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The Dissociation Rate of S_2 Produced from COS Pyrolysis

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The disappearance rate of S_2, which was produced from the pyrolysis of COS, was measured behind incident shock waves by monitoring the UV emission in the temperature range of 4500—6000 K and in the pressure range of 0.32—0.5 atm. It was found that two processes could possibly account for the disappearance of S_2:

$$S_2 + Ar \longrightarrow 2S + Ar \qquad (3)$$

and

$$\left\{\begin{array}{ll} S_2 + Ar \longrightarrow S_2^* + Ar & \qquad (4) \\ S_2^* + Ar \longrightarrow 2S + Ar & \qquad (5) \end{array}\right.$$

and the following rate equation was obtained:

$$-d[S_2]/dt = k_{II}[S_2][Ar] \text{ mol cm}^{-3}\text{ s}^{-1}$$

where

$$k_{II} = 10^{13.68} \exp(-77 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The recombination of S atoms and the dissociation of the S_2 molecule play important roles in the combustion system of sulfur-containing compounds. Despite the importance of these reactions, there are no data for the rate of S_2 dissociation. At room temperature, some authors[1-3] have determined the rate constant for the recombination of S atoms, but the values determined were very different from one another. Fair and Thrush[1] generated ground-state sulfur atoms in a discharge-flow system by means of a rapid reaction between H and H_2S in order to observe the emission from the radiative recombination of S atoms; they determined the rate constant of S atom recombination from the emission intensity and the Franck-Condon factor as:

$$k_{-5} = 1 \times 10^{15} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}.$$

This may be the most reliable data, since the rate constant of atom recombination is generally of the order of 10^{15} cm^6 mol^{-2} s^{-1} at room temperature.

The thermal decomposition of carbonyl sulfide was studied by Hay and Belford[4] and by Schecker and Wagner[5] in the temperature range of 1550—3200 K. The results of these studies showed that S_2 was mainly produced by these reactions:

$$COS + Ar \longrightarrow CO + S + Ar \qquad (1)$$

$$COS + S \longrightarrow CO + S_2, \qquad (2)$$

and that the rate constants for Reaction 1 determined by these two groups agreed with each other. Thus, the mechanism of COS pyrolysis is rather simple compared with those of the other sulfur-containing compounds and the concentration of S_2 formed during the reaction can be easily calculated under the conditions presently studied.

The purpose of this study is to investigate the behavior of the S_2 molecule at higher temperatures (above 4500 K). There are two spectrophotometric methods for monitoring the concentration change of S_2. The absorption method is preferable for the measurement of the ground-state sulfur molecules. However, this method was not successful because of the very strong interference of S_2 emission at temperatures above 4500 K. Therefore, in this study the concentration change of S_2 in the $B^3\Sigma_u^-$ state (S_2^*) was followed by monitoring the UV emission at 392.5 nm.

Experimental

The shock tube was 3.8 cm in internal diameter, with a 2.5-m test section and a 1.5-m driver section. The system was pumped off by means of an oil-diffusion pump to less than 1×10^{-4} Torr before each run. All experiments were performed behind incident shock waves which were generated by high-pressure hydrogen. The UV emission at 392.5 nm, selected by means of a grating monochromator, was detected by means of a photomultiplier through a quartz window which was placed at a position 2.1 m downstream from the diaphragm. Only the S_2 molecule has an emission band around this wavelength corresponding to the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ transition.

Carbonyl sulfide obtained from a commercial cylinder was degassed at the temperature of liquid N_2–ethanol slash and purified by fractional distillations between this temperature and −197 °C. The gas mixtures studied were 0.5 and 1% COS in Ar. The post shock pressure and temperature were in the 0.32—0.5 atm and 4500—5800 K ranges, respectively. The temperature drop due to the pyrolysis of COS was estimated to be about 100 K for 1% COS and about 50 K for 0.5% COS in Ar mixture. The boundary-layer effects on the particle time, temperature, and density were estimated by the method of Mirels.[6] It was found that at $t_l = 30$ μs (at the end of the observation time) the maximum time correction was 20%, the maximum temperature shift was 6.2%, and the maximum density increase was 9.4%.

Results and Discussion

At temperatures above 4500 K, the emission intensity reached a maximum value within 5 μs of laboratory time and then decreased exponentially to a steady value. A typical oscillogram is shown in Fig. 1 (a).

