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Measurements of the Apparent Rate Constant for the Reaction of Iodine Monoxide with Chlorine Monoxide To Form Iodine Atoms

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Abstract—An apparatus for measuring the resonance fluorescence signals of iodine and chlorine atoms is constructed to study iodine monoxide reaction with chlorine monoxide. A technique using the reaction of chlorine atoms with C_2H_6 is developed to calibrate the sensitivity of the apparatus to chlorine atoms. The apparent rate constants for the reaction between $IO^\bullet$ and $ClO^\bullet$ radicals producing iodine atoms was measured at 295 K $k_{app} = (2.62 \pm 0.57) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

INTRODUCTION

Until recently, it was generally accepted that iodine-containing compounds, which are a source of the active iodine in the atmosphere, decomposed in the lower troposphere, that is, at altitudes of kilometers, because the time of their travel to the stratosphere seemed to be too long as compared to the time of their photochemical and chemical conversion. However, several authors have shown that fast convective fluxes at low latitudes could transport compounds to the upper troposphere and even to the lower stratosphere just for few hours [1, 2]. This fact has led to the reconsidering of the role of active iodine in the stratospheric chemistry and ozone depletion.

Natural powerful sources of iodine-containing compounds are, for example, phytoplankton and algae emitting methyl iodide [3, 4]. Data on the emission of chloroiodomethane and other biogenic hydrocarbons are also available [5, 6].

The lifetime of methyl iodide in the lower troposphere in the tropics is a few days [7], and the compound is poorly soluble in water. Therefore, if the hypothesis on fast tropical convection is correct, methyl iodide, as well as other iodinated hydrocarbons, can reach the tropopause and even the stratosphere.

The ocean is the main source of iodinated hydrocarbons in the atmosphere. In spite of wide use of CH_3I in fire extinguishing, this anthropogenic source adds only a few percents. However, widely used biomass combustion can substantially increase the content of iodine in the stratosphere. It should be noted that the amount of iodine in the biomass is equal to or probably higher than the amount of bromine and chlorine [8]. Biomass is burnt mostly in tropical areas where powerful convective currents exist. According to calculations [9], even a few volume parts of iodine per 10^{-13} can essentially affect the amount of ozone in the atmosphere. The calculations used a rate constant of about 10^{-10} cm^3 molecule^{-1} s^{-1} for the reaction of $IO^\bullet$ with $ClO^\bullet$.

Recent measurements led to a five times lower value [10, 11] and cast doubt on the result of [9].

This paper reports on the study of the reaction between iodine and chlorine monoxides using the kinetic flow technique with the registration of a reaction product, namely iodine atoms.

EXPERIMENTAL

We built an apparatus for measuring the resonance fluorescence signals of atomic iodine and chlorine to study the reaction of iodine monoxide with chlorine monoxide. The instrument contained a reactor, a source of iodine and chlorine atoms, a system for the registration of the atoms, and a system for the admittance of gases into the reactor.

Reactor. Figure 1 shows the scheme of the quartz cylindrical reactor with an inner diameter of 1.7 cm. The inner surface of the reactor was covered with a Teflon-like compound F32-L to reduce the heterogeneous decay of atoms and radicals. The reactor pressure was measured with a MACE-3M pressure gauge with an accuracy of 0.05 torr. Oxygen, ozone, helium, and ethane were introduced into the reactor through side holes. A source of iodine atoms was sealed in the reactor. The inlet of iodine atoms was positioned 8.5 cm from the registration zone. It was possible to introduce chlorine atoms at any point along the reactor axis through a movable nozzle. The nozzle was built of a quartz tube with an outer diameter of 6 mm and the wall depth of 1 mm. The inner surface of the tube was covered with hydrocarbon grease to reduce the heterogeneous decay of chlorine atoms. A collapsible Teflon

