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LETTERS

Shock Tube Kinetic Study for the Reaction of H Atoms with SO_2: Comparison between Experiments and Theory

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The bimolecular rate constant for the reaction of $H + SO_2 \rightarrow$ products (1) was determined to be $k_1 = 1.0 \times 10^{-11} \exp(-66.1\ \mathrm{kJ{\cdot}mol^{-1}}/RT)\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}}$ in the temperature range of 1400−2200 K by measuring the temporal profiles of H atoms behind the reflected shock of $C_2H_5I/SO_2/Ar$ mixtures. The rate constant obtained in this study is in good agreement with that calculated using the rate constants of the reverse reaction $OH + SO \rightarrow H + SO_2$ and is also consistent with the rate constants predicted by the master equation analysis.

Introduction

The influence of fuel sulfur on combustion processes has been the subject of many researchers because of the industrial significance. For example, Corley et al.[1] reported that the presence of fuel sulfur had profound effects on NO_x formation. The effect of fuel sulfur on soot formation was also reported.[2] Among them, one of the most important contributions for understanding such effects was the finding that the addition of small amounts of sulfur dioxide resulted in a substantial decrease in radical concentrations. Although Alzueta et al.[3] claimed that the principle radical sink in fuel-rich flames could be explained by the catalytic recombination of H atoms in SO_2 doped flames

$$H + SO_2 + M \rightarrow HOSO + M \qquad (1a)$$

$$HOSO + H \rightarrow H_2 + SO_2 \qquad (2)$$

no experimental investigations for the kinetics of these reactions were performed so far. On the other hand, Frank et al.[4] and Goumri et al.[5] carried out the theoretical investigations of H/S/O/O potential-energy surfaces. The schematic figure of the potential energy diagram of the $H + SO_2$ system is depicted in Figure 1. According to the energy diagram shown in Figure 1, the reaction proceeds via two intermediate structures, HSO_2 and HOSO. It was also suggested that the dissociation from HOSO to OH and SO proceeds without any reaction barrier

$$H + SO_2 + Ar \rightarrow HOSO + Ar \qquad (1a)$$

$$H + SO_2 + Ar \rightarrow HSO_2 + Ar \qquad (1b)$$

$$H + SO_2 \rightarrow OH + SO \qquad (1c)$$

Recently Huges et al.[6] theoretically investigated the temperature and pressure dependence of the rate constants in the $H + SO_2$ system using a master equation model based on the potential-energy surfaces calculated by Frank et al.[4] and Goumri et al.[5] They proposed that at lower temperatures below 700 K reactions (1a) and (1b) were equilibrium conditions, but at higher temperatures above 700 K the dissociation pathway (1c) occurred to form OH and SO. At the temperature range above 1000 K, only reaction (1c) became important and the equilibriums between the intermediate species such as HSO_2 and

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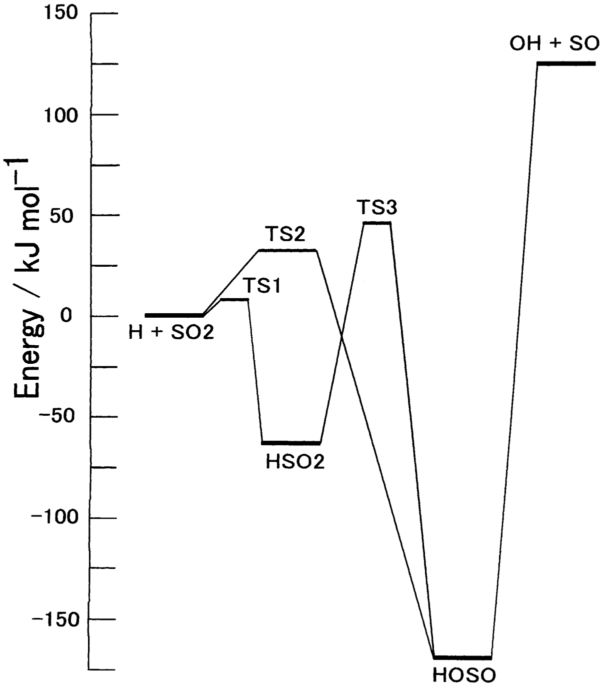

Figure 1. Schematic figure of the potential-energy diagram of H + SO_2 system taken from ref 6.

HOSO were not significant. They also predicted the rate expressions for the H + SO_2 system to model the combustion systems in the presence of fuel sulfur, but no experimental evidences for their predictions are not given yet.

Here we report the first experimental investigations of the bimolecular rate constant for the overall reaction H + SO_2 → products (1) in the temperature range of 1400−2200 K at total densities of 5.3×10^{18} to 8.9×10^{18} molecules cm^{-3} by measuring the temporal profiles of H atoms behind the reflected shock of $C_2H_5I/SO_2/Ar$ (2/600−1000 ppm) mixtures.

