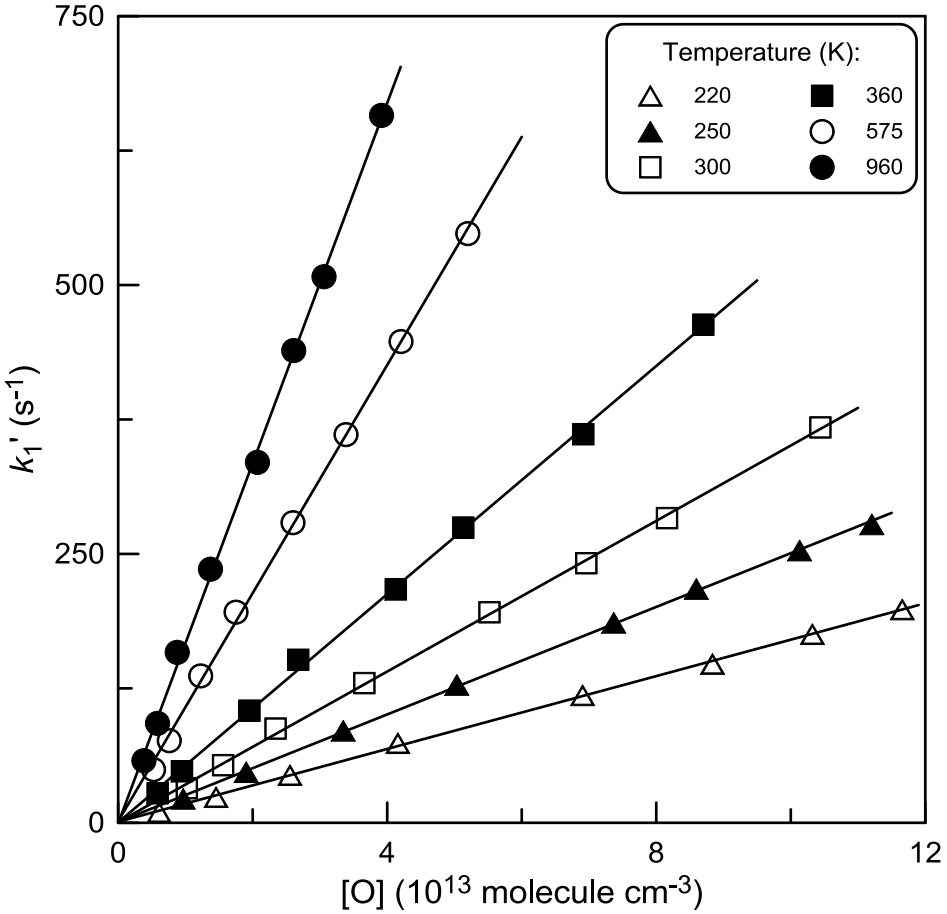


Figure 1. Pseudo-first order rate constant, $k_1' = k_1[O]$, as a function of the O-atom concentration at different temperatures.

In experiments, the kinetics of SO growth was monitored and $[SO]_\infty$ was determined upon total consumption of oxygen atoms. The observed dependence of the pseudo-first-order rate constant, $k_1' \approx k_1 \times [CS_2]$, versus CS_2 concentration is shown in Figure S4 (SI). The slope of the straight line in Figure S4 provides k_1 (± 2σ) = $(1.53 \pm 0.04) \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ at T= 815 K, in good agreement with the k_1 data obtained from the kinetics of CS_2 consumption (Table 1). It should be noted that initial concentration of O atoms in these experiments was low

enough ($[O]_0 \approx 1.5\times10^{11}$ molecule cm^{-3}) to minimize the potential impact of the secondary reaction

$$O + CS \rightarrow CO + S \qquad (2)$$

$k_2 = 2.7\times10^{-10} \exp(-760/T)$ $cm^3 molecule^{-1} s^{-1}$ (T = 150 – 305 K)[16]

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

T (K)[a]	[O][b]	*k*[c]	Reactor surface[d]
220	0.61-11.7	1.69	HW
235	0.62-11.4	1.94	HW
250	0.97-11.2	2.50	HW
270	0.60-11.3	2.85	HW
295	0.63-8.99	3.42	HW
300	1.02-10.4	3.50	Q
320	0.48-9.58	4.20	HW
335	0.22-5.97	4.31	Q
360	0.59-8.70	5.30	Q
380	0.27-6.71	5.57	Q
410	0.63-7.15	6.42	Q
445	0.38-4.85	7.19	Q
500	0.39-5.96	8.61	Q
545	0.27-4.14	10.1	Q
575	0.53-5.20	10.6	Q
695	0.29-3.64	12.5	Q
720	0.35-4.29	13.6	Q
885	0.38-3.19	16.5	Q
960	0.38-3.92	16.7	Q

[a] 8-12 kinetic runs with different [O] at each temperature. [b] Units of 10^{13} molecule cm^{-3}. [c] units of 10^{-12} $cm^3 molecule^{-1} s^{-1}$; statistical 2σ uncertainty is ≤ 2%; total estimated uncertainty is 15 %. [d] HW: halocarbon wax; Q: quartz.

