

## Investigation on the Insertion Channel in the S(<sup>3</sup>P) + H<sub>2</sub> Reaction

Hiroumi Shiina, Akira Miyoshi, and Hiroyuki Matsui\*

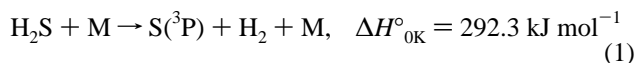
Department of Reaction Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

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To reexamine the possibility of the spin-forbidden, molecular-elimination mechanism of the thermal decomposition of H<sub>2</sub>S, H<sub>2</sub>S + M → S(<sup>3</sup>P) + H<sub>2</sub> + M (1), recently indicated by experimental and theoretical studies, as well as to examine the cause of discrepancies of its rate constants among recent works, the reverse insertion channel of the S(<sup>3</sup>P) + H<sub>2</sub> reaction, S(<sup>3</sup>P) + H<sub>2</sub> + M → H<sub>2</sub>S + M (−1), has been investigated. The experiments have been conducted with an excimer-laser photolysis (248 nm) in a shock tube at a lower temperature range, 900–1050 K, and a higher pressure range up to 4 atm, than previous studies, where the insertion process (−1) was estimated to be dominant over the simple hydrogen-atom-transfer reaction, S(<sup>3</sup>P) + H<sub>2</sub> → H + HS (2). The decay rate of S(<sup>3</sup>P) atoms has been measured by using an atomic resonance absorption spectrometry technique. The measured rate constant agreed well with the extrapolation of the previous measurements for reaction 2, showing that the recombination channel (−1) is still minor at these experimental conditions. The upper limit of the rate constant for reaction 1 derived in the present study was shown to be consistent with the theoretical rate constant calculated by the Troe's formula with the ab initio threshold energy for the intersystem crossing and with reasonable weak collision factors derived from the rate constant for reaction 1 reported by Shiina et al. [*J. Phys. Chem.* **1996**, *100*, 2136].

### Introduction

The reactions involving the third-row atoms in the periodic table often exhibit interesting features different from those involving second-row atoms. For example, the thermal decomposition of SiH<sub>4</sub> is known to produce SiH<sub>2</sub> + H<sub>2</sub> via a three-center transition state, while CH<sub>4</sub> decomposes via a simple C–H bond fission. Similarly, recent experimental studies by Woiki and Roth<sup>1</sup> and Olschewski et al.<sup>2</sup> have indicated that a hydrogen molecule is directly produced in the thermal decomposition of H<sub>2</sub>S, although it is a spin-forbidden process, i.e.,



An ab initio (MRCI+Q) calculation of the singlet and triplet surfaces of H<sub>2</sub>S by Shiina et al.<sup>4</sup> indicates that the lowest crossing point of the repulsive <sup>3</sup>B<sub>2</sub> and the ground <sup>1</sup>A<sub>1</sub> surfaces is located 65.6 kJ mol<sup>−1</sup> above the S(<sup>3</sup>P) + H<sub>2</sub> but 17.2 kJ mol<sup>−1</sup> below the dissociation threshold to HS + H. This supports the above experimental indication and suggests that, at least at low-pressure limit, the H<sub>2</sub> elimination pathway dominates over the simple H–S bond fission which had been assumed in the earlier studies on the thermal decomposition of H<sub>2</sub>S.<sup>4–6</sup>

Experimentally, the molecular mechanism (1) is supported only by the fact that the rate of production of S(<sup>3</sup>P) measured by Woiki and Roth<sup>1</sup> is in agreement with the decomposition rate of H<sub>2</sub>S measured by Olschewski et al.<sup>2</sup> However, the rate constants given by these two groups are about an order of magnitude larger than those reported by other groups.<sup>3–6</sup> Although the reason for this discrepancy is not still clear, this implies that the mechanism of reaction 1 should also be left in question.

The main issue of the present study is to reinvestigate the mechanism and the rate constant for the thermal decomposition

of H<sub>2</sub>S through the measurements on the backward reaction,



Also, this reaction itself implies the potential role of this and analogous insertion reactions of S atoms into hydrocarbons, S(<sup>3</sup>P) + RH + M → RSH + M, in the combustion of H<sub>2</sub>S and sulfur-containing fuels. Although the reactions of S(<sup>3</sup>P) with unsaturated hydrocarbons have been investigated and reported to be the recombination reactions, such insertion reactions of S(<sup>3</sup>P) into saturated bonds have not been well investigated nor discussed, but they may play an important role in the sulfur-containing systems.