2. Experimental Section

The shock tube apparatus was the same as that used in previous works carried out in our laboratory.[7] A diaphragmless shock tube of 46 mm inner diameter and 3.6 m long at a low-pressure section was used, and the shocks were generated by high- pressure helium filled in the driver section. Before each run, the driven section was pumped down to pressures below 2×10^{-5} Torr. The incident shock velocity was measured by four piezoelectric gauges and a time counter. The temperatures and pressures behind the shock waves were calculated from the incident shock velocity. The observation windows were set at 40 mm from the end plate of the shock tube. Time-resolved optical measurements were performed through these windows. The resonance radiation of H atoms (121.6 nm) was produced by microwave excitation of He containing a few percent of H_2. The radiation from the lamp passing through the shock tube was led to a monochromator and finally detected at the photomultiplier. The time-resolved signals detected in the photomultiplier were stored in a digital oscilloscope and used for further analysis.

C_2H_5I were degassed and purified by a thaw−freeze−pump cycle. Ar (99.9999%) and SO_2 (99.9%) were used without further purification.

Results and Discussion

To investigate the rate constant for the overall reaction H + SO_2 → products (1), it is necessary to find out a proper precursor that produces H atoms behind the reflected shock waves. Since several researchers[8,9] have already used the thermal decomposition of C_2H_5I

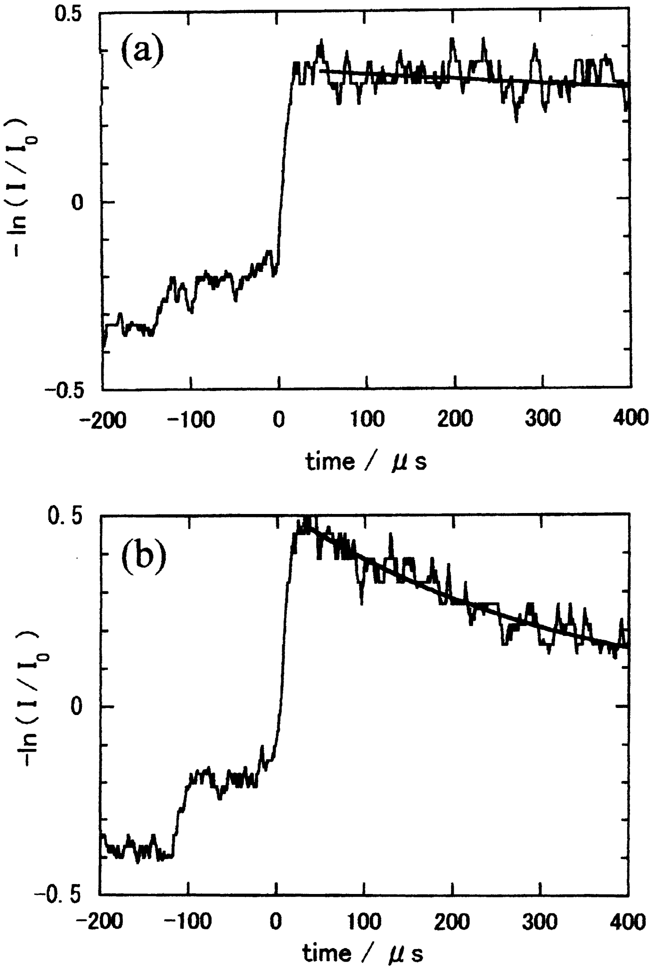

Figure 2. Examples showing the time dependences of the H atom behind the reflected shock of $C_2H_5I/SO_2/Ar$ mixtures. (a) C_2H_5I/SO_2 = 2/1000 ppm, Ar = 7.2×10^{18} molecules cm^{-3}, $T = 1470$ K, $P = 1.44$ atm. (b) C_2H_5I/SO_2 = 2/1000 ppm, Ar = 8.2×10^{18} molecules cm^{-3}, $T = 1920$ K, $P = 2.13$ atm.

$$C_2H_5I \rightarrow C_2H_5 + I \qquad (3a)$$

$$C_2H_5 \rightarrow C_2H_4 + H \qquad (3b)$$

as the precursor of H atoms, we also used the same precursor to produce H atoms behind the reflected shock waves. Because C_2H_5I molecules dissociate to produce H atoms within a few microseconds over the temperature range above 1400 K, the temporal decay of H atoms by the reaction of H + SO_2 can be analyzed without any influences of the dissociation rates of C_2H_5I and C_2H_5.