3.2. Relative measurements of k_1. In this series of experiments, the rate constant of reaction 1 was determined using conventional relative rate method, which consisted of the

measurements of the consumption of CS_2 and reference compound, NO_2 (reaction 3) or Br_2, in reactions with oxygen atoms:

$$O + CS_2 \rightarrow \text{products} \quad (1)$$

$$O + Br_2 \rightarrow Br + BrO \quad (5)$$

$k_5 = 9.85\times10^{-16}\times T^{1.41} \exp(543/T)$ $cm^3 molecule^{-1} s^{-1}$ (T = 220 – 950 K)[18]

The relative consumptions of CS_2 and reference compound in the reaction with O-atoms are related by the ratio of the corresponding rate constants:

$$\ln\frac{[CS_2]_0}{[CS_2]} = \frac{k_1}{k_{\text{ref}}} \times \ln\frac{[\text{Ref}]_0}{[\text{Ref}]} \quad (\text{I})$$

The typical dependences of $\ln([CS_2]_0/[CS_2])$ on $\ln([NO_2]_0/[NO_2])$ and $\ln([Br_2]_0/[Br_2])$ presented in Figures 2 and S5 (SI), respectively, allow, according to eq. I, to determine the ratio of the respective rate constants.

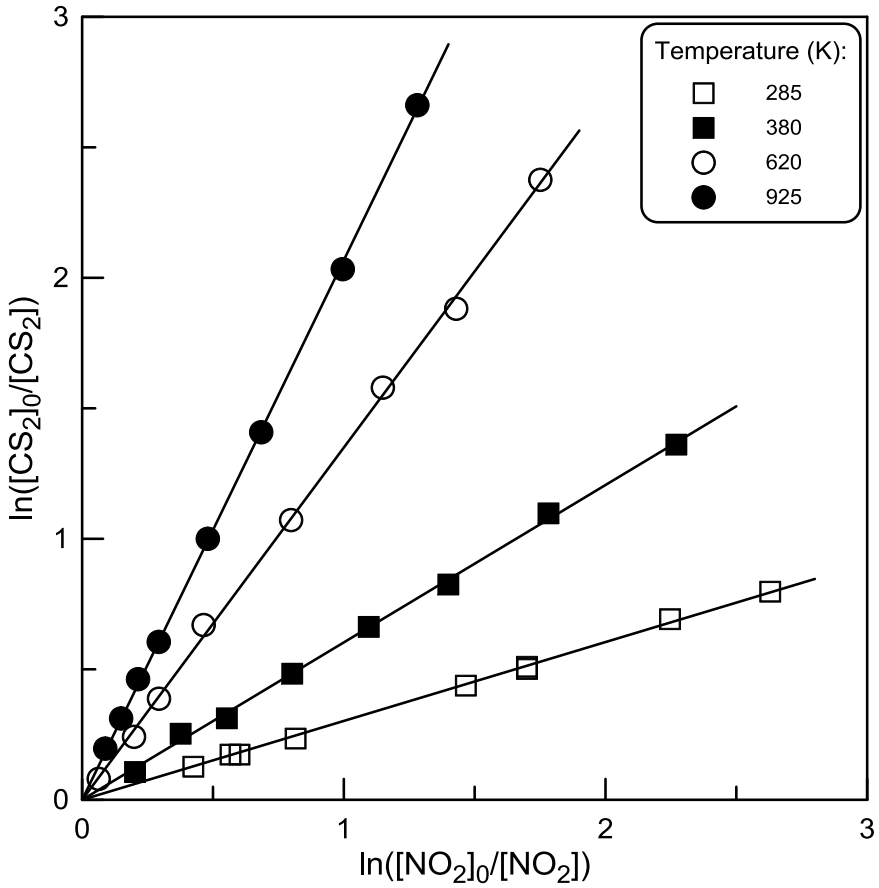


Figure 2. Examples of the dependence of $\ln([CS_2]_0/[CS_2])$ on $\ln(NO_2]_0/[NO_2])$ observed at different temperatures.

