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Experimental Evidence for Acceleration of Reaction between Iodine Monoxide and Chlorine Monoxide at the Reactor Surface

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Abstract—The reaction of iodine monoxide with chlorine monoxide resulting in atom escape to the gas phase is studied at $T = (303 \pm 5)$ K and $P = 2.5$ Torr using a flow setup for measuring the resonance fluorescence signals of atomic iodine and chlorine. The heterogeneous reaction between chlorine monoxide and iodine monoxide occurring at the reactor surface covered with an F32-L Teflon-like compound and treated by the reaction products is characterized by the rate constant $k = (4.9 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This value is substantially higher than the rate constant for the homogeneous reaction $IO^{\bullet} + ClO^{\bullet}$ ($k_1 \le 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}).

INTRODUCTION

The possible role of reactions of active iodine (iodine atoms and $IO^{\bullet}$ radicals) in the processes resulting in the ozone layer depletion has been actively discussed during the last decade. Earlier, iodine compounds were believed not to reach the stratosphere, that is, a height of 20–30 km, where most of the ozone is located, because their lifetime in the atmosphere is measured in several days or weeks and because they rapidly decompose in chemical and photochemical reactions at a low height (0–10 km). However, more recently [1, 2] it has been shown that convective fluxes can transport water-insoluble compounds very rapidly from the lower height to the upper troposphere or even to the stratosphere. Gaseous radon, which is formed exclusively near the earth’s surface and has as a short lifetime as 3.8 days, was detected over the tropical tropopause [3].

It is known [4] that biomass is rich in iodine. Biomass is mainly burned in the tropical regions with strong convective fluxes, which transport iodine-containing compounds to the stratosphere. McCormick [5] observed a dramatic depletion of the ozone layer in the stratosphere at a height of less than 20 km not only in polar regions but also at middle latitudes and even in tropical regions, where the concentrations of active bromine and, especially, chlorine are much lower than that of active iodine [6]. He explained ozone depletion at low and middle latitudes observed during the last decade by the presence of a small concentration of active iodine (≤1pptv), which reacts with the chlorine and bromine compounds. If ozone depletion were exclusively due to the reaction of $IO^{\bullet}$ and $ClO^{\bullet}$ resulting in atomic iodine and chlorine or their precursors, the rate constant of this reaction would be of the order of 10^{-10} cm^3 molecule^{-1} s^{-1} at the above-mentioned concentration of active iodine.

In 1977, Bejanian *et al.* [7] measured the rate constant for the reaction of $IO^{\bullet}$ with $ClO^{\bullet}$ at 298 K by mass spectrometry using a discharge flow system:

$$k = (1.1 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Three thermochemically acceptable channels of this reaction were considered:

$$IO^{\bullet} + ClO^{\bullet} \longrightarrow I + OClO^{\bullet}, \quad \Delta H = -(4.0 \pm 0.2) \text{ kcal/mol}, \qquad \text{(Ia)}$$

$$IO^{\bullet} + ClO^{\bullet} \longrightarrow I + Cl + O_2, \quad \Delta H = -(2.3 \pm 1.2) \text{ kcal/mol}, \qquad \text{(Ib)}$$

$$IO^{\bullet} + ClO^{\bullet} \longrightarrow ICl + O_2, \quad \Delta H = -(47.5 \pm 1.2) \text{ kcal/mol}. \qquad \text{(Ic)}$$

The fractions of pathways (Ia), (Ib), and (Ic) were (0.55 ± 0.03), (0.25 ± 0.02), and (0.2 ± 0.02), respectively.

The rate constant for the reaction of $IO^{\bullet}$ with $ClO^{\bullet}$ was also measured in [8] using an induced resonance fluorescence laser in a flow system at 200–362 K. The kinetics of $IO^{\bullet}$ radical consumption was monitored in excess of the second reactant $ClO^{\bullet}$, that is, under conditions of a pseudomonomolecular process. The following expression for this rate constant was derived:

$$k(T) = (5.1 \pm 1.7) \times 10^{-12} \exp[(280 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

At 298 K,

$$k = (1.17 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The fraction of the pathways that do not produce atomic iodine was (0.14 ± 0.04) at 298 K.

The results of the above two studies agree perfectly, whereas the measured rate constants were nearly an order of magnitude lower than that required to explain the ozone loss in the lower stratosphere observed during the last decade.

Moreover, the $IO^\bullet$ concentration in the stratosphere was lower than 1 pptv and equal to at most $0.2^{+0.3}_{-0.2}$ pptv [9].

The above data suggest that the reaction of $IO^\bullet$ with $ClO^\bullet$ proposed in [6] cannot lead to a decrease in the ozone concentration in the lower stratosphere, because reactions responsible for this process should occur much more rapidly.

It is known that surface reactions are usually faster than reactions in the gas phase. This may be due to both an increase in the reaction rate constant (due to a decrease in the activation energy) and an increase in the local concentration of active species. It is the heterogeneous reactions in polar stratospheric clouds that cause the formation of ozone holes in the north hemisphere in spring. The reactions occurring on surfaces such as glass and Teflon, as well as on ice particles, are much more rapid than those occurring in the gas phase [10, 11]. The introduction of these processes into the computer models of the atmosphere resulted in an increase in the calculated ozone loss by an order of magnitude. Many researchers [12] suggested that chemical reactions could also occur on dust and soot particles liberated during volcano eruption. When studying the reactions of $IO^\bullet$ radicals with a number of sulfur-containing compounds, we also showed [13] that heterogeneous reactions between these components are much faster than the same reactions in the gas phase.

