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Measurement of the Rate Constants of the Reactions of the Chlorine Atom with C_3F_7I and CF_3I Using the Resonance Fluorescence of Chlorine Atoms

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Abstract—The rate constants of the reactions of the chlorine atom with C_3F_7I (k_1) and CF_3I (k_2) have been measured using the resonance fluorescence of chlorine atoms in a flow reactor at 295 K: $k_1 = (5.2 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_2 = (7.4 \pm 0.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. No iodine atoms have been detected in the reaction products.

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Many recent works have been devoted to reactions of chlorine atoms with iodine-containing hydrocarbons of both natural and anthropogenic origin [1–6]. The natural sources of these substances are ocean biomass [7, 8] and photochemical processes occurring in sea water [9, 10]. The anthropogenic sources are industry and fire-extinguishing means [11]. Some contribution is also made by biomass combustion and by cultivation of rice fields [12, 13]. Chlorine atoms form in the marine atmosphere due to heterogeneous processes involving marine aerosol particles. On the surface of these particles, rather stable chlorine-containing compounds, such as HCl and $ClONO_2$, turn into weakly bound Cl_2, HOCl, and $ClNO_2$ molecules, which decompose under UV irradiation to yield chlorine atoms [14–16]. Owing to these processes, the concentration of chlorine atoms in the atmosphere can reach 10% of the concentration of $OH^{\cdot}$ radicals [17, 18]. The rate constants of the reactions of chlorine atoms with halogen-containing hydrocarbons, which are important in atmosphere chemistry, often considerably exceed the rate constants of the reactions of the $OH^{\cdot}$ radical with these substances. These reactions exert a marked effect on the ozone concentration in the atmosphere. In addition, halogen-containing hydrocarbons absorb infrared radiation in the atmospheric transmission window (~10 μm), and their accumulation in the atmosphere can affect the climate of the Earth.

This work is devoted to measurement of the rate constants of the reactions of chlorine atoms with CF_3I and C_3F_7I. Both halides are low-toxic and are presently considered as promising alternatives for bromine-containing refrigerants used in fire extinguishing [19, 20]. Furthermore, they decompose efficiently in the troposphere and do not cause a noticeable damage to the ozone layer [21]. In addition, C_3F_7I is widely used in radical polymerization [22] and in the manufacturing of chemical lasers [23, 24].

EXPERIMENTAL

In order to determine reaction rate constants by the resonance fluorescence method, we recorded the signal from chlorine atoms. The measured resonance fluorescence signal (J^{Cl}) is related to the concentration of chlorine atoms by the expression

$$J^{Cl} = A[Cl]\exp(-\sigma L[Cl]). \quad (1)$$

The coefficient A accounts for the sensitivity of the system to chlorine atoms. It was determined from the results of titration performed at high concentrations of chlorine atoms. The exponential term reflects the effect of absorption of resonance emission of chlorine atoms in the detection zone shown in Fig. 1. The 118.9-nm line of the chlorine atom is a doublet occurring at 118.875 and 118.877 nm. The recommended value of σ for the unresolved doublet is 2.47×10^{-13} cm^2 [25]. The quantity L in Eq. (1) is the length of the zone in which Cl atoms are observed. This zone was bounded by the metallic collimators of the resonance lamp and photon counter, and its length was 0.8 cm.

Detection of Chlorine Atoms

Chlorine atoms were generated by producing a discharge with a frequency of 254 MHz and a power of 2.5 W in a mixture of molecular chlorine and helium (1 : 10000) (Breid resonator). The surface of the discharge zone was treated with orthophosphoric acid.