These data as well as the final values of k_1 calculated with $k_3 = 6.1 \times 10^{-12}$ exp(155/T) and $k_5 = 9.85\times10^{-16}\times T^{1.41}$ exp(543/T) $cm^3molecule^{-1}s^{-1}$ (T = 220 – 950 K)[17] are given in Table 2.

The possible impact of secondary chemistry on the results of the relative rate measurements can be discussed. When reaction 5 is used as a reference one, the most probable secondary reactions potentially leading to the additional consumption of CS_2 and Br_2 are

$$Br + CS_2 \rightarrow \text{products} \quad (6)$$

$$BrO + CS_2 \rightarrow \text{products} \quad (7)$$

$$S + Br_2 \rightarrow SBr + Br \quad (8)$$

$k_8 = (9.5 \pm 1.7)\times10^{-11}$ $cm^3molecule^{-1}s^{-1}$ (T = 298 K)[21]

Overall, the impact of the secondary reactions was minimized by use of the relatively low concentrations of CS_2 and Br_2: $(4 – 5)\times10^{10}$ and $((5 – 6)\times10^{11}$ molecule cm^{-3}, respectively, and short reaction time ≤ 0.01 s. Reactions of Br and BrO with CS_2 are too slow to contribute to CS_2 consumption. This could be verified directly by mixing Br and BrO, generated in the reaction of O atoms with excess Br_2 in the movable injector, with CS_2 in the main reactor. For example, the upper limit of 10^{-15} $cm^3molecule^{-1}s^{-1}$ was determined for the rate constant of reaction 6 at T = 298 – 960 K. Although the rate constant of reaction 8 is very high, S-atoms formed in reactions 1b and 2 are partly removed by O_2, which was present in the reactive system in concentrations at least by two orders of magnitude higher than that of Br_2:

$$S + O_2 \rightarrow SO + O \quad (9)$$

$k_9 = 1.6\times10^{-12}$ exp(100/T) $cm^3molecule^{-1}s^{-1}$ (T = 252 - 878 K)[16]

In addition, in order to minimize the possible contribution of reaction 8 to the consumption of Br_2 compared to the primary reaction with oxygen atoms, the initial concentrations of Br_2 in these experiments were more than an order of magnitude higher than those of CS_2. Similarly, in the experiments where reaction $O+NO_2$ was used as a reference, to minimize the relative

contribution of the reactions of S and SO with NO_2 much higher concentrations of NO_2 compared to $[CS_2]$ were used ($[NO_2]_0/[CS_2]_0 > 50$):

$$S + NO_2 \rightarrow SO + NO \quad (10)$$

$k_{10} = 4.9\times10^{-10} \exp(84/T)$ cm^{3}molecule^{-1}s^{-1} (T = 296 - 410 K)[22]

$$SO + NO_2 \rightarrow SO_2 + NO \quad (11)$$

$k_{11} = 6.7\times10^{-12} \exp(295/T)$ cm^{3}molecule^{-1}s^{-1} (T = 220 - 960 K)[23]

Table 2. Summary of the Relative Measurements of k_1

T (K)	k_1/k_{ref} (±2σ)	k_1[a]	Reference reaction
260	0.232±0.002	2.56	$O+NO_2$
285	0.307±0.007	3.22	$O+NO_2$
305	0.374±0.005	3.79	$O+NO_2$
345	0.254±0.008	4.57	$O+Br_2$
380	0.603±0.010	5.53	$O+NO_2$
530	0.486±0.016	9.25	$O+Br_2$
620	1.350±0.022	10.6	$O+NO_2$
850	0.582±0.009	14.7	$O+Br_2$
925	2.068±0.016	14.9	$O+NO_2$

[a] Units of 10^{-12} cm^3 molecule^{-1} s^{-1}, estimated total uncertainty on k_1 is nearly 20% and includes that on reference reaction.

3.3. Temperature dependence of k_1. All available kinetic data for the temperature dependence of k_1 are shown in Figure 3. One can note good agreement between the results obtained in the present work using different methods: the absolute one with monitoring of CS_2 and SO kinetics and relative rate method employing two reference reactions. The exponential fit to the present absolute measurements of k_1 (solid line in Figure 3) yields the following Arrhenius expression:

$k_1 = (3.35\pm0.10)\times10^{-11}\exp(-(665\pm15)/T)$ cm^{3}molecule^{-1}s^{-1} at T= 220-960 K,

where quoted uncertainties represent statistical 2σ precision on the fit. The overall uncertainty on k_1 was estimated to be about 15% combining statistical error (≤ 2%) and those on the

measurements of the absolute concentration of O atoms (~10%), flows (3%), pressure (2%) and temperature (1%).

