Chemical Physics Letters 707 (2018) 140–143

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Kinetics of the thermal decomposition of CH_2F_2

Akira Matsugi *, Hiroumi Shiina

National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

ARTICLE INFO

Article history:
Received 14 June 2018
In final form 23 July 2018
Available online 24 July 2018

Keywords:
Shock tube
Master equation
Rate constant
Difluoromethane
Thermal decomposition

ABSTRACT

Kinetics of the thermal decomposition reaction $CH_2F_2 \rightarrow CHF + HF$ was studied by laser absorption measurements in a shock tube. The rate constants were determined by analyzing temporal profiles of HF produced in pyrolysis of CH_2F_2 over the temperature range 1577–2214 K at pressure of ~100 kPa in Ar bath. The results were well reproduced by master equation analysis based on RRKM theory and classical trajectory calculations, which gave the following rate constant expressions: $k_\infty = 2.34 \times 10^{15}$ exp $(-41{,}550\ \mathrm{K}/T)\ \mathrm{s}^{-1}$, $k_0 = 5.33 \times 10^{25}\ (T/\mathrm{K})^{-8.635} \exp(-44{,}190\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, and $F_\mathrm{cent} = 0.13$.

1. Introduction

Hydrofluorocarbons (HFCs) are primary constituents of refrigerants for heat pump and refrigeration cycles. HFCs generally have high global-warming potentials (GWPs) due to their high chemical stability in atmosphere. Compounds such as difluoromethane (CH_2F_2; R32) and tetrafluoropropenes (R1234yf and R1234ze) have been proposed and used as alternative refrigerants for air-conditioning systems owing to their low GWPs compared to the conventional HFC refrigerants such as R410A and R134a. Besides the concern on their atmospheric chemistry and environmental impacts, elucidation of their flammability and combustion characteristics is critical to ensure safe use of the low-GWP alternative refrigerants.

Combustion properties of CH_2F_2 have been subjected to several experimental investigations [1–4]. Kinetic modeling studies on the oxidation and combustion of HFCs have also been undertaken [4–7]. Among them, a recent study on CH_2F_2 flames [4] suggested that the thermal decomposition of CH_2F_2

$$CH_2F_2 \rightarrow CHF + HF \tag{R1}$$

was particularly important for predicting the laminar flame speed of CH_2F_2. However, the knowledge on its kinetics is very limited [6,8–10]. In the present study, this reaction was studied by shock tube experiments and master equation analysis to experimentally determine the rate constant and theoretically corroborate and extrapolate the experimental results.

2. Methods

2.1. Experiment

The experimental method has been described elsewhere [11,12]. Briefly, temporal profiles of HF produced from the thermal decomposition of the sample gas, 20–50 ppm of CH_2F_2 diluted in Ar, were monitored by its IR absorption in a shock tube [11]. The rate constants for the reaction (R1), k_1, were then derived by kinetic analysis of the profiles. The measurements were performed for the temperature range 1577–2214 K at pressure of ~100 kPa.

2.2. Calculations of secondary kinetics

To account for contribution of secondary reactions to the observed HF profiles, the reaction pathways and rate constants for the reactions:

$$CHF + CHF \rightarrow \text{products} \tag{R2}$$

$$CHF + CH_2F_2 \rightarrow \text{products} \tag{R3}$$

were investigated computationally. Geometries and harmonic vibrational frequencies of stationary points were obtained at the ω B97X-D/6-311++G(d,p) level [13–15], and single-point energies at the optimized structures were calculated at the CCSD(T)-F12b/cc-pVTZ-F12 level [16–20].

The reaction (R2) was found to begin with barrierless association of two CHF radicals; therefore, its rate constant was calculated by the variational transition state theory. The rate constant for the reaction (R3) was calculated by the transition state theory with the

---

* Corresponding author.
E-mail address: a.matsugi@aist.go.jp (A. Matsugi).

https://doi.org/10.1016/j.cplett.2018.07.054

Table 1
Molecular and transition state properties used in the RRKM/master equation calculation.

Property	Species	Values
Vibrational frequencies (scaled)/cm^{-1}	CH_2F_2	505, 1040, 1068, 1123, 1215, 1390, 1453, 2923, 2996
	TS	967*i*, 198, 423, 974, 1110, 1221, 1384, 1850, 2907
Rotational constant/GHz	CH_2F_2	49.5, 10.6, 9.24
	TS	51.7, 6.35, 5.80
Rotational symmetry number	CH_2F_2	2
	TS	1
Number of optical isomers	CH_2F_2	1
	TS	2
ZPE-corrected barrier height/kJ mol^{-1}		332
ZPE-corrected reaction energy/kJ mol^{-1}		319

semiclassical tunneling correction assuming an asymmetric Eckart potential [21]. The partition functions were estimated by rigid-rotor and harmonic-oscillator approximations. The frequency and zero-point energy (ZPE) scaling factors [22] of 0.950 and 0.975, respectively, were adopted.

2.3. RRKM/master equation calculation

The rate constant for the reaction (R1) was calculated by the RRKM/master equation analysis [23–25] based on the classical trajectory calculation of the collisional energy transfer process [25,26]. The computational method and procedure are same as those described in ref 24 except that the tunneling correction assuming an asymmetric Eckart potential [21] was adopted. The rate constants were calculated only for the reaction channel forming the CHF + HF products because this is expected to be a single dominant channel in the decomposition of CH_2F_2 [9]. The rovibrational properties and energies of the reactant and transition state were calculated using the same method as described above and are summarized in Table 1.

