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Kinetics and Mechanism of the Photolysis of CF_2ClBr Exposed to Light with a Wavelength of 253.7 nm

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Abstracts—CF_2ClBr mixed with oxygen was photolyzed using a low pressure mercury lamp, and the kinetics of photolysis was studied. The absorption spectra of the starting material and products of photolysis were recorded in the wavelength range from 200 to 900 nm on an Agilent 8453 spectrophotometer. The concentrations of the main photolysis products at different irradiation times were calculated by the mathematical processing of the absorption spectra. The scheme of CF_2ClBr photolysis was suggested, the model calculations according to this scheme were performed, and the results of simulation were compared with experimental data.

Keywords: halons, photolysis, absorption spectra

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In 1987 in Montreal industrialized countries signed a protocol on the gradual reduction and subsequent complete cessation of halon production [1]. Halons is a technical name of hydrocarbons containing not only fluorine and chlorine atoms, but also bromine atoms. Previously, these substances were used in various fields of human activity. A particularly important role was played by their use in fire fighting. However, these products are hazardous to the ozone layer of the Earth and are able to absorb infrared radiation from the Earth in the transmission window of the atmosphere, resulting in global warming [2].

Risk of halons for the Earth's ozone layer is due to the fact that, getting into the stratosphere, they fall under the action of ultraviolet radiation to form bromine atoms, which effectively destroy the stratospheric ozone as a result of chain processes. The most important of them are the following [3]:

$$\text{I. } Br + O_3 \rightarrow BrO + O_2$$

$$BrO + O \rightarrow Br + O_2$$

Result: $O + O_3 \rightarrow 2O_2$.

$$\text{II. } Br + O_3 \rightarrow BrO + O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$BrO + ClO \rightarrow Br + Cl + O_2$$

Result: $O_3 + O_3 \rightarrow 3O_2$.

$$\text{III. } Br + O_3 \rightarrow BrO + O_2$$

$$BrO + NO_2 + M \rightarrow BrONO_2 + M$$

$$BrONO_2 + h\nu \rightarrow Br + NO_3$$

$$NO_3 + h\nu \rightarrow NO + O_2$$

Result: $O_3 + O_3 \rightarrow 3O_2$.

It is known that halons are much more dangerous for the ozone layer than those hydrocarbons which contain only fluorine or chlorine atoms. Calculations [4] show that the effectiveness of bromine is 45 times higher than the efficiency of chlorine atoms. The difference in effectiveness between chlorine and bromine was estimated at 40 to 400 [5, 6]. The different in stratospheric ozone depletion efficiency between chlorine and bromine atoms is due to two factors. The first factor is that the bromine atom has a weaker bond with the rest of the molecule than the chlorine atom. Because of this, the halon decay occurs mainly at low altitudes of about 20 km, where the ozone density is close to its maximum. The second factor is the difference in chain length. This difference is due to the difference in atmospheric lifetime between the reservoir gases HCl and HBr, whose formation which temporarily interrupt the chain process until it is resumed by Cl and Br atoms returning to the chain. The atmospheric lifetime of HCl at the stratospheric altitudes is substantially longer than that of HBr [3], which leads to longer chain lengths in the bromine cycle. The main species of this cycle is the BrO radical, the chain carrier in the process responsible for stratospheric ozone depletion. It is known that 50% of the stratospheric bromine compounds exist as BrO radicals or Br atoms. The role of these reactive species is particularly great in the chemical processes that take place at altitudes of 12–15 km [3].

Another feature of halons is that they have a large absorption cross section in the IR region near the

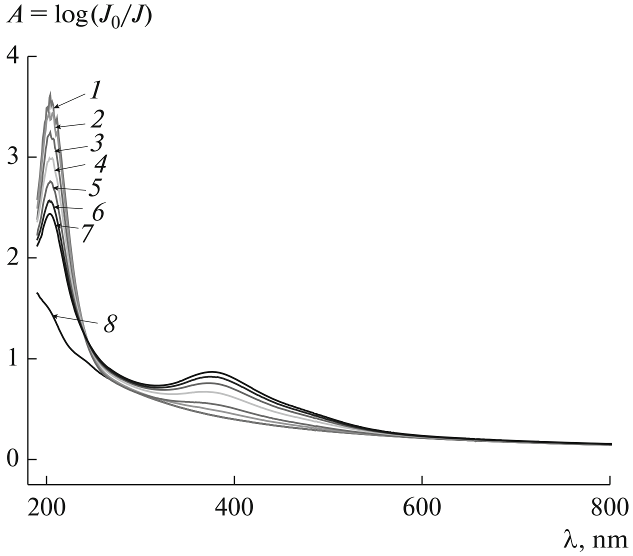

Fig. 1. Spectra of CF_2ClBr and its photolysis products at various irradiation times, s: (*1*) 0, (*2*) 960, (*3*) 2400, (*4*) 4800, (*5*) 7200, (*6*) 9600, and (*7*) 11 520; (*8*) empty cell.

