Atomic resonance absorption spectroscopy monitoring of various halogen atoms formation in pyrolysis reactions behind shock waves

N S Bystrov¹,², A V Emelianov¹, A V Eremin¹ and P I Yatsenko¹,²
¹ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
² Bauman Moscow State Technical University, 2nd Baumanskaya Street 5, Moscow 105005, Russia
E-mail: aemelia@ihed.ras.ru

Abstract. The work is devoted to application of a high sensitive and precise method of atomic resonance absorption spectroscopy for the measurements of the time profiles of concentration of various halogen atoms (chlorine, bromine, iodine), formed in pyrolysis of relevant inhibitors of combustion (CCl₄, C₂F₄Br₂, CF₃I). The experiments were performed at temperatures of 1000–2000 K and a pressure of 2–3 bar behind reflected shock waves. In results the rate constants of dissociation of C₂F₄Br₂, CF₃I and their activation energy were measured.

1. Introduction

The method of atomic resonance absorption spectroscopy (ARAS) is the most sensitive and precise method of measuring of small atomic concentrations. This method has become a kind of “gold standard” in the investigations of the kinetics of dissociation of di- and polyatomic molecules.

The first application of ARAS method in a shock tube was carried out by Myerson and Watt [1] and later the method was developed by Roth and Just [2, 3]. This method has got the successful use in the study of gas-phase reactions behind shock waves, as it allows carrying out precise quantitative time resolved measurement of atoms concentration in the very low range 10¹¹–10¹⁴ cm⁻³. The method is based on the resonant absorption by the given atom of the radiation from the excited atoms of the same sort. With this method, high temperature elementary reactions have been investigated behind shock waves and the rate constants of decomposition of variety of molecules was obtained, including CO, CN, N₂, CO₂, etc [4, 5].

The high sensitivity of the method to low atomic concentrations is due to large oscillator strength of the atomic transition (which are about two orders of magnitude greater than the oscillator strength of the molecular transition) and a resonant absorption character. As a source of probing radiation a discharge containing the excited atoms of the same sort is used. Usually the glow and microwave frequency discharges are applied. A narrow spectral range is cutted by a spectral instrument, such that the in-band influence of emission from shock heated mixture was negligible, but for the other hand, the entire broadened line completely was captured. In
Figure 1. Experimental setup for measurements with the ARAS method: 1—shock tube; 2—windows of MgF$_2$; 3—vacuum monochromator; 4—photomultiplier; 5—solid state generator; 6—quartz tube (QT); 7—the pumping of mixture through the QT; 8—oscilloscope; 9—vacuum uv monochromator.

In this case, an intensity of absorption $W_i$ depends on the atomic concentration by Lambert–Beer law and it is independent of temperature. Lambert–Beer law has a simple form:

$$W_i = 1 - \exp(-\sigma_i[n]l),$$

where $\sigma_i$ is the absorption cross section in the $i$–line, $[n]$ is atoms concentration, $l$ is the length of the optical path. Before the study of kinetics of given atom formation, the calibration measurements in the equilibrium zone behind the shock wave at a known atoms concentration were carried out. At these calibration experiments the dependence of the absorption intensity on the atoms concentration must be determined. The non-linear character of this dependence is associated, in particular, with the influence of the effect of self-absorption, which is particularly noticeable in the strong lines.

This work is devoted to the use of the ARAS method for studying the kinetics of pyrolysis of various inhibitors of combustion. One of the main scientific problems in combustion and detonation is an accurate measurement of the kinetics of the most important reactions that determine the influence of chemically active additives on the processes of initiating of ignition of various combustible gases. In the experiments the time profiles of various halogen atom concentrations (chlorine, bromine, iodine) were measured, which are formed by pyrolysis of corresponding inhibitors (CCl$_4$, C$_2$F$_4$Br$_2$, CF$_3$I) behind reflected shock waves at temperatures of 1000–2000 K and a pressure of 2–3 bar.

