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Temperature Dependent Rate Constant for the Reaction of H-Atoms with Carbonyl Sulfide

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Abstract

The kinetics of the reaction of H-atom with carbonyl sulfide (OCS) has been investigated at nearly 2 Torr total pressure of helium over a wide temperature range, T = 255 – 960 K, using a low-pressure discharge flow reactor combined with an electron impact ionization quadrupole mass spectrometer. The rate constant of the reaction H + OCS $\rightarrow$ SH + CO (1) was determined under pseudo-first order conditions, monitoring the kinetics of H-atom consumption in excess of OCS, $k_1 = 6.6\times10^{-13}\times(T/298)^3\times\exp(-1150/T)$ cm^3 molecule^{-1} s^{-1} (with estimated total uncertainty on k_1 of 15% at all temperatures). Current measurements of k_1 at intermediate temperatures (520-960 K) appear to reconcile previous high and low temperature data and allow the above expression for k_1 to be recommended for use in the extended temperature range between 255 and 1 830 K with a conservative uncertainty of 20%.

Keywords: Hydrogen atom, OCS, kinetics, rate coefficient, non-Arrhenius temperature dependence.

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1 INTRODUCTION

The title reaction is of importance in combustion chemistry and industrial processes and is included in a detailed chemical kinetic model for oxidation of carbonyl sulfide (OCS):[1]

$$H + OCS \rightarrow \text{products} \quad (1)$$

Reaction (1) has three possible channels:[2]

$$H + OCS \rightarrow SH + CO \qquad \Delta_r H° = -44 \text{ kJ mol}^{-1} \quad (1a)$$

$$\rightarrow OH + CS \qquad \Delta_r H° = 241 \text{ kJ mol}^{-1} \quad (1b)$$

$$\rightarrow S + HCO \qquad \Delta_r H° = 243 \text{ kJ mol}^{-1} \quad (1c)$$

There is experimental[3,4] and theoretical[5] evidence that the main reaction pathway leads to SH + CO formation, the reactions (1b) and (1c) being strongly endothermic.

The rate constant for reaction (1) has been measured in four studies: by Rommel and Schiff at room temperature[3], Tsunashima et al. at T = (300 - 525) K,[6] Lee et al.[4] at T = (261 – 500) K and by Woiki and Roth in the temperature range (1200 - 1830) K.[7] The extrapolation of the temperature-dependent data obtained for k_1 at $T \leq 525$ K[4,6] to temperatures between 1200 and 1830 K leads to values of k_1 up to 20 times lower than the measurements of Woiki and Roth.[7] This observation suggests that a significant curvature of the temperature dependence of the reaction rate constant can be expected. To examine this hypothesis and harmonize the experimental data obtained previously at high and low temperatures, the measurements of k_1 at intermediate temperatures are clearly needed. This was the aim of the present paper which reports measurements of the rate constant of the reaction of hydrogen atoms with OCS as a function of temperature over a wide temperature range, 255-960 K.

2 EXPERIMENTAL

Experiments were carried out in a conventional discharge flow reactor combined with a modulated (by a tuning-fork chopper (35 Hz)) molecular beam electron ionization mass spectrometer.[8-10] MKS mass flow controllers were used to control the bath gas (Helium, nearly 2 Torr total pressure) flow rate. Two flow reactors (45 cm length and 2.4 cm i.d.) available in the laboratory, a Pyrex tube covered with halocarbon wax with a jacket for the circulation of thermostatically controlled ethanol and an electrically heated uncoated Quartz

tube, allow kinetic measurements between 220 and 1000 K. MKS mass flow controllers were used to control the bath gas (He) flow rate.

The rate constant of reaction (1) was measured under pseudo-first order conditions, by monitoring the decays of the H atoms in excess of OCS. The configuration of the flow reactor used in the experiments is shown in Figure 1.