When we measured the rate constant for iodine atom formation during the reaction of the $IO^\bullet$ radicals with $ClO^\bullet$ [14], we noticed that, as the reaction vessel walls were treated with the reaction products, the reaction rate constant increased until it attained a constant value, thus indicating the possibility of the heterogeneous process.

In this work, we present the results of experiments carried out in the reaction vessel with the walls pretreated with an F32-L Teflon-like compound and then with the products of the $IO^\bullet$ with $ClO^\bullet$ reaction.

The aim of this work was to determine whether the reaction under study is homogeneous or not under our operating conditions and, if not, to determine the ratio of the rates of the homogeneous and heterogeneous pathways of this reaction under these conditions.

EXPERIMENTAL

Experimental Setup

To study the reaction of iodine monoxide and chlorine monoxide, a setup was constructed that allowed the resonance fluorescence signals of atomic iodine and chlorine to be measured simultaneously. Measurements were conducted at (303 ± 5) K and a pressure inside the reactor of 2.5 Torr. The setup contained a reactor, sources of iodine and chlorine atoms, systems for the registration of the iodine and chlorine atoms, and a system for the supply of gases into the reactor.

The flow setup, the sources of iodine and chlorine atoms, the systems for the registration of the iodine and chlorine atoms, and the systems for the supply of gases into the reactor were described in detail in [14]. Therefore, we will present here only a brief description of them, giving more attention to reactor modifications.

Two reactor modifications were used for the studies.

The reactor of modification (a) is schematically shown in Fig. 1. The inner surface of the reactor was covered with an F32-L Teflon-like compound to reduce the heterogeneous decay of atoms and radicals. Oxygen, ozone, helium, and ethane were introduced into the reactor through side holes. A source of iodine atoms was installed inside the reactor. The distance between the inlet of iodine atoms and their registration zone was 8.5 cm. It was possible to supply chlorine atoms to any point along the reactor axis through a mobile nozzle. The mobile nozzle consisted of a quartz tube with an outer diameter of 6 mm and a wall thickness of 1 mm. The inner surface of the nozzle was covered with hydrocarbon grease to reduce the heterogenous decay of chlorine atoms. A collapsible Teflon connection enabled one to move the nozzle without depressurizing the reactor.

Another reactor, modification (b), differed from the first one in that it had a mobile source of iodine atoms and an immobile source of chlorine atoms. This reactor was used to study changes in the concentration of iodine atoms or $IO^\bullet$ radicals with changes in the contact time.

Two different substances were used to produce iodine atoms in various experiments. Iodine atoms were generated by the photolysis of a CH_3I (or C_3F_7I) mixture diluted with oxygen (0.1–0.5% of CH_3I or C_3F_7I in O_2). The surface of a flow chamber of photolysis was treated with orthophosphoric acid to reduce the heterogeneous decay of iodine atoms. Photolysis was conducted at $\lambda = 253.7$ nm.

Molecular oxygen was stored in commercial metallic cylinders under pressures of 150–100 Torr and supplied to the reactor using a system ensuring the constant flow rate accurate to 2% for several hours. The starting reactants for iodine atom production CH_3I and C_3F_7I (reagent grade) were stored in a dark glass cylinder in the liquid phase. The CH_3I or C_3F_7I vapors were introduced through a fine-control valve into an oxygen flow

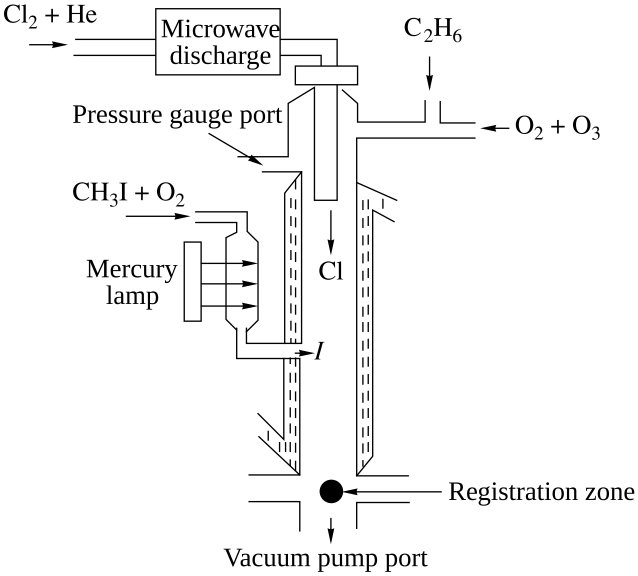

Fig. 1. Reactor of modification (a) for studying the reaction of $\mathrm{IO}^{\bullet}$ and $\mathrm{ClO}^{\bullet}$ radicals.

passing through the iodine atom source. The flow rate was determined by measuring the pressure decrease in a calibrated volume. Chlorine was stored in glass cylinders and added through a capillary to a helium flow, which then passed the flow resonance lamp acting as a chlorine atom source. The molecular chlorine flow was varied by changing the Cl_2 pressure at the capillary inlet.