The present value of the rate constant at T = 300 K, k_1 = (3.65±0.55)×10^{-12} $cm^3molecule^{-1}s^{-1}$, is in good agreement with previous room temperature measurements (T = 298-302 K, not shown in Figure 3) of Callear and Hedges, 3.65,[9] Slagle et al., 4.0±0.3[10] and Borisenko et al., (3.6±0.1)×10^{-12} $cm^3molecule^{-1}s^{-1}$.[15] Temperature dependent data from the present work agree within the experimental uncertainty with previous measurements by Smith,[7] Westenberg and deHaas,[8] Wei and Timmons,[11] Graham and Gutman.[12] However, the present measurements of k_1 at high temperatures are lower by a factor of 1.5-1.9 than those of Homann et al. (T = 695 – 920 K).[6] Homann et al.,[6] using an experimental setup similar to that of the present study, determined the rate constant of reaction 1 from the kinetics of CS_2 consumption and SO formation in an excess of O atoms over CS_2. In our opinion, the most likely reason for the discrepancy between the two studies is the accuracy of the measurement of the absolute concentrations of oxygen atoms in the work of Homann et al.,[6] although, unfortunately, the relevant experimental details are not presented in their work. It can be added that in this work we used four different methods for determining k_1 at elevated temperatures (Figure 3), and all of them led to similar (within an uncertainty of 15%) values of the rate constant.

Current recommendation of the NASA Panel for data evaluation, k_1 = 3.2×10^{-11} exp(-650/T) $cm^3molecule^{-1}s^{-1}$ at T = (218 – 543) K (dotted line in Figure 3),[16] is practically identical to the Arrhenius expression for k_1 derived in the present study. In a theoretical study of the O+CS_2 reaction, Saheb[24] calculated the following non-Arrhenius expression for the overall rate constant: k_1 = 8.38×10^{-13}×$T^{0.54}$×exp(-506/T) $cm^3molecule^{-1}s^{-1}$. The calculations of Saheb[24] are in very good agreement with our experimental data, although we do not observe a slight curvature of the Arrhenius plot predicted by theory (Figure 3).