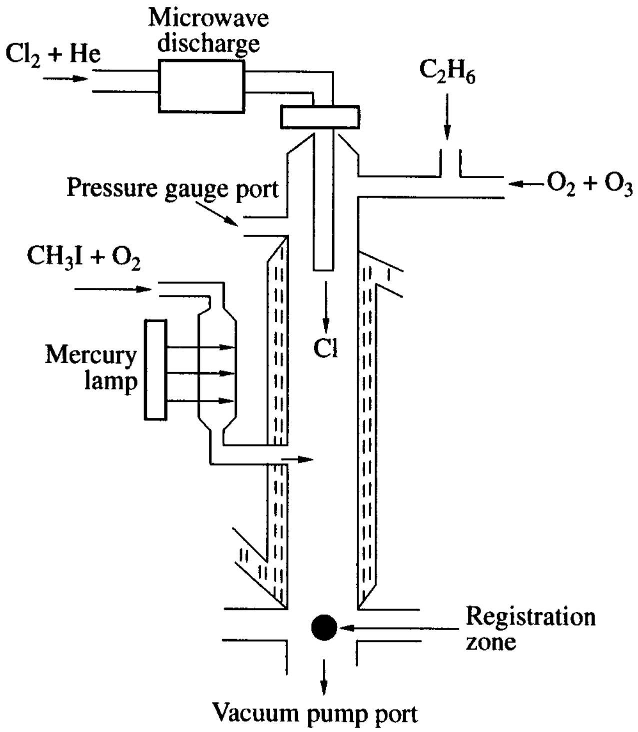

Fig. 1. Schematic of the reactor.

connection enabled us to move the nozzle without depressurizing the reactor.

Source of atomic iodine. The photolysis of a CH_3I mixture dilute with oxygen (0.1–0.5% CH_3I) generated iodine atoms. A quartz tube (with an inner diameter of 1 cm) covered with orthophosphoric acid to reduce the heterogeneous decay of iodine atoms was used as a built-in source. A low-pressure 8-W mercury lamp was set up parallel to the tube. Photolysis at 253.7 nm produced iodine atoms and $CH_3^{\bullet}$ radicals as well, which reacted with oxygen and formed unreactive $CH_3O_2^{\bullet}$ radicals. The processes in the source of iodine atoms were described in detail elsewhere [10].

System for the registration of iodine atoms. The resonance fluorescence technique with photon counting [12] was used to detect iodine atoms. A flow lamp was activated by a 254-MHz discharge. The lamp worked on a mixture of helium and molecular iodine (1×10^{17} and 1×10^{13} molecule/cm^3, respectively); the emission wavelength was 178 nm. We constructed a photoionization counter working on a mixture of argon, nitrogen dioxide, and diethylferrocene to detect the emission. The detector had no response to sunlight and could be used without darkening the reactor. The resonance lamp and the counter were positioned at a right angle to each other and in the plane perpendicular to the reactor axis. 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 of ~1×10^8 atom/cm^3. The typical concentration of iodine atoms in the experiments was ~3×10^{10} atom/cm^3. We used the following procedure to calibrate the absolute sensitivity of the registration system. The reaction of molecular iodine with excess oxygen atoms produced a known amount of atomic iodine according to the following reactions:

$$\text{(a)}\ O + I_2 \longrightarrow IO^{\bullet} + I,$$

$$k_a = 1.38 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ [13];$$

$$\text{(b)}\ O + IO^{\bullet} \longrightarrow I + O_2,$$

$$k_b = 5 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ [14];$$

$$\text{(c)}\ I + \text{wall} \longrightarrow 1/2 I_2,\ k_c < 10\ \text{s}^{-1}.$$

Oxygen atoms were generated in a microwave discharge in 4% O_2 + He mixture. The concentration of oxygen atoms was measured by chemiluminescent titration with NO_2 [15]. The concentration (~10^{14} atom/cm^3) was three orders of magnitude higher than that of iodine atoms. The steady-state concentrations of molecular iodine and iodine monoxide were much lower than 1% of the iodine atom concentration.

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

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

The concentration of oxygen atoms was three orders of magnitude higher than [I]. Therefore, heterogeneous decay was the major pathway of oxygen atom consumption. Thus, the source of iodine atoms was capable of producing a known amount of atoms and transporting them to a distance controlled by the efficiency of the atomic oxygen heterogeneous decay. The concentration of atomic iodine was virtually invariable.

Source of chlorine atoms. We generated chlorine atoms by flowing a dilute Cl_2/He mixture through a 254-MHz discharge with a power of 2.5 W. The surface of the reactor in the discharge zone was treated with orthophosphoric acid. The downstream part of the nozzle was coated with hydrocarbon grease. The nozzle had two right-angle bends between the discharge and the reactor to prevent the penetration of UV radiation into the reactor and the photon counter.