2. Experiment

All experimental results were obtained in a high-vacuum kinetic shock tube. The stainless steel shock tube has internal diameter of 108 mm and a total length of 8 m. Driven and driver section of shock tube have length of 6 and 2 m, respectively and are separated by a diaphragm. Before the experiment shock tube was evacuated by scroll oil-free pump and turbo molecular pump to a pressure of $(4–6) \times 10^{-7}$ mbar.

As the radiation source a microwave discharge lamp was used. For the excitation of the lines of atomic radiation, the mixtures of CCl$_4$, Br$_2$ or CF$_3$I in He were used. To obtain a stable discharge the solid state microwave generator Sairem GMS-200 at a frequency of 2.45 GHz has been applied. The power of the microwave discharge produced by the generator was 60 W. The pressure in the quartz tube (QT) (5–10 mbar) was measured with a pressure gauge. If necessary, it was regulated by means of the vacuum pump. The radiation was detected by a vacuum monochromator (VM) Acton VM-502 and the PMT-181 detector with a sensitivity region of 112 to 830 nm. The experimental setup and equipment is shown schematically in figure 1. A more detailed description of the installation is given in [6]. The test experiments in pure argon carried out before a series of calibration and pyrolysis experiments have confirmed that the absorption at a selected wavelength was not observed.
3. Results and discussion

Calibration measurements for atoms Cl, Br and I were performed in the mixtures with various initial concentrations CCl$_4$, Br$_2$ and CF$_3$I in Ar respectively. The concentrations were varied in the range 5–500 ppm CCl$_4$ + Ar at the temperatures 4000 ± 100 K, 5–1000 ppm Br$_2$ + Ar at the temperatures 2300 ± 100 K, and 1–4 ppm CF$_3$I + Ar at the temperatures 2300 ± 300 K. These temperatures are typical for total dissociation CCl$_4$, Br$_2$, CF$_3$I into atoms of Cl, Br and I. At the same time the experimental results were checked for independence of the absorption cross section on the temperature for the lines measured. The spectral resolution of the monochromator was 0.2 nm for the Cl atom, 0.8 nm for atom Br and 0.4 nm for atom I. The difference in spectral resolution is determined by the choice of the maximum level of signal/noise ratio and the presence of adjacent lines of the atom, so that the line is certainly does not get into the selected interval. The results of these calibrations are shown in figure 2. The lowest concentration that could measured for the iodine atom is 10$^{12}$ cm$^{-3}$.

An attempt to summarize calibration measurements for the different elements, based on the obtained absorption cross section of the used lines, the aperture factor and oscillator strengths of line has led to the following result:

\[ n^* = n_i \sigma_i \frac{f_i}{A_i} R_{0.3}, \]

where \( \sigma_i \) is absorption cross section measured on the line for each element (for Cl (at a wavelength \( \lambda = 138.97 \) nm)—1.5 \( \times \) 10$^{-14}$ cm$^2$, for Br (\( \lambda = 154.07 \) nm)—3.0 \( \times \) 10$^{-15}$ cm$^2$, for I (\( \lambda = 183.04 \) nm)—5.2 \( \times \) 10$^{-15}$ cm$^2$), \( A_i \) is aperture factor (proportional to the resolution of the monochromator at a given wavelength), \( f_i \) is the oscillator strength of the selected lines (for Cl—0.0001, for Br—0.05, for I—0.012). Figure 3 shows the generalization of calibration dependencies.

One can state that the formula (2) quite well generalizes the calibration dependence. It means that the increase of the spectral resolution of the monochromator does not result in obtaining lower values of measured concentration, that agrees with the requirement to measure only on a single line, free from the interference of closely spaced resonant and non-resonant lines of the measured element that can lead to errors of measurement of investigated reaction rate constants by ARAS. Thus, the lowest values of the measured atomic concentrations by ARAS are possible for the lines of the selected atoms, which have a maximum absorption cross section on the line. From (2) it follows that if the oscillator strength of selected line of measurement is higher, that the lower values of the concentrations can be registered.

