Measurement of the Reaction Rate Constants of Oxygen Atoms with Chlorine and Iodomethane Using a Resonance Fluorescence Technique

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Abstract—The following reaction rate constants of oxygen atoms with iodomethane and chlorine were measured using resonance fluorescence under jet conditions at 298 K: $k_1 = (2.4 \pm 0.5) \times 10^{-15}$ and $k_2 = (6.9 \pm 0.2) \times 10^{-14}$ cm^3/s, respectively.

INTRODUCTION

Minor components of the atmosphere, whose concentrations may be no higher than 10^5 molecule/cm^3, nevertheless, play a leading role in the chemistry of the atmosphere. The most important function of the ·OH radical as a troposphere scavenger is well known, although its concentration in this layer is as low as 10^6 molecule/cm^3. Oxygen atoms participate in many processes of ozone consumption and formation. The importance of iodine and chlorine atoms and their compounds with oxygen to the chemistry of the troposphere and the stratosphere is difficult to overestimate. Their reactions with ozone, hydrocarbons, and sulfur and nitrogen compounds should be taken into account in the consideration of the most important current problems such as the conservation of the ozone layer, which prevents the biosphere of the earth from destructive solar UV emission and processes resulting in global warming. For example, it is well known that halogen-containing hydrocarbons of both natural and anthropogenic origins seriously affect the concentration of ozone in the atmosphere. A widespread halogenated hydrocarbon such as iodomethane is formed in large amounts by the decay of phytoplankton and marine algae [1]; it is also released to the atmosphere during the combustion of organic matter in tropical and subtropical zones [2]. Note that the concentration of iodine compounds in biomass is at least the same as or, most likely, higher than that of bromine and chlorine compounds [3]. The lifetime of iodomethane in the atmosphere is a few days, and this substance is sparingly soluble in water [4].

Currently, the ocean is the main source of iodomethane. However, because of the continuously increasing current use of CH$_3$I in firefighting, it is likely that the contribution of anthropogenic iodomethane, which is a few percent of the amount of iodomethane of oceanic origin, will continuously increase. This is related to the fact that climates in many regions of the earth become drier and warmer to cause an increase in the number of fires. An increase in industrial production also results in a great number of fires.

Chlorine atoms are formed in the stratosphere by the degradation of Freons under the action of hard UV radiation, whereas so-called halogen activation is responsible for the appearance of chlorine atoms in the lower atmosphere. This halogen activation consists in that heterogeneous processes with the participation of marine aerosol particles are accompanied by the rapid conversion of chlorine-containing compounds such as HCl and ClONO$_2$ into the weakly bound molecules of Cl$_2$ and HOCl [5]. In the photolysis of molecular chlorine and HOCl, chlorine atoms are formed; these atoms interact with iodomethane to generate atomic iodine. The replacement of chlorine atoms by iodine atoms considerably increased the length of chains in chain reactions with the participation of active iodine because, unlike chlorine, iodine does not have chemically and photochemically stable derivatives. Cicerone [6] noted that marine aerosols often contained less NaCl than seawater, whereas the NaI content of aerosols was occasionally higher than that of ocean water by a factor of 1000 or even 10000. This suggests the occurrence of a chemical mechanism for the replacement of chlorine atoms in the aerosols of marine salts by iodine atoms.