Figure 2 shows the typical examples of the time profiles of H atoms behind the reflected shock of $C_2H_5I/SO_2/Ar$ mixtures. As shown in Figure 2, absorption of SO_2 was overlapped to the time profile of H atoms behind the incident and the reflected shock waves. To subtract the absorbance of SO_2 from each time profile, the absorbance of SO_2 at 121.6 nm was independently determined by measuring the absorbance of SO_2 behind the reflected shock of SO_2/Ar mixtures. Since the concentration of SO_2 is much larger than that of H atoms, the absorbance of SO_2 behind the reflected shock waves is quite constant. Therefore the simple subtraction of the absorbance which

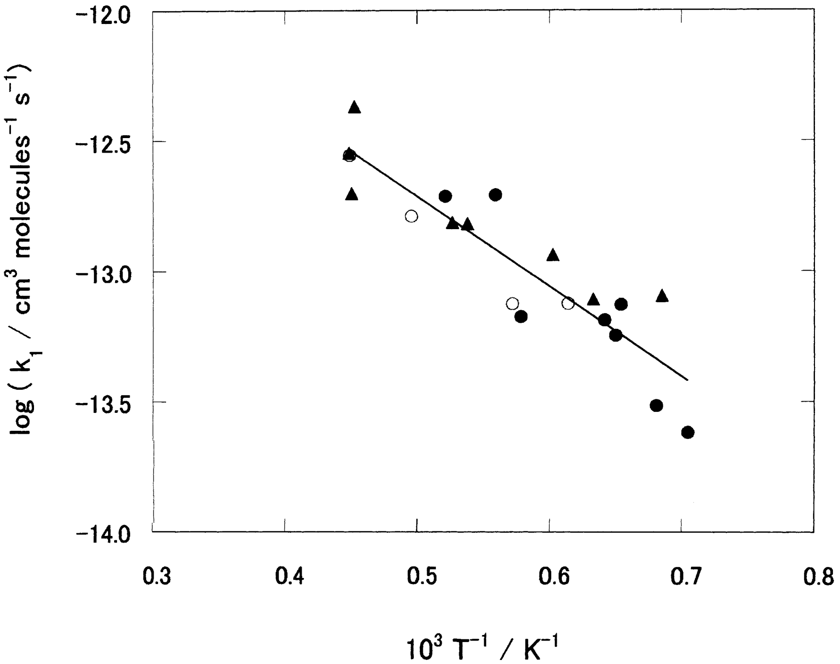

Figure 3. Arrhenius plot of the bimolecular rate constant for reaction 1. Experimental results: ○, C_2H_5I /SO_2 = 2/600 ppm; ▲, C_2H_5I/SO_2 = 2/790 ppm; ●, C_2H_5I/SO_2 = 2/1000 ppm. Solid line: The least-squares fit to the present data.

TABLE 1: Conditions and Results of Experiments to Determine k_1

T/K	[Ar][a]	[C_2H_5I][b]	[SO_2][c]	k_{first}[d]	$k_1/10^{-13}$ cm^3 molecules^{-1} s^{-1}
1420	8.38	1.68	8.38	0.40	0.48
1460	5.33	1.07	4.19	0.67	1.61
1470	7.19	1.44	7.19	0.44	0.61
1530	8.16	1.63	8.16	1.22	1.49
1540	8.87	1.77	8.87	1.01	1.13
1560	7.39	1.48	7.39	0.96	1.30
1580	5.58	1.12	4.38	0.68	1.56
1630	6.62	1.32	3.97	0.60	1.50
1660	5.75	1.15	4.52	1.05	2.31
1730	7.77	1.55	7.77	1.04	1.34
1750	6.88	1.38	4.13	0.62	1.50
1790	7.92	1.58	7.92	3.11	3.93
1860	6.08	1.22	4.78	1.45	3.04
1900	6.11	1.22	4.80	1.48	3.08
1920	8.15	1.63	8.15	3.16	3.88
2020	7.31	1.46	4.38	1.43	3.26
2210	6.48	1.30	5.09	4.36	8.55
2220	6.52	1.30	5.12	2.04	3.99
2230	7.61	1.52	4.56	2.54	5.57
2230	6.09	1.22	4.79	2.72	5.68

[a] Concentrations of the bath gas (argon) in units of 10^{18} molecules cm^{-3}. [b] Concentrations of C_2H_5I in units of 10^{13} molecules cm^{-3}. [c] Concentrations of SO_2 in units of 10^{15} molecules cm^{-3}. [d] Rate constant for reaction 1 using pseudo-first-order analysis in units of 10^3 s^{-1} as described in the text.

corresponds to the initial concentration of SO_2 behind the reflected shock waves gives the time profile of H atoms behind the reflected shock of $C_2H_5I/SO_2/Ar$ mixtures. Time profiles given in Figure 2 are those that have already subtracted the absorbance of SO_2 behind the reflected shock waves. As shown in Figure 2, the temporal decay of the absorbance of H atoms was not observed at a lower temperature range, but at a higher temperature range, the temporal decay of the absorbance of H atoms became prominent.