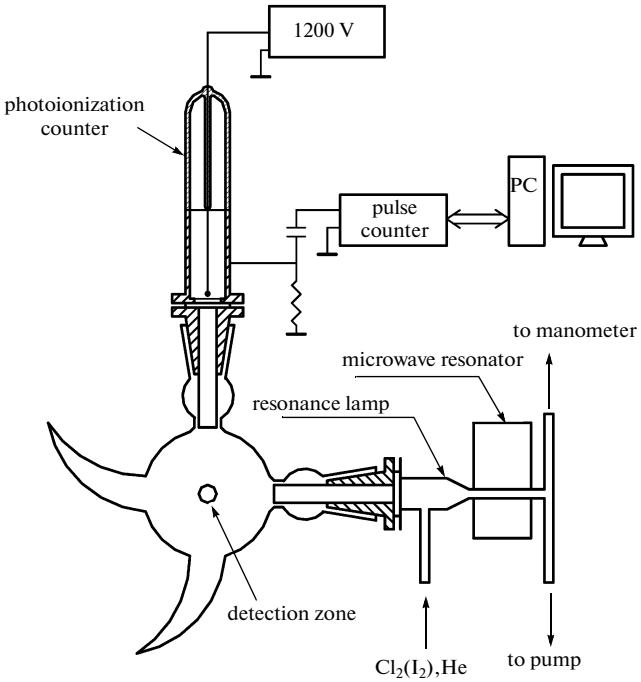

Fig. 1. Zone of detection of chlorine and iodine atoms by the resonance fluorescence method.

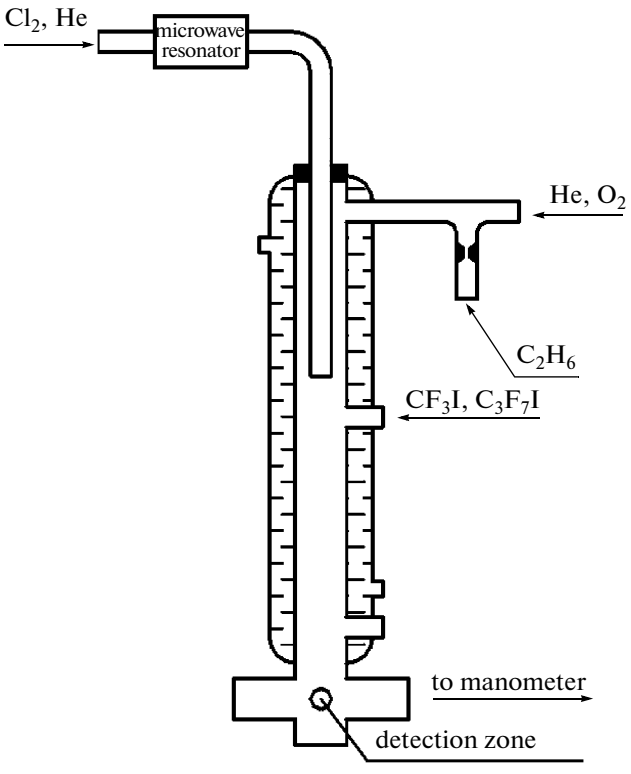

Fig. 2. Schematic of the reactor.

The system for detection of chlorine atoms as their resonance fluorescence consisted of a flow-through chlorine lamp emitting at 118.9 nm, a source of chlorine atoms, and a photoionization counter operating in the 117–134 nm range and detecting photons reemitted by the chlorine atoms. The counter was filled with a mixture of argon and nitrogen(II) oxide (10 Torr NO + 230 Torr Ar). The long-wavelength limit of the counter was determined by the ionization potential of NO, 8.7 eV [26], and was ~133.8 nm. The lamp and the counter were equipped with MgF_2 glasses with a short-wavelength transmission cutoff of 117 nm. This made it possible to work at the resonance absorption line of the chlorine atom at 118.9 nm, i.e., in the range in which there is almost no absorption of dioxygen present in the reactor. The signal from the counter was input, through a frequency meter operating in the pulse counting mode, in a computer for accumulation and subsequent processing.

Calibration of the Absolute Sensitivity of the Setup to Chlorine Atoms

The absolute sensitivity to chlorine atoms was calibrated using titration with ethane, which was carried out by introducing C_2H_6 at a low, controlled flow rate through a capillary into the oxygen stream. The C_2H_6 flow rate was measured as pressure drop in a calibrated container filled with C_2H_6 at 700 Torr, which was placed at the side inlet of the reactor. Ethane was added to the chlorine atom flow until the resonance fluorescence signal of chlorine atoms decreased to zero.