Oxygen atoms are the representatives of so-called odd oxygen, and they occur where ozone is present in the atmosphere because they are weakly retained by the ozone molecule. The photodissociation of molecular oxygen into atoms under the action of UV radia-
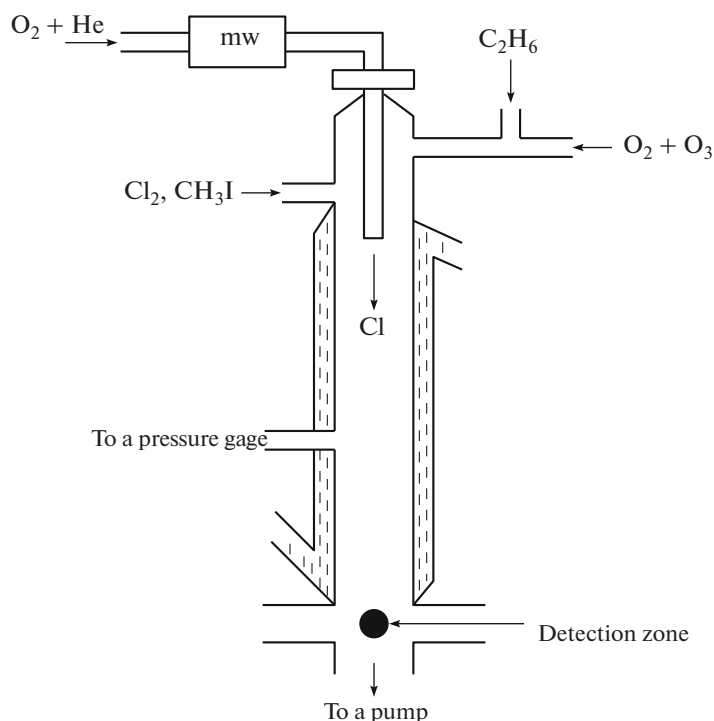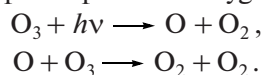
Fig. 1. Schematic diagram of the reactor.

tion followed by the rapid interaction of these atoms with the O_2 molecule to form O_3 is the only reason for the appearance of ozone in the stratosphere at a height of above 30 km. The decay of atmospheric ozone also occurs with the participation of oxygen atoms:

$$O_3 + h\nu \longrightarrow O + O_2,$$
$$O + O_3 \longrightarrow O_2 + O_2.$$

The action of all of the other atmospheric components of both natural and anthropogenic origins is reduced to only an acceleration of the latter of these reactions [7].

Although the concentration of oxygen atoms in the troposphere is low, their reactions with halogens occur by a chain mechanism, and they can also result in the appearance of an additional amount of halogen atoms in the atmosphere. With consideration for an increase in the concentration of ozone in the lower atmosphere, it is likely that the concentration of oxygen atoms in the lower atmosphere will also increase [7].

A kinetic system, in which resonance fluorescence was used to detect chlorine and iodine atoms, was developed in our laboratory. The high sensitivity of this technique allowed us to measure for the first time the rate constant of formation of iodine atoms in the reaction of iodomethane with oxygen atoms:

$$O + CH_3I \longrightarrow I + \text{products.} \qquad (I)$$

Earlier, we were the first to observe the formation of iodine atoms in the interaction of chlorine atoms with iodomethane [8] by detecting both the disappearance of chlorine and the appearance of iodine.

To adjust a procedure for the resonance fluorescence detection of chlorine atoms, we used the reaction of oxygen atoms with molecular chlorine

$$O + Cl_2 \longrightarrow ClO + Cl. \qquad (II)$$

This reaction was also studied by other researchers (e.g., see [9]); however, the published data are inconsistent.

EXPERIMENTAL

Reactor

The experiments were performed under jet conditions in a reactor, which is shown in Fig. 1. The reactor with a movable source of oxygen atoms was a quartz cylinder with an inner diameter of 1.7 cm. To decrease the rate of heterogeneous decay of atoms and radicals, its inner surface was protected with F-32L fluoroplastic. For this purpose, the reactor surface was coated with the liquid fluoroplastic and then kept at 160°C for several hours. Oxygen, helium, chlorine, and ethane were supplied to the reactor through side holes. Iodomethane was also fed through a side inlet. To supply reagent gases other than CH_3I and chlorine, regulators were used, which made it possible to maintain a constant gas flow rate to within 2–3% for 10–15 h. The mass flow rates of reagent and carrier gases were measured based on the outflow of the gases from a calibrated volume per unit time. Pressure changes were monitored using a reference pressure gage. High-purity helium and oxygen were used in all of the exper-

iments. The supply line for Cl_2 was made of glass tubes with Teflon shutoff valves, which were developed at the Institute of Chemical Physics, Russian Academy of Sciences; this line contained no vacuum grease. Molecular chlorine was obtained by the oxidation of HCl with potassium permanganate, purified by low-temperature distillation, kept in glass cylinders, and added to a flow of helium through a capillary. This flow of helium passed through a flow resonance lamp and a source of Cl atoms. To vary the flow of Cl_2, the pressure of chlorine at the capillary inlet was changed. Chemically pure iodomethane was kept in glass cylinders in a liquid phase away from light. In the course of the experiment, the cylinders were dipped into thawing ice and CH_3I vapor in a mixture with oxygen was supplied to the reactor through a fine regulation valve. The flow rate was determined from the pressure drop in a calibrated volume.