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

Ozone was produced in an O_2 flow passing an ozonator. Oxygen from the glass cylinder was fed into a flowmeter with the constant pressure equal to 1 Torr at its outlet. Upon purification in a low-temperature trap with dry ice, oxygen passed a flow-control valve and entered an Ozon-2 ozonator designed at the Institute of Chemical Physics of the Russian Academy of Sciences (Moscow). Then an oxygen–ozone mixture passed through a glass cell (length, 10 cm) placed inside the spectrometer to measure the ozone concentration by the change in the optical density at $\lambda = 253.7$ nm.

The atom resonance fluorescence technique with photon counting was used to detect iodine atoms. A flow lamp with a mixture of helium and molecular iodine vapors (1×10^{13} and 1×10^{17} molecule/cm^3, respectively) was employed as a source of resonance emission. A resonance lamp activated by a 254-MHz discharge emitted at $\lambda = 178$ nm. A photoionization counter was constructed in our laboratory to detect photons. The signal from the counter was sent to a computer for storage and further analysis. The accumulation time was 60 s. The signal/noise ratio was 2 at an iodine atom concentration [I] ~1×10^8 atom/cm^3. The typical concentration of iodine atoms in the experiments was ~3×10^{10} atom/cm^3.

Chlorine atoms were generated with a discharge of frequency 254 MHz and an intensity of 2.5 W in a Cl_2 flow diluted with helium.

The resonance-fluorescence technique with photon counting was also used to detect chlorine atoms. The source of the resonance emission consisted of a flow lamp with a mixture of Cl_2 and helium (1×10^{13} and 1×10^{17} molecule/cm^3, respectively). The lamp was activated by a 254-MHz discharge. A homemade photoionization counter was used to detect the emission. The counter was filled with a mixture of argon and nitrogen monoxide and operated at $\lambda = 133.8$ nm. MgF_2 windows of the lamp and the counter enabled us to use the 119-nm chlorine line for registration, that is, to work in the spectral region virtually free of the absorption of molecular oxygen, which was present in the reactor. The computer system for the accumulation and analysis of the chlorine signal was similar to that employed for iodine. A signal/noise ratio equal to 2 was attained at [Cl] = 1×10^{10} atom/cm^3. The typical chlorine atom concentration in our experiments was 10^{12}–10^{13} atom/cm^3.

EXPERIMENTAL METHOD

The method of investigating the $\mathrm{IO}^{\bullet} + \mathrm{ClO}^{\bullet}$ reaction is based on the chain process involving two chain propagation reactions:

the reaction studied

$$\mathrm{IO}^{\bullet} + \mathrm{ClO}^{\bullet} \xrightarrow{k_1} \mathrm{I} + \text{products} \qquad (\mathrm{I})$$

and the reaction

$$\mathrm{I} + \mathrm{O}_3 \xrightarrow{k_2} \mathrm{IO}^{\bullet} + \mathrm{O}_2. \qquad (\mathrm{II})$$

If only two reactions, (I) and (II), occur in the reactor, the steady-state concentration of iodine atoms $[\mathrm{I}]_{ss}$ is achieved if the time of the reactant contact is longer than the characteristic time of reaction (II). This steady-state concentration can be found by the equation

$$k_2[\mathrm{O}_3][\mathrm{I}]_{ss} = k_1[\mathrm{ClO}^{\bullet}][\mathrm{IO}^{\bullet}]_{ss}\,. \qquad (1)$$

Here, $[\mathrm{IO}^{\bullet}]_{ss}$ is the steady-state concentration of $\mathrm{IO}^{\bullet}$ radicals. If there are no chain termination reactions of iodine atoms or $\mathrm{IO}^{\bullet}$ radical decay, the following relation is true:

$$[\mathrm{I}]_{ss} + [\mathrm{IO}^{\bullet}]_{ss} = [\mathrm{I}]_0, \qquad (2)$$

where $[\mathrm{I}]_0$ is the initial concentration of iodine atoms in the reactor. Combining Eqs. (1) and (2), we arrive at

$$\frac{[\mathrm{I}]_0}{[\mathrm{I}]_{ss}} = \frac{k_2[\mathrm{O}_3]}{k_1[\mathrm{ClO}^{\bullet}]} + 1. \qquad (3)$$

The straight line representing the $[I]_0/[I]$ vs. $[O_3]/[ClO^\bullet]$ dependence should intercept the y axis at the point equal to unity ($[I]_0/[I] = 1$). From the slope of this line, one can determine the k_2/k_1 ratio and calculate the k_1 value using the rate constant for the reaction of $IO^\bullet$ with ozone (k_2) obtained earlier in a wide temperature range [15].

Equation (3) is only applicable to homogeneous reaction (I) if its every step results in the formation of iodine atoms.

Measurement of the Initial Resonance Fluorescence Signal of Iodine Atoms in the Reactor—J_0

The flows of O_2 and He through the iodine atom source, the ozonator, and the capillary were the same as in the experiment. The pressure in the reactor was $P = 2.5$ Torr, and the linear flow rate was $v = 450$–500 cm/s. The concentration of iodine atoms was $\sim 3 \times 10^{10}$ molecule/cm^3 and practically did not change along the reactor axis. The rate constant for the heterogeneous decay of iodine atoms was measured in special experiments and found equal to $k \le 1$ s^{-1}. The contact time was at most 2×10^{-2} s; therefore, the concentration of iodine atoms in the registration zone was equal to their initial concentration within ±2%. The initial resonance fluorescence signal of iodine atoms was 500–1000 counts per 10 s in different experiments.