System for the registration of chlorine atoms. We used the resonance-fluorescence technique to detect chlorine atoms. The source of the resonance emission consisted of a flow lamp working on 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 self-made photoionization counter was used to detect the emission. The counter was filled with a mixture of argon and nitrogen dioxide. The operating wavelength of the counter was shorter than 133.8 nm. MgF_2 windows of the lamp and the counter enabled us to use the 119-nm chlorine line, that is, to work in the spectral range free from the absorption of molecular oxygen, which was present in the reactor. The signal from the counter was sent to the computer for accumulation and further analysis. At [Cl] = 1×10^{10} atom/cm^3, we had the signal/noise ratio equal to 2. Titration with C_2H_6 was used to calibrate the sensitivity of the system to chlorine atoms.

Titration of Cl atoms. We chose C_2H_6 as a titrating agent because of the following reasons. First, C_2H_6 rapidly reacts with chlorine atoms:

$$Cl + C_2H_6 \longrightarrow HCl + C_2H_5^{\bullet}.$$

The gas-phase rate constant of this reaction is $k = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [16]. Second, the reaction of C_2H_6 with hydrogen atoms is slow: the rate constant for the reaction is lower than 1.1×10^{-16} cm^3 molecule^{-1} s^{-1} [17]. Hydrogen-containing compounds were present in small amounts in helium used in the resonance lamp and in the discharge for dilution. Because hydrogen atoms have a high absorption cross-section at 121.6 nm, they have a considerable resonance fluorescence signal in the absence of molecular chlorine. However, if molecular chlorine was present in the discharge, hydrogen atoms reacted with chlorine rapidly and the signal disappeared. The photon counter was unable to distinguish the signals of atomic chlorine (119 nm) and atomic hydrogen (121.6 nm). By adding C_2H_6, we determined whether hydrogen atoms were present in the system. If no molecular chlorine was present in the discharge and the observed signal was independent of the C_2H_6 concentration, it belonged to hydrogen atoms. If upon the addition of C_2H_6, the signal went down to zero, then it belonged to atomic chlorine.

Figure 2 illustrates the titration procedure. A mixture of helium and molecular and atomic chlorine entered the oxygen flow through the nozzle. The distance between the nozzle and the registration zone was 21.5 cm. The additional oxygen flow passed through the source of iodine atoms and entered at 8.5 cm from the registration zone. Gas flows corresponded to those used in further measurements of the rate constant for the reaction between iodine and chlorine monoxides. We considered only the processes after iodine atoms entered the reactor, that is, in the part of the reactor where the final values of the gas flows and stream velocities were set constant.

We should also consider the difference between the flows and the stream velocities in the two parts of the reactor. We denote the stream velocity between the nozzle and the inlet of iodine atoms (zone *I*) as v_1, and the stream velocity between the latter and the registration point (zone *II*) as v_2.

Titration was performed by the addition of small calibrated flows of C_2H_6 into the oxygen flow through a capillary. The C_2H_6 flow was found from the pressure drop in a calibrated volume positioned upstream from the capillary. The volume contained C_2H_6 at 700 torr. To calculate other flows, we assumed that the flow was proportional to the square of a pressure decrease at the capillary entrance.

We used titration to measure rather high concentrations of chlorine atoms (1×10^{13} atom/cm^3). Ethane was added to the flow of chlorine atoms until the signal of the resonance fluorescence went down to zero. Note that at this moment, the C_2H_6 concentration was somewhat higher than that of atomic chlorine. When these two concentrations were equal, we observed a residual signal. The signal slowly decreased in inverse proportion to the squared time. At a chlorine atom concentration of $>1 \times 10^{14}$ atom/cm^3, the effect was negligible. At concentrations of 1×10^{12}–1×10^{13} atom/cm^3, numerical modeling taking into account the difference in the stream velocities and concentrations in the two parts of the reactor was necessary. The profiles of atomic chlorine and C_2H_6 concentrations along the reactor axis were calculated using some invariable initial concentrations of chlorine atoms $[Cl]_0$ and various initial concentrations of C_2H_6. Figure 3 shows calculated concentrations of chlorine atoms versus time (t) for different titration conditions. The initial concentrations $[Cl]_0$ and $[C_2H_6]_0$ in the figure caption are the concentrations in zone *II* in the reactor and the registration zone. The concentrations are higher in zone *I*. Line *1* in Fig. 3 shows the level of the chlorine atom concentration in the absence of C_2H_6. The steps result from the additional dilution with oxygen flowing through the source of iodine atoms.

