BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 965—968 (1976)

S_2 Formation during the Pyrolysis of H_2S in Shock Waves

Tetsuo HIGASHIHARA, Ko SAITO, and Hitoshi YAMAMURA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730

(Received April 28, 1975)

The rate of S_2 formation from shock-heated H_2S was measured by means of the UV absorption technique in the temperature range of 2380—3000 K. At all the temperatures measured, the S_2 absorption during the reaction could be represented by $(S_2)_t=(S_2)_\infty\{1-\exp(-kt)\}$, where:

$$k=10^{9.2}\exp(-72\text{ kcal}/RT)\text{ s}^{-1}.$$

The mechanism of the S_2 formation was proposed, and the value of the second-order rate constant, k_1, for the primary reaction, $H_2S+M \to SH+H+M$, was estimated as follows:

$$k_1 = 10^{13.1}\exp(-92\text{ kcal}/RT)\text{ l mol}^{-1}\text{ s}^{-1}.$$

The effects of the addition of NO and O_2 on the rate of S_2 formation were also investigated. The results showed the validity of the proposed reaction mechanism.

The thermal decomposition of H_2S was studied by a static method by Darwent *et al.*[1] in pure H_2S at pressures between 30 and 300 Torr and in the temperature range of 720—970 K. At the temperatures above 900 K, they found that the reaction was second-order with respect to the concentration of H_2S and that its apparent activation energy was about 50 kcal/mol. The reaction was suggested to be $2H_2S \to 2H_2+S_2$. In shock waves at temperatures above 1000 K, on the other hand, the primary step of the decomposition of H_2S, which is diluted in an inert gas, may be considered to be as follows:

$$H_2S + M \to SH + H + M \tag{1}$$

such as has been reported for the other triatomic molecules. However, no data about the pyrolysis of H_2S in shock waves have been reported, although in the oxidation of H_2S Reaction (1) was recognized to be the primary step.[2] It was then stated that the difficulty in the evaluation of the kinetic data for Reaction (1) was due to the effects of oxygen and other oxidizers which could not be removed from the reactant.[3] In this work, we observe the rate of the S_2 formation from shock-heated H_2S in Ar by using a reactant purified carefully, and discuss the mechanism of the H_2S decomposition.

Experimental

The experiments were conducted in a 5-cm-diameter shock tube with a 4.3-m-long test section. The shocks were generated by high-pressure hydrogen in a 1.7-m-long driver section. The system was pumped by an oil-diffusion pump to less than 1×10^{-4} Torr before each run. All the measurements were made behind the incident shock waves. The light source used for the absorption measurements was a 300W Xe lamp (Ushio Electric Co.). The light was focused with a mirror on the entrance slit of a monochromator (Jarrell-Ash, 0.25 m) which had been placed on the side opposite the light source with respect to the shock tube. The selected light was detected by a photomultiplier (MS9SY), whose output was recorded on a single sweep of an oscilloscope. The rise time of the electronics was 2 μs or less. The concentration of S_2 was followed by observing the absorption intensity at 320 nm (${}^3\Sigma_g^- \to {}^3\Sigma_u^-$ system). Although the SH absorption band lies around 320 nm, the measured absorption at this wavelength was attributed to S_2, since the absorption due to SH was negligibly small compared to the strong absorption of S_2.[4]

Hydrogen sulfide was produced by dropping a saturated NaS aqueous solution into a 10% H_2SO_4 aqueous solution and was dried by passing it through calcium chloride and phosphorus pentoxide. The gas thus obtained was solidified and degassed at -115 °C (mp of EtOH) and then purified by fractional distillations between -115 °C and -196 °C. Mixtures of 5%H_2S–95%Ar, 5%H_2S–1%NO–94%Ar, and 5%H_2S–1%O_2–94% Ar were prepared and kept in 8-l flasks for more than 12 hr before use.

The experimental conditions were as follows: $P_1=8$—16 Torr, $P_2=300$—460 Torr, $T_2=2380$—3000 K and ρ_2(total density)$=(3.2$—$6.2)\times10^{-6}$ mol/cm^3, where the subscript 2 denotes the condition just behind the shock front (chemically frozen condition).