Measurement of the Background Signal—F

Upon measuring and recording the initial resonance fluorescence signal of iodine atoms; more than 4×10^{14} molecule/cm^3 of ozone was introduced into the reactor without changing other parameters of the flow. This resulted in the fast formation of $IO^\bullet$ radicals via the reaction of iodine with ozone (II).

The rate constant for reaction (II) is 1.1×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K [15] and the ozone concentrations used. The characteristic time of the reaction was at most 2×10^{-3} s. Therefore, more than 99.9% of iodine atoms transformed into $IO^\bullet$ radicals under the experimental conditions.

Thus, the background signal was largely associated with the light scattering on the molecules of substances, which were present in the reactor (mainly on CH_3I).

Measurement of the Steady-State Resonance Fluorescence Signal of Iodine Atoms—J

When the initial resonance fluorescence signal almost disappeared, that is, when almost all the iodine atoms introduced into the reactor transformed into $IO^\bullet$ radicals, chlorine atoms produced by a discharge were added to the reactor. As before, the reactant flow parameters were kept constant. Chlorine atoms introduced into the reactor transformed into $ClO^\bullet$ radicals in the fast reaction

$$Cl + O_3 \xrightarrow{k_3} ClO^\bullet + O_2. \tag{III}$$

The rate constant for this reaction is $k_3 = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 295 K [16]. Therefore, the $ClO^\bullet$ concentration was equal to the concentration of the chlorine atoms introduced and, in our experiments, changed from 1×10^{12} to -1×10^{13} molecule/cm^3. The technique for measuring the chlorine atom concentration is described in [14]. The reaction of $IO^\bullet$ and $ClO^\bullet$ radicals (reaction (I)) resulted in the formation of a steady-state concentration of iodine atoms.

RESULTS AND DISCUSSION

Taking into account that the initial concentration of iodine atoms introduced into the reactor $[I]_0$ is proportional to the measured difference between signals $(J_0 - F)$ and that the steady-state concentration of iodine atoms $[I]_{ss}$ is proportional to the signal difference $(J - F)$, Eq. (3) can be rearranged into the form

$$\frac{J_0 - F}{J - F} = \frac{k_2[O_3]}{k_1[ClO^\bullet]} + 1. \tag{4}$$

Recall that we derived Eq. (3) for a completely homogeneous reaction with the generation of iodine atoms by every step of the process. In this case, a plot of $(J_0 - F)/(J - F)$ versus $[O_3]/[ClO^\bullet]$ should be a straight line that intersects the Y axis at $y = 1$.

Figure 2 presents the $(J_0 - F)/(J - F)$ vs. $[O_3]/[ClO^\bullet]$ plot obtained in the experiments carried out in the reactor, which was treated with the reaction products many times, at a constant ozone concentration and a variable $[ClO^\bullet]$ concentration. The experimental points are extrapolated with a straight line, which, however, intersects the y axis at a point that is well above $y = 1$. This is an indication of the heterogeneous nature of the reaction of the reactants and the possible decay of active chain carries in chain termination reactions.

As noted above, the reaction of $IO^\bullet$ with $ClO^\bullet$ can occur via different pathways, one of which (Ic) results in chain termination. If during the contact, reaction (Ic) occurs to a significant extent, the steady-state signal of iodine atoms is lower than the initial one even at $[O_3]/[ClO^\bullet] \longrightarrow 0$ and relation (4) is not fulfilled.

We considered both of the above possibilities. First, we studied the possibility of the heterogeneous reaction. Taking into account that heterogeneous processes are faster than homogeneous ones, we hypothesized that the rate constant (higher than that reported in [7, 8]) of the reaction studied was due to the occurrence of a heterogeneous reaction along with a homogeneous one. The technique used allowed us to distinguish these two

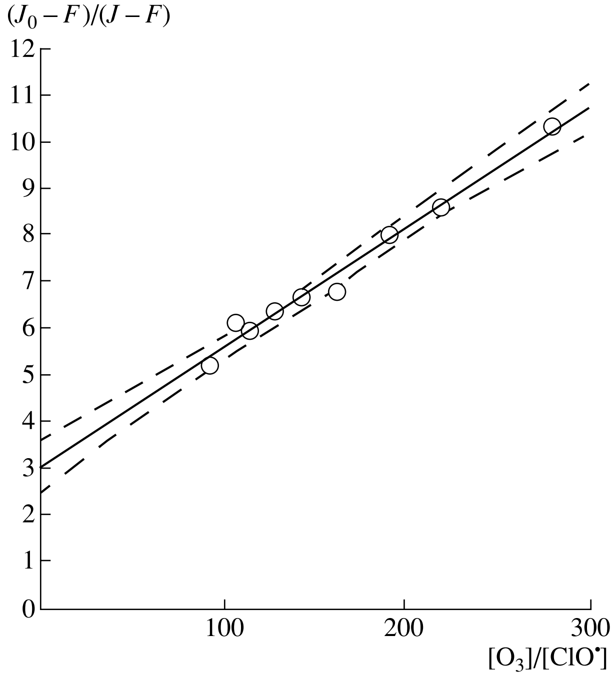

Fig. 2. $(J_0 - F)/(J - F)$ vs. $[O_3]/[ClO^\bullet]$ plot obtained in experiments performed at a constant ozone concentration equal to 4.38×10^{14} molecule/cm^3 and a variable $[ClO^\bullet]$ concentration. The dotted line corresponds to a 98% confidence interval.

processes. In the case of the chain process in the reactor, the characteristic time of every elementary step may be shorter than that of active species diffusion to the wall, thus permitting one to distinguish the homogeneous and heterogeneous reaction pathways.