maximum of thermal radiation of the Earth, where the optical absorption of the atmosphere is low, thereby contributing to global warming (greenhouse effect). Although the greatest contribution to the greenhouse effect is currently made by carbon dioxide [7], absorption by this gas at the center of its bands is saturated, and an increase in the absorption can only be due to the sides of the bands. This results in a logarithmic dependence of the IR absorbance on the CO_2 concentration, whereas it is directly proportional to the halon concentration.

A considerable number of scientific papers have been devoted to halon 1211, whose chemical formula is CF_2ClBr. This is due to the fact that, before the Montreal Protocol, which bans the production of substances hazardous to the ozone layer, was signed, three halons—CF_3Br, $C_2F_4Br_2$, and CF_2ClBr—were recognized as the most effective inhibitors of the chain combustion reactions and were widely used in fire fighting.

The ability of halonsto suppress flame is due to the fact that they are involved in the inhibition of chain combustion reactions by reacting with the hydrogen atom branching the chain [8]:

$$H^{\bullet} + RBr \rightarrow HBr + R^{\bullet}.$$

As was mentioned above, the production of all of these substances was banned, but in Russia they were allowed up to 2000. At present, these substances are only used in extinguishing especially difficult fires, for example, in submarines and military aircraft. Note that, among these three substances, CF_2ClBr has the lowest ozone depletion potential (ODP = 8) and the smallest value of global warming potential (GWP = 1940) [9].

The upper limit of the rate constant of the reaction between the OH radical and CF_2ClBr was measured to be 1.5×10^{-16} cm^3 $molecule^{-1}$ s^{-1} [10]. In the same study, the absorption cross-section was measured for this substance in the wavelength range from 190 to 320 nm at 210–296 K. From these data, the atmospheric lifetime in of CF_2ClBr was calculated to be 16 years.

Note that, although the ODP and GWP of $C_2F_4Br_2$ are 18.4 and 2270, respectively [9], exceeding the same parameters for CF_2ClBr, $C_2F_4Br_2$ was used as a fire extinguishing agent in Russian submarines until 2008.

EXPERIMENTAL

Reactant mixtures were prepared in a molybdenum-glass vacuum apparatus in which shutoff valves were made only of glass and teflon. Oxygen (pure grade) and CF_2ClBr were stored in glass flasks. Before beginning the experiments, CF_2ClBr was purified by low-temperature distillation. Pressure was measured with vacuum gauges and a Sapfir manometer (Russia) calibrated against the water vapor pressure at 273 K. Pressures in the 0–30 Torr range were measured with an accuracy of 0.1 Torr; pressures in the 30–760 Torr range, with an accuracy of 3 Torr.

The optical system for photolysis at a wavelength of 253.7 nm consisted of a quartz cell with a diameter of 4 cm and a length of 10 cm and a BUV-15 low-pressure bactericidal mercury lamp (Russia). More than 92% of the radiation from the lamp had a wavelength of 253.7 nm. The typical width of a spectral line at this wavelength is no larger than a few nanometers.

To determine the intensity of the lamp (*I*), experiments on two actinometers—HBr and CH_3Br—were conducted. The average value of the lamp radiation intensity was $(1.7 \pm 0.1) \times 10^{15}$ photon cm^{-2} s^{-1}.

Absorption spectra and the absorbances of the analyzed components were recorded on an Agilent 8453 spectrophotometer (United States).

Before beginning the measurements, the optical cell was evacuated with a fore pump to a residual pressure of 3×10^{-3} Torr and purged with helium several times. Thereafter, the spectrum of the evacuated cell was recorded and the cell was filled with a mixture to be examined. The mixture was irradiated for certain periods of time, and the spectra of the cell contents were recorded in the wavelength range from 200 to 900 nm. The absorbance of the cuvette was subtracted from the total spectrum. The variation of the absorbance of the mixture in the absorption range of the halon and in that of the photolysis products (330–500 nm) allowed us to study the kinetics of photolysis.

