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Rate Constant and Products of the Reaction of O(^{3}P) Atoms with Thiirane over the Temperature Range 220–950 K

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Abstract

A discharge-flow, modulated molecular beam mass spectrometry technique has been used to determine the rate constant for the reaction of ground state oxygen atoms with C_2H_4S in the temperature range 220 – 950 K. The reaction rate constant has been determined directly by monitoring C_2H_4S in an excess of O atoms and through competitive reaction of oxygen atoms with C_2H_4S and Br_2. Weak, negative temperature dependence is observed below 300 K, whereas positive temperature dependence is observed above 380 K: $k = 1.13\times10^{-12} (T/298)^{2.18} \exp(733/T)$ cm^3 molecule^{-1} s^{-1}. We estimate this expression to be accurate within 15 % over the investigated temperature range. SO and C_2H_4 have been detected as reaction products and a branching ratio of unity (with uncertainty of 10%) has been found for the channel forming these two species in the temperature range 300 - 900 K, confirming that the title reaction is an efficient source of SO radicals.

Keywords: Oxygen atom, Thiirane, SO, Rate constant, Non-Arrhenius

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1 INTRODUCTION

Reactions of thiirane (ethylene sulfide, C_2H_4S) with various atoms (O, H, Cl, S) are known to be rapid and proceed through S-atom abstraction leading to almost stoichiometric formation of ethylene and sulfur containing radicals.[1-5] Thus, the desulfuration reactions of C_2H_4S are a convenient source of sulfur-containing radicals for use in laboratory studies of their reactions.

The title reaction

$$O + C_2H_4S \rightarrow \text{products} \quad (1)$$

potentially leads to the formation of SO radicals, which are important intermediates in atmospheric and combustion chemistry. SO radicals are involved in the mechanisms of sulfur oxidation, where they are formed, for example, in the reactions of oxygen atoms with OCS and CS_2 and are further oxidized to SO_2 by reactions with O_2 and NO_2. The title reaction has only been studied in one previous work. Lee et al.[4] used flash photolysis-resonance fluorescence method to measure its kinetics between 268 K and 424 K. To our knowledge, the yield of SO has never been measured.

The objective of the present work was to determine the rate constant and products of the title reaction over an extended temperature range, T = 220 - 950 K, in order to provide a new kinetic and mechanistic data set for use in laboratory studies and, potentially, in theoretical reaction rate calculations.

2 EXPERIMENTAL

Experiments have been carried out in a discharge-flow apparatus at 2 Torr total pressure of Helium using electron-impact ionization (25–30 eV energy) mass spectrometry to measure the concentrations of the species involved.[6-9] The flow reactor used at low temperatures (Figure S1, Supporting Information (SI)), T = 220 – 325 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. The high temperature reactor, employed at T = 310 – 950 K, was an electrically heated Quartz tube (45 cm length and 2.5 cm i.d.) with water-cooled extremities (Figure S2, SI).[10]

Oxygen atoms were produced by discharging trace amounts of O_2 in He and were detected at their parent peak, m/z = 16 (O^+): the contribution of O_2 at this mass due to fragmentation of the molecular oxygen in the ion source of the mass spectrometer was

properly taken into account. The contribution of O_2 to m/z = 16 could be easily determined by simultaneous detection of the signals from O_2 at m/z = 32 and 16 and was approximately 5 % of the intensity of the parent O_2 peak. The resulting contribution of O_2 to the O atom signal was up to 40%.

To ensure the accuracy of the measurements of [O] (directly propagating to the uncertainty on the measurements of the reaction rate constant) two independent procedures were employed. The absolute concentrations of the O atoms were determined from the decrease of the O_2 concentration upon initiation of the microwave discharge ($\Delta[O_2] = 2[O]$). In another method, oxygen atoms were titrated with excess NO_2,

$$O + NO_2 \rightarrow NO + O_2 \qquad (2)$$

$k_2 = (6.1 \pm 0.4) \times 10^{-12} \exp((155 \pm 18)/T)$ cm^3 molecule^{-1} s^{-1} (T = 220 – 950 K),[6] and their absolute concentrations could be determined from the consumed fraction of $[NO_2]$ and [NO] and $[O_2]$ formed: $[O] = \Delta[NO_2] = [NO] = [O_2]$. Both methods gave essentially identical (within 10%) results. In a previous study from this group, we have checked for the presence of electronically excited oxygen atoms $O(^1D)$ in the microwave source of O atoms. It was shown that the fraction of $O(^1D)$ in the total concentration of oxygen atoms entering the reactor is less than 0.5%,[9] i.e. the possible impact of the presence of $O(^1D)$ on the results reported in the present study can be considered as negligible.