The concentrations of iodine and chlorine atoms were measured using resonance fluorescence in accordance with a procedure that was described in detail previously [10, 11]. In the measurements of the rate constants of reactions (I) and (II), the resonance fluorescence signals of iodine and chlorine atoms, respectively, were measured.

Detection of Iodine Atoms

The system for the resonance fluorescence detection of iodine atoms included a iodine resonance lamp, a photoionization counter for the detection of photons reemitted by iodine atoms, and a Ch3-63/1 frequency meter.

The detection zone of iodine atoms was formed by tubes ~10 mm in diameter and ~10 mm in length, which were crosswise sealed in the reactor. The brass cones of the resonance lamp, the photon counter, and the Wood horn were attached to the ground-glass quartz ends of the tubes with the use of vacuum grease. The tubes were coated with MgO on the inside to make the probability of the heterogeneous decay of iodine atoms close to unity. The diameter of the detection zone was ~5 mm.
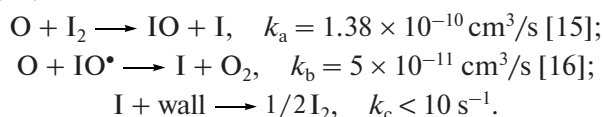
The flow resonance lamp operated at the wavelength $\lambda = 178.3$ nm, at which the absorption cross section of the resonance emission of iodine atoms was $\sigma^{res}(I) = 5 \times 10^{-13}$ cm^2 [12]. The lamp was made of UV quartz with the short-wave transmission cutoff of 160 nm. An indium membrane was used to provide vacuum tightness. A mixture of helium with molecular iodine in a ratio of about 10 000 : 1 was passed through the lamp. The concentration of molecular iodine at the inlet of the resonance lamp was $\sim 7 \times 10^{12}$ cm^{-3}. To generate a discharge in the lamp, a Broida microwave resonator was used. The reemitted photons were detected using the photoionization counter over the range of 160−185 nm. The signal from the counter arrived at the Ch3-63/1 frequency meter and simulta-

neously at an S1-107 oscillograph. In the course of an experiment, from 500 to 10^4 pulses were accumulated at each point. Before the measurements, the counter was initially evacuated with a diffusion pump to a pressure of 5×10^{-5} Torr and then filled with a mixture of NO (10 Torr) and Ar (230 Torr). A drop of diethylferrocene was placed in a glass finger and an equilibrium was established between its vapor and liquid phases. The long-wave transmission cutoff of the counter, which was determined by the ionization potential of diethylferrocene (6.3 eV [13]) was 185 nm. Thus, the photoionization counter simultaneously served as a monochromator to restrict the spectral range of wavelengths from 160 to 185 nm. Before the experiments, the system was calibrated in terms of sensitivity to iodine atoms.

Calibration of the Absolute Sensitivity of the System to Iodine Atoms

The calibration of the absolute sensitivity of the system to iodine atoms was performed in the following manner: A carrier gas (helium) with molecular iodine at a known concentration, which was calculated from the time of outflow of a mixture of helium with saturated vapor of I_2 from a calibrated volume at 0°C, was introduced into the reactor, where iodine reacted with oxygen atoms. These oxygen atoms were obtained by the action of a microwave discharge on a mixture of O_2 with He. The concentration of O atoms was higher than the concentration of I atoms by three orders of magnitude.