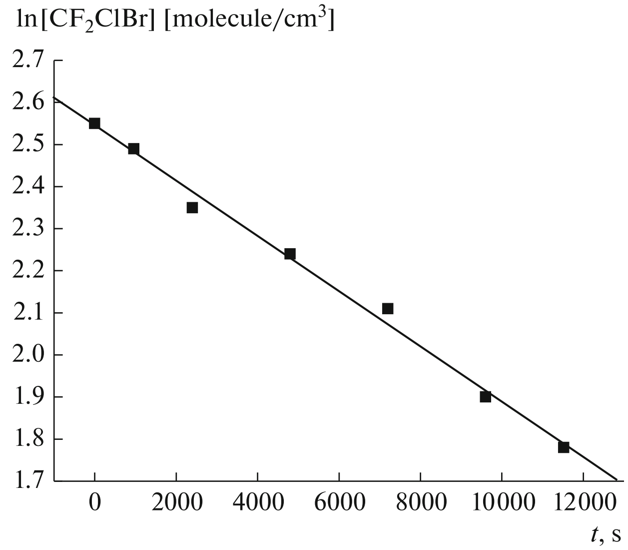

Fig. 2. Logarithm of the CF_2ClBr concentration as a function of irradiation time.

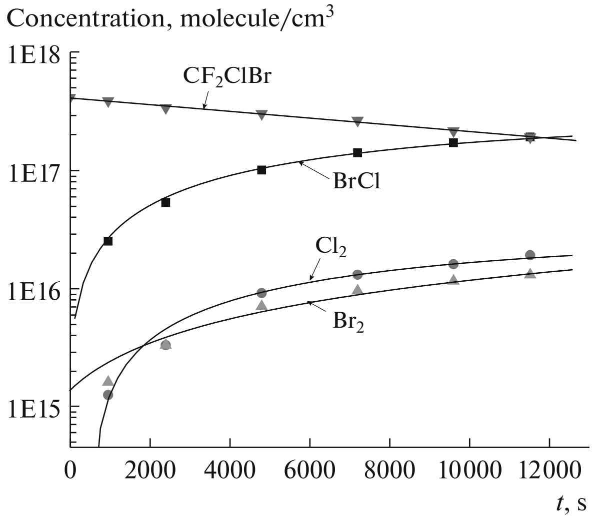

Fig. 3. CF_2ClBr, BrCl, Br_2, and Cl_2 concentrations as a function of photolysis time for the CF_2ClBr (12.8 Torr) + oxygen (150 Torr) mixture.

RESULTS

The photolysis of CF_2ClBr at a wavelength of 253.7 nm was carried out at halon pressures of 4 to 21.5 Torr and an oxygen pressure of 150 Torr. Oxygen was added to mimic the natural photolysis conditions.

Figure 1 shows the spectrum obtained in the course of the photolysis of a CF_2ClBr (12.8 Torr) + oxygen (150 Torr) mixture at various irradiation times. The measurements were performed on an Agilent 8453 spectrophotometer. CF_2ClBr concentrations at different irradiation times were calculated from spectrometer readings, $\log(J_0/J)$, using the following formula:

$$2.3\log(J_0/J) = \sigma l[CF_2ClBr], \qquad (1)$$

where [CF_2ClBr] is the concentration of the substance (molecule/cm^3), σ is the absorption cross section of the substance at a wavelength of 253.7 nm (cm^2), l is the optical path of the cell (cm), and J_0 and J are the intensities of the spectrometer signal at the times 0 and t, respectively.

Using these data, one can calculate the quantum yield for the halon (α) using the dependence of the CF_2ClBr concentration on the irradiation time:

$$-d[CF_2ClBr]/dt = I\alpha\sigma[CF_2ClBr], \qquad (2)$$

where σ is the absorption cross section of $CClF_2Br$ at 253.7 nm, ~3.8×10^{-20} cm^2 [11]; I is the power of the lamp radiation, 1.7×10^{15} photon cm^{-2} s^{-1}.

Integrating with respect to time yielded the following expression:

$$\ln[CF_2ClBr] = I\alpha\sigma t. \qquad (3)$$

Figure 2 shows the plot of the logarithm of the CF_2ClBr concentration versus the irradiation time. As calculated from the slope of the line in this figure, the quantum yield of the halon is unity with a high degree of accuracy.