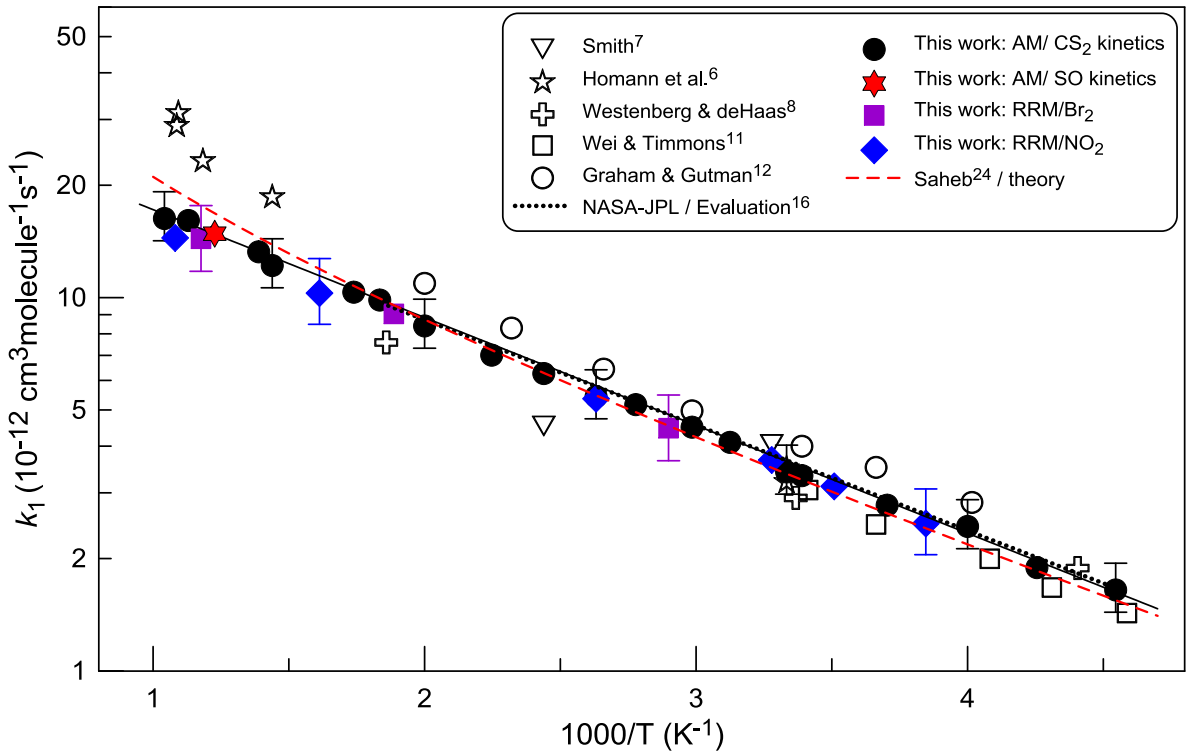


Figure 3. Summary of the temperature dependent measurements of the rate constant of the reaction O+CS_2. Partially shown error bars on the values of k_1 from the present study correspond to the estimated 15 and 20% uncertainties on the absolute and relative measurements, respectively.

The rate of CS_2 removal in the stratosphere by atomic oxygen can be roughly compared with that in reaction with OH radical:

$$OH + CS_2 \rightarrow CS_2OH\ (+O_2) \rightarrow \text{products} \qquad (12)$$

$k_{12} = (1.256\times10^{-16}\ \exp(4550/T))/(T+1.81\times10^{-3}\ \exp(3400/T))\ cm^3molecule^{-1}s^{-1}$ [16]

So, for example, at altitudes of 25-30 km, the rate constants of the respective reactions are: $k_1 \approx 2\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ (this work) and $k_{12} \leq 10^{-11}$ $cm^3molecule^{-1}s^{-1}$ (upper limit because the recommended expression is for the total pressure of one atmosphere).[16] Considering that concentration of atomic oxygen at these altitudes (> 10^7 molecule cm^{-3})[25,26] is by two orders of magnitude higher than that of OH radicals (~ 10^5 molecule cm^{-3}),[27] the O-atom initiated oxidation of stratospheric CS_2 is much more efficient process compared with OH+CS_2 reaction, and should be taken into account when modeling the chemistry of sulfur compounds in the stratosphere.

3.4. Products of reaction 1. Experiments were focused on the measurements of SO and OCS yields corresponding to the branching ratios for the reactions 1a and 1b, respectively. The yield of SO in reaction 1 was measured relative to that in reaction of O atoms with thiirane (reaction 4), for which the yield of SO is known to be of nearly 100%.[20] Experiments consisted in a consecutive titration of oxygen atoms with CS_2 and C_2H_4S and detection of the SO formed. Typical experimental data observed at extreme temperatures of the study are shown in Figure 4. The branching ratios for the SO forming channel of reaction 1, determined at different temperatures between 220 and 960 K from slopes of the straight lines like those in Figure 4, are summarized in Table 3.