If S_2^* (the $B^3\Sigma_u^-$ state of S_2) was mainly produced by the recombination of S atoms, the emission intensity should maintain the equilibrium value observed by Bott and Jacobs[7] at relatively lower temperatures (2300—4800 K) and high pressures (10—20 atm), since the S atom concentration did not overshoot

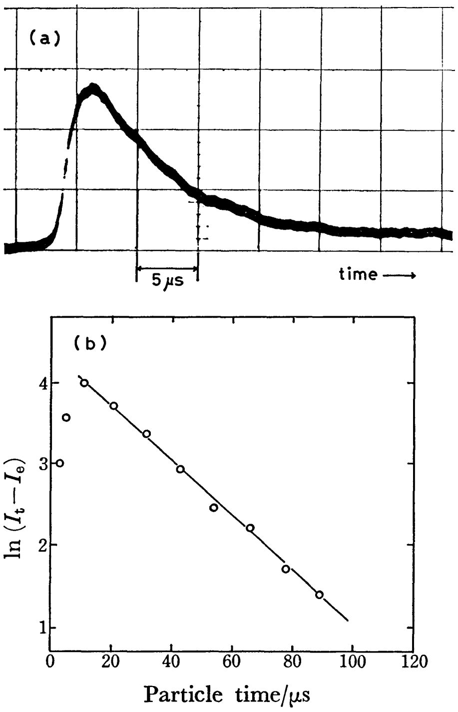

Fig. 1. (a): Typical oscilloscopic trace of S_2 emission at 392.5 nm, 0.5% COS in Ar mixture; post shock temperature=5507 K. (b): Plot of ln (I_t-I_e) *vs.* particle time.

behind the shock front, as is shown in Fig. 6. Therefore, the phenomenon shown in Fig. 1 (a) should be due to the thermal excitation from the ground electronic state of S_2. If so, the temperature dependence of the peak intensity per unit of S_2 concentration should give the energy difference between the ground and excited electronic states (90.6 kcal/mol). Figure 2 shows the Arrhenius plot of the peak intensity per unit of the initial concentration of COS. The apparent activation energy of this plot is 72.6 kcal/mol, smaller by about 20 kcal/mol than the energy difference of the two electronic states. This can reasonably be explained by considering that the yield of S_2 at the peak is temperature-dependent. If we plot the peak intensity per unit of S_2 concentration against $1/T$ (broken line of Fig. 2), where the S_2 concentration was calculated by using Reactions 1 and 2, the apparent activation energy becomes 114 kcal/mol, greater by about 20 kcal/mol than the energy difference of the two electronic states of S_2. However, if we use a value of $k_2=10^{13.92}$ exp $(-27.2\ \text{kcal}/RT)$ cm^3 mol^{-1} s^{-1} for the rate constant of Reaction 2, which was estimated by Kondratiev,[10] the apparent activation energy of the peak intensity becomes about 90 kcal/mol. Thus, the yield of S_2 (and the resulting apparent activation energy) is strongly influenced by the rate constants of Reactions 1 and 2. Unfortunately, since we have no reliable rate constants for these reactions at higher temperatures, we could not decide whether or not, at the peak, the thermal equilibrium between the $^3\Sigma_u^-$ and $^3\Sigma_g^-$ states of S_2 was maintained, but it may be reasonable to assume that the equilibrium was maintained. If such is the case, the decrease in the emission intensity after the peak corresponds to the dissociation rate of the S_2 molecule. Similar phenomena were observed for the emission of C_2 during the pyrolysis of CH_4, CCl_4, CF_4, and C_2H_2 by Fairbarn[8] and of C_2H_2 by Beck and Mackie.[9] In those studies, it was found that the thermal equilibrium between the electronically ground and excited states of C_2 was maintained.

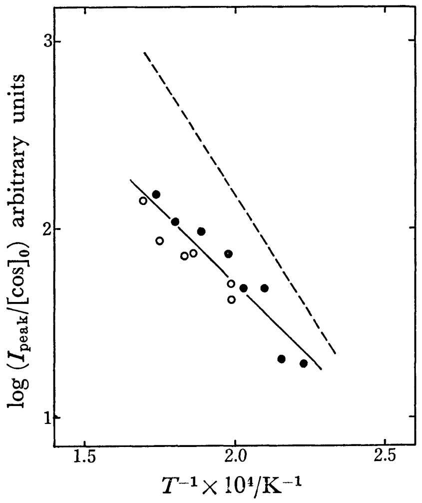

Fig. 2. ○ and ●: Arrhenius plot of peak intensity per unit initial concentration of COS, ○: 1% COS in Ar mixture; ●: 0.5% COS in Ar mixture. ----: Arrhenius plot of peak intensity per unit S_2 concentration.