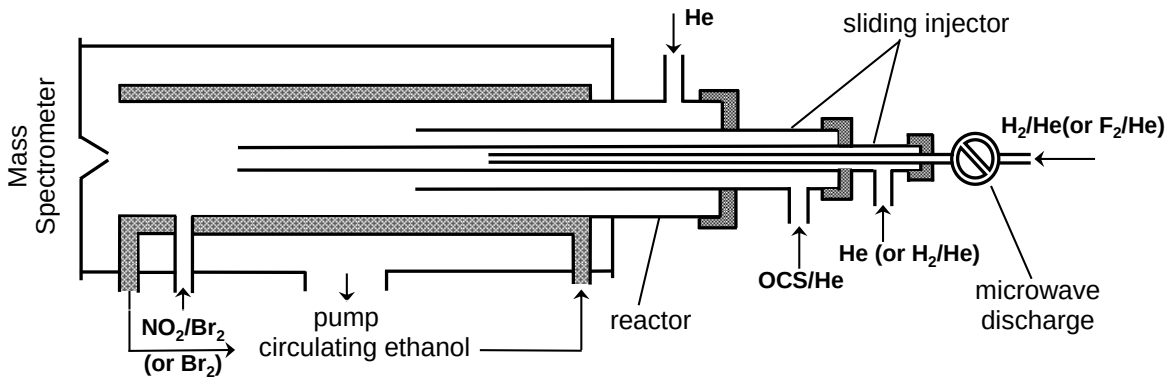

FIGURE 1 Configuration of the flow (low temperature) reactor used in the kinetic measurements.

Hydrogen atoms were produced using two methods: from the microwave discharge in H_2/He mixtures and in reaction of fluorine atoms with H_2,[11]

$$F + H_2 \rightarrow H + HF \quad (2)$$

$k_2 = 1.24 \times 10^{-10} \exp(-507/T)$ cm^3 molecule^{-1} s^{-1} (T = 220 – 960 K).

Fluorine atoms were generated by discharging trace amounts of F_2 in He. Mass spectrometric monitoring of molecular fluorine showed that more than 95% of F_2 was dissociated in the microwave discharge.

To enable the detection of low concentrations of H atoms by mass spectrometry, a chemical conversion of H atoms to stable species HOBr (m/z = 96/98) was employed upon addition of the NO_2/Br_2 mixture at the end of the reactor (Figure 1):

$$H + NO_2 \rightarrow OH + NO \quad (3)$$

$k_3 = (1.47 \pm 0.26)\times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (T = 195 – 2000 K),[12]

$$OH + Br_2 \rightarrow Br + HOBr \quad (4)$$

$k_4 = 2.16 \times 10^{-11} \exp(207/T)$ cm^3 molecule^{-1} s^{-1} (T = 220 – 950 K).[13]

The concentrations of NO_2 and Br_2 were chosen so as to provide $k_3[NO_2] >> k_5[Br_2]$:

$$H + Br_2 \rightarrow Br + HBr \quad (5)$$

k_5 = 7.06 × 10^{-11} $(T/298)^{0.88}$ exp(182/T) cm^3 $molecule^{-1}$ s^{-1} (T = 220 – 950 K).[14] In a few experiments with high concentrations of H atoms, they were monitored at m/z = 80/82 (HBr^+) after being transformed to HBr in reaction (5).

The absolute concentrations of HOBr were determined using OH titration with excess Br_2 via reaction (4) and relating the consumed fraction of Br_2 to the concentration of HOBr produced: [HOBr] = Δ[Br_2]. The absolute concentrations of Br_2, HBr, NO_2, F_2, H_2 and OCS in the reactor were derived from their flow rates from monometrically prepared mixtures. All stable species were detected by mass spectrometry at their parent peaks: m/z= 160 (Br_2^+), 46 (NO_2^+), 96/98 ($HOBr^+$), 80/82 (HBr^+), 38 (F_2^+), 60 (OCS^+).

The purities of the gases used were as follows: He > 99.999 % (Alphagaz); OCS (15% in He, Messer) > 99.99 %; Br_2 > 99.99% (Aldrich); F_2, 5% in helium (Alphagaz); HBr > 99.8% (Praxair); NO_2 > 99% (Alphagaz); H_2 > 99.998 % (Alphagaz).

