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CHEMICAL PHYSICS OF ATMOSPHERIC PHENOMENA

Mechanism of CF_3Br Photolysis at the Wavelength of 253.7 nm

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Abstract—The kinetics of the photolysis of CF_3Br (Halon 1301) at various durations of irradiation of CF_3Br–oxygen mixtures at a wavelength of 253.7 nm is studied. The spectra and absorbances of the reactants are obtained within the range of 200–900 nm using an M-40 spectrophotometer. Kinetic data are determined from a change in the absorption spectra at a wavelength of 416 nm, which corresponds to the maximum absorption of molecular bromine. A kinetic mechanism of CF_3Br photolysis is proposed, and the quantum yield and the absorption cross section of CF_3Br at this wavelength are determined.

Keywords: bromine atoms, halons, ozone layer, global warming, photolysis

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INTRODUCTION

Saturated hydrocarbons containing chlorine and bromine atoms pose a danger to the ozone layer of the Earth and contribute to global warming. Therefore, in 1987, industrial countries signed the Montreal protocol on the gradual reduction and then the complete cessation of the production of such hydrocarbons [1]. The lifetime of CF_3Br in the atmosphere is 65 years, its ozone destruction potential (ODP) is 12 (ODP of Freon 11 (CCl_3F) is 1), and its global warming potential (GWP) is 7030 (GWP of Freon 11 is 4680) [2].

The indicated lifetime of CF_3Br ensures its presence in the middle and upper stratosphere, where the intensity of ultraviolet radiation (including 253.7-nm radiation) is high enough for its photolysis. This process produces bromine atoms, which destroy ozone in chain reactions. The chain length of the bromine-induced ozone destruction cycle is tens of times greater than that for chlorine atoms [3]. In addition, the bromine atom has a weaker bond with the rest of the molecule than the chlorine atom. Therefore, halons largely decompose at altitudes of ~20 km, that is, where the ozone layer density is close to the maximum. These two factors also make bromine-containing compounds more dangerous to the ozone layer [4].

The aforementioned GWP of CF_3Br, 7030, is significantly higher than the corresponding values for the other halons. For example, the GWP values for $C_2F_4Br_2$ (Halon 2402) and CF2ClBr (Halon 1211) are 1860 and 1620, respectively [2]. This means that CF_3Br has a large absorption cross section in the infrared region near the maximum of the thermal radiation of the Earth, where the optical density of the atmosphere is small. Although the greatest contribution to global warming (from anthropogenic constituents) currently comes from carbon dioxide, its IR radiation absorption at the center of the bands has reached saturation, so an increase in absorption is possible only due to absorption in the wings of the lines. This leads to a logarithmic dependence of the absorption of CO_2 on its concentration, while the contribution of halons to the greenhouse effect is directly proportional to their concentration.

Previously, CF_3Br (Halon 1301) was widely used in many countries to put out fires. Among compounds containing bromine atoms, CF_3Br is most effective, both in inhibiting combustion reactions and in reducing the flame speed. Note that Halon 1301 is still used in extinguishing fires under special conditions, for example, fires in mines, warships, museums and in airplanes. This is due to the ability of this compound to quickly and effectively suppress the burning of various materials, as well as to extinguish fires in electrical equipment under voltage.

The mechanism of action of CF_3Br as an inhibitor of combustion processes is that it binds the hydrogen atom, the branching species of combustion chain reaction, thereby terminating the chain: $H^{\cdot} + CF_3Br \rightarrow HBr + CF_3^{\cdot}$, $HBr + OH^{\cdot} \rightarrow H_2O + Br^{\cdot}$, $HBr + O^{\cdot} \rightarrow OH^{\cdot} + Br^{\cdot}$ [5].

EXPERIMENTAL

The setup for photolysis of CF_3Br consisted of a quartz cuvette, 4 cm in diameter and 10 cm in length, a BUV-1 low-pressure bactericidal lamp, and an M-40 spectrophotometer for recording the absorption spec-

