The study of $\text{C}_2\text{F}_4\text{Br}_2$ dissociation kinetics using methods of atomic and molecular resonance absorption spectroscopy behind shock waves

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Abstract. Measurements of atomic bromine and $\text{CF}_2$ radical concentration profiles, formed at the dissociation of $\text{C}_2\text{F}_4\text{Br}_2$ molecules behind shock waves, were carried out by means of atomic resonance absorption spectroscopy and molecular resonance absorption spectroscopy. The experiments were performed in mixtures with various concentrations of $\text{C}_2\text{F}_4\text{Br}_2$ in $\text{Ar}$ at the temperatures of 1000–3500 K and pressures of 2–17 bar. As a result the mechanism of $\text{C}_2\text{F}_4\text{Br}_2$ pyrolysis was investigated and the $\text{C}_2\text{F}_4$ radical dissociation rate constant was determined: $k_{\text{dC}_2\text{F}_4} = A \exp(-E/RT)$, where $A = 4.76 \times 10^7 \text{ s}^{-1}$ is constant, $E = 96 \text{ kJ mole}^{-1}$ is the activation energy, $R$ is the perfect gas constant and $T$ is the temperature.

1. Introduction

Various halogenated hydrocarbons are used for explosion safety of technological equipment, using flammable gases [1, 2]. Combustion suppression efficiency occurs not only from halogenated carbons endothermicity during pyrolysis, when the temperature of mixture decreases rapidly, but also due to chemical inhibition of chain combustion reactions. Freon 114B2 (1,2-dibromotetrafluoroethane) is considered to be one of the most effective additives to the combustible mixtures, which effectively inhibits ignition and detonation processes in methane–air and hydrogen–air mixtures [2, 3]. Despite its wide practical application the kinetics and mechanism of decomposition of $\text{C}_2\text{F}_4\text{Br}_2$ was studied very superficially. Besides one work on the primary dissociation of 1,2-dibromotetrafluoroethane into $\text{C}_2\text{F}_4\text{Br}$ and Br [4] no other information was found. There is an assumption that one of the secondary decomposition products is $\text{CF}_2$ radical. However, this additive not only inhibits the combustion under certain conditions but can even accelerate the ignition of the methane–air mixtures [5].

Therefore, the study of $\text{C}_2\text{F}_4\text{Br}_2$ dissociation kinetics will allow obtaining new data about mechanism of its pyrolysis in a wide temperature range and also will help to determine the rate constants of formation of some secondary products of $\text{C}_2\text{F}_4\text{Br}_2$ dissociation.
2. Experimental

2.1. Experimental setup

The experiments were performed behind reflected shock waves in a shock tube made of stainless steel with 108 mm internal diameter. The shock tube consists of pressure driven section 6 meter long and the 2 meter driver section. Sections of the shock tube were divided with copper (170 µm thickness) or aluminum (80 µm thickness) diaphragm. Before the experiment the shock tube was pumped by fore-vacuum and turbomolecular pumps to the pressure of $(4–8) \times 10^{-10}$ bar. The experimental setup and equipment are shown in figure 1. More detailed description of experimental setup is given in [6].

The mixtures with various initial concentrations of Br$_2$ in Ar and CF$_3$H in Ar were compiled for the calibration, while the experiments were carried out in mixtures with various compositions of C$_2$F$_4$Br$_2$ in Ar. All studied mixtures were prepared in stainless steel vessel, which was previously pumped to $9 \times 10^{-10}$ bar. Because of the high sensitivity of ARAS and MRAS techniques to different impurities, all gases used were of ultra-purity: Ar—99.9999%, Br$_2$—99.9% and C$_2$F$_4$Br$_2$—99.66%.

The measurements of atomic Br and CF$_2$ radicals were implemented using ARAS (atomic resonance absorption spectroscopy) and MRAS (molecular resonance absorption spectroscopy) techniques and source of resonance radiation was the microwave discharge in the quartz tube (QT) in previously prepared mixtures (0.4%Br$_2$ + He and 1%CF$_3$H + He). The solid generator Sairem GMS-200 at 2.45 GHz operating at 80–110 W was used for the producing stable discharge. The pressure in QT (5–10 mbar) was measured with an Edwards pressure gauge. If necessary, it was regulated by means of the fore-vacuum pump. Molecules of Br$_2$ and CF$_3$H dissociated under the action of microwave discharge, and the emission line spectrum of atomic bromine and the band of CF$_2$ radical appeared, figure 2. Based on works [7, 8], one of the most powerful resonance lines of atomic bromine at wavelength of 154.07 nm and band of CF$_2$ at wavelength of 251.9 nm were selected for kinetics study of C$_2$F$_4$Br$_2$ dissociation. Test experiments with shock waves in pure argon confirmed the absence of any radiation absorption at selected wavelengths.
2.2. Calibration experiments

Since the spectral shape of the lines emitted by the resonance lamp is not known in detail, the calibration experiments are necessary for conversion of the absorption intensity to the concentration.