Consideration of the Heterogeneous Reaction $IO^\bullet + ClO^\bullet$

If heterogeneous reaction (k_1^{het}) with the rate constant k_1^{het} occurs in the reactor along with homogeneous one (I), Eq. (3) should be rewritten in the form

$$\frac{[I]_0}{[I]_{ss}} = \frac{k_2}{k_1 + k_1^{het}\dfrac{0.5k_{diff}}{k_1^{het}[ClO^\bullet] + 0.5k_{diff}}}\frac{[O_3]}{[ClO^\bullet]} + 1, \quad (5)$$

where $k_{diff} = 23D/4R^2$, $k_1^{het}[ClO^\bullet]$ is the rate constant of the kinetically controlled reaction, D is the diffusion coefficient of $IO^\bullet$ radicals, and R is the reactor diameter (cm). $D = D_0(760/P)$, where D_0 is the diffusion coefficient of $IO^\bullet$ radicals at 760 Torr and P is the reactor pressure (Torr). $D_0 = 0.12$ cm^2/s at $T = 296$ K.

The fact that the coefficient at k_{diff} in Eq. (5) is lower than unity suggests that the reactor configuration near the registration zone is not cylindrical and that the whole reactor surface is not available for active species. This coefficient was chosen in [13] to be 0.5 when the theoretical curves were fitted into the experimental data.

Note that the study of the heterogeneous reaction mechanism was not our task. We tried to show that the reaction, whose rate depends on the reactant concentrations, as well as the rate of the bimolecular homogeneous reaction, still occurs at the surface. This explains the fact that the rate constants of the same reaction measured in different studies sometimes differ by orders of magnitude. Clearly, the rate constant k_1^{het} considered here can only be used under our experimental conditions and in the given reactor.

It follows from Eq. (5) that the $[I]_0/[I]_{ss}$ vs. $[O_3]/[ClO^\bullet]$ plot also intersects the y axis at the point $y = 1$ if experiments are performed at a rather low $ClO^\bullet$ concentration when $k_1^{het}[ClO^\bullet] \ll 0.5k_{diff}$. In this case, the rate constant of the reaction determined from the slope of the curve is a sum of the rate constants for the homogeneous and heterogeneous reactions. If experiments are conducted at a constant and relatively low $ClO^\bullet$ concentration, the reaction rate constant determined on the basis of their results might not be the rate constant of the homogeneous process. Obviously, this explains why our rate constant for the $IO^\bullet + ClO^\bullet$ reaction is higher than reported values [14].

The experimental curve presented in Fig. 2 was obtained under conditions when the ozone concentration remained unchanged and the $ClO^\bullet$ concentration changed broadly. The steady-state concentration of iodine atoms was 10^{10}–10^{11} molecule/cm^3.

We determined the sum of the rate constants for the heterogeneous and homogeneous reactions and, then, using mathematical modeling based on Eq. (5), obtained the fraction of the homogeneous component in the reaction rate constant. The simulation results indicated the heterogeneous character of the reaction.

We conducted experiments varying the ozone concentration in the course of the run with a constant $ClO^\bullet$ concentration. The results of these experiments are given in Fig. 3. It presents the $(J_0 - F)/(J - F)$ vs. $[O_3]/[ClO^\bullet]$ plot obtained at two different $ClO^\bullet$ concentrations, as well as the results of mathematical modeling using the rate constant of the heterogeneous reaction calculated from the data of Fig. 2.

Curve *1a* corresponds to $[ClO^\bullet] = 4.5 \times 10^{12}$ molecule/cm^3 and $k_1^{het} = 4.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, whereas curve *2a* corresponds to $[ClO^\bullet] = 1.4 \times 10^{12}$ molecule/cm^3 and $k_1^{het} = 4.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

As can be seen, neither of these curves adequately describes the experimental data. It is also clear that this dependence cannot be extrapolated by a straight line that intercepts the y axis at the point $y = 1$. Note that the curves passing the extremum points intercept the y axis at $y < 1$ at $[O_3]/[ClO^\bullet] \longrightarrow 0$. This suggests that the steady-state signal of iodine atoms is stronger than the initial signal; that is, the system contains an additional iodine atom source.

In our opinion, chlorine atoms produced by reaction (1b) in our reactor can enter either the reaction with ozone (III) or the reaction with methyl iodide:

$$Cl + CH_3I \xrightarrow{k_4} I + \text{products}. \qquad \text{(IV)}$$

At low ozone concentrations, reaction (IV) prevails over reaction (III) and an additional iodine atom source appears in the reactor.