Thiirane was supplied to the reactor by flowing the helium over a liquid C_2H_4S or from a calibrated volume with known gaseous C_2H_4S/He mixture and was detected by mass spectrometry at its parent peak at m/z = 60 ($C_2H_4S^+$). Absolute concentrations of all stable species (C_2H_4S, SO_2, C_2H_4, O_2, NO_2, NO and Br_2) were derived from measured flow rates of their manometrically prepared gas mixtures.

He and O_2 were taken directly from high-pressure tanks and had stated purities better than 99.99% (Alphagaz). The SO_2, C_2H_4, NO_2, NO were Alphagaz products (> 99.9%, > 99.95%, > 99% and > 99%, respectively). The purities of C_2H_4S (Merck) and Br_2 (Aldrich) were 98% and 99.99%, respectively.

3 RESULTS AND DISCUSSION

3.1 Rate Constant of Reaction (1)

The rate constant of reaction (1) was determined using two approaches: by absolute and relative-rate measurements. Consistent results were observed with both methods.

Absolute measurements. The absolute measurements of k_1 were carried out under pseudo-first order conditions in an excess of oxygen atoms over C_2H_4S ($[C_2H_4S]_0$ = (2–3.5)×10^{11} molecule cm^{-3}). The time dependence of $[C_2H_4S]$ and [O] was monitored by changing the position of the movable injector (Figures S1 and S2, SI), and the measured distance between the injector head and the sampling cone of the mass spectrometer was converted into reaction time using the linear flow velocity of the gas mixture in the reactor. Figure 1 shows typical data obtained in this manner. The linearity of the semilogarithmic plots in Figure 1 clearly illustrates that the C_2H_4S decays are first order, $\ln([C_2H_4S]_0/[C_2H_4S]) = k_1'\times t$, where $k_1' = k_1\times[O]$.

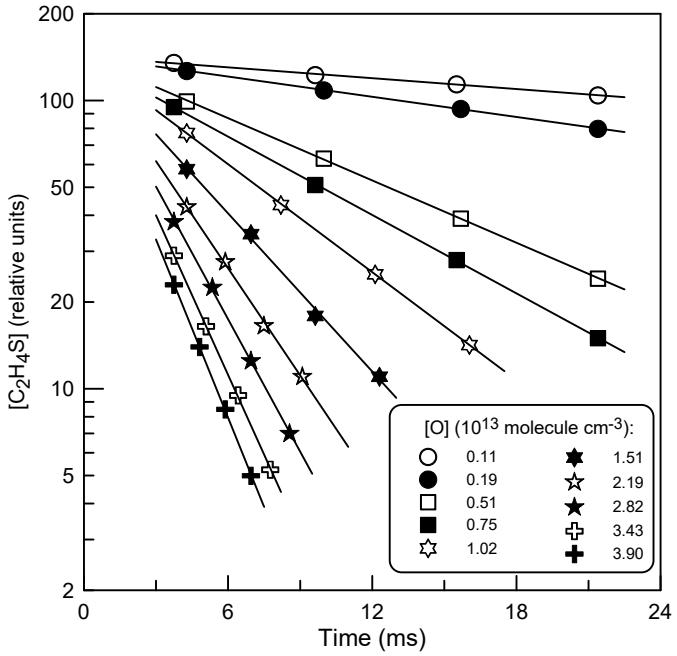

Figure 1. Typical decay profiles of C_2H_4S in the presence of different concentrations of O atoms observed at T = 360 K.