At high temperatures and at moderate pressures, the mechanism of the S + H<sub>2</sub> reaction has been reported to be a simple H atom abstraction reaction,



By the measurements of absolute concentrations of S and H atoms, Shiina et al.<sup>3</sup> confirmed that reaction 2 dominates over reaction −1 at the temperatures between 1050 and 1660 K and the pressures below 2 atm. Also, they found that the activation energy for reaction 2 was 82.5 kJ mol<sup>−1</sup>, which is very close to the endothermicity of the reaction. Similar conclusions were also reported by Woiki and Roth.<sup>8</sup>

However, at lower temperatures or at higher pressures, the contribution of the insertion reaction (−1) is expected to be significant since this reaction is in the low-pressure limit and since its temperature dependence is estimated to be negative from the equilibrium constant and the activation energy for reaction 1. If we estimate the rate constant for reaction −1 from the equilibrium constant and the extrapolation of the rate constant<sup>3</sup> for reaction 1, significant turnover of the overall rate constant ( $k_2 + k_{-1}$ ) is expected at around 1000 K under the

\* To whom correspondence should be addressed.

pressure of  $\sim 4$  atm, which could not be observed in the temperature and pressure range of the previous study.<sup>3</sup> However, such contribution of the insertion reaction (-1) should be verified experimentally since the uncertainty of the rate constant for reaction 1 is large at this temperature range due to the extensive extrapolation.

Thus, in the present study, the measurement of the rate constant for  $S + H_2$  reaction has been extended down to the temperature of 900 K and up to the pressure of 4 atm, to investigate the possible contribution of the insertion reaction (-1). The preferred rate constant for the reverse reaction, the thermal decomposition of  $H_2S$  (1), at lower temperatures will be discussed from the experimental results.

### Experimental Section

The experimental system used in the present study was essentially the same as in our previous studies,<sup>3</sup> except that the  $MgF_2$  optics were replaced by stronger quartz ones for the experiments at higher pressures. The  $S(^3P)$  atoms were produced by KrF excimer-laser (248 nm) photolysis in a diaphragmless shock tube of 5 cm i.d. and 4.8 m long, where COS was used as a precursor for S atoms.  $S(^1D)$  atoms produced by the photolysis were effectively converted into  $S(^3P)$  atoms by a collisional quenching process within 1  $\mu s$  under the present experimental conditions. The decay rate of  $S(^3P)$  atoms was measured by using atomic resonance absorption spectrometry (ARAS) behind reflected shock waves in  $COS-H_2$  mixtures highly diluted in Ar. The ARAS system consisted of a microwave discharge lamp for supplying resonant radiation at 182.6 nm using a mixture of 0.1%  $SO_2$  diluted in He, a monochromator with a focal length of 20 cm, and a solar-blind photomultiplier (Hamamatsu, R972).

As was indicated in the previous studies, the effective absorption coefficient of  $S(^3P)$  atoms is pressure dependent, and thus, a calibration curve for the S atom ARAS was constructed for the high-density range of the present experiments for the  $S(^3P) + H_2$  reaction. The curvature of the calibration curve was determined assuming the single-exponential decay of S atom concentrations by the pressure-independent reference reaction,<sup>3,8</sup>

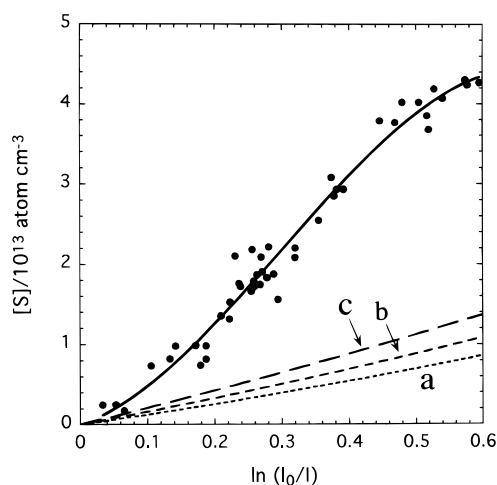


The obtained calibration curve for the high-pressure range is shown in Figure 1, where those at lower pressure range used in the previous study are shown for comparison.