The concentration of oxygen atoms was determined by chemiluminescence titration with the use of NO_2 [14]. The following reactions occurred in the system:

$$O + I_2 \longrightarrow IO + I, \quad k_a = 1.38 \times 10^{-10} \text{ cm}^3/\text{s [15]};$$
$$O + IO^\bullet \longrightarrow I + O_2, \quad k_b = 5 \times 10^{-11} \text{ cm}^3/\text{s [16]};$$
$$I + \text{wall} \longrightarrow 1/2\, I_2, \quad k_c < 10 \text{ s}^{-1}.$$

The steady-state concentrations of molecular iodine and $IO^\bullet$ radicals in this system were also much lower than 1% of the concentration of I atoms. Indeed,

$$[I_2] = \frac{k_c}{2k_a[O]}[I] < 10^{-3}\,[I],$$

$$[IO^\bullet] = \frac{k_c}{2k_a[O]}[I] < 10^{-4}\,[I].$$

The concentration of O atoms was higher than [I] by almost three orders of magnitude; therefore, heterogeneous decay was the main process of consumption of these atoms. Consequently, a specified amount of iodine atoms could be obtained by this procedure and transferred at a distance restricted by the heterogeneous decay of atomic oxygen. In this case, the concentration of atomic iodine remained almost unchanged. The maximum absolute sensitivity of the system to iodine atoms reached in our experiments was 2.9×10^7 cm^{-3} at a signal-to-noise ratio of 1 and a

pulse accumulation time of ~100 s. Various factors, such as the contamination of optical windows with chemical reaction products or a deterioration of discharge parameters in the lamp, could result in a decrease in sensitivity. Therefore, we performed calibration before the onset of each particular experiment in the cases when it was of importance to determine the absolute concentration of iodine atoms.

Detection of Chlorine Atoms

The device for the resonance fluorescence detection of chlorine atoms consisted of a chlorine flow lamp as a resonance emission source with a wavelength of 118.9 nm, a photoionization counter operating in the range of 117−134 nm designed for measuring the number of photons reemitted by chlorine atoms, a Ch3-63/1 frequency meter connected to a computer.

The flow lamp was filled with a mixture of Cl_2 with helium (1×10^{13} and 1×10^{17} cm^{-3}, respectively), which was exposed to a discharge with a frequency of 254 MHz. A Broida resonator was used to generate this discharge with a power of 2.5 W. The pressure in the lamp was varied from 0.5 to 1 Torr. Its inner surface in the discharge zone was treated with orthophosphoric acid.

The signal from the counter through the frequency meter was supplied in the pulse count mode to the computer for data acquisition and processing. At the concentration [Cl] = 1×10^{10} cm^{-3}, the signal-to-noise ratio was 2. Titration with C_2H_6 was used to calibrate the absolute sensitivity of the device to chlorine atoms.

The photoionization counter was filled with a mixture of argon with nitrogen monoxide (230 and 10 Torr, respectively). The long-wave transmission cutoff of the counter was 133.8 nm, which was determined by the ionization potential of NO (8.7 eV [13]). The lamp and the counter were equipped with optical glasses of MgF_2, which allowed us to perform measurements at a wavelength of 118.9 nm corresponding to the absorption of the chlorine atom, that is, to operate in the region where the absorption of radiation by molecular oxygen present in the reactor was almost absent.

Calibration of the Absolute Sensitivity of the System to Chlorine Atoms

To calibrate the system, it was necessary to produce a known concentration of chlorine atoms in the reactor. In this case, the amount of molecular chlorine should be very low because its presence causes the appearance of a spurious signal. Ethane was chosen as a titration agent for two reasons. First, C_2H_6 rapidly reacts with chlorine atoms:

$$Cl + C_2H_6 \xrightarrow{k_3} HCl + C_2H_5. \qquad (III)$$
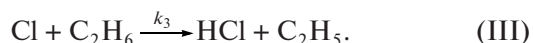
At 298 K, the rate constant of the gas-phase reaction is $k_3 = 5.7 \times 10^{-11}$ cm^3/s [17]. Second, ethane slowly reacts with hydrogen atoms. The rate constant of this reaction is lower than 1.1×10^{-16} cm^3/s [18]. Hydrogen-containing compounds were present in small amounts as impurities in helium, which was used as a diluent in the resonance lamp and in a discharge for generating chlorine atoms. Because of the high absorption cross section of radiation with a wavelength of 121.6 nm in the absence of molecular chlorine, H atoms gave a detectable resonance fluorescence signal. However, this signal disappeared in the presence of molecular chlorine because hydrogen atoms rapidly react with Cl_2.