The concentrations of the main products of the photolysis—BrCl, Cl_2, and Br_2—were calculated using experimental values of $\log(J_0/J)$ obtained on the Agilent 8453 spectrophotometer. For this purpose, the system of equations shown below was solved using the MathCAD program for wavelengths of 360, 380, and 430 nm.

In writing the system of equations, we used the absorption cross section of the photolysis products inform Ref. [11].

$$\begin{aligned}\log(J_0/J)0.23 &= [BrCl]35.03\times10^{-20}\\ &+ [Cl_2]13.22\times10^{-20} + [Br_2]8.66\times10^{-20},\end{aligned} \qquad (4)$$

$$\begin{aligned}\log(J_0/J)0.23 &= [BrCl]39.26\times10^{-20}\\ &+ [Cl_2]5.00\times10^{-20} + [Br_2]30.7\times10^{-20},\end{aligned} \qquad (5)$$

$$\begin{aligned}\log(J_0/J)0.23 &= [BrCl]14.63\times10^{-20}\\ &+ [Cl_2]0.732\times10^{-20} + [Br_2]60.1\times10^{-20}.\end{aligned} \qquad (6)$$

The results of solving the system of equations (4)–(6) are shown in Fig. 3. It can be seen that the main photolysis product absorbing in this range of wavelengths is BrCl. In addition, Br_2 and Cl_2 form in much smaller amounts.

Our experimental data were compared with data calculated using the photochemical box model developed in the Laboratory of Chemical Physics of Atmosphere, Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences [12]. The following photolysis scheme was used in the model, in which all the constants are given for 298 K:

$CF_2BrCl + h\nu \rightarrow Br^{\bullet} + {}^{\bullet}CClF_2$ $k_I = 6.5 \times 10^{-5}\ s^{-1}$, (I)

$Br_2 + h\nu \rightarrow Br^{\bullet} + Br^{\bullet}$ $k_{II} = 7.1 \times 10^{-6}\ s^{-1}$, (II)

$BrCl + h\nu \rightarrow Br^{\bullet} + Cl^{\bullet}$ $k_{III} = 6.8 \times 10^{-5}\ s^{-1}$, (III)

$Cl_2 + h\nu \rightarrow Cl^{\bullet} + Cl^{\bullet}$ $k_{IV} = 2.0 \times 10^{-6}\ s^{-1}$, (IV)

${}^{\bullet}CClF_2 + Br_2 \rightarrow CF_2BrCl + Br^{\bullet}$ $k_V = 1.6 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ [13], (V)

${}^{\bullet}CClF_2 + O_2 \rightarrow CF_2O^* + ClO$ $k_{VI} = (1.3 \times 10^{-11} \pm 7.0 \times 10^{-12})\ cm^3\ molecule^{-1}\ s^{-1}$ [14], (VI)

${}^{\bullet}CClF_2 + O_2 \rightarrow CClF_2OO$ $k_{VII} = 1.0 \times 10^{-11}\ (\pm 8.0 \times 10^{-12})\ cm^3\ molecule^{-1}\ s^{-1}$ [14], (VII)

${}^{\bullet}ClO + {}^{\bullet}ClO \rightarrow O_2 + Cl_2$ $k_{VIII} = 4.8 \times 10^{-15}\ cm^3\ molecule^{-1}\ s^{-1}$ [15], (VIII)

$Cl_2 + Br^{\bullet} \rightarrow BrCl + Cl$ $k_{IX} = (2.41 \times 10^{-15} \pm 1.99 \times 10^{-16})\ cm^3\ molecule^{-1}\ s^{-1}$ [16], (IX)

$Br_2 + Cl \rightarrow Br^{\bullet} + BrCl$ $k_X = (1.4 \times 10^{-10} \pm 1.2 \times 10^{-11})\ cm^3\ molecule^{-1}\ s^{-1}$ [17], (X)

$BrCl + Cl \rightarrow Cl_2 + Br^{\bullet}$ $k_{XI} = (1.45 \times 10^{-11} \pm 1.99 \times 10^{-12})\ cm^3\ molecule^{-1}\ s^{-1}$ [18], (XI)

$Br^{\bullet} + Br^{\bullet} + M \rightarrow Br_2 + M$ $k_{XII} = 1.2 \times 10^{-32}\ cm^3\ molecule^{-1}\ s^{-1}$ [19], (XII)

$Br_2 + Cl_2 \rightarrow 2BrCl$ $k_{XIII} = 3.32 \times 10^{-22}\ cm^3\ molecule^{-1}\ s^{-1}$ [20]. (XIII)

The rate constants of reactions (I)–(IV) were calculated using the values of the absorbance cross sections [11] and radiation lamp power presented above.