We included reaction (IV) into the chain process scheme and performed computer simulation for the experimental data given in Fig. 3. In this case, curve *1b* corresponds to $[ClO^\bullet] = 4.5 \times 10^{12}$ molecule/cm^3, $k_1^{het} = 4.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and $k_4 = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, whereas curve *2b* corresponds to $[ClO^\bullet] = 1.4 \times 10^{12}$ molecule/cm^3, $k_1^{het} = 4.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and $k_4 = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

As can be seen, the results of computer simulation perfectly agree with the experimental data at these values of k_1^{het} and k_4. The experimental estimate of the rate constant of reaction (IV) obtained more recently was

$$k_4 = (3.1 \pm 1.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

To eliminate the effect of reaction (IV), we used C_3F_7I instead of methyl iodide as a source of iodine atoms. In preliminary experiments, we showed that no iodine atoms were formed during the reaction of C_3F_7I with chlorine atoms. Figure 4 presents the experimental data obtained with C_3F_7I at $[O_3] = 5.0 \times 10^{14}$ molecule/cm^3, $P = 2.54$ Torr, $v = 488$ cm/s, and $T = 303$ K, as well as the results of mathematical modeling including the heterogeneous process (I^{het}).

Figure 4 shows that our experimental data largely correspond to the heterogeneous reaction pathway. However, the same data may be interpreted assuming that chain termination (Ib) occurs at a noticeable rate along with reaction (Ic).

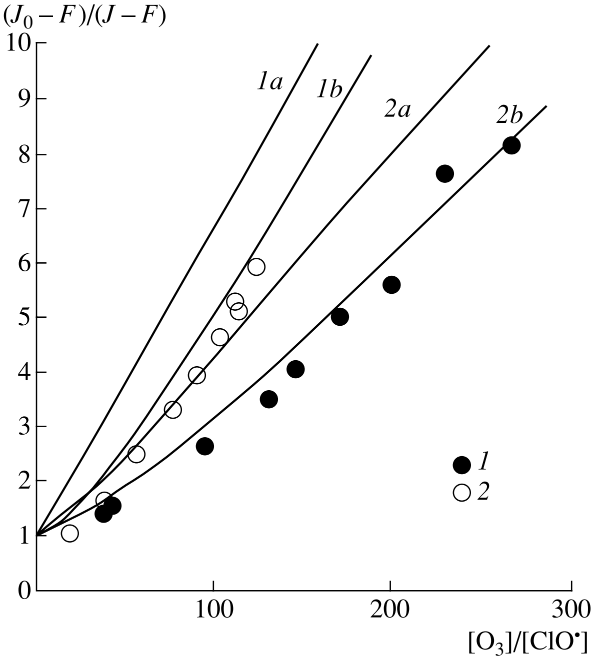

Fig. 3. $(J_0 - F)/(J - F)$ vs. $[O_3]/[ClO^\bullet]$ plot obtained at variable $[O_3]$ and constant $[ClO^\bullet]$ concentration equal to (*1*) 4.5×10^{12} and (*2*) 1.4×10^{12} molecule/cm^3. The points correspond to the experiment, and the lines correspond to the results of the mathematical modeling with due regard for (*1a*, *2a*) the heterogeneous pathway of reaction (I) and (*1b*, *2b*) the simultaneous occurrence of the heterogeneous process and reaction (IV); $k_1^{het} = 4.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_4 = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, (*1a*, *1b*) $[ClO^\bullet] = 4.5 \times 10^{12}$, and (*2a*, *2b*) 1.4×10^{12} molecule/cm^3.

This should result in a decrease in the active iodine concentration ($[I] + [IO^\bullet]$) along the reactor. The experimental iodine concentration [I] should be lower than that predicted by Eq. (I), and the experimental points of the $(J_0 - F)/(J - F)$ vs. $[O_3]/[ClO^\bullet]$ plot should be above those predicted by Eq. (5). Figure 5 presents the processing of the experimental data obtained when C_3F_7I was used as an iodine atom source. Figure 5 shows that our experimental data can be attributed to both the heterogeneous character of reaction (I) and chain termination (Ic) with the rate constant

$$k_{1c} = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

To distinguish between these two cases, we studied how the resonance fluorescence signal of atomic iodine changed with the time of reactant contact. If the rate constant for reaction (Ic) is low, the reaction

$$IO^\bullet + \text{wall} \xrightarrow{k_5} (IO)_{ads} \qquad \text{(V)}$$

is slow and the active iodine concentration ($[I] + [IO^\bullet]$) does not noticeably change during the contact time, the resonance fluorescence signal of iodine atoms should be independent of the contact time for both the homogeneous and heterogeneous pathways of reaction (I). On the contrary, the iodine signal should markedly decrease along the reactor axis if the rate constant for termination k_{1c} is high.