The emission intensity is proportional to the concentration of S_2*. As is shown in Fig. 1 (b), since a semilogarismic plot of (I_t-I_e) *vs.* the time gives a straight line after the maximum, the variation in the S_2* concentration with the time is expressed by the following relation:

$$\ln(I_t-I_e)\propto\ln([S_2^*]_t-[S_2^*]_e)=k_\mathrm{I}t,$$

where the subscripts t and e denote the time t and the time needed to reach an equilibrium respectively. Although the emission intensity profile as experimentally recorded reflects the time variations in the gas temperature and density, in this study these corrections were not carried out and the mean temperature and density were used for the date reduction, since the observation time was very limited (from about 5 μs to about 20 μs laboratory time). Since COS decomposes almost completely at the time when the emission intensity reaches a peak (see Fig. 6), there is no need to consider the effect of S_2 formation on the rate of S_2 disappearance. Thus, the value of k_I gives a quasi-first-order rate constant of S_2 disappearance. Furthermore, taking into consideration the fact that S_2 disappears mainly as a result of the collision with Ar, the second-order rate constant of S_2 disappearance (k_II) is obtained from the $k_\mathrm{II}=k_\mathrm{I}/$[Ar] equation. The Arrhenius plot of k_II thus obtained is shown in Fig. 3 for 0.5 and 1% COS in Ar mixtures. The best-fitting line gives:

$$k_\mathrm{II}=10^{13.68}\exp(-77\ \text{kcal}/RT)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}.$$

The formation and disappearance of S_2 were considered to be governed by the reactions listed in Table

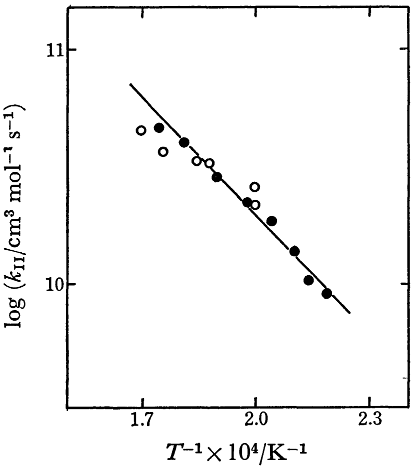

Fig. 3. Arrhenius plot of k_{II}, ○: 1% COS in Ar mixture; ●: 0.5% COS in Ar mixture.

1. In order to check the reliability of the assumption of the equilibrium between S_2 and S_2^* and the resultant rate constant, k_{II}, for the S_2 disappearance, the concentration change of S_2^* with the time was calculated at the temperatures of 5025 and 5753 K by using a reaction mechanism including the 11 elementary reactions listed in Table 1, and was compared with that obtained experimentally. The values of k_1,[4,5] k_2,[10] k_{-4}[1] at 298 K, k_{-5}[1] at 298 K, k_6[1] have been determined by other investigators, but there are no rate data for the rest. Therefore, the rate constants of these reactions were estimated in the following way. The rate constants of Reaction 4 were calculated from the simple collision theory, by assuming that the molecular diameters of S_2, S_2^*, and Ar were 3.88, 4.47, and 3.42 Å respectively, as

$$k_4 = \lambda_4 \times 8.46 \times 10^{12}\, T^{1/2} \exp(-90.6\ \mathrm{kcal}/RT)\ \mathrm{cm^3\,mol^{-1}\,s^{-1}}$$

$$k_{-4} = \lambda_{-4} \times 9.89 \times 10^{12}\, T^{1/2}\ \mathrm{cm^3\,mol^{-1}\,s^{-1}}.$$