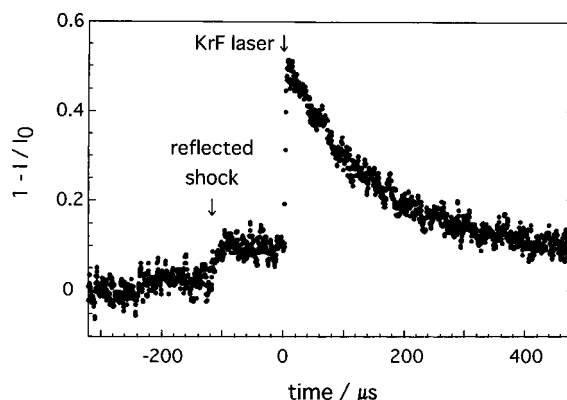
Sample gases used in this study were the mixtures of 1.51–10.1%  $H_2$  and 100–201 ppm COS diluted in Ar. COS was purified by a trap-to-trap procedure. Research grade (>99.9999%) Ar and  $H_2$  were decontaminated by passing through a cold trap when introducing into the Pyrex glass container. They were mixed manometrically and stored more than 24 h before use to ensure complete mixing.

### Experimental Results

The present study has been conducted in a temperature range of 910–1050 K and total pressure range of 0.4–4.2 atm. Experiments were limited to  $\leq 4$  atm due to the limit of the mechanical strength of optics used in the ARAS system. A KrF excimer laser was fired with a delay time of 100  $\mu s$  after the reflected shock wave passed through the observation station. The time dependence of the concentration of  $S(^3P)$  atoms was monitored by the ARAS system. H atom measurements were not performed at high pressures because of the restriction of



**Figure 1.** Calibration curves for S atom ARAS. Solid line denotes the calibration curve for the total density of  $2.8 \times 10^{19}$  molecules  $cm^{-3}$  constructed in the present study. Broken lines denote the calibration curves at lower total densities: (a) 2.54, (b) 4.98, and (c)  $7.42 \times 10^{18}$  molecules  $cm^{-3}$ .

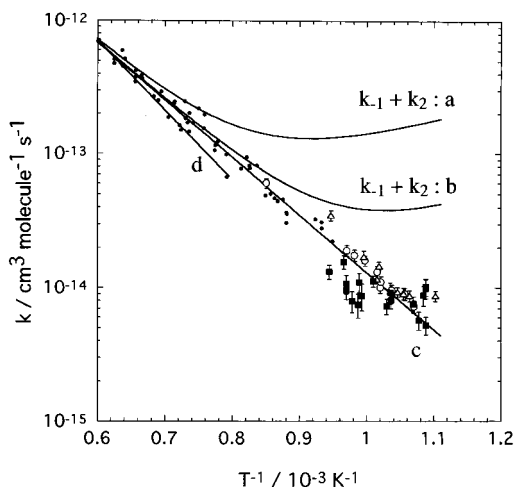


**Figure 2.** Example of the time profile of the S atom resonant absorption at 182.6 nm. Experimental conditions:  $T = 1060$  K, total density =  $2.8 \times 10^{19}$  molecules  $cm^{-3}$ ,  $[COS] = 119$  ppm, and  $[H_2] = 1.51\%$ .

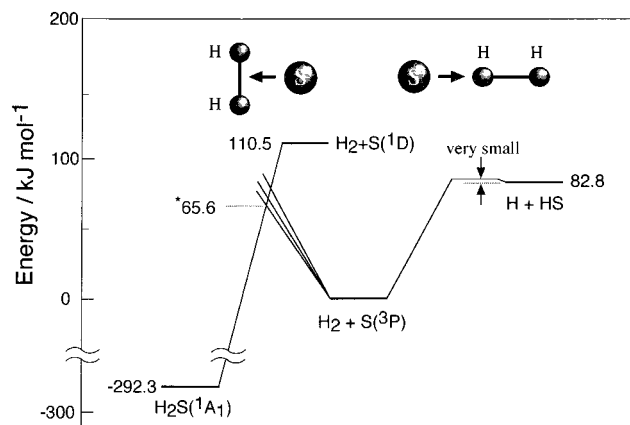
the VUV transmission of the quartz optics. The initial concentrations for COS and  $H_2$  were chosen so that the pseudo-first-order condition for the reaction of  $S(^3P)$  was satisfied, i.e.,  $[S(^3P)]_{t=0} \ll [H_2]$ .