Diffusion corrections[11] (calculated with the diffusion coefficient of C_2H_4S in He D_0 = 290 × $(T/298)^{1.85}$ Torr cm^{-2} s^{-1})[12] on the pseudo-first order rate constants, $k_1' = k_1\times[O]$ (obtained from the slope of the semilogarithmic plots), typically did not exceed a few percent. The consumption of the excess reactant, oxygen atom, in reaction (1) and, mainly, due to the heterogeneous loss (≤ 10 s^{-1}) was within a few percent, although reaching up to 15% in a few kinetic runs. In all cases, the average concentration of the oxygen atoms along the reaction

zone was used in the calculations. Examples of the second-order plots observed at different temperatures are shown in Figure 2. A linear least-squares fit of these data at each temperature gave the bimolecular rate constant. A summary of the absolute measurements of k_1 is given 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 O atoms (~10%), flows (3 %), pressure (2 %) and temperature (1 %).

The small (close to zero) intercepts in Figure 2 are consistent with the experimental observation of the absence of any consumption of thiirane in the absence of the oxygen atoms in the reactor. This indicates a negligible role of the thermal decomposition of thiirane[13] under experimental conditions of the kinetic measurements, even at highest temperatures of the study.

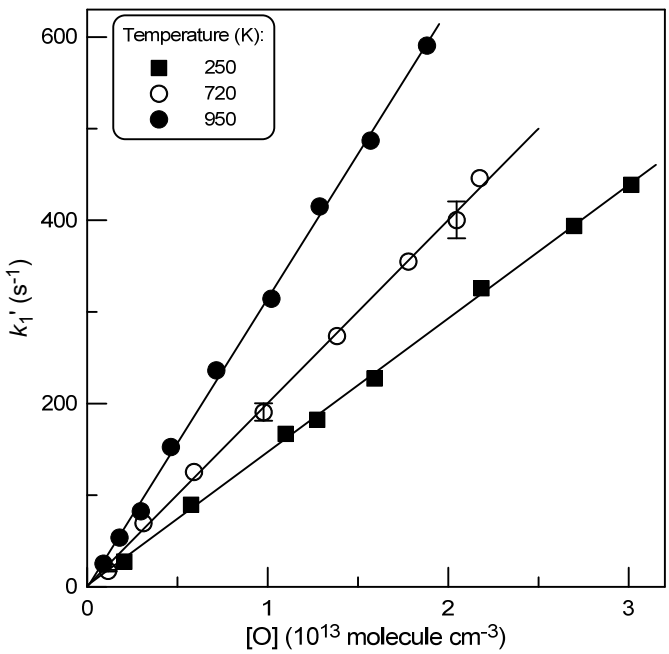

Figure 2. Dependence of the pseudo-first order rate constant, $k_1' = k_1[O]$, on the concentration of oxygen atoms at different temperatures. Partially shown error bars represent typical uncertainties (≤ 5%) on the determination of k_1'.

Table 1 Experimental conditions and results of the current absolute measurements of k_1

T (K)	[O] (10^{13} molecule cm^{-3})	k_1 (± 2σ) (10^{-11} cm^3 molecule^{-1} s^{-1})	Reactor surface[(a)]
220	0.13-2.64	1.60±0.03	HW
235	0.12-2.85	1.48±0.02	HW
250	0.21-3.01	1.46±0.02	HW

270	0.12-2.91	1.41±0.03	HW
298	0.19-3.51	1.37±0.02	HW
325	0.15-3.57	1.35±0.02	HW
360	0.11-3.90	1.33±0.02	Q
410	0.34-2.81	1.38±0.02	Q
475	0.24-2.86	1.46±0.03	Q
575	0.05-1.73	1.77±0.02	Q
720	0.12-2.17	2.00±0.04	Q
880	0.13-1.94	2.85±0.03	Q
950	0.09-1.88	3.16±0.05	Q

[a] HW: halocarbon wax; Q: quartz.