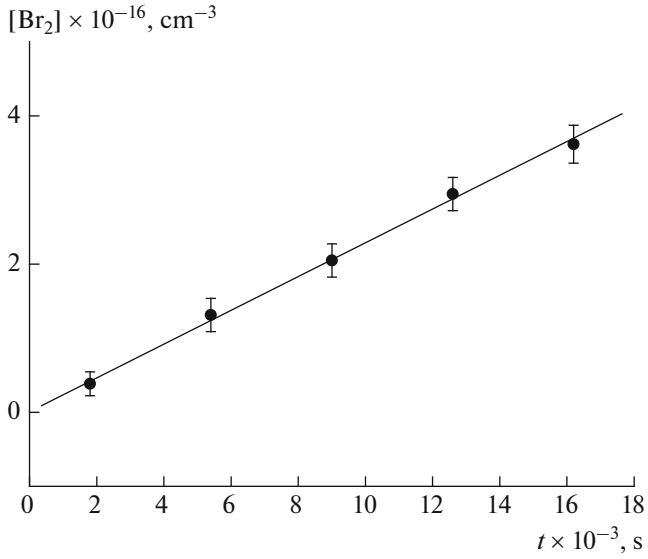

Fig. 1. Time dependence of the of molecular bromine concentration on the irradiation time at CF_3Br and O_2 pressures of 96 and 600 Torr, respectively.

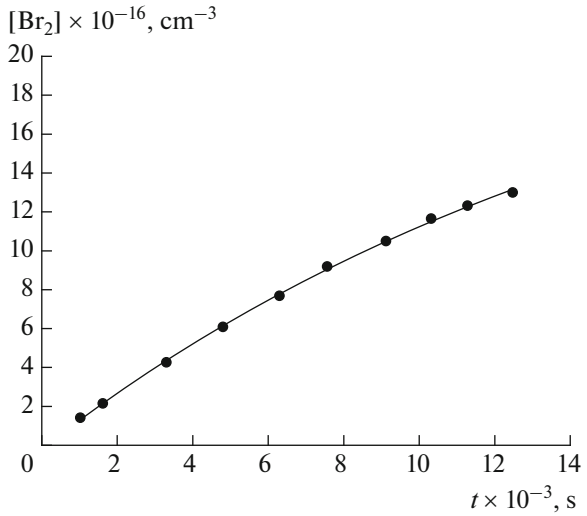

Fig. 2. Time dependence of the molecular bromine concentration on the irradiation time at CF_3Br and O_2 pressures of 650 and 23 Torr, respectively.

tra of the test substances in the ultraviolet and visible regions. More than 92% of the radiation of the bactericidal lamp accounted for a wavelength of 253.7 nm.

The kinetics of CF_3Br photolysis was studied by measuring the optical density of CF_3Br–oxygen mixtures. The measurements were carried out in the absorption region of CF_3Br and at a wavelength of 416 nm, which corresponds to the maximum absorption of molecular bromine. Since the absorption cross section of CF_3Br at a wavelength of 253.7 nm is rather small, the time of irradiation of the mixture reached several hours.

The radiation intensity of the bactericidal lamp, determined using hydrogen bromide as an actinide, was found to be $(1.87 \pm 0.2) \times 10^{15}$ quantum/(cm^2 s).

Before the measurements, the optical cell was evacuated with a forepump to a pressure of 3×10^{-3} Torr and washed several times with helium. Then, the spectrum of the evacuated cuvette was recorded. After the cuvette was filled with the test mixture, the spectrum was recorded again. Next, the mixture of substances was irradiated for a certain period of time, at the end of which spectra of the mixture in the cuvette were again recorded in the wavelength range 200–900 nm. Unfortunately, the 253.7-nm absorption cross section of one of the main photolysis products, $CF_3O_2^{\bullet}$ is almost five hundred times higher than that of CF_3Br, so we measured the optical density of the mixture near 416 nm, which allowed monitoring the kinetics of the accumulation molecular bromine, one of the products of CF_3Br photolysis.

The optical density $D(\lambda)$ measured by the spectrophotometer is related to the concentration of the analyte in the optical cell according to the Lambert–Beer law,

$$D(\lambda) = n\sigma(\lambda)l, \quad (1)$$

where n is the analyte concentration (molecule cm^{-3}), $\sigma(\lambda)$ is the absorption cross section of the substance at a wavelength of 253.7 nm in cm^2, l is the length of the cuvette in cm.

At the beginning of the experiments, a calibration was made, which determined the correspondence of the optical density at 416 nm to the molecular bromine vapor pressure. From these data, the absorption cross section of molecular bromine at 416 nm and 295 K was determined:

$$\sigma_{416\ nm} = 6.3 \times 10^{-19}\ cm^2.$$

This value agrees well with that measured in [6].

