A Measurement of the Thermal Decomposition of CS₂ behind Reflected Shock Waves

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Synopsis.   The thermal decomposition of CS_2 in Ar was investigated in the temperature range of 2000—2900 K by monitoring both the UV absorption and the visible emission of CS_2. A typical induction zone was observed during the decomposition. It was found that the rate constant of the initiation reaction obtained from the induction zone was smaller than that reported by previous workers.

Shock-tube studies of the pyrolysis of CS_2 diluted in Ar have been reported by four research groups in the past.[1-5] In the low-pressure region, the rate of CS_2 disappearance is expressed generally as: $-d[CS_2]/dt=k[CS_2][Ar]+k'[CS_2]^2$, and for highly diluted mixtures, with only a small percentage of CS_2, the second term is neglected. k does not necessarily correspond to the rate constant of the $CS_2+Ar \rightarrow CS+S+Ar$ reaction. However, the values of k reported by the previous workers are consistent with each other within a factor of two, although different experimental conditions, techniques, and data analyses were employed. Among the previous experiments, Arnold et al.'s data[5] for k correspond clearly to the complex reaction after an induction period. In our present study by using the UV absorption technique, the induction zone was also found in the CS_2 concentration profile behind reflected shock waves below 3000 K. Moreover, it appeared that the second-order rate constant for the CS_2 decay rate in the induction zone was much smaller than the previous results. At temperatures higher than 3000 K, the induction period was so short that the CS_2 profile showed a simple decay curve, as if the decomposition proceeded via a simple mechanism. In this paper, therefore, only the case in which the induction zone apparently exists in the absorption profile is considered.

Experimental

Reaction mixtures containing 0.25 and 0.5 mol% CS_2 in Ar were heated by reflected shock waves in a shock tube 5 cm in inner diameter, previously described elsewhere,[6] and the CS_2 dissociation rate was deduced by monitoring the UV absorption at 220±0.8 nm. In some experimental runs, the emission from the electronically excited CS_2 was monitored at 435±5 nm simultaneously with the absorption record. The experimental conditions were as follows: temperature = 1980—2930 K; total concentration = $(3.3—8.0) \times 10^{-6}$ mol cm⁻³; $[CS_2] = (1.5—4.0) \times 10^{-8}$ mol cm⁻³. At 220 nm, the observed absorption coefficient of CS_2 was around 1×10^7 cm² mol⁻¹ and Lambert-Beer's law was ascertained to hold, at least up to 8×10^{-8} mol cm⁻³ of CS_2.

Results and Discussion

Figure 1 shows a typical trace of the UV absorption. The absorption of CS_2 rises to a maximum just behind the reflected shock front and then begins to decrease

slightly; then, after a certain period (we call this the induction period of CS_2 decomposition), it rapidly falls to a steady value. From the two different slopes in the profile, as indicated by I and II in the figure, the corresponding rate constants, k_I and k_{II}, can be determined for each experiment. The visible emission, on the other hand, rose to a peak behind the reflected shock front with a relatively long rise time, while at the end of the induction zone it began to decrease towards a steady value. In the induction zone, the emission profile did not show any such gradient in its intensity as appeared in the simultaneous absorption record. Thus, from the emission profile, the rate of CS_2 disappearance was measured only from the slope behind the induction zone. Figure 2 shows an Arrhenius plot of the second-order rate constants, together with the previous data. The values of k_I and k_{II} were determined from the absorption profile as: $-d(ln[CS_2])/dt/[Ar]$, while the values of k_{III} were obtained by the emission profile as: $-d(lnI)/dt/[Ar]$, where I is the emission intensity. This figure shows that the second-order rate constants, k_{II} and k_{III}, fall in the range of the previous data, although our data show a somewhat larger scatter and, if k_{III} is considered alone, the data seem to have a different temperature dependence because of the lack of data over a wide temperature range. The plot of k_I, the apparent rate constant in the induction zone, lies below that of the previous data, but it shows the same temperature dependence.