An example of the time dependence of the resonant  $S(^3P)$  atom absorption is shown in Figure 2. As was observed in our previous study,<sup>3</sup> the  $S(^3P)$  atoms were rapidly produced when COS was photolyzed, then decreased with nearly a single-exponential time dependence. From the observed decay rates (after correcting the contribution from the reaction  $S + COS$  (3)), bimolecular rate constants for the reaction(s)  $S(^3P) + H_2 \rightarrow$  product(s) were evaluated and plotted in Figure 3, compared with previous studies<sup>1,3</sup> for reaction 2.

As shown in the figure, no pressure dependence of the rate constant was observed in this study up to 4 atm. The extrapolation of the rate constants for reaction 2 measured at higher temperature ranges in the previous experiments agrees very well with the rate constant of this study at lower temperatures. A slight deviation of the rate constants at the highest density seen in the figure is not significant considering the possible uncertainty in the calibration curve. Therefore, it is reasonable to conclude that even at the higher pressure ranges and the low temperatures employed in this study simple hydrogen atom transfer reaction 2 is still dominant over the recombination reaction (-1) in the reactions of  $S(^3P) + H_2$ .



**Figure 3.** Arrhenius plot of the rate constant for  $S(^3P) + H_2$  reaction. Rate constants measured at different total densities ( $\rho$ ) are marked with different symbols:  $\rho = (3.2\text{--}3.8) \times 10^{18}$  (O),  $(4.7\text{--}7.1) \times 10^{18}$  ( $\Delta$ ), and  $(2.7\text{--}2.9) \times 10^{19}$  ( $\blacksquare$ ) molecules  $\text{cm}^{-3}$ . Solid circles (O) denote the rate constant reported in the previous study<sup>3</sup> at  $\rho = (3.57\text{--}12.5) \times 10^{18}$  molecules  $\text{cm}^{-3}$ . Curves a and b indicate the calculated overall rate constants ( $k_{-1} + k_2$ ) from the extrapolation of  $k_1$  reported by Woiki and Roth<sup>1</sup> and Shiina et al.,<sup>3</sup> respectively. Curve c shows the Arrhenius fit to the present (O,  $\Delta$ , and  $\blacksquare$ ) and previous ( $\bullet$ ) results;  $k_2 = 2.2 \times 10^{-10} \exp(-80.7 \text{ kJ mol}^{-1}/RT)$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Curve d is the rate constant reported by Woiki and Roth.<sup>7</sup>

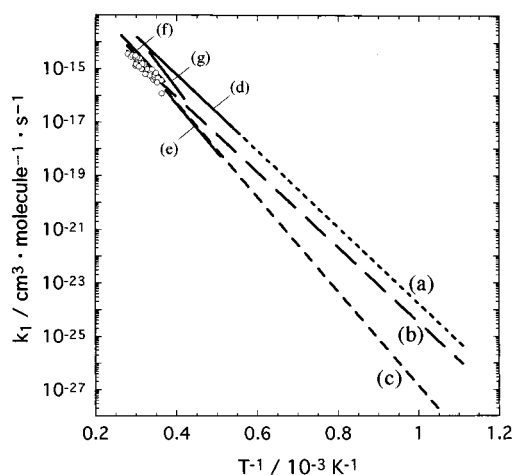


**Figure 4.** Energy diagram of the  $S(^3P) + H_2$  reaction. Indicated values are the energy relative to the ground-state  $H_2 + S(^3P)$  [ $\text{kJ mol}^{-1}$ ]. The barrier height for the collinear H atom transfer is expected to be very small from the experimental results. The energy of the  $C_{2v}$  intersystem crossing is an estimate based on the ab initio calculation (see text).

Also, it is of importance to discuss the reported rate constants for the dissociation of  $H_2S$  (1). The overall rate constants for the reaction  $S(^3P) + H_2$  including both reactions -1 and 2 calculated at the highest pressure range of this study are also shown in Figure 3. Curve a and curve b denote the calculated rate constant using the equilibrium constant and the extrapolations of the rate constants for reaction 1 reported by Woiki and Roth,<sup>1</sup> and Shiina et al.,<sup>3</sup> respectively. It is clear that the simple extrapolation of either rate constant for reaction 1 to such a low-temperature range is not appropriate.