In the calibration of the absolute sensitivity of the system, a signal-to-noise ratio of 2 was obtained at $[Cl] \approx 1 \times 10^{10}$ molecule/cm^3. Rate constants were measured at chlorine atom concentrations substantially exceeding this value.

Reactor and Feeding of Reactants

Experiments were carried out under jet conditions in the reactor shown in Fig. 2. The reactor was a quartz cylinder with an internal diameter of 1.7 cm. The reactor surface was covered with fluoroplastic F-32L to reduce the heterogeneous decay rate of atoms and radicals. The diluent gases (oxygen and helium) and ethane were fed into the reactor through side holes, and CF_3I and C_3F_7I were fed through a side inlet. The mass flow rates of the reactants and carrier gases were determined by measuring the amount of gas flowing out of a calibrated volume per unit time. Pressure variation was monitored with a standard manometer. High-purity-grade helium and oxygen were used in all experiments. Molecular chlorine and iodine supply pipelines contained no vacuum grease and were made of glass and Teflon shutoff valves. Chlorine was synthesized by HCl oxidation with $KMnO_4$, was purified by low-temperature distillation, and was stored in glass cylinders. It was added to the He stream passing through the flow-through resonance lamp and through the source of chlorine atoms. The reactants

CF_3I and C_3F_7I were stored in lightproof glass cylinders and were fed into the reactor as their mixtures with helium or oxygen through a metering valve. The flow rate was determined by measuring the pressure drop in the calibrated volume. Reagent-grade CF_3I and C_3F_7I were used.

Ethane used in the calibration of the absolute sensitivity of the system to chlorine atoms was stored in a glass cylinder and was introduced directly into the reactor through a capillary.

Detection of Iodine Atoms

The system for detection of iodine atoms as their resonance fluorescence consisted of an iodine resonance lamp, a photon counter, and a frequency meter. The signal from the latter was input in a personal computer (PC). From 500 to 10^4 pulses per data point were coadded. The lamp emitted the resonance line of iodine atoms at a wavelength of 178.3 nm, for which the resonance radiation absorption cross section of iodine atoms was 5×10^{-13} cm^2 [27]. The lamp was made of quartz (UF brand) with a short-wavelength transmission cutoff of 160 nm. A He + molecular iodine mixture (~10000 : 1) was pumped through the lamp. Reemitted quanta were detected with a photoionization counter sensitive in the wave range 160–185 nm. The glass body of the counter was soldered to a vacuum system, was pumped to a residual pressure of 5×10^{-5} Torr, and was then filled with a mixture of 10 Torr NO and 230 Torr Ar. A diethylferrocene drop was placed into an appendix soldered to the counter. The short-wavelength cutoff of the counter (160 nm) was determined by the transmission of its quartz window, whereas the long-wavelength cutoff (185 nm) was determined by the ionization potential of diethylferrocene, which is 6.3 eV [26]. Thus, the counter also served as a monochromator filtering the spectral range from ~160 to ~185 nm.

Calibration of the Absolute Sensitivity of the Detection System to Iodine Atoms

The following procedure was used to calibrate the absolute sensitivity of the detection system. A known amount of atomic iodine was obtained via the reaction between molecular iodine and oxygen atoms. Molecular iodine was fed into the reactor as follows. A 220-cm^3 flask containing iodine crystals was placed in melting ice, at the temperature of which the saturation vapor pressure of molecular iodine is 3.2×10^{-2} Torr. The flask was then filled with helium and attached to the reactor through a Teflon valve. The rate of pressure variation in the calibrated volume, i.e., the rate of gas outflow from the flask was measured with an MASE-3 metallic bellows manometer with an accuracy of 0.01 Torr. The pressure in the reactor was measured with a VDG-1 manometer. The total flow in the reactor was determined by summing the helium and oxygen flow rates.