An appropriate reaction mechanism was assumed for the CS_2 decomposition involving the 14 elementary reactions listed in Table 1. The simulation by using this mechanism clearly showed a radical chain behavior; thus, the existence of the induction zone, i.e., a rapid decrease in CS_2, began after a time, and was followed by a rapid increase in the sulfur atom. A typical example of the calculation is shown in Fig. 3. Although the mechanism and the rate constants
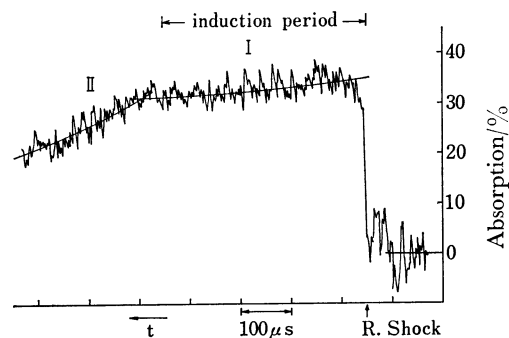

Fig. 1.   Typical UV absorption trace.
Conditions: T=2460 K, [Ar]=3.45×10^{-6} mol cm⁻³, [CS₂]=1.73×10^{-8} mol cm⁻³. Rate constants: k_I=1.06×10^8 cm³ mol⁻¹ s⁻¹, k_{II}=7.45×10^8 cm³ mol⁻¹ s⁻¹.
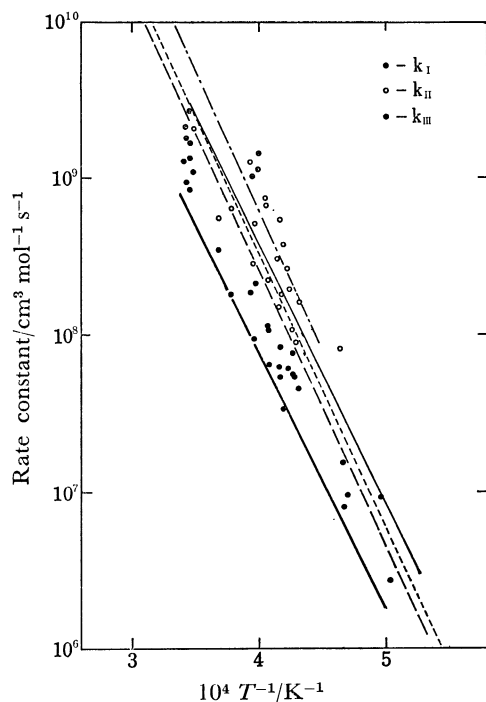
Fig. 2. Arrhenius plot of second order rate constants. k_I, k_{II}, and k_{III} are explained in the text. ——·——: Ref. 1, ————: Ref. 2, —————: Ref. 5, ———: Ref. 7, ———: k_1 determined in this work.

TABLE 1. MECHANISM AND KINETIC DATA

Reaction	Forwards rate constant[a]		
	log A	E	Sources
1 $CS_2 + Ar = CS + S + Ar$	14.4	74	a
2 $CS_2 + S = CS + S_2$	14.0	4.07	b
3 $CS_2 + CS_2 = CS + S + CS_2$	14.22	43.7	c
4 $S_2 + Ar = S + S + Ar$	13.6	80.2	d
5 $CS_2 + S + Ar = CS_3 + Ar$	log $k = 17.48$		e
6 $CS_2 + S_2 = CS + S_3$	log $k = 8.63$		f
7 $S_3 + Ar = S_2 + S + Ar$	14.39	22.7	g

a) Units: mol cm⁻³ for concentration, s for time, and kcal mol⁻¹ for energy. The backwards rate constants were estimated using the equilibrium constants.
a. Obtained in this work. b. K. Howman, G. Krome, and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, **74**, 650 (1970). c. Ref. 1. This reaction probably proceeds via a two-step process: $2CS_2 \rightarrow CS_3 + CS$ and $CS_3 + Ar \rightarrow CS_2 + S + Ar$. d. T. Higashihara, K. Saito, and I. Murakami, unpublished results. e. N. Basco and A. E. Peason, *Trans. Faraday Soc.*, **63**, 2684 (1967). f. Assumed from the data for $CO_2 + O_2 = CO + O_3$. g. Adjusted value to fit the experimental data.

used are not necessarily true, the simulation has significance in the sense that the induction period appears also in the calculation.