Relative rate measurements. In the relative-rate measurements, the decays of C_2H_4S and the reference compound Br_2 were monitored in the presence of a common reactant (O-atoms),

$$O + C_2H_4S \rightarrow \text{products} \quad (1)$$

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

$k_3 = 9.85\times10^{-16}\times T^{1.41} \exp(543/T)$ cm^3 molecule^{-1} s^{-1} (T = 220 – 950 K).[6] The initial concentrations of C_2H_4S and Br_2 in these experiments were in the range (2.5 – 5) and (2 – 4)× 10^{11} molecule cm^{-3}, respectively. The relative consumptions of C_2H_4S and Br_2 in the reaction with O-atoms are linked by the ratio of the corresponding rate constants:

$$\ln\frac{[C_2H_4S]_0}{[C_2H_4S]} = \frac{k_1}{k_3} \times \ln\frac{[Br_2]_0}{[Br_2]} \quad (I)$$

Reaction (3) produces BrO radicals and Br atoms, which can potentially react with C_2H_4S. Given that there are no rate constant data available for these reactions, we tested the possible impact of this secondary chemistry under the experimental conditions of the relative rate measurements. Br and BrO (≈ 5×10^{11} molecule cm^{-3}) were generated in the reaction of O atoms with excess Br_2 in the movable injector and mixed with C_2H_4S (≈ 3×10^{11} molecule cm^{-3}) in the main reactor. Monitoring of C_2H_4S showed that the presence of Br and BrO did not lead to its observable consumption at 310 – 900 K, temperature range of the relative rate measurements.

Typical dependences of ln($[C_2H_4S]_0/[C_2H_4S]$) on ln($[Br_2]_0/[Br_2]$) are presented in Figure 3. According to equation (I) the slopes of the straight lines in Figure 3 correspond to the k_1 to k_3 ratio. The final k_1 values calculated from k_3 and the slopes are given in Table 2. We estimate the total uncertainty of the k_1 values obtained from relative-rate measurements to be 20%.

The uncertainty is slightly higher than in the direct measurements because of the uncertainty of the rate constant of the reference reaction.

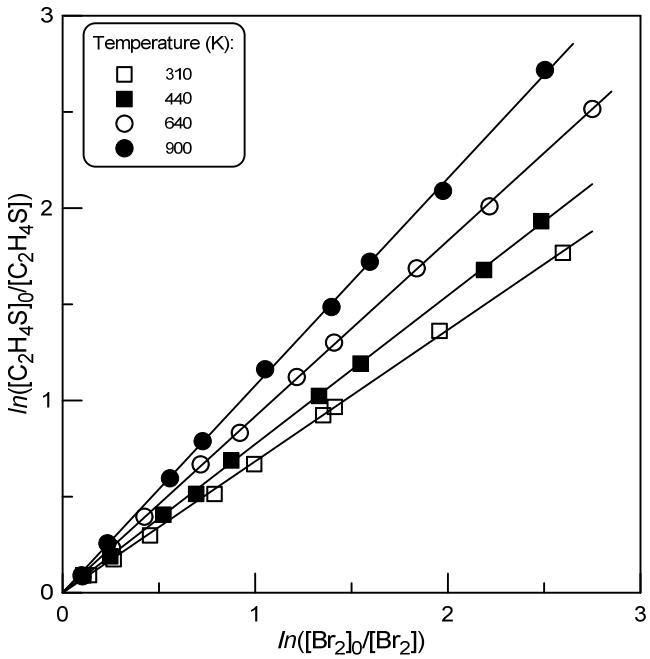

Figure 3. Examples of the dependence of $\ln([C_2H_4S]_0/[C_2H_4S])$ on $\ln([Br_2]_0/[Br_2])$ observed at different temperatures.

Table 2 Results of the current relative measurements of k_1

T (K)	k_1/k_3 (±2σ)	k_1 (10^{-11} cm^3 molecule^{-1} s^{-1})
310	0.690±0.006	1.28
380	0.741±0.004	1.32
440	0.773±0.005	1.40
515	0.816±0.011	1.54
640	0.913±0.004	1.90
820	0.971±0.007	2.38
900	1.077±0.010	2.84

The current results are plotted as a function of temperature in Figure 4 together with the measurements of Lee et al.[4] One can note close agreement between the absolute and relative measurements of this study and with the previous literature determination.[4] The rate constant of the reaction of O atom with thiirane clearly exhibits non-Arrhenius behavior. Interestingly, weak, negative temperature dependence is observed below 300 K, whereas positive temperature dependence is observed above 380 K.

