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Thermal Decomposition of COS

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Synopsis. Thermal decomposition of COS was investigated by shock tubes between 1140—3230 K. The decay of COS and S was monitored by IR emissions and atomic resonance absorption spectrometry (ARAS) coupled with laser flash photolysis technique, respectively. The rate constants for the reactions $COS+M \rightarrow CO+S+M$ (1) and $COS+S \rightarrow CO+S_2$ (2) were determined as $k_1=(4.07\pm1.83)\times10^{-10}\exp(-257\pm24\ \mathrm{kJ}/RT)$, T: 1900—3230 K and $k_2=(3.91\pm1.18)\times10^{-11}\exp(-28.3\pm0.9\ \mathrm{kJ}/RT)$ cm^3 molecule^{-1} s^{-1}, T: 1140—1680 K.

A number of investigators have studied the thermal decomposition of carbonyl sulfide in static reactors at low temperatures, however, there is still lack of reliable kinetic data at high temperatures.

The mechanism over 900 K at low pressures involves a unimolecular, first-order rupture (1) followed by bimolecular atom abstractions (2),

$$\mathrm{COS}(^1\Sigma) + \mathrm{M} \rightarrow \mathrm{CO}(^1\Sigma) + \mathrm{S}(^3\mathrm{P}) + \mathrm{M} \qquad \Delta H^\circ_{298} = 305\ \mathrm{kJ\,mol^{-1}} \quad (1)$$

$$\mathrm{COS} + \mathrm{S}(^3\mathrm{P}) \rightarrow \mathrm{CO} + \mathrm{S_2} \qquad \Delta H^\circ_{298} = -121\ \mathrm{kJ\,mol^{-1}}. \quad (2)$$

Hay and Berford[1)] studied the thermal decomposition of COS in the temperature range 2000—3200 K in shock tube experiments using a quadrupole mass filter. The authors estimated the rate constants as $k_1=1.84\times10^{-13}\ T^{1/2}[299\ \mathrm{kJ}/RT]^{1.87}\exp[-299\ \mathrm{kJ}/RT]$ cm^3 molecule^{-1} s^{-1}, and $k_2 = 9.97\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 2570 K. Schecker and Wagner[2)] investigated the thermal decomposition of COS in the temperature range 1500—3100 K in three shock tubes of different diameter behind incident and reflected waves by monitoring IR emission of COS at 4.9 μm. The rate constant was found to be $k_1=2.63\times10^{-10}\exp(-255\ \mathrm{kJ}/RT)$ cm^3 molecule^{-1} s^{-1}, however, COS was not selectively isolated in the study because of interfering spectra of product CO. Woiki and Roth[3)] studied the thermal decomposition of COS behind reflected shock waves in the temperature range 1750—2990 K by monitoring S(^{3}P) atom using ARAS. The rate constant was found to be $k_1=4.82\times10^{-10}\exp(-266\ \mathrm{kJ}/RT)$ cm^3 molecule^{-1} s^{-1}. In the present study, therefore, thermal decomposition of COS was investigated in a shock tube behind incident shock waves by monitoring IR emission intensities at 4.7 and 5.3 μm simultaneously, where the relative sensitivities for COS and CO were calibrated at these wavelengths.

Woiki et al.[4)] studied the consecutive reaction (2) behind reflected shock waves in the temperature range 1200—1670 K by using ARAS. From the decay of the S atom absorption signals, the rate constant of reaction (2), $k_2=9.97\times10^{-11}\exp(-37.9\ \mathrm{kJ}/RT)$ cm^3 molecule^{-1} s^{-1}, was determined by assuming first order kinetics. In this study, reaction (2) was directly measured by monitoring S atom using ARAS, where, S atoms were produced via 193 nm laser photolysis of COS behind reflected shock waves. The results of this study are compared with those of previous studies.

Experimental

The details of the apparatus have been described elsewhere.[5)] The conventional stainless-steel shock tube of 5 cm diameter and 4 m long was used to obtain the rate constant of reaction (1). A sample gas mixture of the 1% COS diluted Ar were heated in incident shock waves between 1900—3230 K. The total pressure between 27.7—123 kPa was applied. The variation of the concentrations of COS and CO was monitored by the IR emission of 5.3 and 4.7 μm.

Also a diaphragmless stainless-steel shock tube of 5 cm diameter and 4 m long was used to obtain the rate constant of reaction (2). Sample gas mixtures of 130 and 520 ppm COS diluted in Ar were heated in reflected shock waves between 1140—1680 K. The total pressure between 124—232 kPa was applied. After the reflected shock wave passed through the observation station, a sample gas was irradiated by an ArF (28 kJ m^{-2}) or KrF (120—320 kJ m^{-2}) excimer laser through a rectangular quartz window located at the end plate of the shock tube. S(^{1}D) atom produced by laser photolysis of COS was very rapidly quenched to its ground state, then the time dependent concentration of S(^{3}P) was monitored by using Atomic Resonance Absorption Spectrometry (ARAS) at the wavelength 182.6 nm. Resonant radiation at the same wavelength from a microwave-excited discharge lamp (0.1% SO_2 in He) was isolated by a 20 cm VUV monochromator and detected by a solar-blind photo multiplier tube. ARAS signals were recorded with a storage oscilloscope.