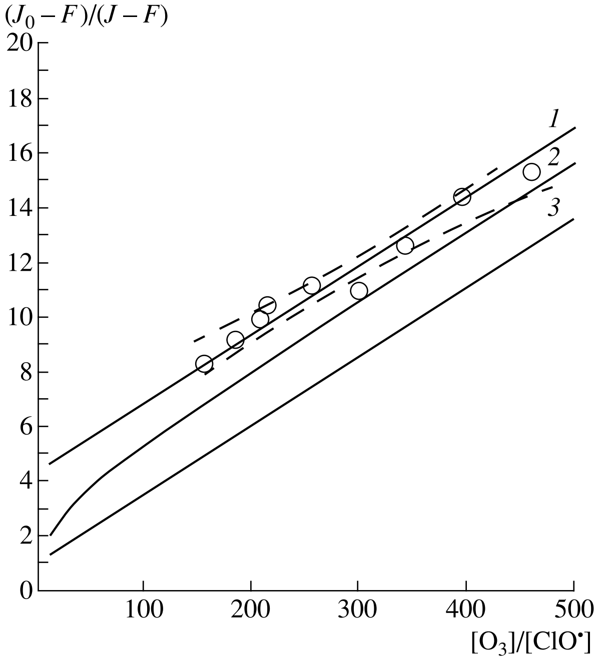

Fig. 4. Experimental data (points) obtained with C_3F_7I used as an iodine atom source at $[O_3] = 5.0 \times 10^{14}$ molecule/cm^3, $P = 2.54$ Torr, $v = 488$ cm/s, and $T = 303$ K, as well as the results of mathematical modeling including the heterogeneous process (I^{het}) at the degree of reaction homogeneity ($k_1/(k_1 + k_1^{\text{het}})$) equal to (*1*) 0, (*2*) 0.2, and (*3*) 1. The dotted line corresponds to a 95% confidence interval.

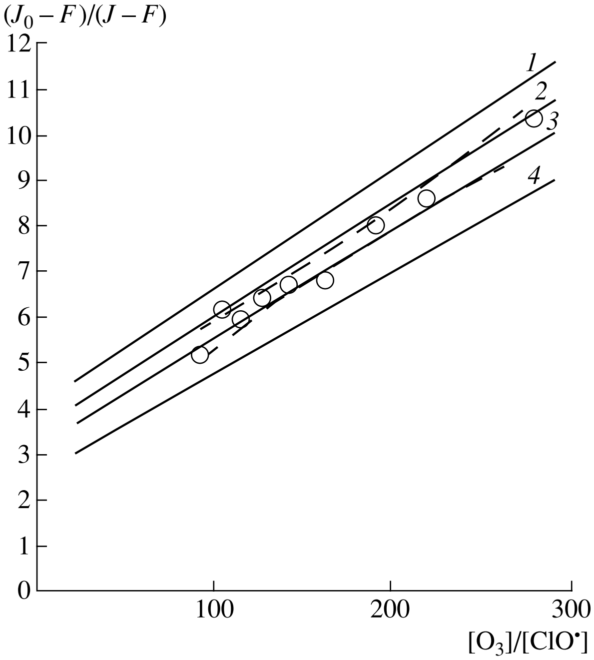

Fig. 5. Results of modeling for the simultaneous occurrence of homogeneous reaction (I) and chain termination (Ic) at $k_1 = 5.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k_{1c} \times 10^{11}$ cm^3 molecule^{-1} s^{-1}: (*1*) 2, (*2*) 1.5, (*3*) 1, and (*4*) 0. The points represent experimental data for C_3F_7I as an iodine atom source; the dotted line corresponds to a 99% confidence interval.

In the case of reaction (Ic), the dependence of the resonance fluorescence signal of iodine atoms on the contact time is described by the equation

$$\ln(J - F) = -k_{\text{eff}}\frac{k_2[O_3]}{k_1[ClO^\bullet] + k_2[O_3]}t \qquad (6)$$

or

$$\ln(J - F) = -k_{\text{eff}}\frac{[IO^\bullet]_{ss}}{[IO^\bullet]_{ss} + [I]_{ss}}t, \qquad (7)$$

where

$$k_{\text{eff}} = k_{1b}[ClO^\bullet] + k_5 \qquad (8)$$

and k_5 is the rate constant for $IO^\bullet$ decay on the reactor walls. The $[IO^\bullet]_{ss}/([IO^\bullet]_{ss} + [I]_{ss})$ can be calculated using the J_0 value (the resonance fluorescence signal of the iodine atoms in the absence of $ClO^\bullet + O_3$) and the resonance fluorescence signal of iodine atoms in the presence of $ClO^\bullet$ and O_3 at $t \longrightarrow 0$, when termination reaction may be neglected.

Figure 6 illustrates the $\ln(J - F)$ vs. t dependence for the experiment with C_3F_7I used as an iodine atom source. Similar relations were also obtained for other $[IO^\bullet]_{ss}/([IO^\bullet]_{ss} + [I]_{ss})$ ratios.

The slope of the curve in the $\ln(J - F) - t$ coordinates is $k_{\text{eff}}\,[IO^\bullet]_{ss}/([IO^\bullet]_{ss} + [I]_{ss})$. Figure 7 presents the $k_{\text{eff}}[IO^\bullet]_{ss}/([IO^\bullet]_{ss} + [I]_{ss})$ vs. $[IO^\bullet]_{ss}/([IO^\bullet]_{ss} + [I]_{ss})$ plot. The slope of this curve is k_{eff}. We should know the k_5 value to determine the rate constant k_{1c}.

As noted above, the reactor surface was covered with an F32-L Teflon compound before the experiment to reduce $IO^\bullet$ decay. To be sure that the heterogeneous decay of $IO^\bullet$ radicals is insignificant, we used their reaction with NO, which was thoroughly studied by resonance fluorescence of iodine atoms in [17]. We showed in that work that only the homogeneous reaction

$$IO + NO \xrightarrow{k_6} I + NO_2 \qquad (VI)$$

occurs on addition of NO to $IO^\bullet$ radicals produced by reaction (II).