The equilibrium constant for these reactions was expressed as

$$K_4 = k_4/k_{-4} = (Q_{S_2^*}/Q_{S_2}) \exp(-90.6\ \mathrm{kcal}/RT),$$

where $Q_{S_2^*}$ and Q_{S_2} are the partition functions of the electronically excited and ground states of S_2. The ratio of $Q_{S_2^*}/Q_{S_2}$ can be calculated from the molecular constants; it is given as 2.15 at 5000 K. From this value, the $\lambda_4/\lambda_{-4}=2.5$ ratio was obtained. In general, the efficiency of electronic excitation is large; therefore, in this study $\lambda_4=1$ was assumed, and $\lambda_{-4}=0.4$ was thus obtained. Fair and Thrush[1] determined the value of k_{-4} at 298 K as

$$k_{-4} = 1.5\times 10^{14}\ \mathrm{cm^3\,mol^{-1}\,s^{-1}}.$$

The collision efficiency, λ_{-4}, was calculated from this value as $\lambda_{-4}=0.88$ at 298 K, in good agreement with that value obtained by assuming $\lambda_4=1$. Fair and Thrush also obtained values of k_{-5} at 298 K and k_6 as

$$k_{-5} = 10^{15}\ \mathrm{cm^6\,mol^{-2}\,s^{-1}}$$

$$k_6 = 10^{7.48}\ \mathrm{s^{-1}}.$$

Assuming that the rate constant of recombination reaction was inversely proportional to the temperature, k_{-5} was expressed as

$$k_{-5} = 10^{17.47}/T\ \mathrm{cm^6\,mol^{-2}\,s^{-1}}.$$

The value of k_5 was obtained from k_{-5} by combining it with the equilibrium constant as

$$k_5 = 10^{13.95} \exp(-6\ \mathrm{kcal}/RT)\ \mathrm{cm^3\,mol^{-1}\,s^{-1}}.$$

The value of k_3 was assumed to be the same as that of k_{II}, and from the value of k_3 and the equilibrium constant, the value of k_{-3} was calculated. Now, we have all the rate constants needed to calculate the concentration changes in COS, CO, S, S_2, and S_2^* with the time. Figures 4 and 5 present comparisons of the experimental (circle) and calculated histories of S_2^* by using different sets of rate constants. As is shown in these figures, if a value of k_3 is set as equal to that of k_{II}(Case a), the calculated rate of S_2^* disappearance becomes larger than that observed. This means that Reaction 4, followed by Reaction 5, contributes to the consumption of S_2. Therefore, the value of k_3 was changed to one-half the value of k_{II} and the concentration change of S_2^* was recalculated (Case b). Although the agreement with the experiment seems to be improved, there remains some difference with regard to the equilibrium concentration of S_2^*. Therefore, in order to check the influence of the values of k_4, k_{-4}, k_5, and k_{-5} on the

TABLE 1. REACTION MECHANISM

Reaction	Rate expression[a]	Ref.
1) $COS + Ar \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO + S + Ar$	$k_1 = 10^{14.2} \exp(-61\ \mathrm{kcal}/RT)$	5
2) $COS + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO + S_2$	$k_2 = 10^{12.23} \exp(-4.0\ \mathrm{kcal}/RT)$	10
3) $S_2 + Ar \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2S + Ar$	See text	
4) $S_2 + Ar \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} S_2^* + Ar$	See text	
5) $S_2^* + Ar \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} 2S + Ar$	See text	
6) $S_2^* \xrightarrow{k_6} S_2 + h\nu$	$k_6 = 10^{7.48}$	1

a) Units: mol/cm^3 for concentration, s for time.

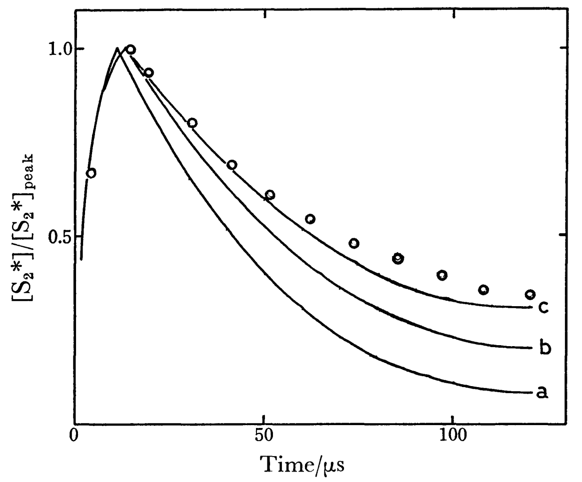

Fig. 4. Comparison of S_2^* profils between the experiment (O) and the calculations (—), 1% COS in Ar mixture; post shock temperature=4851 K; mean temperature between 5 and 20 μs laboratory time=5025 K.