Several series of experiments were performed to study the photolysis mechanism: at CF_3Br pressures of 23 to 650 Torr and oxygen pressures of 10 to 600 Torr. The dependence of the molecular bromine concentration on the irradiation duration at a temperature of 293 K, CF_3Br pressure of 96 Torr, and an oxygen pressure of 600 Torr is shown in Fig. 1. The dependence is linear throughout the irradiation time.

However, the dependence displayed in Fig. 2 shows that, under other irradiation conditions, namely, at a CF_3Br pressure of 650 Torr and an oxygen pressure of 23 Torr, the dependence of the molecular bromine concentration on the irradiation time deviates from linearity.

To explain these regularities, we proposed the following photolysis mechanism:

$$CF_3{-}Br + h\nu \rightarrow CF_3{-}Br^*, \quad (I)$$

$$CF_3{-}Br \rightarrow CF_3^{\bullet} + Br^{\bullet}, \quad (II)$$

$$CF_3{-}Br^* + M \rightarrow CF_3{-}Br + M, \quad \text{(III)}$$

$$CF_3^{\bullet} + O_2 + M \rightarrow CF_3O_2^{\bullet} + M, \quad \text{(IV)}$$

$$CF_3^{\bullet} + Br_2 \rightarrow CF_3{-}Br + Br^{\bullet}, \quad \text{(V)}$$

$$CF_3^{\bullet} + CF_3^{\bullet} \rightarrow C_2F_6, \quad \text{(VI)}$$

$$Br^{\bullet} + Br^{\bullet} + M \rightarrow Br_2 + M. \quad \text{(VII)}$$

If the oxygen pressure exceeded 1 Torr, then the inequality $k_{IV}[O_2] \gg k_{VI}[R]$ was satisfied. This follows from the fact that the ratio of the rate constants k_{IV} and k_{VI} [7, 8] is close to 1, while the ratio $[O_2]/[CF_3^{\bullet}]$ under the conditions of our experiments was ~10^4. Therefore, the reaction (VI) can be ignored.

Applying the steady-state concentration method [9], we obtained the following expression for the rate of CF_3Br consumption and molecular bromine accumulation, assuming that all the bromine atoms produced by CF_3Br photolysis combined to form molecular bromine:

$$d[Br_2]/dt = (1/2)\sigma_d(253.7) \times I[CF_3{-}Br]\alpha k_{IV}[O_2]/(k_{IV}[O_2] + k_V[Br_2]), \quad (2)$$

where $\sigma_d(253.7)$ is the dissociation cross section of CF_3Br (cm^2) at a wavelength of 253.7 nm, I is the radiation flux (photon/cm^2 s) at the same wavelength, $\alpha = k_{II}/(k_{II} + k_{III}[M])$ is the fraction of CF_3Br molecules that have avoided deactivation and formed bromine atoms, $k_{IV}[O_2]/(k_{IV}[O_2] + k_V[Br_2])$ is a term that takes into account the formation of CF_3Br in the reaction of $CF_3^{\bullet}$ with Br_2. If $k_V[Br_2]$ is markedly higher than $k_{IV}[O_2]$, the presence of this term in (2) makes the time dependence of the Br_2 concentration nonlinear (Fig. 2).

However, at the initial stage, when $k_V[Br_2] \ll k_{IV}[O_2]$, the dependence of the Br_2 concentration on the irradiation time is linear (Fig. 1), described by

$$d[Br_2]/dt = (1/2)\sigma_d(253.7)\, I\alpha[CF_3Br]. \quad (3)$$

Experiments conducted at oxygen pressures of 50 to 600 Torr and nitrogen pressures from 60 to 480 Torr showed that, at a given partial pressure of CF_3Br, the rate of molecular bromine from accumulation is independent of the oxygen or nitrogen pressure. This suggests that the coefficient α in expression (3) is 1.

Taking this into account and denoting the Br_2 accumulation rate as W, we obtain

$$W_1 = (1/2)\sigma_d(253.7)\, I[CF_3Br]. \quad (4)$$

The quantum yield φ is determined from the ratio of the dissociation cross section σ_d at the corresponding wavelength to the absorption cross section σ at the same wavelength:

$$\varphi = \sigma_d/\sigma. \quad (5)$$

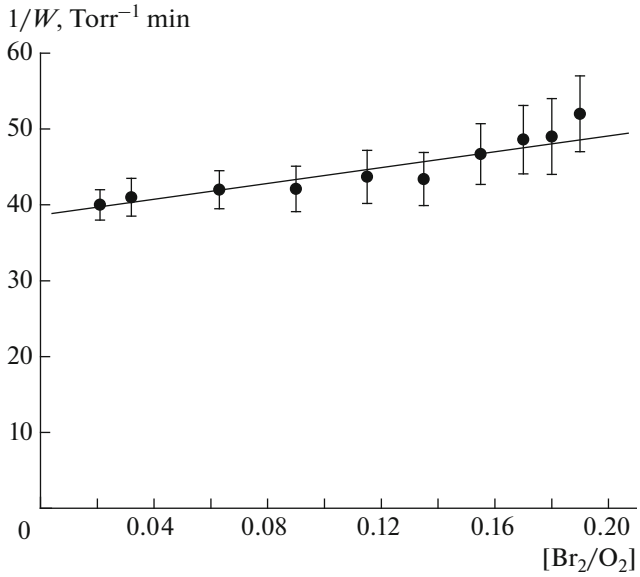

Fig. 3. $1/W$ as a function of $[Br_2]/[O_2]$ at a CF_3Br pressure of 650 Torr.

Given that the quantum yield of bromine atoms for the photolysis of CF_3Br at the wavelength of 253.7 nm is 1 [10], then from Fig. 1 and expressions (4) and (5), we determine the absorption cross-section for CF_3Br at this wavelength: ~8.0×10^{-22} cm^2. From similar dependences obtained at CF_3Br pressures of 56 and 51 Torr, the absorption cross sections were found to be 7.9×10^{-22} and 8.3×10^{-22} cm^2, respectively. The mean value of the absorption cross section of CF_3Br at 253.7 nm was $(8.1 \pm 0.4) \times 10^{-22}$ cm^2. This value agrees well with the data from [11].

After simple transformations, expression (2) can be recast as

$$1/W = (1/W_1)(1 + k_V[Br_2]/k_{IV}[O_2]). \quad (6)$$

The $1/W$ versus $[Br_2]/[O_2]$ dependence for a CF_3Br pressure of 650 Torr is shown in Fig. 3. The slope of the straight line in Fig. 3 yields the ratio between the rate constants of reactions (IV) and (V):

$$k_V/k_{IV} = 1.7.$$

The experiments were carried out at CF_3Br pressures of 286, 375, and 600 Torr. The k_V/k_{IV} ratios obtained from these experiments were 1.7, 2.0, and 1.9, respectively. The average value of this ratio is 1.8 ± 0.2.

The rate constants of reactions (IV) and (V) were measured in [7] and [12], respectively. The ratio of the rate constants for reactions (IV) and (V), calculated using the data of [7] and [12], is 2.2, slightly exceeding the value obtained in the present work: 1.8 ± 0.2.

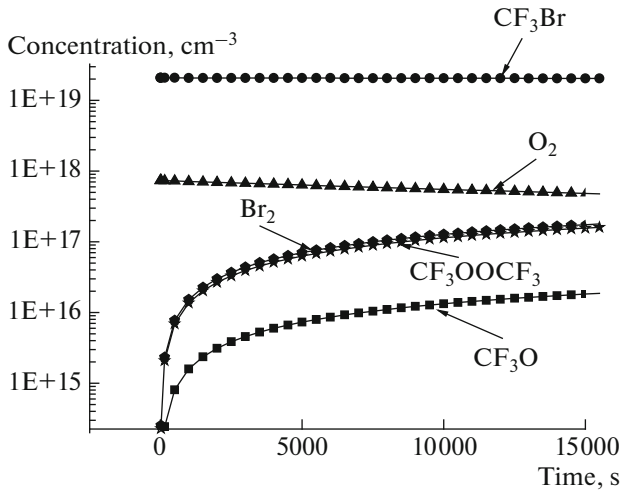

Fig. 4. Time dependences of the calculated concentrations of the 253.7-nm photolysis products of CF_3Br at CF_3Br and O_2 pressures of 650 and 23 Torr, respectively.

RESULTS AND DISCUSSION

Since our experimental technique allowed us to measure only the concentration of Br_2 formed during the photolysis of CF_3Br, without the probably of further monitoring the fate of the CF_3O_2 radicals, we were interested in comparing our experimental results with data obtained by the works in which the products of interaction of these radicals were identified. For the reaction

$$CF_3O_2^{\bullet} + CF_3O_2^{\bullet} \rightarrow \text{products} \qquad \text{(VIII)}$$

the authors of [13] reported the following value of the apparent rate constant:

$$k_{app} = 3.1 \times 10^{-12}\ cm^3/(\text{molecule s}).$$

This value agrees perfectly with the data obtained in [14] for the same reaction.