The exponential-down model [23] was employed for modeling the collisional energy transfer. The model parameter α and collision frequency Z were determined by the classical trajectory calculation [25] at 1000–2500 K, and are represented as functions of temperature T as $\alpha \approx 390\,(T/1000\text{ K})\text{ cm}^{-1}$ and $Z \approx 2.2 \times 10^{-10}\,(T/\text{K})^{1/6}\text{ cm}^3$ molecule^{-1} s^{-1}.

3. Results and discussion

Examples of the HF time profiles are shown in Fig. 1. The mole fractions of HF increased after the passage of the reflected shock waves at time zero. At high temperatures, the apparent yield of HF (relative to the initial CH_2F_2 mole fraction) reached an asymptotic value of approximately 1.5, which indicates existence of secondary reaction(s) contributing to the profiles.

Fig. 2 shows the calculated energy diagrams for the potential secondary reactions, R2 and R3. For comparison, the reaction enthalpies at 0 K obtained from the Active Thermochemical Tables (ATcT) [27,28] based on version 1.122 of the Thermochemical Network [29] are also shown. The former reaction proceeds with formation of chemically-activated *cis*-/*trans*-CHFCHF, which can isomerize to each other or dissociate to the CHCF/CCHF + HF products. The barrier height for the isomerization (dotted line in Fig. 2) was not calculated but is expected to be ~300 kJ mol^{-1} based on the calculation of a similar system [30]. The dissociations from the activated CHFCHF can take place directly because of the large

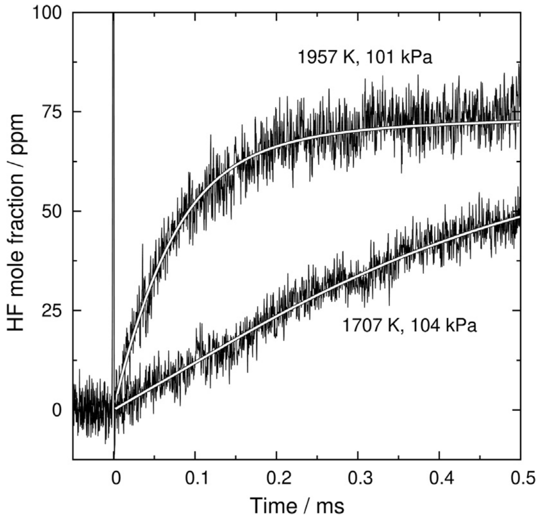

Fig. 1. HF mole fraction profiles observed in the decomposition of CH_2F_2 (50 ppm in Ar) behind the reflected shock waves at 1707 and 1957 K. The white lines represent the fitted profiles.

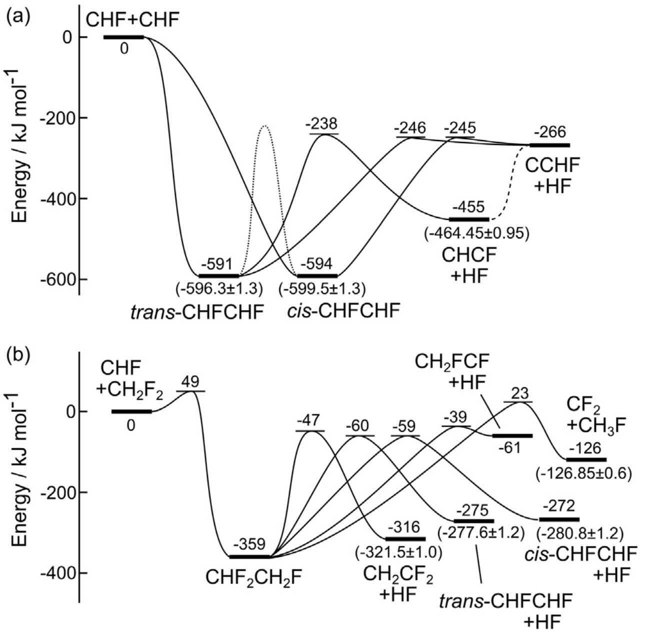

Fig. 2. Energy diagrams for the (a) CHF + CHF and (b) CHF + CH_2F_2 reactions. ZPE-corrected energies relative to the reactants are shown. The values in the parentheses are the ATcT [27–29] reaction enthalpies at 0 K.

excess energies available. Since CCHF rapidly isomerizes to CHCF, the overall process can be represented as

$$\text{CHF+CHF} \rightarrow \text{CHCF+HF} \tag{R2a}$$

with the rate constant k_{2a} close to the sum of those for the two association channels, which was calculated to be $k_2 = 6.2 \times 10^{-11}\text{ cm}^3$ molecule^{-1} s^{-1} without significant temperature dependence over 1000–2500 K.

The CHF + CH_2F_2 reaction begin with insertion of the CHF radical to the C-H bond of CH_2F_2, generating chemically-activated CHF_2CH_2F, which can then decompose to various products. The insertion has a barrier height of 49 kJ mol^{-1}, and the calculated rate constant in the high-pressure limit is expressed as $k_3 = 1.6 \times 10^{-23}\,(T/\text{K})^{3.22}\exp(-4820\text{ K}/T)\text{ cm}^3$ molecule^{-1} s^{-1} over