The concentration of molecular iodine getting into the reactor was calculated via the formula

$$[I_2] = \frac{Q_{He+I}[I_2]_{amp}}{Q_\Sigma} P \times 3.16 \times 10^{16}, \quad (2)$$

where Q_{He+I} is the flow rate of the gas from the calibrated ampule, $[I_2]_{amp}$ is the fraction of molecular iodine in the ampule (%), Q_Σ is the total mass flow rate through the reactor, P is the pressure in the reactor, and 3.16×10^{16} is the number of molecules at a pressure of 1 Torr and $T = 298$ K.

The following reactions occurred in the system:

(a) $O + I_2 \rightarrow IO^\cdot + I$,

$k_a = 1.38 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [28],

(b) $O + IO^\cdot \rightarrow I + O_2$,

$k_b = 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [29],

(c) $I + \text{wall} \rightarrow \frac{1}{2}I_2$,

$k_c < 10$ s^{-1}.

Oxygen atoms were obtained via microwave discharge in a mixture of 4% O_2 with He. The concentration of oxygen atoms was estimated by chemiluminescence titration using NO_2 [30]. The concentration of oxygen atoms (~10^{14} molecule/cm^{-3}) was three orders of magnitude hogher than the concentration of iodine atoms. The steady-state concentration of molecular iodine and the $IO^\cdot$ radical in this source of iodine atoms was considerably lower than 1% of the concentration of iodine atoms:

$$[I_2] = [I]\frac{k_c}{2k_a[O]} \le [I] \times 2 \times 10^{-3} \text{ molecule/cm}^3, \quad (3)$$

$$[IO^\bullet] = [I]\frac{k_c}{2k_b[O]} \le [I] \times 2 \times 10^{-3} \text{ molecule/cm}^3. \quad (4)$$

It follows from (3) and (4) that the entire molecular iodine was converted into atomic iodine under our experimental conditions. This source made it possible to obtain a certain number of iodine atoms and to transport them to the distance determined by the heterogeneous disappearance rate of oxygen atoms. The concentration of iodine atoms remained almost unchanged. A signal-to-noise ratio of 2 was obtained at $[I] \approx 1 \times 10^8$ molecule/cm^3.

RESULTS AND DISCUSSION

Determination of the Rate Constant of the Reaction of C_3F_7I with Cl Atoms by the Detection of Cl Atoms

The chlorine atoms that formed as the helium + molecular chlorine mixture was passed through the Breid resonator were fed into the reactor through a thin tube connected to the reactor using a Teflon sleeve gasket and was moved along the reactor axis without impairing the reactor tightness. At a certain distance from the detection zone, the chlorine atoms

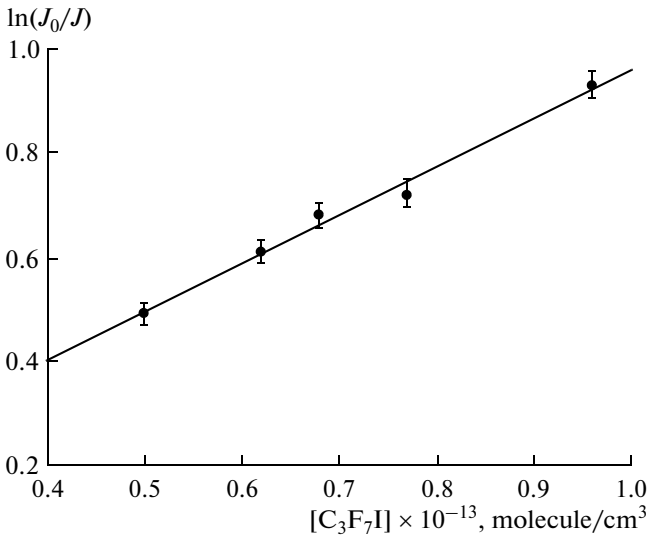

Fig. 3. Resonance fluorescence signal of chlorine atoms versus C_3F_7I concentration; T = 295 K, P = 1.5 Torr, [Cl] ≈ 1.1×10^{12} molecule/cm^3.