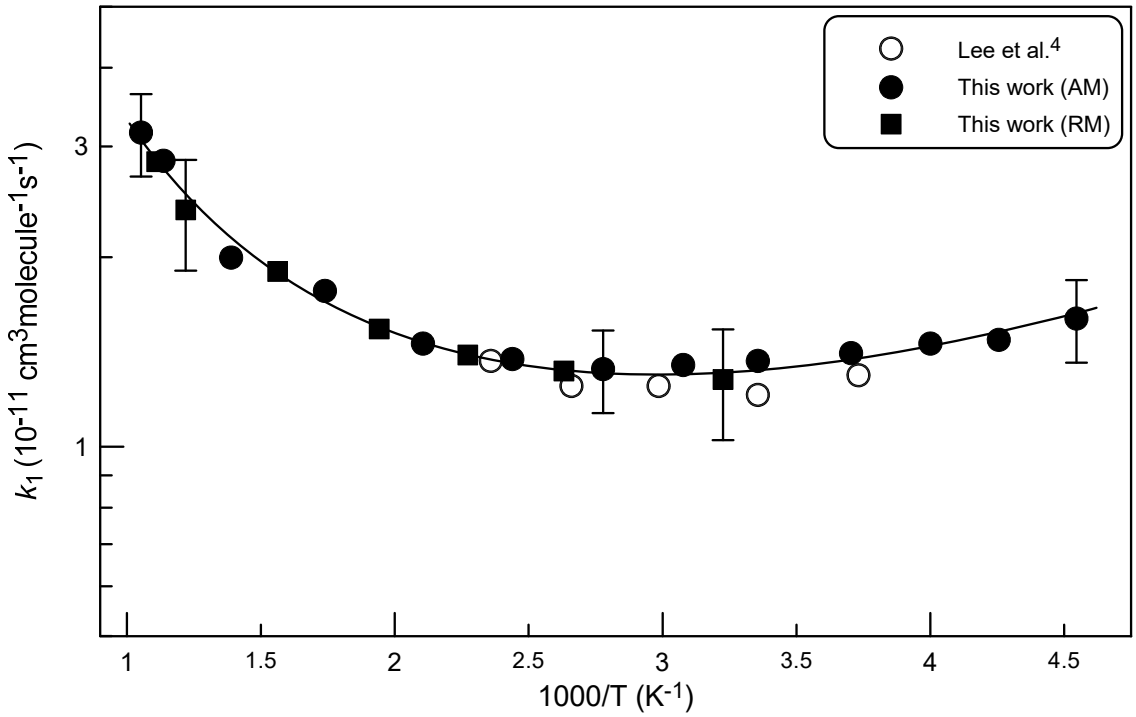

Figure 4. Summary of the measurements of k_1: AM, absolute measurements; RM, relative rate method. Uncertainties are shown for selected measurements of k_1 and correspond to 15 and 20% for the absolute and relative measurements, respectively.

A modified Arrhenius fit to the current results yields the following expression:

$k_1 = 1.13\times10^{-12}\,(T/298)^{2.18}\exp(733/T)$ cm^3 molecule^{-1} s^{-1} at T = 220 950 K.

We recommend this expression be used in kinetic models. The expression is expected to be accurate within 15 % between 220 K and 950 K.

3.2 Products of reaction (1)

To examine if the change in temperature dependence is caused by a change in the reaction mechanism (new reaction pathways), we measured the branching ratio of the SO + C_2H_4 forming channel at 298 K and 900 K. The reaction products, SO and C_2H_4, were detected upon total consumption of O atoms in an excess of C_2H_4S. The determination of their yields consisted in the measurements of the consumed [C_2H_4S] and the formed concentrations of the products. The SO radical was monitored at m/z = 48 (SO^+) and at m/z = 64 (SO_2^+) after being scavenged with an excess of NO_2 ([NO_2] ~ 10^{14} molecule cm^{-3}), added in the end of the reactor 5 cm upstream of the sampling cone, as shown in Figure S3 (SI):