COS (Matheson Company, Inc.) was purified by trap to trap distillation. Ar was passed through a dry-ice cold trap to remove water vapor.

Results and Discussion

An example of the evolution of the IR intensities at 4.7 and 5.3 μm is shown in the insert of Fig. 1. Because the consecutive reaction (2) is much faster than the initiation reaction (1) for the present experimental condition, the rate of disappearance of COS should be

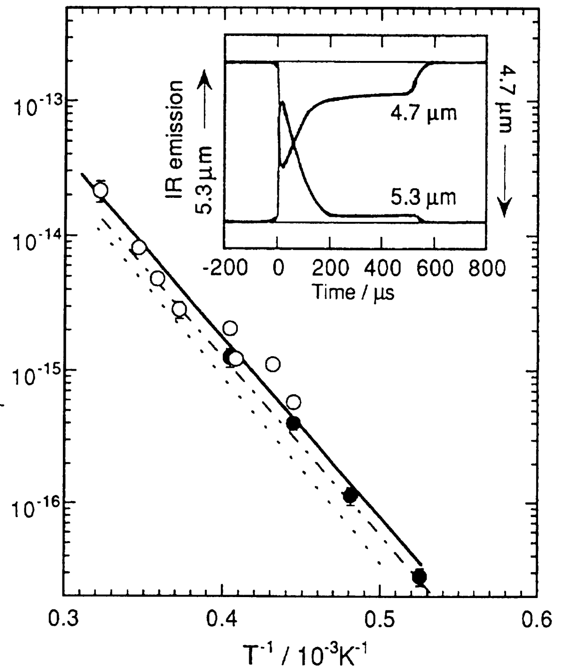

Fig. 1. Arrhenius plot of the rate constant of the reaction, COS+M→CO+S+M, obtained by IR emission experiments. (○) (—) This work obtained from the emission of 5.3 μm (Method(a)). (●) This work obtained from the emission of 5.3 and 4.7 μm (Method(b)). (– – –) H. G. Schecker and G. Wagner (Ref. 2). (- - -) A. J. Hay and L. Berford (Ref. 1). The insert shows an example of the IR emission signals at 5.3 and 4.7 μm in COS/Ar system. COS/Ar=1/99, T=2494 K, P=101 kPa.

twice of that of (1). In order to exclude the contribution of CO in the observed IR emissions, the following two procedures were employed.

Method (a): This analysis is essentially the same as that used in Ref. 2. At high temperatures above 2250 K, decomposition of COS is very fast. Therefore final steady state of the observed IR emission was due to CO only. Also IR emission at $t=0$ should be only from COS, then the following relation can be used to evaluate the rate constant k_1.

$$I(t) - A_1 = (A_2 - A_1)e^{-2k_1(\mathrm{M})t}, \qquad (3)$$

where $I(t)$ the observed IR emission intensity at 4.7 or 5.3 μm, A_1 the IR intensity after COS is completely decomposed, A_2 the emission intensity at $t=0$, and M denotes the third body, respectively. A_1 and A_2 can be decided from the single profile of IR emission at 4.7 or 5.3 μm independently. However, relative intensity of COS against CO is larger in the IR emission at 5.3 μm than that at 4.7 μm, therefore, experimental data at 5.3 μm were used to evaluate the rate constant of (1) in this study.

Method (b): At low temperatures below 2070 K, steady state for IR intensities was not attained even at the final stage of the observation time. Thus emission intensities of COS and CO were calibrated as functions of temperature and wavelength i.e., the coefficients a_{ij} in the following relations were measured in COS/Ar and CO/Ar mixtures for a wide temperature range,

$$I_{5.3} = a_{11}(\mathrm{COS}) + a_{12}(\mathrm{CO}),$$
$$I_{4.7} = a_{21}(\mathrm{COS}) + a_{22}(\mathrm{CO}),$$

where $I_{5.3}$, and $I_{4.7}$ are the emission intensity of 5.3 and 4.7 μm respectively. By using these calibration curves, concentration of COS in the COS/CO mixtures can be evaluated by analyzing the IR intensities at these two wavelengths.

At temperature between 2250 and 2450 K, both methods (a) and (b) could be adopted.