Two series of calibration experiments behind shock waves were carried out:

(i) Using ARAS method at wavelength of 154.07 nm in the mixture of Br₂ + Ar at the temperature \( T_3 = 2250 \pm 150 \) K, pressure \( P_3 = 2.35 \pm 0.05 \) bar, and initial concentration of Br₂ from 0.1 to 0.0005\% the radiation absorption dependence on atomic bromine concentration was obtained.

(ii) Using MRAS method at wavelength of 251.9 nm in the mixture CF₃H + Ar at the temperature \( T_5 = 1900 \pm 400 \) K, pressure \( 1.5 < P_5 < 16 \) bar, and initial concentration of CF₃H from 0.0038 to 2.7\% the radiation absorption dependence on CF₂ radical concentration was obtained.

The temperature ranges were chosen in order to Br₂ and CF₃H at the experimental time conditions have been fully dissociated into Br [9] and CF₂ + HF [10, 11] accordingly. The concentration range was determined by the limit of setup sensitivity on the one hand and condition of secondary reactions influence elimination on the other.

The typical absorption profiles are shown in figure 3. Change of the intensity of transmitted radiation behind the reflected shock wave, which is caused by the investigated components appearance, was seen. By measuring this level and comparing it with the exact concentration in initial mixture, taking into account the full dissociation of initial molecules, calibration curves were plotted (figure 4).

Similar to works [12,13], the calibration curves were approximated by means of the modified Lambert–Beer law because of the possible different processes of broadening and shift of the emitted and absorbed lines in QT and shock wave [12]:

\[
\frac{I}{I_0} = 1 - \exp(\sigma L[N])^n,
\]

where \( I/I_0 \) is the ration of radiation intensity passed through studied mixture to initial radiation, \( \sigma \) is the absorption cross section in cm\(^2\), \( L = 10.8 \) cm is the optical path (shock tube internal diameter), \( [N] \) is the concentration of the component in the mixture in cm\(^{-3}\), and \( n \) is the exponent coefficient. The \( \sigma \) and \( n \) coefficients were varied. The best fit with the experimental
Figure 3. Typical absorption profiles: (a) mixture of 0.00875% CF$_3$H + Ar at the wavelength of 251.9 nm, $T_0 = 1567$ K, $P_0 = 15.6$ bar; (b) mixture of 0.05% Br$_2$ + Ar at the wavelength of 154.07 nm, $T_0 = 2354$ K, $P_0 = 2.4$ bar; 1—incident shock wave (ISW); 2—reflected shock wave (RSW).

Figure 4. Calibration curves: (a) CF$_2$ radical for different mixtures of CF$_3$H in Ar; (b) Br-atom for different mixtures of Br$_2$ in Ar.

data was attained at $n = 0.5$, $\sigma = 1.49 \times 10^{-17}$ cm$^2$ for Br calibration curve and at $n = 0.8$, $\sigma = 3.86 \times 10^{-18}$ cm$^2$ for CF$_2$ calibration curve. Further, using these calibration curves, current concentration of studied atoms or molecules in different gas mixtures can be accurately determined.

2.3. Experiments in the mixture of C$_2$F$_4$Br$_2$ + Ar
The main experiment series was carried out in the mixture of C$_2$F$_4$Br$_2$ + Ar at the temperature from 1000 K to 3500 K, pressure from 2 to 17 bar and initial concentration of C$_2$F$_4$Br$_2$ from 0.05 to 0.002%. In total, 25 experiments at wavelength of 251.9 nm and 30 experiments at wavelength of 154.07 nm were performed. In figures 5 and 6 the typical concentration profiles of Br–atom and CF$_2$ radical behind shock wave are presented.
3. Result

3.1. Dissociation of $\text{C}_2\text{F}_4\text{Br}_2$ in Ar

In figure 5 the sharp growth of bromine concentration behind shock wave front is clearly seen while further decrease indicates its recombination in $\text{Br} + \text{Br} \rightarrow \text{Br}_2$ reaction. The reaction of bromine recombination at pyrolysis of $\text{C}_2\text{F}_4\text{Br}_2$ was studied before [14]. According to work [4] pyrolysis of $\text{C}_2\text{F}_4\text{Br}_2$ occurs as follows:

\begin{align*}
\text{C}_2\text{F}_4\text{Br}_2 + \text{Ar} & \rightarrow \text{C}_2\text{F}_4\text{Br} + \text{Br} + \text{Ar}, \\
\text{C}_2\text{F}_4\text{Br} + \text{Ar} & \rightarrow \text{C}_2\text{F}_4 + \text{Br} + \text{Ar}.
\end{align*}

Also in that work it is stated, that the reaction (2) proceeds more quickly than the reaction (3). However, experiments, carried out at wavelength of 251.9 nm, indicated that CF$_2$ radical (figure 6), which occurs at C$_2$F$_4$ radical dissociation, is formed rapidly behind shock waves together with Br atom. It is obvious that the formation of CF$_2$ radical may occur only after separation of two Br atoms from C$_2$F$_4$Br$_2$ molecule. Moreover, if to correlate experimental data with CF$_2$ maximum possible concentration, which corresponds to C$_2$F$_4$ radical complete pyrolysis, then CF$_2$ concentration level is close to 100%. Further signal decrease, which was observed at the high temperatures, figure 6(a), indicates the CF$_2$ dissociation, that is in good agreement with the other works [15].
Figure 7. Black line is the dissociation rate constant of C$_2$F$_4$ radicals obtained in this study. Red line is the dissociation rate constant of C$_2$F$_4$ molecules [16].