$$SO + NO_2 \rightarrow SO_2 + NO \qquad (4)$$

k_4 = (6.7±0.2)×10^{-12} exp((295±10)/T) cm^3 $molecule^{-1}$ s^{-1} (T = 220 - 960 K).[14] This allowed the determination of the absolute concentrations SO radicals considering their stoichiometric conversion to SO_2: [SO] = [SO_2]. C_2H_4 was detected at m/z = 26 ($C_2H_2^+$). The reaction time was ≈ 0.02 s and $[C_2H_4S]_0$ = (2.5-3.0)×10^{13} molecule cm^{-3}. Under these experimental conditions, O atoms were completely consumed in the reaction with C_2H_4S. The experimental data observed at T = 298 and 900 K are shown in Figures 5 and 6.

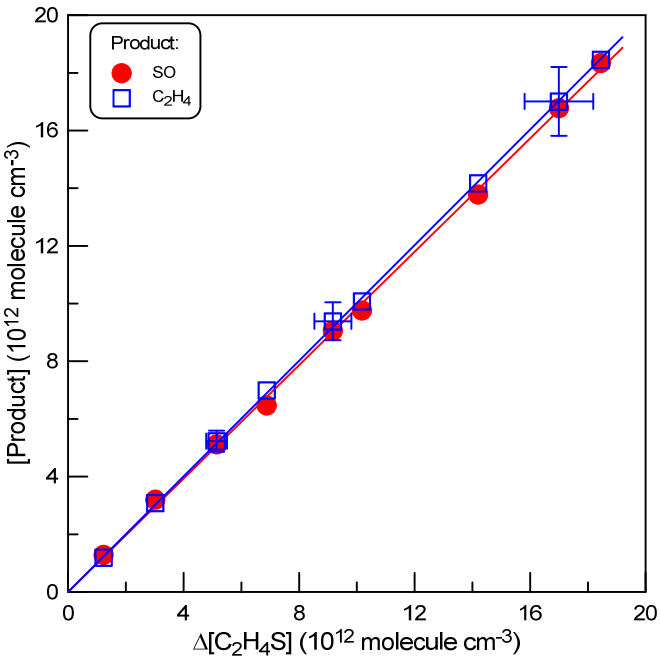

Figure 5. [SO] and [C_2H_4] formed in reaction (1) at 298 K as a function of the consumed concentration of C_2H_4S. Error bars are shown for selected points and correspond to typical (5-7)% uncertainties on the determination of the absolute concentrations of the relevant species.

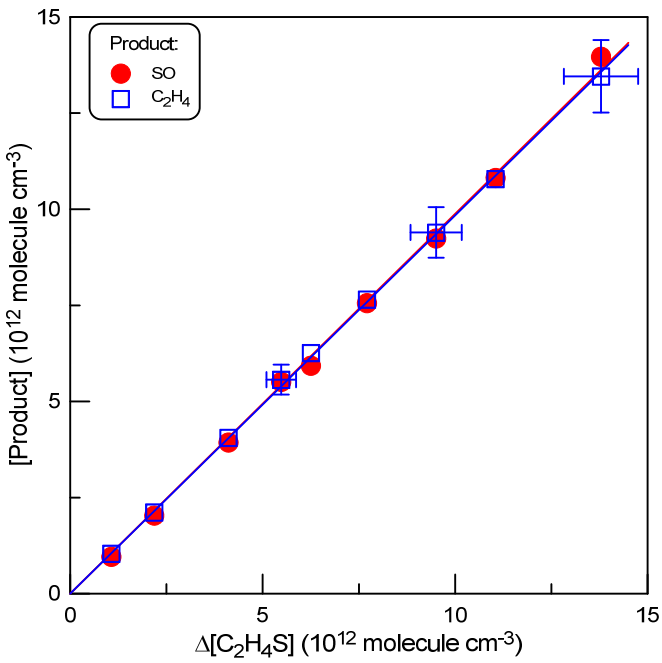

Figure 6. [SO] and [C_2H_4] formed in reaction (1) at 900 K as a function of the consumed concentration of C_2H_4S. Error bars are shown for selected points and correspond to typical (5-7)% uncertainties on the determination of the absolute concentrations of the relevant species