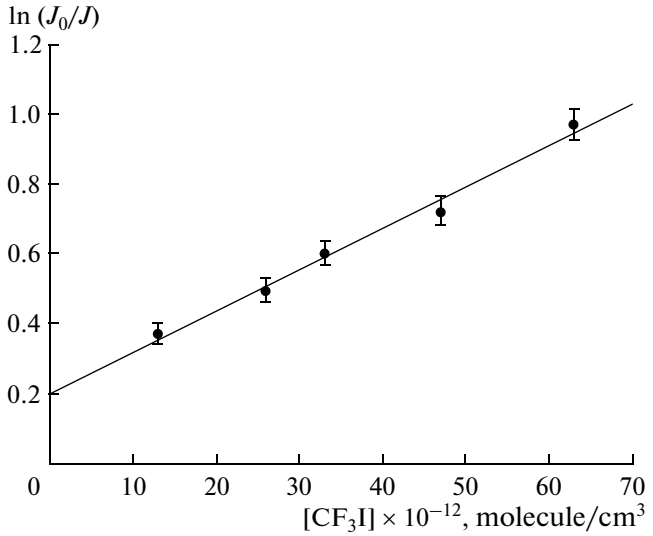

Fig. 4. Resonance fluorescence signal of chlorine atoms versus CF_3I concentration; T = 295 K, P = 1.6 Torr, [Cl] ≈ 1.3×10^{12} molecule/cm^3.

interacted with excess C_3F_7I diluted with helium or oxygen:

$$Cl + C_3F_7I \rightarrow \text{products}. \quad (I)$$

The consumption of chlorine atoms in reaction (I) was monitored by measuring the resonance fluorescence signal of chlorine atoms. Assuming that the chlorine atoms can react not only with C_3F_7I but also with the reactor wall, we can write the expression for the rate of disappearance of chlorine atoms in the reaction as follows:

$$\frac{d[Cl]}{dt} = -k_1[Cl][C_3F_7I] - k_{het}[Cl], \quad (5)$$

where k_1 is the rate constant of the bimolecular reaction of chlorine atoms with C_3F_7I (cm^3 molecule^{-1} s^{-1}) and k_{het} is the rate constant of the disappearance of chlorine atoms on the reactor wall (s^{-1}).

Integrating Eq. (5), we obtain

$$\ln\frac{[Cl_0]}{[Cl]} = k_1[C_3F_7I]\tau + k_{het}\tau, \quad (6)$$

where $[Cl_0]$ is the maximum concentration of chlorine atoms at the zero concentration of the atmospheric reactant and at the zero value of τ; τ is the contact time of the reactants, equal to z/v_0, z is the distance between the point of mixing of the reactants and the detection zone; and v_0 is the linear velocity of the reactants determined from the equation

$$Q_\Sigma = Pv_0S, \quad (7)$$

where Q_Σ is the total flow rate of the diluent gases and reactants through the reactor (cm^3 Torr s^{-1}), P is the pressure in the reactor (Torr), and S is the cross-sectional area of the reactor (cm^2).

Under our experimental conditions, the maximum linear velocity of the reactants was 700 cm/s. The corresponding Reynolds number did not exceed 60; i.e., the gas flow was definitely laminar.

The resonance fluorescence signal of chlorine atoms, J, is proportional to their concentration; i.e., $J \sim [Cl]$. Therefore, accepting that J_0 is the resonance fluorescence signal corresponding to the maximum "zero" concentration of chlorine atoms $[Cl_0]$ measured at the zero concentration of C_3F_7I and extrapolated to the zero value of τ, we readily obtain the following equation from Eq. (6):

$$\ln\frac{J_0}{J} = k_1[C_3F_7I]\tau + k_{het}\tau. \quad (8)$$

The plot of $\ln(J_0/J)$ versus $[C_3F_7I]$ obtained at 295 K, a pressure of 1.5 Torr in the vessel, and a chlorine atom concentration of ~1.1×10^{12} molecule/cm^3 is shown in Fig. 3. The reaction time was 0.018 s.