The only way that $IO^\bullet$ radicals disappear in the absence of their homogeneous decay is their decay on the reactor walls. If the k_5 value is very low, as in the case of the reactor coverage with the F32-L Teflon com-

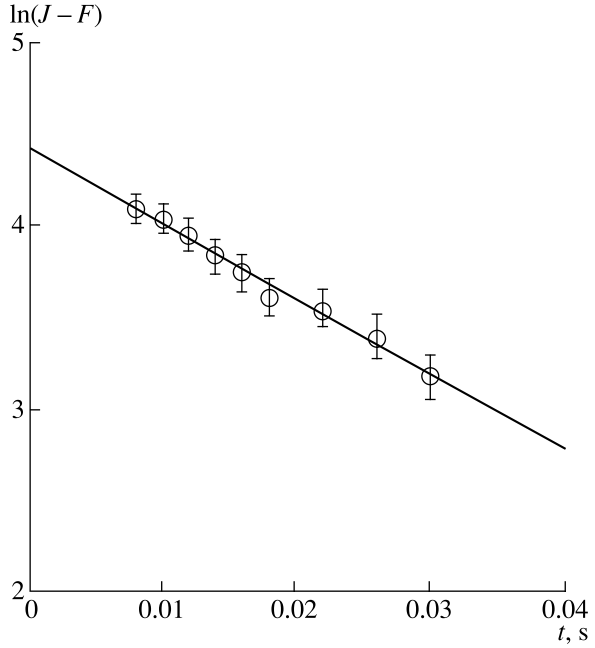

Fig. 6. ln(J – F) vs. time of the experiment with C_3F_7I used as an iodine atom source.

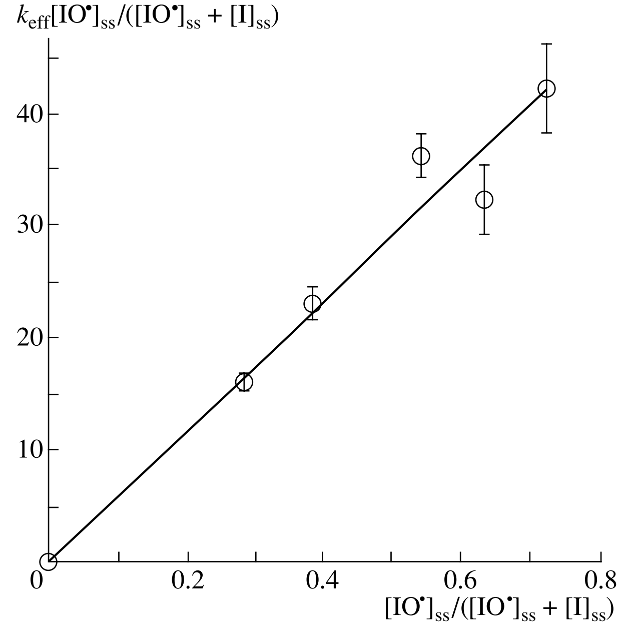

Fig. 7. $k_{eff}[IO^{\bullet}]_{ss}/([IO^{\bullet}]_{ss} + [I]_{ss})$ vs. $[IO^{\bullet}]_{ss}/([IO^{\bullet}]_{ss} + [I]_{ss})$.

pound, the iodine atom concentration does not change along the reactor. Similar experiments were performed after studying the reaction of $IO^{\bullet}$ and $ClO^{\bullet}$ radicals. The obtained dependence of ln(J – F) on the contact time ($t = L/v$, where L is the reaction zone length) suggests that the heterogeneous decay of $IO^{\bullet}$ radicals is insignificant:

$$k_5 = (7.6 \pm 5.2)\ \mathrm{s}^{-1}.$$

Using Eq. (8) and knowing the concentration $[ClO^{\bullet}] = 8.3 \times 10^{12}$ molecule/cm^3 and the values of k_{eff} and k_5, we can determine the rate constant for reaction (Ic):

$$k_{1c} = (5.9 \pm 1.5) \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}.$$

Note that this value is the upper limit of the rate constant of chain termination in our reactor. This is due to the fact that, although the rate constant for the heterogeneous decay of iodine atoms was determined before and after experiments and its values perfectly agreed, it could be higher in the course of the experiment because of the treatment of the reactor walls by the reaction products. This means that we obtained a lower value of the rate constant for chain termination.

Nevertheless, even our rate constant for the termination reaction k_{1c} is too low to explain the experimental data presented in Fig. 5. Therefore, reaction (I) in our reactor occurs mainly on the reactor walls and its contribution is maximal if the reactor wall is treated by the reaction products. Figure 4 shows that the fraction of the homogeneous component of reaction (I) is at most 0.2; that is, the rate constant of the homogeneous reaction (I) is

$$k_1 \le 1 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}.$$

This value agrees well with the data of [7, 8].

Thus, our data support the findings reported in [7, 8] that the homogeneous reaction of iodine monoxide with chlorine monoxide occurs too slowly to confirm the calculations of Solomon *et al.* [6], who assumed that this reaction is very important in stratospheric ozone depletion, especially taking into account that the $ClO^{\bullet}$ and $IO^{\bullet}$ concentrations are too low to ensure this process at even lower rate constants of this reaction [9]. The possible role of much faster heterogeneous processes requires further investigation.

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