By adding C_2H_6 to the reaction mixture, we could determine whether hydrogen atoms were present in the test system. If the signal intensity observed in a discharge in the absence of molecular chlorine was independent of the concentration of C_2H_6, the signal was due to hydrogen atoms. However, if molecular chlorine was present in the discharge zone, the signal intensity decreased to zero upon the addition of C_2H_6.

Titration was performed by introducing small fixed flows of C_2H_6 into the flow of oxygen through a capillary. The flow rate of ethane was measured based on a pressure drop in a calibrated reservoir, which contained C_2H_6 at a pressure of 700 Torr, arranged at the capillary inlet. Ethane was added to the flow of chlorine atoms until the resonance fluorescence signal intensity of Cl atoms decreased to zero. The titration of chlorine atoms with ethane was described in more detail elsewhere [19].

Generation and Titration of Oxygen Atoms

Oxygen atoms were generated by passing molecular oxygen diluted with helium (4% O_2) through a microwave discharge. The concentration of atomic oxygen was determined using a method described in the monograph [14].

If a steady-state concentration of oxygen atoms was reached in the reaction vessel and nitrogen dioxide was supplied to this vessel, bright green fluorescence (which can be clearly seen in a slightly darkened room) initially appeared due to the formation of the electronically excited NO_2^* molecule:

$$O + NO_2 \longrightarrow NO + O_2, \qquad (IV)$$

$$NO + O + M \longrightarrow NO_2^*. \qquad (V)$$

As soon as the concentrations of NO_2 and O became equal, the green fluorescence instantaneously disappeared. The concentration of NO_2 was determined from the NO_2 pressure drop in a calibrated volume.
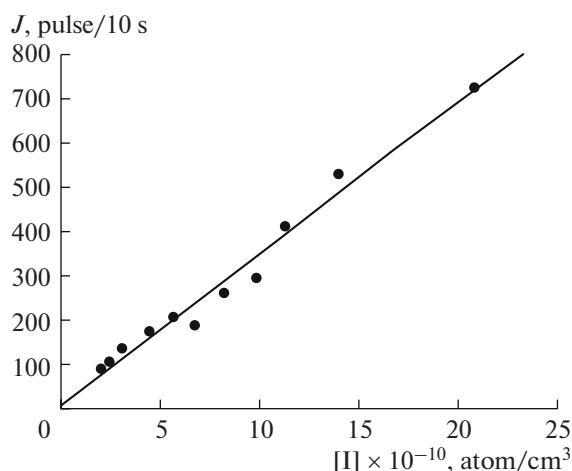
J, pulse/10 s

Fig. 2. Dependence of the number of resonance fluorescence pulses in 10 s on the concentration of iodine atoms (calibration straight line) obtained before the onset of experiments on the measurement of the rate constant of reaction (I).

$\ln J$

Fig. 3. Dependence of ln J on τ obtained before the onset of experiments on the measurement of the rate constant of reaction (I).

RESULTS AND DISCUSSION

Rate Constant of the Reaction of Oxygen Atoms with Iodomethane

The iodine atoms formed in reaction (I) were detected using resonance fluorescence. Oxygen atoms were generated by the action of a microwave discharge on a mixture of oxygen with helium (1 : 25). Their concentration was 8.5×10^{14} cm^{-3}, and the reaction time was $\tau = 4 \times 10^{-2}$ s.

The change in the concentration of iodine atoms in the course of reaction (I) is described by the rate equation

$$d[I]/dt = k_1 [CH_3I][O] - k_h [I], \qquad (1)$$

where k_1 is the rate constant of reaction (I), and k_h is the rate constant of heterogeneous decay of I atoms.

In all of the experiments, the reaction time and the concentration of oxygen atoms remained unchanged; only the concentration of iodomethane, which was lower than the concentration of oxygen atoms by approximately one order of magnitude, changed.

Under steady state conditions,

$$[I] = k_1[CH_3I][O]/k_h . \qquad (2)$$

To determine the concentration of iodine atoms from the intensities of resonance fluorescence signals, corresponding calibration was performed in accordance with the above procedure immediately before measurements. Figure 2 shows the dependence of the number of pulses J (resonance fluorescence signal intensity) on the concentration of iodine atoms. From this calibration curve, it follows that a pulse in 10 s corresponds to the concentration $[I] = 3.1 \times 10^8$ cm^{-3}.