The stiff ordinary differential equations describing the time evolution of the system were solved by inverse differentiation. A Cauchy problem was solved for the system. The initial concentrations of the gas components and the coefficients of photolysis of light-sensitive components were set according to the experimental conditions. The calculated data are plotted in Fig. 4. The main photolysis products appearing in Fig. 4 are CF_2O and BrCl.

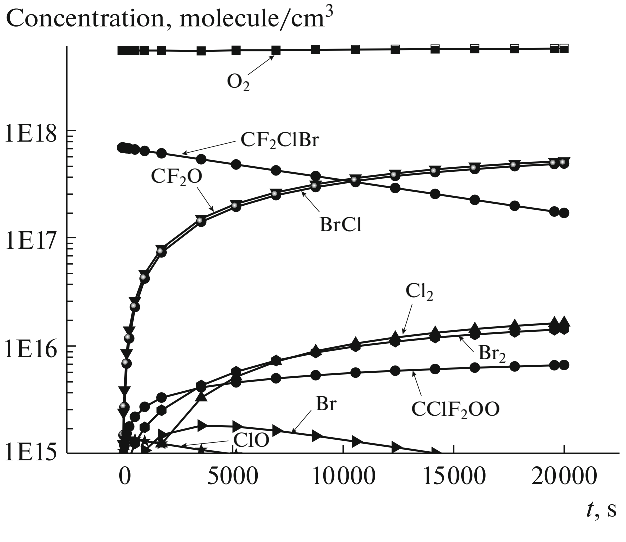

Fig. 4. Simulated time variation of the CF_2ClBr, BrCl, and Br_2 concentrations in the photolysis of the CF_2ClBr (12.8 Torr) + oxygen (150 Torr) mixture. Radiation wavelength, 253.7 nm; temperature, 295 K.

Similar experiments and calculations were performed for CF_2ClBr photolysis at different pressures. A simple mathematical rearrangement of Eq. (2) yielded the following relationship between the pressure of the halon decomposed as a result of photolysis ($p_0 - p_t$) and the initial halon pressure (p_0):

$$p_0 - p_t = kp_0(t - t_0). \quad (4)$$

For plotting $p_0 - p_t$ versus $p_0(t - t_0)$, we chose t = 4800 s, the point in time at which the concentrations of the resulting products are low enough and obviously cannot have a significant effect on the kinetics of the process. The results are shown in Fig. 5. The value of k calculated from the slope of the line in Fig. 5 is $(6.1 \pm 0.6) \times 10^{-5}\ s^{-1}$, which agrees fairly well with the value of k calculated from the plot in Fig. 2. Note that, throughout the pressures range examined, the concentration of BrCl formed as a result of photolysis is one order of magnitude higher than the concentrations of molecular chlorine and bromine.

DISCUSSION

One of the aims of our work was to check whether it is possible to calculate the concentrations of the photolysis products resulting from the irradiation of CF_2ClBr from experimental absorption spectra under conditions such that several substances with overlapping absorption spectra are formed. The concentrations of the photolysis products calculated in this way can be compared with theoretical values obtained using the above-mentioned photochemical box model. Comparing Figs. 3 and 4 shows that the agreement between these data is satisfactory.

The photolysis of CF_2ClBr was studied previously. In [21], this compound was photolyzed using a high-pressure mercury lamp whose radiation was filtered with a cyanide perchlorate solution. The emission maximum was at 248 nm, but the width of the spectrum was about 20 nm. The primary event of photolysis yielded bromine atoms (quantum yield of ≥0.78) and BrCl (quantum yield of ~0.013). The formation of chlorine atoms was considered unlikely because of the significantly stronger bond of the chlorine atom with the rest of the molecule. The photolysis products were molecular bromine and various hydrocarbons containing chlorine and bromine atoms. The extent of photolysis was not greater than 0.1%. To increase the extent of photolysis, various substances binding the radicals resulting from photolysis (radical scavengers) have been used, but no effective scavenger has been found. Molecular oxygen proved a more effective scavenger [22]. The primary event of photolysis was the formation of a bromine atom: $CF_2ClBr + h\nu \rightarrow CF_2Cl^\bullet + Br$, and the resulting radicals reacted with an oxygen molecule, which prevented the reverse reaction and significantly increased the extent of photolysis: $CF_2Cl + O_2 + M \rightarrow CF_2ClOO + M$.