3 RESULTS AND DISCUSSION

3.1 Measurements of the rate constant of reaction (1)

The rate constant of the title reaction was determined under pseudo-first order conditions monitoring H-atom decays in excess of OCS, [H] = $[H]_0$×exp(-k_1'×t), where [H] and $[H]_0$ are the time-dependent and initial concentrations of H atoms, respectively, and k_1' = k_1×[OCS]+k_w is the pseudo-first-order rate constant with k_w representing the wall loss of hydrogen atoms. Initial concentrations of H atoms in these experiments were in the range (0.8 – 2.0) × 10^{11} molecule cm^{-3}. The flow velocity in the reactor was in the range (470-3830) cm s^{-1}, increasing with temperature, to provide experimental conditions suitable for the measurements of k_1 which increases significantly with temperature.

Examples of H-atom decays observed at T = 960 K (highest temperature of the study) are shown in Figure 2. The pseudo-first order rate constants, k_1', corresponding to different concentrations of excess reactant, OCS, were determined from the exponential fit to the hydrogen atom consumption kinetics. All measured values of k_1' were corrected for axial and radial diffusion of H atoms using diffusion coefficient of hydrogen atom in He, D_0 = 0.078×$T^{1.74}$ Torr cm^2 s^{-1}.[15] Typically, diffusion corrections were less than 10%, but in several kinetic runs (at high temperatures) they reached 30 %. Dependencies of the pseudo-first

order rate constant, $k_1' = k_1 \times [OCS] + k_w$, on concentration of OCS observed at different temperatures of the study are shown in Figures 3 and 4, for lower and higher temperatures, respectively.

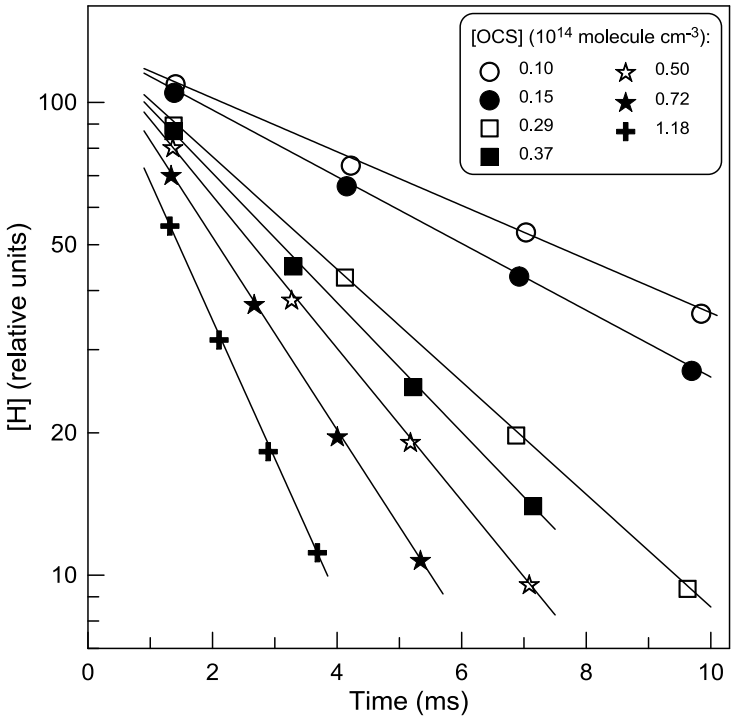

FIGURE 2 Example of pseudo-first-order decays of hydrogen atoms observed at *T*=960 K.