Results and Discussion

Rate of S_2 Formation. In preliminary experiments, it was found that the rate of the S_2 formation was greatly influenced by trace amounts of oxygen. Therefore, the purification of H_2S was carefully performed in the manner described in the experimental section. For the mixture of 5%H_2S–95%Ar, no induction period of the S_2 formation was observed over the temperature range measured. A typical oscilloscopic trace of S_2 absorption is shown in Fig. 1 (a). The variation in the concentration of S_2 with the time was expressed by the following relation:

$$\ln\{(S_2)_\infty/((S_2)_\infty-(S_2)_t)\} = kt \tag{I}$$

where $(S_2)_\infty$ denotes the concentration of S_2 at the steady state, which is reached within the observation time. In Fig. 1(b), a plot of the value of the left-hand side of Eq. I is shown as a function of the laboratory time. The experimental conditions and the values of k determined from the above relation are listed in Table 1. The Arrhenius plots of k are shown in Fig. 2, where the data obtained in preliminary experiments are also included for comparison (lines (a) and (b)). In the preliminary experiments, samples were purified by solidifying, degassing, and distilling by using liquid N_2 and were used without further purification. Therefore, it is thought that slight amounts of air were still present in the samples. From this figure, it appears that trace amounts of an impurity accelerate the rate

TABLE 1. EXPERIMENTAL CONDITIONS AND RATE CONSTANTS

Run No.	P_1 Torr	P_2 Torr	T_2 K	ρ_2 mol/cm^3	k s^{-1}	k_1 l mol^{-1} s^{-1}
274	13	419	2640	5.08×10^{-6}	1.80×10^{3}	3.54×10^{5}
276	15	432	2380	5.83	0.682	1.17
279	14	414	2440	5.45	1.09	1.99
280	11	376	2780	4.86	3.31	7.62
282	9	329	2950	3.58	7.60	21.4
283	8	300	3000	3.19	11.4	35.8
284	10.5	375	2890	4.81	5.44	11.3
285	9	321	2890	3.57	5.13	14.4
287	9.5	335	2860	3.76	5.38	14.3
289	16	460	2380	6.20	0.738	1.19
290	14	438	2570	5.48	1.04	1.89

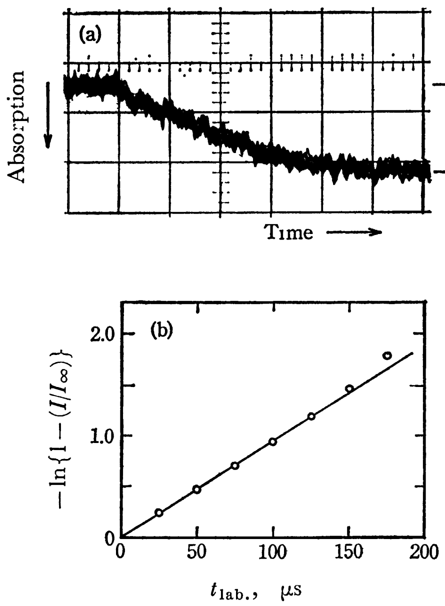

Fig. 1. (a): Sypical oscilloscopic trace of S_2 absorption at 320 nm, 5% H_2S-95% Ar; $T_2=2570$ K; sweep time=50 μs/cm. (b): Plot of $-\ln\{1-(I/I_\infty)\}$ *vs.* laboratory time.

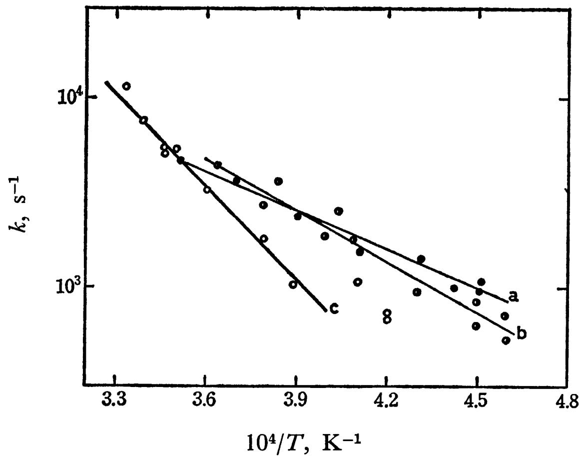

Fig. 2. Arrhenius plots of the rate constant k for S_2 formation. Data around lines (a) and (b) were obtained in preliminary experiments for 5% H_2S-95% Ar mixtures. Data around line (c) were obtained in this experiment for 5% H_2S-95% Ar mixture.