The resulting calibration curves were used for the measurement of the rate constants of following reactions:

\[ C_2F_4Br_2 = C_2F_4Br + Br \]
Figure 3. Generalization of calibration data for lines of atomic chlorine, bromine and iodine.

Figure 4. Typical absorption profiles of Br atoms at the line 154.07 nm in mixture 100 ppm \( \text{C}_2\text{F}_4\text{Br}_2 \) in Ar: (a) \( T_5 = 1334 \text{ K}, \ P_5 = 2.5 \text{ bar} \), (b) \( T_5 = 1268 \text{ K}, \ P_5 = 2.8 \text{ bar} \). ISW—insident shock wave; RSW—reflected shock wave.

and

\[ \text{CF}_3\text{I} = \text{CF}_3 + \text{I}. \]  

(4)

The time profiles of the concentration of bromine atoms at the pyrolysis of \( \text{C}_2\text{F}_4\text{Br}_2 \) were measured in the mixtures 100 and 500 ppm \( \text{C}_2\text{F}_4\text{Br}_2 + \text{Ar} \) at the temperatures of 1200–1800 K and pressures of 2–3 bar. Typical examples of Br-line absorption observed in a mixture \( \text{C}_2\text{F}_4\text{Br}_2 + \text{Ar} \) behind shock wave are shown in figure 4. In more detail, these measurements are described in [7].

One can see that in the pyrolysis \( \text{C}_2\text{F}_4\text{Br}_2 \) the time of formation of bromine atom in the reaction (3) takes about 50–70 \( \mu \text{s} \). But at the temperatures above 1500 K, this time becomes shorter and is comparable with the resolution time of the measurement system, so all data on the rate constant of reaction (3) are given for the temperatures not exceeding 1500 K. In figure 5 the rate constant of reaction (3) in the Arrhenius coordinates and data of [8] estimated by methods RRKM (Rice–Ramsperger–Kassel–Marcus) are given.

The best fit of experimental data (figure 5) for the rate constant of reaction (3) is

\[ k_1 = A_1 \exp(-E_1/RT), \]  

(5)

where \( A_1 \) is pre-exponential factor equal \( 7.93 \times 10^{13\pm0.6} \text{ s}^{-1} \) and \( E_1 \) is activation energy of reaction (3) equal \( 243 \pm 15 \text{ kJ/mol} \), determined from the slope angle of the dependence in figure 5, \( R \) is
the gas constant. The asymptotic standard error is determined by processing the experimental data by the least squares method. One can see that the found value of $k_1$ is in a good agreement with the RRKM estimation [8] for the lower temperature range.

The time profiles of the concentration of I atoms at the pyrolysis of CF$_3$I were measured in the mixtures 1–4 ppm CF$_3$I + Ar at the temperatures of 900–1400 K and pressures of 2–3 bar. Typical examples of I-line absorption on a wavelength of 183.04 nm at different temperatures observed in a mixture CF$_3$I + Ar behind shock wave are shown in figure 6. One can see the rise of the absorption signal caused by the formation of I atoms behind reflected shock wave and it approaching to the stationary level.

In figure 7 the rate constant of pseudo-first-order of reaction (4) in Arrhenius coordinates is shown. The corresponding Arrhenius expression has the form:

$$k_2 = A_2 \exp(-E_2/RT),$$

(6)

where $A_2$ is pre-exponential factor equal $8.44 \times 10^{11} \pm 0.2$ s$^{-1}$ and $E_2$ is activation energy of reaction (4) equal $182 \pm 5$ kJ/mol, $R$ is the gas constant. One can see that this value of $k_2$ is a bit different from the values obtained in [9, 11]. In [11], measurements of this rate constant were carried out by the decay of concentration of initial molecule CF$_3$I in the mixtures of 3–5%
CF$_3$I in argon. In these experiments the drop in optical density on the long wavelength wing ($\lambda = 316$ nm) of electronic band of CF$_3$I was registered. In [9] the measurements were carried out by the rate of accumulation of iodine atoms obtained from the intensity of the fluorescence in a wide spectral range of 300–1100 nm generated in the mixtures of 0.2–1% CF$_3$I in argon.