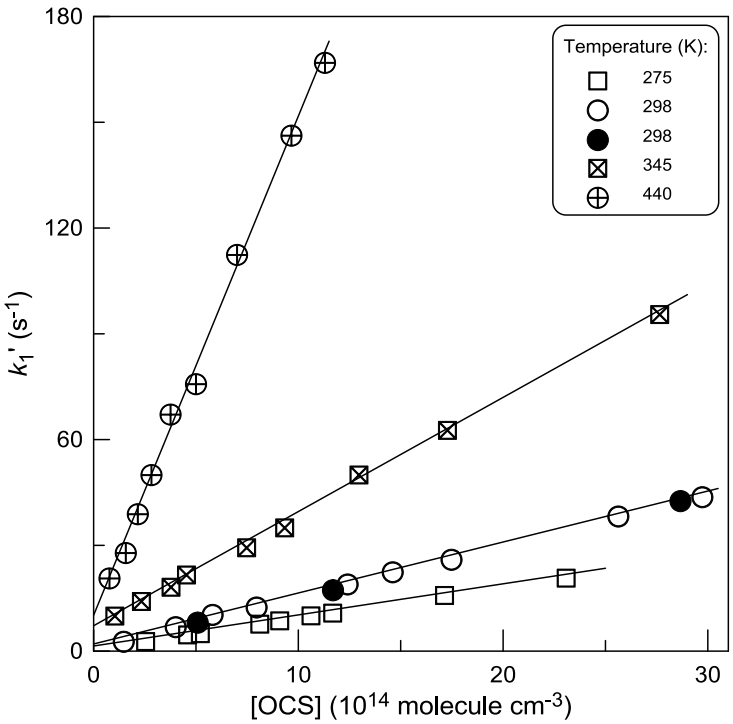

FIGURE 3 Pseudo-first-order rate constant (k_1') as a function of the concentration of OCS measured at different temperatures in the reactor. For T = 298 K, open symbols: $[H]_0 = 2\times10^{11}$ molecule cm^{-3}; filled symbols: $[H]_0 = 0.8\times10^{11}$ molecule cm^{-3}.

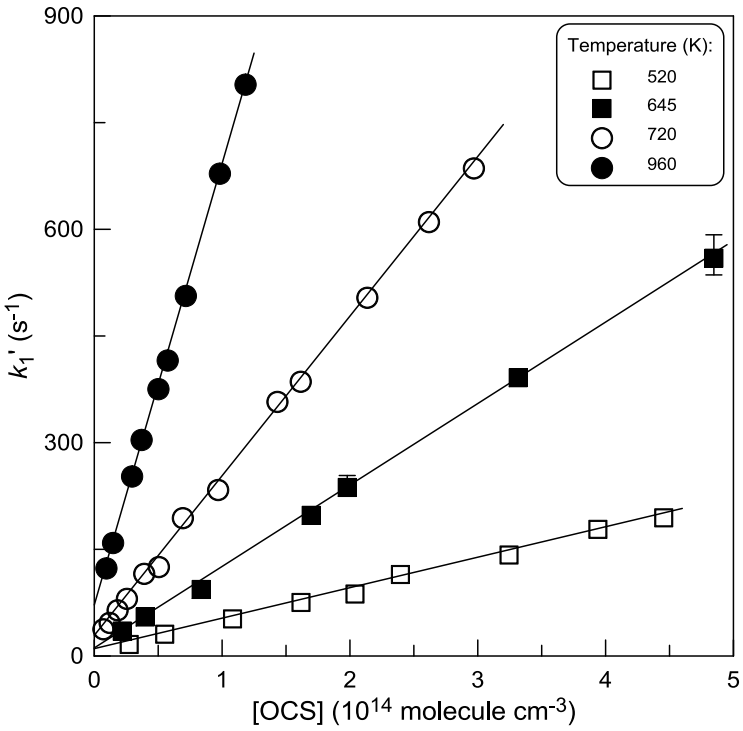

FIGURE 4 Dependence of the pseudo-first-order rate constant (k_1') on concentration of OCS at different temperatures in the reactor. Partially shown error bars represent typical uncertainties (≤ 5%) on determination of k_1'.

The wall loss rate of H atoms, k_w, measured in the absence of OCS in the reactor was between 0.5 and 10 s^{-1} (increasing with temperature) in both reactors. The intercepts of the linear dependencies of k_1' on [OCS] (Figures 3 and 4) are in good agreement with k_w for the experiments carried out at T < 400 K. However, at higher temperatures, the intercepts increase with temperature (up to 70 s^{-1} at T = 960K), indicating increased H-atom wall loss in the uncoated quartz reactor in the presence of OCS. It should be noted that, in any case, the rate of heterogeneous removal of hydrogen atoms remains insignificant compared to that in the reaction with OCS.

The final values of k_1 determined from the slopes of the straight lines in Figures 3 and 4 are presented in Table 1. The estimated total uncertainty (2σ) on the individual measurements of k_1 is approximately 15 % and includes statistical error (see Table 1) and those on the measurements of the flows, pressure, temperature and absolute concentration of OCS.