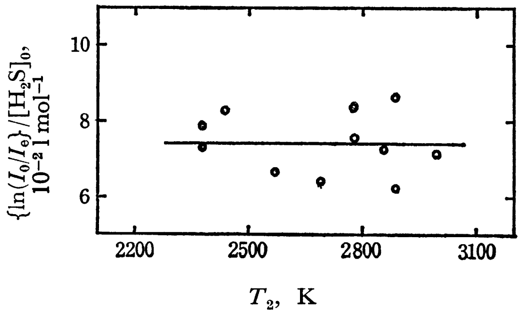

Fig. 3. Plot of $\{\ln(I_0/I_e)\}/(H_2S)_0$ against temperature, where I_0 and I_e are transmitted light intensities at shock front and at equilibrium, respectively.

of S_2 production. The data obtained in this experiment, corresponding to the most purified H_2S, show a large temperature dependence compared with the other two sets of data, (a) and (b). The best fitting straight line (c) gives the following expression in the temperature range of 2500—3000 K:

$$k = 10^{9.2}\exp(-72\ \text{kcal}/RT)\ \text{s}^{-1}.$$

In Fig. 3, the values of $\{\ln(I_0/I_e)\}/(H_2S)_0$ are plotted as a function of T, where I_e is the light intensity at the equilibrium and where the subscript o denotes the condition just behind the shock front. Since the extinction coefficient of S_2 does not vary with the temperature,5) it appears that the quantity of S_2 produced from the unit concentration of H_2S is almost constant over the temperature range measured. This fact means that the recombination of S atoms does not play a dominant role in the S_2 formation because the composition between S_2 and S at the equilibrium, $S_2 \rightleftarrows 2S$, varies largely with the temperature in the range considered.

A possible mechanism of the pyrolysis of H_2S accompanying the S_2 formation is considered to be as follows:

	ΔH°_{298} (kcal/mol)6)	
$H_2S + M \rightarrow H + SH + M$	90.9	(1)
$H_2S + H \rightarrow H_2 + SH$	-13.3	(2)

$2SH \rightarrow H_2S + S$ − 6.1 (3)
$H_2S + S \rightarrow 2SH$ 6.1 (−3)
$2SH \rightarrow H_2 + S_2$ −37.3 (4)
$SH + H \rightarrow H_2 + S$ −19.4 (5)
$SH + S \rightarrow H + S_2$ −17.9 (6)

From the above reaction scheme and the observed result that there existed no induction time for the S_2 formation, it is assumed that the consumption of the intermediates, H, SH, and S, is very rapid compared with their production rate through the primary reaction. Therefore, it is reasonable to use the steady-state method for these radicals. Also, we assume that $(S_2)_\infty = C(H_2S)_0$ and $(S_2)_\infty - (S_2)_t = C(H_2S)_t$, where C is a constant. With these relations, Eq. I is rewritten as:

$$\ln \{(H_2S)_0/(H_2S)_t\} = kt \qquad \text{(II)}$$

It appears that k is the first-order rate constant for the overall reaction of H_2S consumption.

For the S_2 formation in the H_2S pyrolysis, we do not have knowledge about which reaction is dominant under those experimental conditions. Reaction (4) was proposed for the flash photolysis of H_2S by Norrish *et al.*[7] On the other hand, Reaction (6) was proposed by Cullis *et al.*[8] in their review of the combustion of sulfur compounds, on the basis of the reason that the latter is much faster than the former in spite of its lower exothermicity. Also, in the discharge flow system of $H + H_2S$,[9] Reaction (6) was taken as a dominant reaction of S_2 formation. In any event, if the steady-state assumption is used for the intermediates, the following conclusion can be obtained whether Reaction (4) or (6) is taken as the main process of S_2 formation. That is, the overall rate of the H_2S decomposition becomes twice the primary reaction rate, as:

$$-d(H_2S)/dt = 2k_1(H_2S)(M) \qquad \text{(III)}$$

Since, in this experiment, the concentration (M) does not vary with the time behind the shock front, the second-order rate constant, k_1, can be determined from Eqs. II and III. The Arrhenius plots of k_1 are shown in Fig. 4, where the preliminary data (corresponding to Lines (a) and (b) in Fig. 2) are also included. It appears that the effects of impurities become apparent at lower temperatures and that, even for the most purified mixture, the data below 2500 K become higher than the (c) line, the one most suitable for the data above 2500 K. It has been shown in the pyrolysis of H_2O and SO_2 that, under the conditions of relatively lower temperatures and higher concentrations of the reactant, the systems involved many bimolecular reactions and that, as a result, the mechanisms were complicated. This seems to hold also for the pyrolysis of H_2S. Thus, the following expression for k_1 was evaluated from the data above 2500 K:

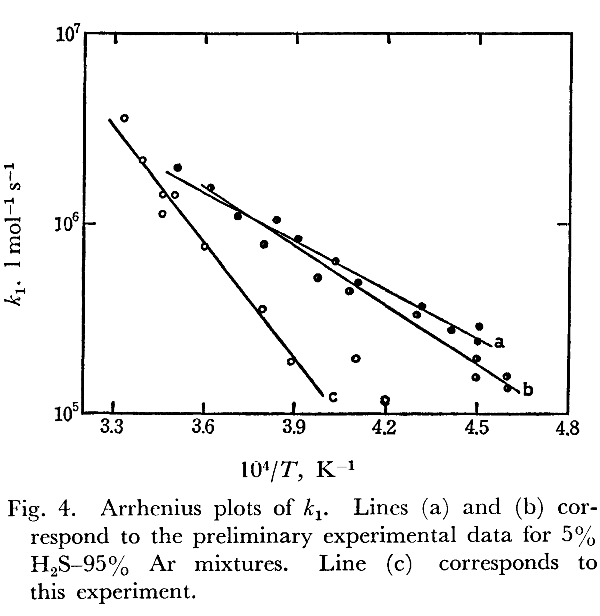

Fig. 4. Arrhenius plots of k_1. Lines (a) and (b) correspond to the preliminary experimental data for 5% H_2S–95% Ar mixtures. Line (c) corresponds to this experiment.

$$k_1 = 10^{13.1} \exp(-92 \text{ kcal}/RT) \text{ l mol}^{-1} \text{ s}^{-1}.$$

Effects of NO and O_2. When a mixture of 5% H_2S+1% NO+94% Ar was shock-heated, it was found that the rate of S_2 formation slowed down extremely. Because of the large effect of NO, the value of k could not be determined for this mixture. This effect suggests that NO acts as a scavenger of radicals. As has been proposed by Bradley *et al.*[10] in the experiment on the $H + H_2S$ flow system, the following reaction is thought to occur in our system also:

$$SH + NO \rightarrow (SHNO)^* \rightarrow \text{removal of SH} \qquad (7)$$

Furthermore, the following reactions may occur to eliminate H atoms from the system:

$$H + NO + M \rightarrow HNO + M \qquad (8)$$
$$H + HNO \rightarrow H_2 + NO \qquad (9)$$

much like the elimination of S atom observed in the photolysis of CS_2 and COS,[11] but at high temperatures these reactions are thought to be less important than Reaction (7).

As is shown in Figs. 2 and 4, in the presence of trace amounts of impurities the rate of S_2 formation was accelerated in the lower-temperature region. The most effective species is thought to be oxygen, which could not be removed from the sample in the usual manner. In the experiment on the 5% H_2S+1% O_2+94% Ar mixture, it was found that the rate of S_2 formation was further accelerated. This can be explained by adding the following bimolecular reactions to the above reaction Scheme 1—6:

$$H + O_2 \rightarrow OH + O \qquad (10)$$
$$H_2S + O \rightarrow SH + OH \qquad (11)$$
$$H_2S + OH \rightarrow SH + H_2O \qquad (12)$$

These reactions contribute to the formation of the SH radical. Thus, the effects of the addition of both NO and O_2 qualitatively support the above reaction scheme proposed for the decomposition of H_2S, although, from this study, it is not apparent whether the main reaction of S_2 formation is Reaction 4 or 6.