Thus, we suggest that not one, but two Br atoms are separated from C$_2$F$_4$Br$_2$ almost immediately even at low temperatures (≈ 1000 K). This means that the processes (2), (3) occur with comparable rates. It allows to replace reactions (2), (3) with the one brutto reaction C$_2$F$_4$Br$_2$ + Ar → C$_2$F$_4$ + 2Br + Ar, which occurs with certain effective rate constant $k_{dC_2F_4Br_2}$. Finally, the mechanism of C$_2$F$_4$Br$_2$ dissociation can be presented in the form:

$$\text{C}_2\text{F}_4\text{Br}_2 + \text{Ar} \rightarrow \text{C}_2\text{F}_4 + 2\text{Br} + \text{Ar},$$

(4)

$$\text{C}_2\text{F}_4 + \text{Ar} \rightarrow 2\text{CF}_2 + \text{Ar}.$$  

(5)

3.2. Dissociation rate constant of C$_2$F$_4$Br$_2$

The C$_2$F$_4$Br$_2$ dissociation rate in the initial time, when concentrations of reaction products are negligible, can be described with the following relation:

$$\frac{d[\text{Br}]}{dt} = 2k_{dC_2F_4Br_2} [\text{C}_2\text{F}_4\text{Br}_2].$$

(6)

In this case, the dissociation rate constant can be determined directly from the experimental data by the tangent of slope angle of initial region of the concentration profile:

$$k_{dC_2F_4Br_2} = \frac{d[\text{Br}]/dt}{2[\text{C}_2\text{F}_4\text{Br}_2]}.$$  

(7)

As it can be seen in figure 5 the separation of Br atoms from the initial molecule occurs under experimental conditions with the rather high velocity. The full time of dissociation into C$_2$F$_4$ + 2Br radicals does not exceed 30–40 µs even at low temperatures (≈ 1000 K). Unfortunately, under such reaction times, it is not possible to measure the rate of C$_2$F$_4$Br$_2$ dissociation with appropriate accuracy, since the value of the derivative d[Br]/dt is limited by the time resolution of present experiments, which is approximately 30 µs. Nevertheless, recently in [14] the value of this rate constant was estimated for the temperature range 1200–1500 K.
3.3. Dissociation rate constant of C$_2$F$_4$

The expression of rate constant for reaction of C$_2$F$_4$ radical dissociation can be written similar to (7):

$$ k_{dC_2F_4} = \frac{d[CF_2]}{dt} = \frac{1}{2(C_2F_4)}. $$

(8)

The results obtained from experimental data are presented in figure 7. As it can be seen in figure 7, the dissociation rate constant can be reliably obtained only for temperatures below 1600 K. At the higher temperatures C$_2$F$_4$ radical also fully dissociates in 30–40 µs, as it can be seen in figure 6. Therefore, the growth of the derivative d[CF$_2$/dt is limited by the time resolution of the experimental setup, the same as at C$_2$F$_4$Br$_2$ dissociation process. That means that the experimental data does not describe the actual behavior of the rate constant at $T > 1600$ K. The activation energy and exponential coefficient were obtained for the rate constant (8) in arrenius form:

$$ k_{dC_2F_4} = A \exp(-E/RT), $$

(9)

where $A = 4.76 \times 10^7$ s$^{-1}$ is exponential coefficient, $E = 96$ kJ mole$^{-1}$ is the activation energy, $R$ is the perfect gas constant and $T$ is the temperature. It should be noted, that the obtained dissociation rate constant of C$_2$F$_4$ radicals differs from the available data on dissociation rate constant of C$_2$F$_4$ molecules (figure 7). According to [16] the activation energy of C$_2$F$_4$ molecules dissociation is $\sim 300$ kJ, which is 3 times more than the activation energy for C$_2$F$_4$ radicals with two unpaired electrons. This fact could be explained with the fact that the single sigma bond in the C$_2$F$_4$ radical is weaker than the double bond in the C$_2$F$_4$ molecule.

4. Conclusion

The joint use of ARAS and MRAS techniques has been successfully applied at the wavelengths of 154.07 nm and 251.9 nm for the measurements of Br atoms and CF$_2$ radicals concentration profiles, which were formed by dissociation of 1,2-dibromotetrafluoroethane. As a result the mechanism of C$_2$F$_4$Br$_2$ dissociation over a wide temperature range was investigated in detail. For the first time the dissociation rate constant of C$_2$F$_4$ radical in the reaction C$_2$F$_4$+Ar $\rightarrow$ 2CF$_2$+Ar was experimentally obtained. Using this data, the activation energy equal to 96 kJ/mole was determined.

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