TABLE 1 Summary of the present measurements of the rate constant of reaction (1)

T (K)[(a)]	[OCS][(b)]	k_1 (± 2σ)[(c)]	Reactor surface[(d)]
255	1.25-14.0	0.0453 ± 0.0011	HW
275	2.54-23.1	0.0882 ± 0.0012	HW
298	1.47-29.7	0.145 ± 0.003	HW
298	0.95-10.7	0.158 ± 0.005	Q
300	4.55-37.9	0.154 ± 0.007	HW
320	2.79-35.0	0.220 ± 0.005	HW
330	0.42-8.25	0.308 ± 0.005	HW
345	1.04-27.6	0.324 ± 0.008	HW
360	1.72-13.6	0.505 ± 0.022	Q
385	0.54-11.7	0.759 ± 0.032	Q
440	0.77-11.3	1.42 ± 0.06	Q
520	0.27-4.45	4.29 ± 0.18	Q
645	0.22-4.85	11.5 ± 0.3	Q
720	0.07-2.97	22.4 ± 0.4	Q
820	0.08-1.47	39.8 ± 1.1	Q
960	0.09-1.18	62.1 ± 0.9	Q

[a] 7-13 H-atom decay traces at each temperature.
[b] units of 10^{14} molecule cm^{-3}.
[c] units of 10^{-13} cm^3 $molecule^{-1}$ s^{-1}.
[d] HW: halocarbon wax; Q: quartz.

Reaction (1) produces SH radicals and the measurements of k_1 can be potentially impacted by the fast secondary reaction:

$$H + SH \rightarrow S + H_2 \qquad (6)$$

The rate constant of reaction (6) is not well established. The available measurements of k_6 (between 1.1×10^{-11} and 4.15×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at room temperature) have been reviewed by Safaric and Strausz[16] who recommended a "best value" for $k_6 = 2.5\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Although the secondary reaction is quite fast, its effect on the measurements of k_1 can be considered as negligible due to low initial concentrations of H atoms used. As shown in Figure 3, variation of the initial concentration of H atoms by a factor of 2.5 had no impact on the measurements of k_1 at T = 298 K.

We performed another series of k_1 measurements with an initial concentration of H atoms as high as $\approx 2 \times 10^{13}$ molecule cm^{-3}. The hydrogen atoms in these experiments were detected as HBr after their chemical conversion in reaction (5) at the end of the reactor.

Under high concentrations of H atoms used, the rate of hydrogen atom consumption is expected to double that of the primary H+OCS reaction, d[H]/dt = 2×k_1[H][OCS], due to the presence of the rapid secondary reaction (6) and assuming a steady-state concentration for SH. Results of these measurements carried out at three temperatures are shown in Figure 5. The derived values of k_1 are given in Table 1. One can note an excellent agreement between the results obtained for k_1 with different (by two orders of magnitude) initial concentrations of H atoms and using two different methods of H-atom detection (conversion to HOBr or HBr).