The authors of this work suggested that two channels of this reaction:

$$CF_3O_2^{\bullet} + CF_3O_2^{\bullet} \rightarrow CF_3O^{\bullet} + CF_3O^{\bullet} + O_2, \qquad \text{(VIIIa)}$$

$$CF_3O_2^{\bullet} + CF_3O_2^{\bullet} \rightarrow CF_3OOCF_3 + O_2. \qquad \text{(VIIIb)}$$

However, the infrared spectrum of the products did not revealed the presence of the CF_3OOCF_3 peroxide, which apparently, means that reaction (VIIIb) does not play a significant role.

The main product of reaction (VIII) is the CF_3OOOCF_3 trioxide. This compound is formed by the reaction

$$CF_3O^{\bullet} + CF_3O_2^{\bullet} + M \rightarrow CF_3OOOCF_3 + M. \qquad \text{(IX)}$$

The reaction rate constant for reaction (IX) was measured to be

$$k_{IX} = 2.5 \times 10^{-12}\ cm^3/(\text{molecule s}).$$

The authors concluded that the rate constant of bimolecular reaction (VIIIa) is:

$$k_{VIIIa} = 1.8 \times 10^{-12}\ cm^3/(\text{molecule s}).$$

In addition, in [14], the absorption spectrum of the $CF_3O_2^{\bullet}$ radical was recorded within 200–280 nm. The absorption cross section at 253.7 nm was found to be

$$\sigma_{253.7} \approx 4.0 \times 10^{-19}\ cm^2.$$

Using this value and the above bactericidal lamp radiation intensity, we calculated the rate constant for the photolysis of $CF_3O_2^{\bullet}$ under the conditions of our experiments:

$$CF_3O_2^{\bullet} + h\nu \rightarrow CF_3^{\bullet} + O_2, \quad k_X = 7.5\times10^{-4}\ s^{-1}. \qquad \text{(X)}$$

We included reactions (VIII), (IX), and (X) into the mechanism of CF_3Br photolysis, and the concentrations of the photolysis products were calculated using a box photochemical model developed at the Laboratory of Atmospheric Chemistry of Tal'roze Institute for Energy Problems of Chemical Physics RAS [15]. The corresponding system of rigid ordinary differential equations describing the time evolution of the chemical system was numerically solved by means of inverse differentiation. For this system, the Cauchy problem was solved. The initial concentrations of the gas components and the photolysis coefficients of light-sensitive components were selected in accordance with the experimental conditions.

The model is based on the above mechanism CF_3Br photolysis, supplemented by the aforementioned three reactions, the rate constants of which were measured in [14]. The rate constants for the remaining reactions included in the photolysis mechanism were $k_I = 1.3 \times 10^{-6}\ s^{-1}$, $k_{IV} = 4.0 \times 10^{-12}\ cm^3/(\text{molecule s})$ [7], $k_V = 1.79 \times 10^{-12}\ cm^3/(\text{molecule s})$ [12], and $k_{VII} = 1.6 \times 10^{-32}\ cm^6/(\text{molecule}^2\ s)$ [16].

The rate constant for reaction (I) was calculated using the absorption cross section given in [11] and the above indicated intensity of the mercury bactericidal lamp we used.

The results of the simulations within the framework of the box model are displayed in Fig. 4. A comparison of Fig. 2 and Fig. 4 shows that the experimental data and simulation results on the formation of molecular bromine are in satisfactory agreement.

CONCLUSIONS

(1) Photolysis of CF_3Br with low-pressure mercury bactericidal lamp at a wavelength of 253.7 nm over a wide range of pressures of CF_3Br and oxygen was carried out.

(2) A mechanism of CF_3Br photolysis is proposed and its correspondence to the experimental data is examined.

(3) The absorption cross section of CF_3Br at a wavelength of 253.7 nm was found to be $(8.1 \pm 0.4) \times 10^{-22}$ cm^2, which agrees well with the published data.

(4) The ratio between the rate constants of the reactions (IV) and (V), was determined, $k_V/k_{IV} = 1.7$.

(5) In accordance with the proposed mechanism of CF_3Br photolysis, the concentrations of photolysis products were calculated using a box photochemical model. The simulation results and experimental data were found to be in close agreement.

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