In the present work, the concentration of SO_2 is always maintained in large excess over C_2H_5I, and therefore H atom removal is always given by the single-exponential decay because of the pseudo-first-order conditions

$$[\mathrm{H}] = [\mathrm{H}]_0 \exp(-k_{\text{first}}t) \tag{4}$$

where

$$k_{\text{first}} = k_1[\mathrm{SO_2}] \tag{5}$$

Since the absorbance of H atoms was always kept lower than 0.5 behind the reflected shock waves, the linear Beer's law is almost valid to the time profiles of H-atom absorbance and therefore the concentration of H atoms is proportional to the absorbance (ABS) $\equiv -\ln(I/I_0)$, where I and I_0 refer to the time-dependent and the incident resonance light intensities, respectively. Hence a single-exponential fit to the time-dependent absorbance of H atoms gives the rate constant $k_{\text{first}} = k_1[SO_2]$ for reaction 1. The overall bimolecular rate constant k_1 was obtained by dividing the value of each k_{first} with the concentration of SO_2 behind the reflected shock waves. The conditions and results of all experiments are summarized in Table 1. Figure 3 shows the Arrhenius plots of the bimolecular rate constant k_1 for the reaction of $H + SO_2 \rightarrow$ products (1). A least-squares fit of the present experimental data in the temperature range of 1400−2200 K gives $k_1 = 1.0 \times 10^{-11} \exp(-66.1\ \mathrm{kJ{\cdot}mol^{-1}}/RT)$ cm^3 molecules^{-1} s^{-1}. Attempts were carried out to observe the pressure dependence by changing the total densities of Ar in the reflected shock waves between 5.3×10^{18} and 8.9×10^{18} molecules cm^3, but no or little pressure dependences were found under these conditions. Figure 4 is the comparison of the rate constants for reaction 1 obtained in this work with those of the previous estimates using the master equation model[6] based on the potential-energy surfaces calculated by Frank et al.[4] The rate constants k_1 calculated from the reverse reaction $OH + SO \rightarrow H + SO_2$ and the equilibrium constant are also shown in Figure 4. As can be seen clearly, excellent agreements were obtained between the present work and the results predicted by the master equation analysis. Good agreements were also obtained between our results and the rate constants calculated from the reverse reaction $OH + SO \rightarrow H + SO_2$. This fact supports the strong negative temperature behavior for the reverse reaction $OH + SO \rightarrow H + SO_2$ as suggested in ref 6. Dagaut

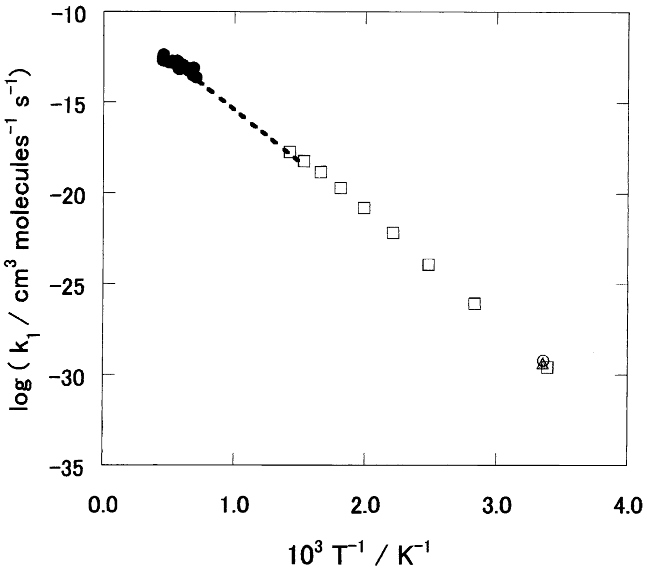

Figure 4. Comparison of the rate constant for reaction 1 between the experimental results of this work (●), the master equation model taken from ref 6 (dashed line), and conversions from the rate constant for the reverse reaction (□, ref 10; ○, ref 11; △, ref 12).

et al.[13] recently pointed out that reaction (1a) was important to model the H-atom removals in flames. However the rate constant for the overall reaction H + SO_2 → products (1) obtained in the present work can be expressed by the exploration of the calculated rate constant predicted by the reverse reaction OH + SO → H + SO_2 and is also consistent with the predictions of the rate constant using the master equation analysis by Hughes et al.[6] Therefore our experimental results support the conclusions by Hughes et al. that only reaction (1c) became important at the temperature range above 1000 K. However these conclusions are only based on the observations of the H-atom decays behind the reflected shock of $C_2H_5I/SO_2/Ar$ mixtures and therefore detections of the products by the reaction of H + SO_2 are highly desired. Detections of SO produced by the reaction of H + SO_2 are underway, and these results will give us new insights for the inconsistencies about the product branching fractions for reaction 3 and 5.

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