The Arrhenius plot of reaction (1) thus obtained is shown in Fig. 1. The rate constant of the reaction determined by two procedures, (a) and (b), is consistent as can be seen in the figure. A least-squares fit of the data shown in Fig. 1 gives the following Arrhenius expression for the rate constant of reaction (1) in the temperature range of 1900 to 3230 K:

$$k_1 = (4.07 \pm 1.83) \times 10^{-10} \exp(-257 \pm 24\ \mathrm{kJ}/RT)$$
$$\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}.$$

The error bars shown in the plot indicate the uncer-

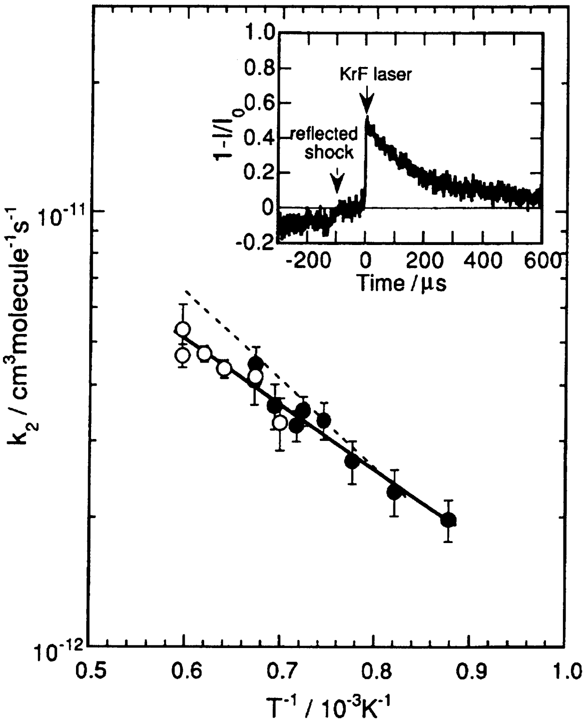

Fig. 2. Arrhenius plot of the rate constant of the reaction, COS+S→CO+S_2, obtained by the laser photolysis of COS experiments. (●) (○) (—) This work closed circles; ArF, open circles; KrF. (- - -) D. Woiki et al. (Ref. 4) The insert shows an example of the absorption signal of S(^{3}P) at 182.6 nm. COS=130 ppm, T=1616 K, P=216 kPa.

Table 1. Reaction Scheme and Rate Parameters

COS–Ar	$\log A$	E	Reference
1) $COS+M=CO+S+M$	−9.39	257	This work
2) $COS+S=CO+S_2$	−10.35	23.8	This work
3) $COS+O=CO+SO$	−10.58	18.8	Baulch (Ref. 6)
4) $CS+O=CO+S$	−9.57	6.3	Atkinson (Ref. 8)
5) $S_2+M=S+S+M$	−7.98	425	Fair (Ref. 7)
6) $S+O_2=SO+O$	−11.65	0.0	Baulch (Ref. 6)

$k=A\ \exp(-E/RT)$, (in units of cm^3, molecule, sec, and kJ). The reverse reactions were included in this calculation.

tainty 2σ. The value of the rate constant for the reaction (1) is found to be consistent with those of previous studies.

The measured apparent activation energy of 257 kJ mol^{-1} in the reaction (1) is compared with those of other similar linear-triatomic molecules, CS_2, which is isoelectronic and involve a singlet-triplet potential energy crossing during thermal decomposition to ground state products. CS_2 decomposes as follows.

$$CS_2(^1\Sigma) + M \rightarrow CS(^1\Sigma) + S(^3P) + M \quad \Delta H^\circ_{298} = 392\ \mathrm{kJ\,mol^{-1}}. \tag{4}$$

The rate constant of this reaction was obtained by Baulch et al.[6] as $k_4 = 4.3\times10^{-9}\exp(-326\ \mathrm{kJ}/RT)$ cm^3 molecule^{-1} s^{-1}. The calculated values of n in the equation, $E_a = E^* - nRT$ based on the simple collision theory vary from 2.57 at 2250 K to 1.79 at 3239 K for COS. These values are consistent with the same spin-forbidden reactions of CS_2, for which the values of n are 3.53 and 2.46 over the same temperature range.

An example of the time dependence of absorption intensity of $S(^3P)$ atom at 182.6 nm is shown in the insert of Fig. 2. ArF excimer laser was fired after 100 μs delay from the arrival of reflected shock wave at the observation station. The sudden increase of the absorption by $S(^3P)$ atoms due to ArF laser photolysis of COS and subsequent exponential decay are shown in this figure. The yield of $S(^3P)$ production in 193 nm photolysis of COS was found to be 2—3% of the initial concentration of COS, so that decay rate of $S(^3P)$ was directly determined by adapting pseudo-first order kinetic analysis. The Arrhenius plot of the rate constant for the reaction (2) thus obtained is shown in Fig. 2. The experimental results are expressed as

$$k_2 = (3.91 \pm 1.18) \times 10^{-11}\exp(-28.3 \pm 0.9\ \mathrm{kJ}/RT)\ \mathrm{cm^3\,molecule^{-1}\,s^{-1}}.$$

The magnitude of the rate constant for reaction (2) is found to agree with those measured by Woiki et al.[4] within the factor of 2, although the values of the activation energy is somewhat different each other.

The rate constants of elementary reactions of COS–Ar system are summarized in Table 1. Sensitivity analysis was performed to ensure the validity of the present analyses. Consequently, consecutive reactions are confirmed to be unimportant in deciding the rate constants of the reaction (1) and reaction (2).

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