On the Value of k_1. Our experimental result for k_1 can be expressed by the equation of the collision theory: $k_1 = \{pZ(D/RT)^{s-1}/(s-1)!\}\exp(-D/RT)$, where p is the steric factor; Z, the collision frequency; s, the number of effective vibrations in the molecule, and D, the critical energy for HS–H bond dissociation. According to the absorption spectrum of H_2S[12], there exists a continuum band with a maximum at about 51000 cm^{-1} and extending to 37000 cm^{-1}. This continuum was also observed in the experiment by Watanabe *et al.*13) and was ascribed to a predissociation. Since, no discrete structure has been observed in the region of further low wave numbers, this continuum is thought to correspond to a nonbonding state which arises from $SH(^2\Pi)+H(^2S)$. Therefore, it may be considered that the dissociation proceeds *via* a crossing point whose potential is higher than the energy state of the products, $SH(^2\Pi)+H(^2S)$. If we take 106 kcal/mol for the critical energy, D,14) we obtain $s=3.5$. By introducing these values into the empirical equation, $E_a=D-(s-1.5)RT$, the activation energy, E_a, is calculated to be 94 kcal/mol at 2750 K. This value is very close to the experimental value. Assuming the collision diameters for H_2S–H_2S and H_2S–Ar pairs to be 3.5 and 3.0 Å respectively, we obtain $p=0.5$, which is comparable to the value of 0.14 for the analogous molecule, H_2O.15) The relatively large values of p for these molecules can be feasibly explained by the spin-allowed reactions.

Although, in this study, we did not consider either the temperature change during the course of the reaction behind the shock front or the boundary-layer effects, it may be thought that the results are not essentially changed by these effects.

References

1) B. De B. Darwent and R. Roberts, *Proc. Roy, Soc., A*, **216**, 344 (1953).

2) J. N. Bradley and D. C. Bobson, *J. Chem. Phys.*, **46**, 2865 (1967).

3) H. H. Homan and A. Haas, "Comprehensive Chemical Kinetics," Vol. 4, ed. by C. H. Bamford and C. F. H. Tipper, Elsevier Publishing Co., New York (1972), Chap. 1.

4) R. A. Fifer, R. Moreau, and S. H. Bauer, "Proceedings of the Ninth International Shock Tube Symposium," Stanford Univ. Press, Calif. (1973), p. 731.

5) A. G. Gaydon, G. H. Kimbell, and H. B. Palmer, *Proc. Roy. Soc., A*, **279**, 313 (1964).

6) S. W. Benson, "Thermochemical Kinetics," Wiley, New York (1968).

7) R. G. W. Norrish and A. P. Zeelenberg, *Proc. Roy. Soc., A*, **240**, 293 (1957).

8) C. F. Cullis and M. F. R. Mulcahy, *Combust. Flame*, **18**, 255 (1972).

9) L. T. Cupitt and G. P. Glass, "Proceedings of the Symposium on Chemical Kinetics Data for the Upper and Lower Atmosphere," ed. by S. W. Benson, John Wiley & Sons, Inc., New York (1975), P. 39.

10) J. N. Bradley, S. P. Truemen, D. A. Whytock, and T. A. Zaleski, *J. Chem. Soc. Faraday*, **69**, 416 (1973).

11) N. Basco and A. E. Pearson, *Trans. Faraday Soc.*, **63**, 2684 (1967).

12) C. F. Goodeve and N. O. Stein, *Trans. Faraday Soc.*, **27**, 393 (1931).

13) K. Watanabe and A. S. Jursa, *J. Chem. Phys.*, **41**, 1956 (1964).

14) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, D. Van Nostrand Co., Princeton, N. J. (1967).

15) K. Kuratani and S. Tsuchiya, "Shock Waves in Chemistry and Physics," Shokabo, Tokyo (1968), Chap. III.