To find the numerical value of the constant k_1, the constant of the heterogeneous decay of iodine atoms k_h should be initially found. For this purpose, we measured the dependence of the resonance fluorescence
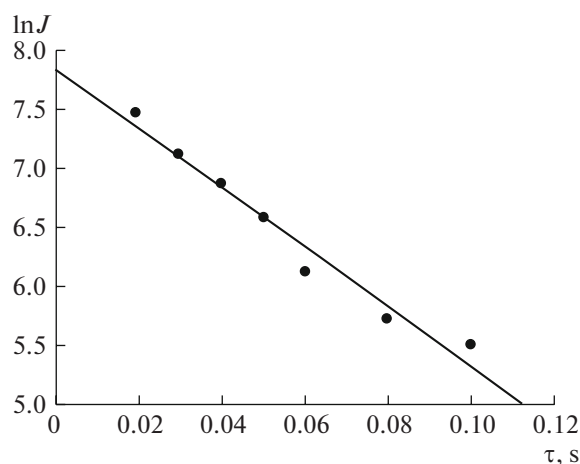
signal intensity of iodine atoms on the distance L between the point of the inlet of atomic iodine into the reactor and the detection zone of these atoms. Ignoring axial diffusion and a radial distribution of the concentration of iodine atoms, we can use the equation

$$[I] = [I]_0 \exp(-k_h\tau), \qquad (3)$$

where [I] and $[I]_0$ are the current and initial concentrations of I atoms, respectively. Hence,

$$k_h = -\frac{1}{\tau}\ln[I]/[I]_0, \qquad (4)$$

where $\tau = L/v$ is the time it takes for atoms to travel the distance L at the average weight linear velocity v.

Figure 3 shows the dependence of ln $\ln[I]/[I]_0$ on τ (the ratio $[I]/[I]_0$ is expressed as J). The value of k_h found from this dependence is 25 s^{-1}.

Figure 4 shows the dependence of the resonance fluorescence signal intensity of iodine atoms on the concentration of iodomethane. Using the calibration curve, we can replace [I] in Eq. (2) by J (the number of pulses per second) and obtain the value of $k_1 = (2.4 \pm 0.5) \times 10^{-15}$ cm^3/s.

Rate Constant of the Reaction of Oxygen Atoms with Chlorine

The concentration of molecular chlorine was varied within the range from 10^{10} to 10^{13} cm^{-3}. Oxygen atoms were obtained by the action of a microwave discharge on a flow of helium containing a few percent of molecular oxygen. The pressure of helium was varied within the range of 1−10 Torr. The concentration of oxygen atoms, which was measured using a procedure proposed in [14], was higher by at least one order of magnitude than the concentration of molecular chlo-
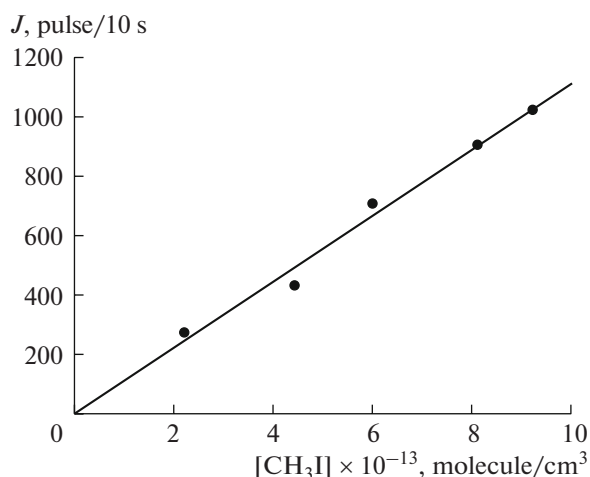
Fig. 4. Dependence of the number of resonance fluorescence pulses in 10 s on the concentration of iodomethane obtained in the study of reaction (I).
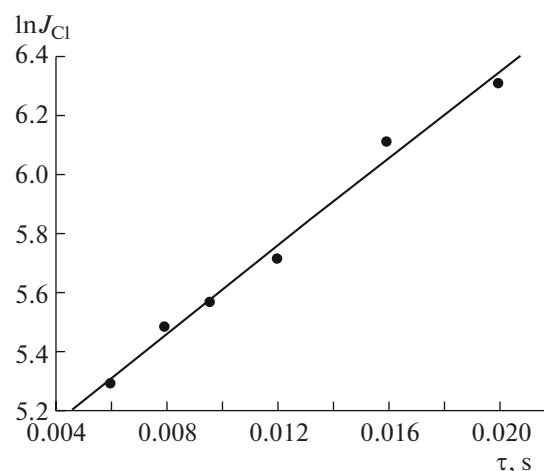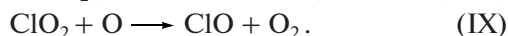