Since the rate of Reaction 1 is very small compared with that of Reaction 2, the concentration of sulfur atoms should rapidly reach a steady value. In fact, the computer simulation showed that a steady concentration was reached within 10 μs under the present experimental conditions (see Fig. 3). An Arrhenius expression for the initiation reaction rate constant

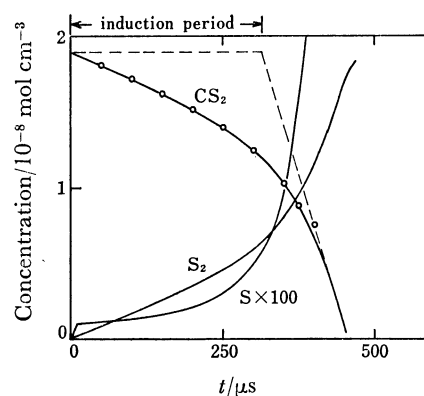Fig. 3. Example of simulation.
Conditions: $T = 2710$ K, $[Ar] = 3.76 \times 10^{-6}$ mol cm⁻³, $[CS_2] = 1.88 \times 10^{-8}$ mol cm⁻³. Open circles are the experimental profile of CS_2 under the same conditions.

was thus obtained from the $k_1 = 2k_1$ relation as:

$$k_1 = 10^{14.4 \pm 0.5} \exp\{-(74.3 \pm 6.5 \text{ kcal mol}^{-1})/RT\}$$
$$\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

where the limits of error are the standard deviations. These results are shown in Fig. 2. The value of k_1 obtained in this study gives a collision efficiency factor, β_c,[8] of about 0.01 at 2500 K. This is considered satisfactory compared with the other spin-forbidden reactions of triatomic molecules.

The experimental conditions of Gaydon *et al.* and Arnold *et al.* are the same as those of the present work. Gaydon *et al.* obtained the rate of the CS_2 decomposition by observing the CS and S_2 absorption with relatively long time resolutions. Arnold *et al.* obtained the overall rate from the intensity gradient after the induction period in the emission profile at 450 nm. Therefore, the values of k_{II} and k_{III} measured in this work may be identified with the values of k measured by these workers. Olschewski *et al.* studied the decomposition rate by monitoring the CS_2 absorption at high total concentrations, 10^{-5}—10^{-4} mol cm⁻³, while the CS_2 concentration was in the same range as in the present study. A calculation using the above assumed mechanism under their experimental conditions showed that the concentration of the sulfur atom reached a steady value within a very short time. Considering this fact, their k_1 values give an overestimate by at least a factor of two.

References

1) A. G. Gaydon, G. H. Kimbell, and H. B. Palmer, *Proc. R. Soc. London, Ser. A*, **279**, 313 (1964).
2) H. A. Olschewski, J. Troe, and H. Gg. Wagner, *Z. Phys. Chem. N. F.*, **45**, 329 (1965).
3) H. A. Olschewski, J. Troe, and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, **70**, 1060 (1966).
4) P. R. Ryason, *Rev. Sci. Instr.*, **38**, 607 (1967).
5) S. T. Arnold, W. G. Brownlee, and G. H. Kimbell, *J. Phys. Chem.*, **74**, 8 (1970).
6) T. Higashihara, K. Saito, and H. Yamamura, *Bull. Chem. Soc. Jpn.*, **49**, 965 (1976).
7) D. L. Baulch, D. D. Drysdale, J. Duxbury, and S. Grant, "Evaluated Kinetic Data for High Temperature Reactions," Vol. 3, Butterworths, London (1976).
8) J. Troe, *J. Chem. Phys.*, **66**, 4745 (1977); **66**, 4758 (1977).