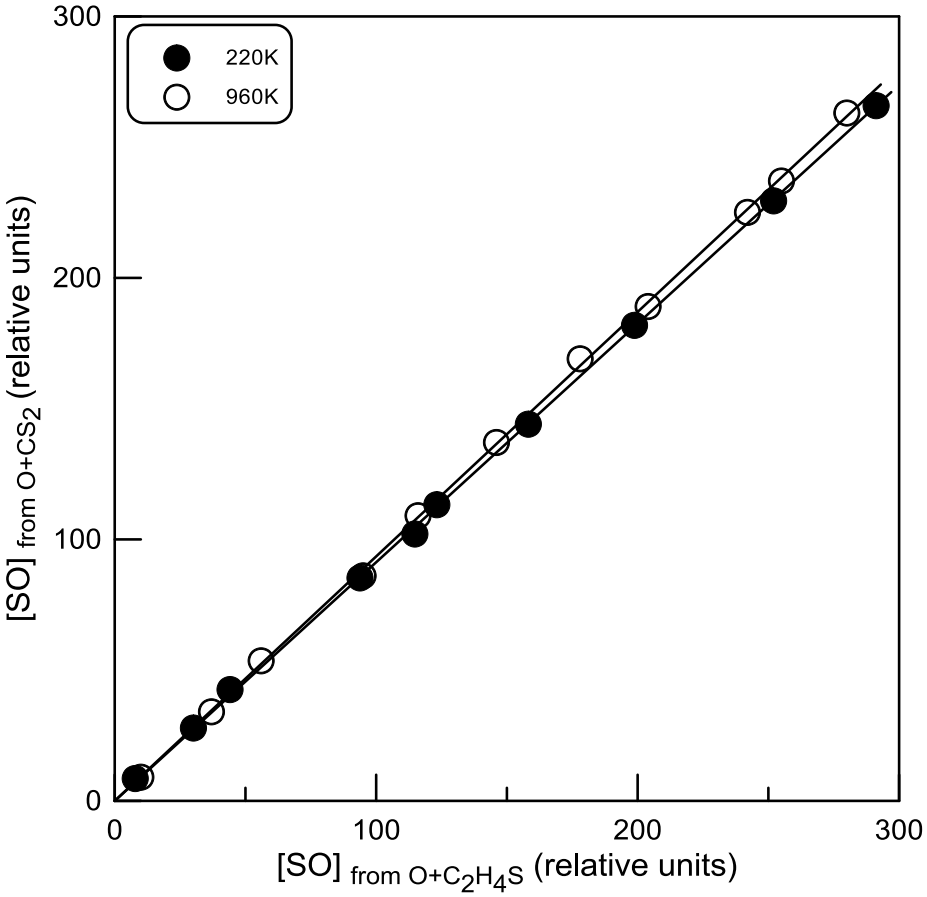


Figure 4. Yield of SO radicals in reaction of O atoms with CS_2 relative to that in reaction $O+C_2H_4S$ upon consumption of the same concentration of oxygen atoms.

Table 3. Branching Ratio Data (%) for the Channels (1a) and (1b) of the $O+CS_2$ Reaction.

T (K)	$100 \times k_{1a}/k_1$ (± 2σ) [a]	$100 \times k_{1b}/k_1$ (± 2σ) [a]	$100 \times (k_{1a}/k_1+k_{1b}/k_1)$
220	91.2±0.4	9.60±0.12	100.8
235	90.3±0.6	9.90±0.06	100.2
250	91.2±0.2	9.06±0.06	100.3
270	91.1±0.2	8.88±0.08	100.0
298	90.4±0.6	8.49±0.04	98.9
320	91.5±0.6	9.01±0.02	100.5
335	90.6±1.8	8.70±0.08	99.3
380	91.0±1.4	8.17±0.11	99.2
445	92.1±0.8	7.90±0.08	100.0
545	92.2±0.6	7.70±0.07	99.9
695	93.2±1.0	7.48±0.06	100.7
960	92.9±0.6	7.52±0.06	100.4

[a] The quoted errors represent the statistical 2σ fit precision, the estimated total uncertainty on k_{1b}/k_1 is about 10%.

In these experiments, the formed concentration of OCS was also measured as a function of consumed concentration of oxygen atoms at T = 380 – 960 K. However, in contrast to the relative measurements of SO yield, the determination of the branching ratio for the OCS-forming channel of reaction 1 required the measurements of the relatively low absolute concentrations of oxygen atoms and those of OCS. The initial concentration of oxygen atoms was determined through their conversion to SO in reaction with excess thiirane: $[O]_0 = [SO]$. The methods employed for the absolute calibration of SO and OCS signals are given in the Experimental section. At lower temperatures (T = 220 – 335 K), where the possible impact on [OCS] of the secondary reaction

$$O + OCS \rightarrow \text{products} \qquad (13)$$

$k_{13} = 1.92\times10^{-12}\times(T/298)^{2.08}\times\exp(-1524/T)$ $cm^3 molecule^{-1} s^{-1}$ at T= 220-960 K.[19]

could be neglected, we conducted a series of experiments in an excess of oxygen atoms over CS_2. Reaction time was in the range (0.02-0.03) s and consumption of CS_2 was more than 95%. The formed concentration of OCS was measured as a function of $[CS_2]$ consumed, i.e. only the stable species were involved in the determining of the branching ratio k_{1b}/k_1. Some

typical experimental data obtained with two methods are shown in Figure 5. The slopes of the straight lines in Figure 5 provide the branching ratios for the OCS forming channel of reaction 1.