The rate constant of reaction (I) calculated from the slope ratio of the straight line in Fig. 3 turned out to be

$$k_1 = (5.2 \pm 0.3) \times 10^{-12}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}.$$

We failed to find any measured value of the rate constant of reaction (I) in the literature. At the same time, the rate constants of the reactions of the chlorine atom with CF_3I and C_2F_5I were reported to be $(5.1 \pm 1.5) \times 10^{-13}$ and $(3.9 \pm 0.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively [31]. Therefore, the rate constant measured by us supplements this series in a natural way. Note that the rate constants measured for the reactions of the chlorine atom with CH_3I, C_2H_5I, and C_3H_7I [32] also increase with an increasing number of carbon atoms in the molecule.

We demonstrated earlier that the heterogeneous formation of iodine atoms takes place in the reaction of the chlorine atom with methyl iodide [33]. To see whether iodine atoms form in reaction (I) not, we per-

formed experiments in which we attempted to detect a signal from iodine atoms under the following conditions: chlorine atom concentration of 2.1×10^{12} molecule/cm^3, C_3F_7I concentration of 1.0×10^{14} to 1.1×10^{15} molecule/cm^3, and reaction time of ~0.02 s. Within the scatter of experimental data, we could not detect any iodine signal stronger than the background signal at the zero concentration of C_3F_7I. This suggests that the rate constant of the channel of the reaction between the chlorine atom and C_3F_7I leading to the formation of iodine atoms does not exceed~10^{-17} cm^3 molecule^{-1} s^{-1}. The sensitivity of the detection system to iodine atoms determined in special-purpose experiments was ~10^8 molecule/cm^3.

Determination of the Rate Constant of the Reaction between CF_3I and Cl by Detection of Cl Atoms

The rate constant of the reaction of CF_3I with chlorine atoms,

$$Cl + CF_3I \rightarrow \text{products} \qquad \text{(II)}$$

was measured in the reactor presented in Fig. 2.

With the replacement of the reactant taken into account, Eq. (8) turns into Eq. (9):

$$\ln\frac{J_0}{J} = k_2[CF_3I]\tau + k_{het}\tau, \qquad (9)$$

where k_2 is the rate constant of reaction (II) and the other designations have the same meaning as those presented above. The rate constant of reaction (II) was measured at 295 K, a pressure of 1.6 Torr in the vessel, and a chlorine atom concentration of ~1.3×10^{12} molecule/cm^3. The reaction time was 0.016 s.

The plot of $\ln(J_0/J)$ versus $[CF_3I]$ is shown in Fig. 4. The rate constant of reaction (II) calculated from the slope ratio of the straight line in Fig. 4 is

$$k_2 = (7.4 \pm 0.6) \times 10^{-13}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}.$$

The value of the rate constant of reaction (III) obtained by us is between the values measured earlier (8.5×10^{-13} cm^3 molecule^{-1} s^{-1} [32] and 5.1×10^{-13} cm^3 molecule^{-1} s^{-1} [31]). Although the rate constant of the reaction of the chlorine atom with CF_3I is almost 30 times larger than the rate constant of the reaction of the OH$^\bullet$ radical with the same refrigerant [34], neither process can compete with the photolysis of CF_3I in the troposphere. We attempted to detect iodine atoms as a reaction product by the resonance fluorescence method. However, up to a CF_3I concentration of 2.3×10^{15} molecule/cm^3, the resonance fluorescence signal of iodine atoms did not exceed its background value measured at the zero concentration of CF_3I. This means that the rate constant of the channel of the reaction of chlorine atoms with CF_3I leading to the formation of iodine atoms does not exceed ~10^{-17} cm^3 molecule^{-1} s^{-1}.

Iodine-containing refrigerants are widely used in kinetic studies as substances generating iodine atoms upon photolysis. If the system contains chlorine atoms, then, as was shown in our earlier study [35], additional iodine atoms will result from the reaction of the chlorine atoms with CH_3I if the latter is used as the source of iodine atoms. Therefore, it is necessary to take into account the contribution from these iodine atoms to the chemical processes in the reactor. Such difficulties will not appear if CF_3I or C_3F_7I is used as the source of iodine atoms.

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