The slopes of the straight lines in Figures 5 and 6 provide the branching ratio for the SO and C_2H_4 forming pathway of reaction (1): [SO]/Δ[C_2H_4S] = 0.98±0.01 and 0.99±0.01, and [C_2H_4]/Δ[C_2H_4S] = 1.00±0.01 and 0.98±0.01 (± 2σ) at T = 298 and 900 K, respectively. One can note an excellent agreement between the results obtained for the yields of SO and C_2H_4. We estimate the total uncertainty of the yields to be around 10 %, which originates mainly from the uncertainties (5 – 10 %) in Δ[C_2H_4S], Δ[SO], and Δ[C_2H_4], combined in quadrature. The current results indicate that the C_2H_4 + SO -forming channel has a branching ratio of unity for reaction (1), at least under the experimental conditions covered in this work.

The non-Arrhenius U-shaped temperature dependence of the reaction rate constant in combination with the identified reaction products seems to indicate a complex addition-elimination reaction mechanism (at least, at low temperatures of the study):

$$O + C_2H_4S \rightarrow [C_2H_4S(O)]^* \rightarrow SO + C_2H_4$$

Negative temperature dependence is often associated with the formation of a pre-reactive complex. The switch from negative to positive temperature dependence of the total rate constant upon increase of temperature can be due to different reasons. For example, due to opening of new reaction channels (leading to different reaction products). This is the case for some reactions of unsaturated organic compounds (for example, Br + trans-2-butene,[15] OH +

p-cymene[16]), where adduct forming and H-atom abstraction channels dominate at low and high temperatures, respectively. The *U*-shaped temperature dependence observed[17] for the rate constant of the reaction OH + HBr $\rightarrow$ H_2O + Br was described by the sum of contributions from complex- (through formation of a collision complex BrH···OH) and direct-mode (direct abstraction mechanism) reactions.[18] A mechanism involving competing reactions, proceeding through a pre-reactive H-bonded complex to form $CH_3C(O)O$ + H_2O and a direct methyl-H abstraction channel, was proposed to explain a complex temperature dependence of the OH+CH_3COOH reaction with a sharp minimum of the reaction rate constant at T = 530 K.[19] Reactions proceeding through the formation of an intermediate complex, separated from the reactants and the reaction products by a loose and a tight (lying below the energy of the reactants) transition states, respectively, are potential candidates for the *U*-shaped temperature dependence of the reaction rate constant.[20-22] Georgievskii and Klippenstein[23] in their theoretical calculations, based on the consideration of the two distinct transition state regimes, reproduced the *U*-shaped (with a strong minimum near 200 K) temperature dependence of the rate constant of the CN+C_2H_6 reaction in the temperature range (25 – 1140) K. It was shown that the low temperature kinetics is governed by the loose outer transition state that leads to the formation of the pre-reactive complex, but as temperature is raised, the properties of the tighter inner transition state become increasingly important. This two transition state model seems highly plausible for the title reaction. Clearly, detailed theoretical calculations are needed to constrain this mechanism; however, this is outside the scope of the present study. The current low-pressure (2 Torr of He) measurements and those of Lee et al.[4] at higher pressures (50–100 Torr of Ar) agree within experimental uncertainty, which indicates that reaction (1) is pressure independent. This suggests that no collisionally stabilized adducts are formed, at least at pressures under 100 Torr.

In conclusion, the rate constant of the title reaction was measured over a wide temperature range, T = 220 - 950 K (for the first time at temperatures above 464 K and below 268 K). Negative temperature dependence is observed below 300 K, whereas positive temperature dependence is observed above 380 K. The SO and C_2H_4 forming channel of the reaction (1) turned out to be the main, if not the only one, with a branching ratio in the range (0.9 - 1.0). The measurements provide a new reliable kinetic and mechanistic dataset

for practical use and an experimental basis for theoretical calculations aimed at elucidating the reaction dynamics.

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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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