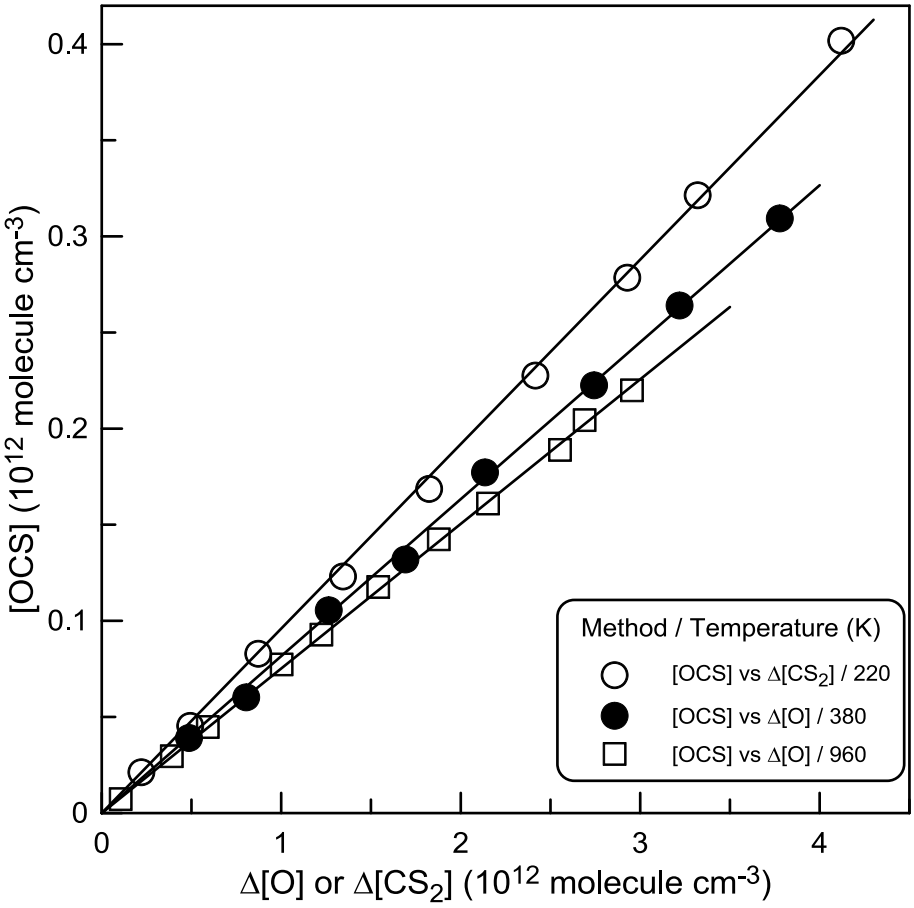


Figure 5. Concentration of OCS formed in reaction of O atoms with CS_2 as a function of the consumed concentration of CS_2 or O atoms.

All the results obtained for k_{1a}/k_1 and k_{1b}/k_1 between 220 and 960 K are presented in Table 3 and Figure 6. The errors on k_{1a}/k_1 and k_{1b}/k_1 shown in the Table correspond to the statistical 2σ precision of the fit to the respective experimental data. The estimated total uncertainty on k_{1b}/k_1 is around 10% and is due to combined uncertainty on the measurements of the absolute concentrations of SO, OCS and CS_2. The sum of the branching ratios for two reactions channels (1a) and (1b) shown in the last column of Table 3 is nearly 100 % at all temperatures of the study. However, this by no means excludes the possible presence of the third, $CO+S_2$ forming, channel of reaction 1 with a branching ratio of a few percent. Indeed, Slagle et al.[10]

in their molecular crossed beam study with photoionization mass spectrometry as a detection method observed, although not quantified, S_2 as the product of reaction 1. Hsu et al.[13] and Cooper and Hershberger[14] reported the branching ratios of (1.4 ± 0.2) % and (3.0 ± 1.0) %, respectively, for the reaction channel (1c) based on the measurements of the other reaction product, CO.