Using the fluorescence resonance method for detection of chlorine and bromine atoms, the quantum yields of these atoms were determined at 193, 222, and 248 nm [23]: for chlorine atoms, 1.03 ± 0.14, 0.27 ± 0.04, and 0.18 ± 0.03, respectively; for bromine atoms, 1.04 ± 0.13, 0.86 ± 0.11, and 0.75 ± 0.13, respectively. In this work, photolysis was not conducted at a wavelength of 253.7 nm, but extrapolation of the results shows that, in the experiments carried out in the absence of oxygen, the dominant product at this wavelength would be molecular bromine; however, atomic chlorine also would form in appreciable amounts. We believe that the chlorine atoms form not in the primary event of photolysis but in subsequent reactions. This assumption is confirmed by a later work in which the following quantum yields are reported: 0.96 for bromine atoms and 0.04 for chlorine atoms in the photolysis of CF_2ClBr at a wavelength of 234 nm [24].

The experimental conditions closest to those of our study were used by Deng et al. [25], who carried out the photolysis of CF_2ClBr at a wavelength of 253.7 nm in an oxygen-containing mixture. At oxygen pressures above 4 Torr, the halon quantum yield was 1, as under our experimental conditions. The dissociation constant of CF_2ClBr was 1.89×10^{-5} s^{-1}. The following chemical equation for the photolysis process is reported [25]:

$$2CF_2BrCl + O_2 + h\nu \rightarrow 2CF_2O + Br_2 + Cl_2.$$

Detection of CF_2O as the main product of photolysis involving oxygen is consistent with our theoretical calculations (Fig. 4). However, in contrast to the results of our work, which indicates that another main product is BrCl, Deng et al. [25] did not include this substance into their scheme of the photolysis, considering that, along with CF_2O, the main photolysis products are Cl_2 and Br_2. At the same time, their spectrum of the products has a maximum intensity at a wavelength of 390 nm, which is also in agreement with our data, and the absorbance maximum for Br_2 is at 430 nm. Molecular chlorine in this wavelength range has a one order of magnitude smaller absorption cross section and could make this change in the absorption spectrum only if its concentration in the photolysis products significantly exceeded the concentration of molecular bromine, but this is impossible from energy considerations. We believe that the photolysis scheme presented in this paper is also applicable to the experimental results described by Deng et al. [25] and that, along with CF_2O, BrCl prevails in the products of CF_2BrCl photolysis under irradiation with light with a wavelength of 253.7 nm in the presence of molecular oxygen. Note that BrCl is very valuable chemical used in wastewater treatment and disinfection of industrial ponds, since it kills harmful bacteria that are resistant to the action of chlorine [26]. Also, this substance is used in analytical chemistry for determining low concentrations of mercury [27] and in some types of Li–SO_2-batteries for increasing their voltage and energy density [28].

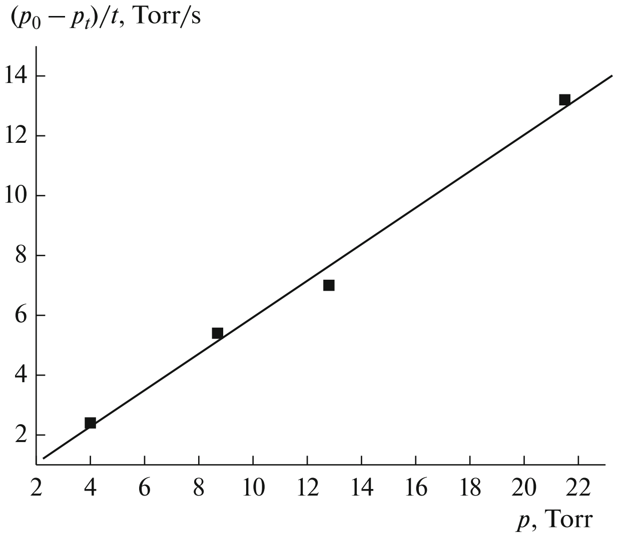

Fig. 5. Pressure of the halon photolyzed in 4800 s versus the initial halon pressure.

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