In [10], measurements were made by the registration of absorption spectrum of CF$_3$I in the range of 230–350 nm for mixtures 0.5% CF$_3$I in argon. In [12], rate constant of the reaction (4) was determined based on uv absorption measurements of radicals CF$_3$ at 290 ± 1.5 nm. In [13] the Arrhenius expression for rate constant over the temperature range from 400 K to 1400 K on basis of the equilibrium constant and the data for the rate of reversal reaction was evaluated. In [14] the rate constant of dissociation CF$_3$I in krypton was measured by ARAS in the spectral range 165–185 nm. However, the rate constant in [14] is given only for the reaction of second order. Thus, none of the published papers failed to find the rate constant of the reaction (4) measured by the registration only one resonance line of iodine in a narrow spectral range. Therefore, this study present the first results of the direct measurements of, the rate constant of reaction (4) by ARAS on only one resonance line of iodine in the spectral range of 183.04 ± 0.4 nm. Consequently, one can assume that the obtained data represent the most accurate real value of the rate constant of the reaction (4) in the measured range of temperatures and pressures.

4. Conclusion
ARAS method has been successfully used to measure concentrations profiles of various halogen atoms (chlorine, bromine, iodine) during the pyrolysis of various halo-carbons. Calibration curves of resonance absorption of the investigated atoms depending on the concentrations were obtained and the corresponding generalizing dependence is proposed. The pseudo-first order rate coefficients and activation energy of the formation of Br and I atoms in the dissociation reactions of C$_2$F$_4$Br$_2$ and CF$_3$I, respectively, are determined. The obtained results can be useful for analyzing the inhibitory properties C$_2$F$_4$Br$_2$ and CF$_3$I, and kinetics calculations for ignition and combustion of complex fuels, containing corresponding halogenated hydrocarbons.

Acknowledgments
The support of this study by grant from the Russian Science Foundation No. 14-19-00025P is gratefully acknowledged.

References
[1] Myerson A L and Watt W S 1968 J. Chem. Phys. 49 425–33
[2] Roth P and Just T 1975 Ber. Bunsenges Phys. Chem. 79 682–6
[3] Just T 1981 Atomic resonance absorption spectrometry in shock tube Shock Wave in Chemistry—1981 ed Lifshitz A (New York: Marcel Dekker) pp 279–318
[4] Orden A V and Saykally R J 1998 Chem. Rev. 98 2313–58
[5] Michael J V and Lim K P 1993 Annu. Rev. Phys. Chem. 44 429–58
[6] Drakon A V, Emelianov A V, Eremin A V and Yatsenko P I 2017 High Temp. 55 239–45
[7] Emelianov A V, Eremin A V and Yatsenko P I 2016 Experimental study of pyrolysis of C2F4Br2 behind shock waves Nonequilibrium Processes in Physics and Chemistry—2016 ed Starik A M and Frolov S M (Moscow: TORUS PRESS) pp 42–9
[8] Tsang W J 1984 J. Phys. Chem. 88 2812–7
[9] Zaslenskaya I S, Mukoseev Yu K, Skorobogatov G A and Khripun V K 1990 Kinet. Catal. 31 1046–52
[10] Brouwer L and Troe J 1981 Chem. Phys. Lett. 82 1–4
[11] Zaslenskaya I S, Mukoseev Yu K, Skorobogatov G A and Slinkin S V 1986 Kinet. Catal. 27 734–9
[12] Saito K, Yoneda Y, Tahara H, Kidoguchi S and Murakami I 1984 Bull. Chem. Soc. Jpn. 57 2661–2
[13] Skorobogatov G A 1982 Kinet. Catal. 23 18–21
[14] Kumaran S S, Su M C, Lim K P and Michael J V 1995 Chem. Phys. Lett. 243 59–63