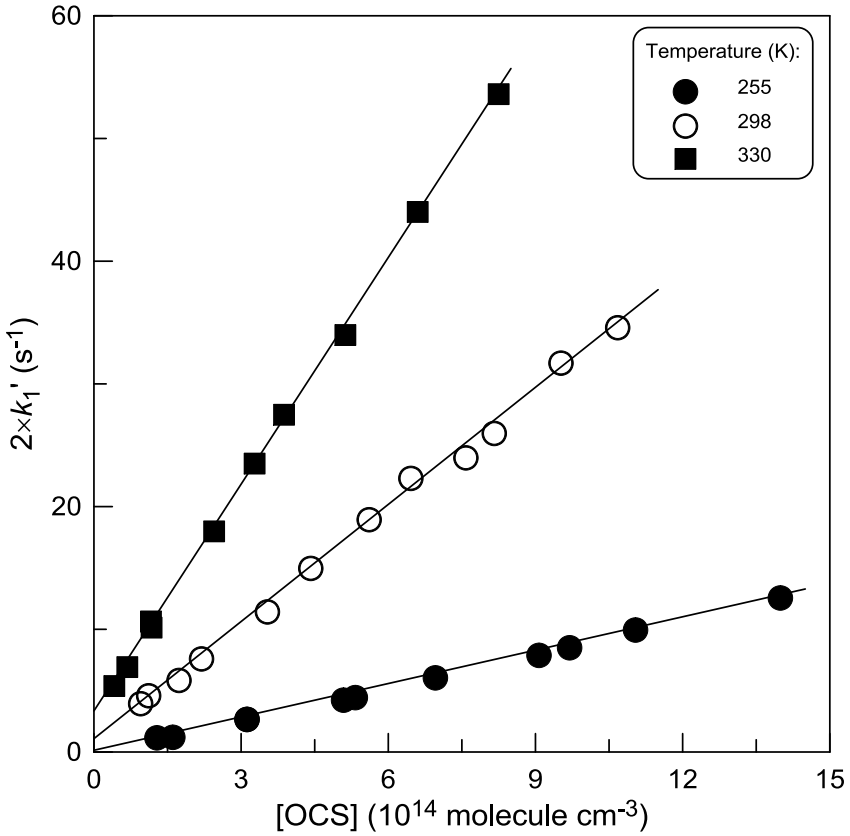

FIGURE 5 Dependence of the pseudo-first-order rate constant of hydrogen atom consumption on concentration of OCS measured at high initial concentration of H atoms ([H] ≈ 2×10^{13} molecule cm^{-3}).

3.2 Comparison with previous data

The results of the previous and current measurements of the rate constant of reaction (1) are shown in Figure 6. In the first measurement of the reaction rate constant, Rommel and Schiff[3] using discharge flow system combined with mass spectrometry reported k_1 = (2.20 ± 0.55)×10^{-14} $cm^3 molecule^{-1} s^{-1}$ at T = 298 K. The rate constant was determined from the OCS

consumption at the initial stage of the reaction and from the integrated rate equation. Tsunashima et al. [6] determined k_1 at four temperatures between 300 and 525 K relative to the rate constant of H atom reaction with H_2S,

$$H + H_2S \rightarrow SH + H_2 \quad (7)$$

monitoring the yield of CO (in off line analysis of CO in the form of carbon dioxide) in the H+OCS/H_2S mixture as a function of the [H_2S]/[OCS] ratio. To place the relative measurements on an absolute basis the authors used k_7 = (1.29±0.15)×10^{-11} exp(-(860±30)/T),[17] which can still be considered valid. Lee at al.[4] reported absolute measurements of k_1 using the flash photolysis – resonance fluorescence method. The rate constant of reaction (1) was determined over the temperature range 261 – 500 K by monitoring H atom consumption in an excess of OCS: k_1 = (9.06 ± 1.53)×10^{-12} exp(-(1938 ± 55)/T) $cm^3 molecule^{-1} s^{-1}$. Finally, Woiki and Roth[7] investigated reaction (1) behind reflected shock waves at temperatures between 1200 and 1830 K, using atomic resonance absorption spectroscopy for monitoring H-atom profiles.