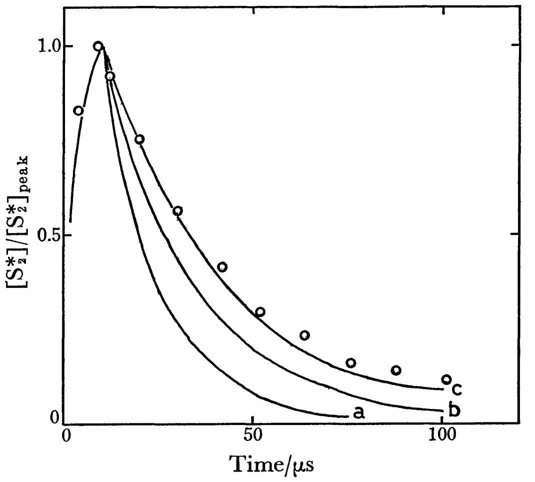

Fig. 5. Comparison of S_2^* profiles between the experiment (O) and the calculations (—), 0.5% COS in Ar mixture; post shock temperature=5507 K; mean temperature between 5 and 20 μs laboratory time=5753 K.

equilibrium concentration of S_2^*, the values of k_4 and k_{-4} were divided by 10, while those of k_5 and k_{-5} were multiplied by 10, leaving $k_3=1/2\ k_{\text{II}}$, and then the concentration change of S_2^* was recalculated (Case c). The results of the calculations are shown in Figs. 4 and 5; the agreement is very satisfactory. Thus, if a set of proper rate constants was selected for Reactions 3, 4, and 5, the concentration change in S_2^* could be reasonably reproduced, but the rate constant for Reaction 3 could not be determined precisely, since the exact values of k_4 and k_5 are not yet available. Therefore, we have the limiting relation, $k_{\text{II}}=k_3$, when the rates of Reactions 4 and 5 are negligibly small; we may conclude that the value of k_{II} is the upper limit of k_3.

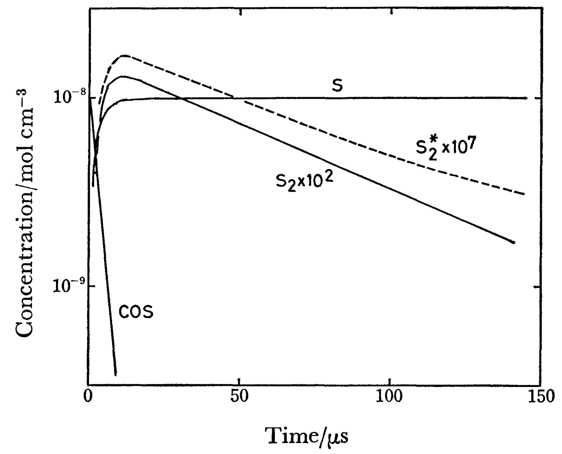

Fig. 6. Time dependent concentration changes of COS, S, S_2, and S_2^*. Experimental conditions are the same as those of Fig. 4.

Figure 6 shows the concentration profiles of COS, S, S_2, and S_2^* with the time; these profiles were calculated by using the rate constants of Case c. As is shown in this figure, although the equilibrium between the concentrations of S_2 and S_2^* was not maintained precisely, it was found that the assumption of the equilibrium did not introduce many errors in estimating the disappearance rate of S_2 from the change in the emission intensity with the time.

The following three reactions are also possible in the decomposition of COS:

$$COS + S \longrightarrow CS + SO \qquad (7)$$

$$COS + SO \longrightarrow CO_2 + S_2 \qquad (8)$$

$$CS + SO \longrightarrow CO + S_2. \qquad (9)$$

The influence of these reactions on k_{II} were examined. Since there are no rate data for Reaction 7, a value of 10^{12} cm^3 mol^{-1} s^{-1} was assumed for k_7. Using values of 10^{11} and 10^9 cm^3 mol^{-1} s^{-1} for k_8[10)] and k_9[10)] respectively, the history of S_2^* was calculated. It was found from this calculation that the concentration of S_2^* was slightly influenced by these reactions, but that the value of k_{II} so determined was not influenced.

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