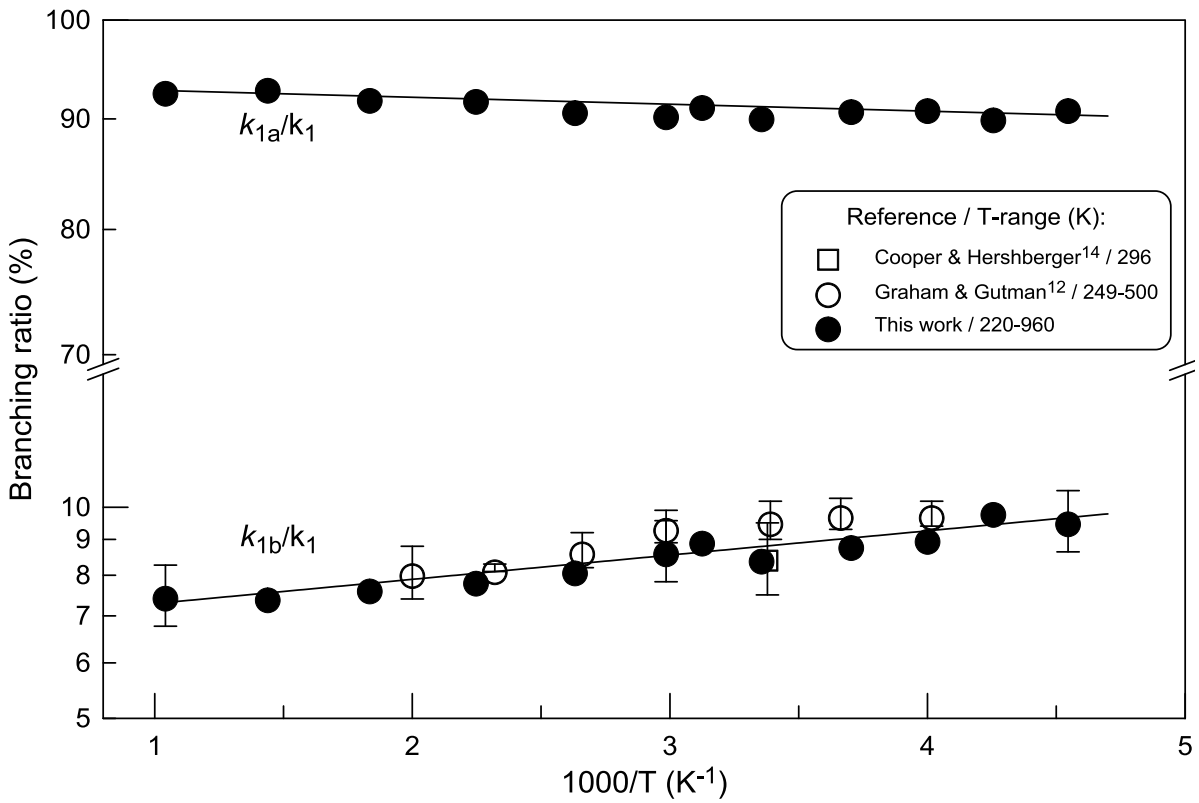


Figure 6. Branching ratio of the SO+CS (k_{1a}/k_1) and S+OCS (k_{1b}/k_1) forming channels of the reaction O+CS_2 as a function of temperature. Partially shown error bars for the present data correspond to estimated uncertainty of 10 % on the measurements of k_{1b}/k_1.

The present data for k_{1b}/k_1 are in good agreement with two previous measurements by Cooper and Hershberger[14] at room temperature and Graham and Gutman at T = 249 – 500 K.[12] An exponential fit to the branching data from the present work provides the following expressions:

$k_{1a}/k_1 = (0.935\pm0.005)\times\exp(-(7.4\pm0.2)/T)$,

$k_{1b}/k_1 = (0.067\pm0.002)\times\exp(80\pm8/T)$ at T = 220 – 960 K,

where uncertainties correspond to the statistical 2σ precision of the fit. Using the Arrhenius expressions for k_{1b}/k_1 and for the total rate constant k_1, k_{1b} can be expressed as k_{1b} = $(2.24\pm0.14)\times10^{-12}\exp(-(585\pm25)/T)$ $cm^3molecule^{-1}s^{-1}$ at T= 220 - 960 K. This expression can be compared with the result of the computational study of Saheb:[24] k_{1b} = $5.23\times10^{-12}\times(T)^{0.41}\exp(-3973/T)$ $cm^3molecule^{-1}s^{-1}$ at T= 200-2000 K. The computed values of k_1 are close to our experimental data at highest temperature of the study (960 K), however are by a factor of 10^5 lower at T = 220 K (see Figure S6). Obviously, there is a very serious disagreement between theory and experiment, which needs to be resolved.

CONCLUSIONS

Absolute and relative measurements of the rate coefficient of carbon disulfide + $O(^3P)$ reaction have been carried out over a temperature range between 220 and 960 K yielding k_1 = $(3.35\pm0.10)\times10^{-11}\exp(-(665\pm15)/T)$ $cm^3molecule^{-1}s^{-1}$. In addition, the branching ratios for the major, SO+CS forming, and minor, S+OCS forming, reaction pathways were measured as a function of temperature at T = 220 – 960 K. The Arrhenius expression for the overall rate constant and, especially information on the reaction products obtained for the first time in an extended temperature range provide an experimental dataset for use in combustion and volcanic plume modeling. Comparison of the current data with a computational study shows a very serious discrepancy between theory and experiment, which indicates the need to refine existing theoretical calculations.

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Supporting Information. Diagrams of the flow reactors (Figures S1 and S2); examples of concentration-time profiles of CS_2 in reaction with excess O (Figure S3); pseudo-first order rate constant, $k_1' = k_1[CS_2]$, as a function of the CS_2 concentration at T = 815 K (Table S4); examples of the dependence of $\ln([CS_2]_0/[CS_2])$ on $\ln(Br_2]_0/[Br_2])$ (Figure S5); temperature dependence of the rate constant of the O + OCS forming channel 1b.

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