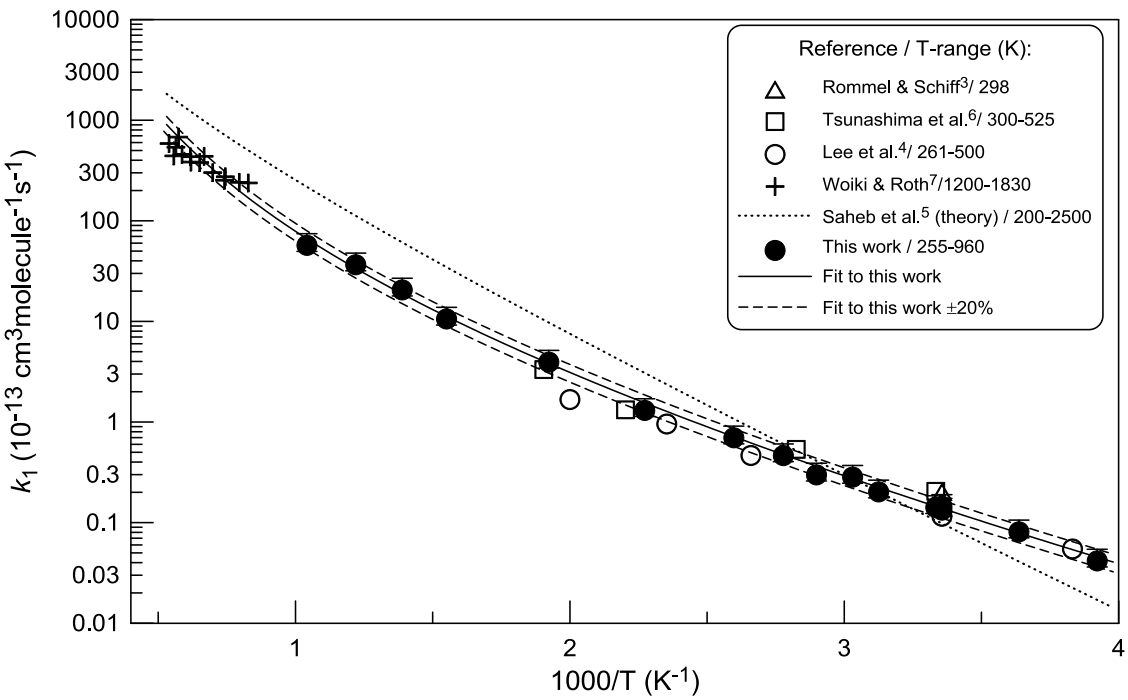

FIGURE 6 Reaction H + OCS: summary of the data for the reaction rate constant. Error bars on the present data correspond to 15% uncertainty on k_1.

The present results are generally in good agreement with previous studies at low temperatures (≤ 500 K), however, they show a well-pronounced curvature of the Arrhenius

plot. The fit of the present data with modified Arrhenius expression (continuous line in Figure 6) yields:

$k_1 = 6.6\times10^{-13}\times(T/298)^3\times\exp(-1150/T)$ cm^3 molecule^{-1} s^{-1}

This expression for k_1 is recommended from the present study in the temperature range (255 -960) K. As is well-known,[18-20] the parameters of the modified Arrhenius equation are highly correlated and the individual uncertainties are therefore not meaningful, but a conservative estimate of the overall 2σ uncertainty in k_1 (independent of temperature) is 15%. Since almost all available experimental data for k_1, including the high temperature results from Woiki and Roth, [7] are well described by the expression above (see Figure 6), it can be recommended to use it at temperatures up to 1830 K with uncertainty of 20% (dashed lines in Figure 6).

The curved Arrhenius dependence of k_1 can be due to various reasons, for example, the temperature dependence of the pre-exponential factor (predicted by collision and transition state theory) and activation energy,[21] and/or a complex reaction mechanism. In a theoretical study of Saheb et al.,[5] it was shown that reaction (1) proceeds mainly through OCS-H intermediate to yield SH and CO as reaction products. The TST/RRKM calculations provided the pressure independent non-Arrhenius expression for the main, SH+CO forming, channel: $k_1 = 1.23\times10^{-10}\,(T/298)^{1.022}\exp(-2812/T)$ cm^{3}molecule^{-1}s^{-1} at T = 200 – 2500 K. It can be noted that theoretical calculations (dotted line in Figure 6) qualitatively describe the growth of k_1 with temperature, but on the absolute basis they deviate significantly from the experimental results (by a factor of up to 2.8 at some temperatures).

The theoretical expression for k_1 computed by Saheb et al.[5] is included in a detailed chemical kinetic model for oxidation of carbonyl sulfide developed by Glarborg and Marshall,[1] based on a critical evaluation of data from the literature. The results of the present study, which confirm previous measurements of k_1, seem to indicate that available experimental data for k_1 are more suitable for use in kinetic models.

CONCLUSION

In this work, using a discharge-flow reactor combined with mass spectrometry, we have measured the rate constant of the reaction of hydrogen atoms with carbonyl sulfide as a function of temperature at T = 255–960 K. The observed non-Arrhenius

behavior of the rate constant allowed us to reconcile previous measurements at low (T < 500 K) and high (1200–1830 K) temperatures and recommend an expression for the reaction rate constant for use in kinetic models at T = 255–1830 K.

ACKNOWLEDGMENT

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the main text of this article..

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