Fig. 5. Dependence of $\ln J_{Cl}$ on τ obtained in the study of reaction (II).

rine. In the reactor, reaction (II) and the following reaction occurred:

$$ClO + O \longrightarrow O_2 + Cl. \tag{VI}$$

The rate constants of these reactions are $k_2 = 7.2 \times 10^{-14}$ [9] and $k_6 = 3.8 \times 10^{-11}$ cm^3/s, respectively [20].

Thus, molecular chlorine was converted into atomic chlorine (the characteristic reaction time is $\sim 10^{-2}$ s). In addition, the following reactions occurred:

$$Cl + O_2 + M \longrightarrow ClO_2 + M, \tag{VII}$$
$$Cl \longrightarrow Cl_2 \text{ (at the reactor wall)}, \tag{VIII}$$
$$ClO_2 + O \longrightarrow ClO + O_2. \tag{IX}$$

The dependence of the concentration of chlorine atoms on the reaction time can be found by solving the following set of differential equations:

$$\partial[Cl]/\partial t = k_2[Cl_2][O] + k_9[ClO_2][O] + k_6[ClO][O]$$
$$- k_7[Cl][O_2][M] - k_8[Cl],$$
$$\partial[ClO]/\partial t = k_2[Cl_2][O] - k_6[ClO][O]$$
$$- k_9[ClO_2][O],$$
$$\partial[Cl_2]/\partial t = -k_2[Cl_2][O] + 1/2k_8[Cl],$$
$$\partial[ClO_2]/\partial t = k_7[Cl][O_2][M] - k_9[ClO_2][O].$$

After reaching quasi-steady-state conditions, the major portion of chlorine continued to occur as atoms, and the quasi-steady-state concentrations of ClO and ClO$_2$ are determined by the relationships

$$[Cl_2]_{st} = [Cl]_{st}k_8/2k_2[O] \leq 5\% [Cl]_{st}, \tag{5}$$
$$[ClO]_{st} = k_2[Cl_2]_{st}/k_6[O] \ll 1\% [Cl]_{st}, \tag{6}$$
$$[ClO_2]_{st} = k_7[Cl]_{st}[O_2][M]/k_9[O] < 1\% [Cl]_{st}. \tag{7}$$

Thus, with a large excess of oxygen atoms with respect to molecular chlorine, the steady-state concentration of chlorine atoms is as high as 90% of the doubled initial concentration of Cl$_2$. The time taken to reach a steady state depends on the characteristic time of reaction (I):

$$[Cl] \approx 2[Cl_2]_0(1 - e^{-k_2[O]\tau}), \tag{8}$$

where $[Cl_2]_0$ is the initial concentration of molecular chlorine introduced into the reactor, [O] is the current concentration of oxygen atoms in the reactor, and τ is the time of contact between the reactants. After finding the logarithm, we obtain the expression

$$\ln [Cl] \approx \text{const} + k_2[O]\tau. \tag{9}$$

Taking into account that $[Cl] \sim J_{Cl}$, where J_{Cl} is the resonance fluorescence signal intensity of chlorine atoms, we obtain the expression

$$\ln J_{Cl} \approx \text{const} + k_2[O]\tau. \tag{10}$$

Figure 5 shows the dependence of $\ln J_{Cl}$ on τ at an oxygen atom concentration of 3.8×10^{15} cm^{-3} in the reactor. The rate constant of reaction (II) can be found from the slope: $k_2 = (6.9 \pm 0.9) \times 10^{-14}$ cm^3/s. This value is consistent with the results obtained by Niki and Weinstock [9].

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