## Discussion

An energy diagram for the two competing  $S(^3P) + H_2$  reaction channels -1 and 2 is illustrated in Figure 4. The reaction path leading to the recombination reaction corresponds to  $C_{2v}$  approach of S atoms to the hydrogen molecule, and the lowest energy for the crossing of repulsive  $^3B_2$  and  $H_2S \tilde{X}^1A_1$  surfaces



**Figure 5.** Arrhenius plot of the rate constant for the thermal decomposition of  $H_2S$ . Curves a and b indicate the simple extrapolations of the rate constants reported by Woiki and Roth<sup>1</sup> and Shiina et al.,<sup>3</sup> Curve c denotes the rate constant estimated by the Troe's formula with  $E_0 = 357.9 \text{ kJ mol}^{-1}$  and  $\beta_c = 0.025$  at 3200 K (see text). Open circles (O) denote the experimental results by Shiina et al.<sup>3</sup> Solid lines denote the experimental results by Woiki and Roth<sup>1</sup> and Olschewski et al.,<sup>2</sup> (d), Roth et al.,<sup>6</sup> (e), Bowman and Dodge<sup>5</sup> (f), and Higashihara et al.<sup>4</sup> (g).

is estimated to be  $65.6 \text{ kJ mol}^{-1}$ . On the other hand, the observed activation energy by Shiina et al.<sup>3</sup> was  $82.5 \text{ kJ mol}^{-1}$ . Ab initio multireference single and double configuration interaction (MRSDCI) calculation of the potential energy surface for reaction 2 was reported by Tsuchiya et al.<sup>9</sup> The direct abstraction reaction proceeds on the collinear  $^3\Pi$  potential energy surface, and the barrier height along the reaction coordinate was found to be small, only  $8.3 \text{ kJ mol}^{-1}$  above the  $SH + H$  asymptote. This calculation supports the experimental finding that the activation energy for the reaction is approximately equal to the endothermicity, which is qualitatively explained as they have an extremely "late" barrier. This is a common feature for the reactions of  $S(^3P)$  with a series of  $C_1\text{--}C_4$  alkanes or with  $H_2S$ .<sup>9</sup> The rate constant for the reaction  $S + H_2$  measured in this study together with our previous work<sup>3</sup> gives the expression

$$k_2 = 10^{-9.65 \pm 0.14} \exp[-(80.7 \pm 0.3) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for  $T = 910\text{--}1660 \text{ K}$ . The Arrhenius preexponential factor,  $10^{-9.65} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , seems to be too large for the spin-forbidden process; thus, it is suggested that the measured rate constant in this study corresponds to the simple abstraction reaction 2. The present experimental result indicates that the spin-forbidden recombination reaction (-1) with the lower threshold energy is minor compared to the direct abstraction channel (2).

From the experimental evidence that the rate of  $S(^3P) + H_2$  reaction even at  $\sim 4 \text{ atm}$  showed no significant contribution of the recombination reaction (-1), the upper limit of the rate constant for reaction 1 over the temperature range of  $910\text{--}1050 \text{ K}$  can be estimated. In Figure 5, the extrapolations of the rate constants for reaction 1 reported by Woiki and Roth<sup>1</sup> (a) and Shiina et al.<sup>3</sup> (b) are compared with the theoretical calculation (c) by using Troe's formula for the low-pressure limit.<sup>10</sup> Here, the parameters used in the calculation are  $E_0 = 357.9 \text{ kJ mol}^{-1}$  (from the ab initio calculation<sup>3</sup>),  $\beta_c \propto T^{-1}$ , and  $\beta_c = 0.025$  at  $T = 3200 \text{ K}$ , which was evaluated from the best fit to the high-

temperature rate constant reported by Shiina et al.,<sup>3</sup> and is a typical value for a molecule of this size. As a rate expression for a wider temperature range,  $T = 900\text{--}3600$  K,

$$k_1 = 10^{0.4235} (T/\text{K})^{-2.613} \exp(-373.1 \text{ kJ mol}^{-1}/RT)$$

was derived from the fit of the calculated values. This expression is consistent with the indicated upper limit of the rate constant for reaction 1, and it suggests that experiments at a much higher pressure range,  $>120$  atm (at 900 K), are necessary to observe the apparent contribution of the insertion reaction (−1) against the abstraction reaction (2).

Although the role of the insertion reaction (−1) is estimated to be insignificant except at extremely high pressures and low temperatures, analogous insertion reactions of S atoms into hydrocarbons should be left for further experimental and theoretical investigations since they are expected to be faster due to the higher efficiencies for the collisional stabilization.

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#### References and Notes

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