Curve *4* describes the case when the initial concentrations of chlorine and ethane are equal. A considerable amount of unreacted Cl atoms are present in the registration zone in this case. We calculated the dependence of the chlorine atom concentration in the registration zone on the initial concentration of C_2H_6 using these profiles.

The resonance fluorescence signal S is related to the concentration of chlorine atoms by the expression

$$S = A[Cl]\exp(-\delta L[Cl]).$$

Coefficient A accounts for the sensitivity of the system to Cl atoms; the exponential term describes the

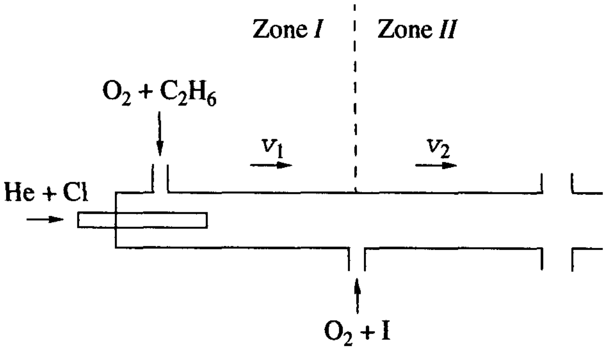

Fig. 2. Experimental setup for the measurement of chlorine atom concentration by titration with ethane.

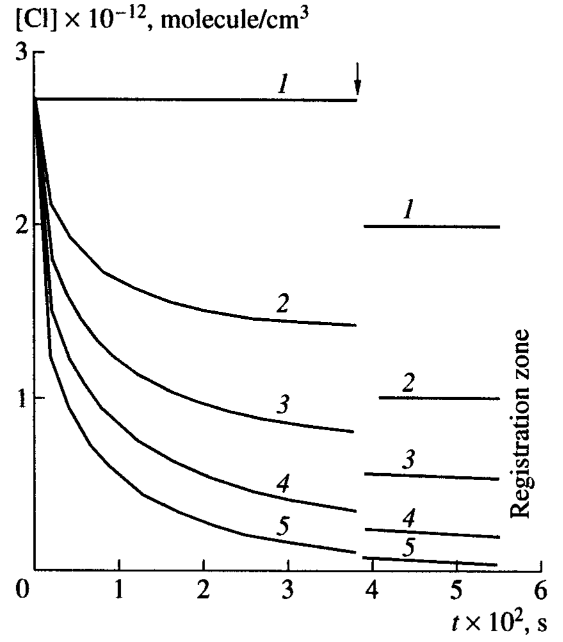

Fig. 3. Calculated concentrations of chlorine atoms versus time at $[Cl]_0 = 2 \times 10^{12}$ molecule/cm^3 and initial C_2H_6 concentrations of (*1*) 0, (2) 1×10^{12}, (*3*) 1.5×10^{12}, (*4*) 2×10^{12}, and (*5*) 2.5×10^{12} molecule/cm^3. The arrow marks the moment when O_2 + I mixture enters.

effect of the self-absorption of the emission by chlorine atoms in the registration zone. The 119-nm band of chlorine atom is a doublet consisting of 118.875 and 118.877-nm bands. The recommended value of δ for the unresolved doublet is 2.47×10^{-13} cm^2. L is the length of the section where Cl atoms are present. The metal collimators of the resonance lamp and of the photon counter are the boundaries of this section, $L = 1.8$ cm.

Figure 4 shows the Cl atom resonance fluorescence signal (S) as a function of the C_2H_6 concentration. Our measurements revealed that the Cl atom concentration is proportional to the flow of molecular Cl_2 through the reactor. The proportionality coefficient depends on the conditions in the discharge; so it was necessary to calibrate the system in each run.

System for gas supply. Molecular oxygen from gas bottles flowed into the reactor through a system that enabled us to maintain a constant flow with an accuracy of 2% for up to several hours. A dark glass cylinder contained liquid CH_3I; during the experiments, we kept the cylinder in melting ice. CH_3I vapor was added through a fine adjustment valve to oxygen flowing through the source of iodine atoms. The flow rate was found from the pressure drop in a calibrated volume. Cl_2 from glass cylinders was added through a capillary to helium flowing through the resonance lamp and the source of Cl atoms. We varied the chlorine pressure upstream the capillary to get various flows of molecular chlorine.

C_2H_6 from a glass cylinder was introduced directly into the reactor through a capillary.

To produce ozone, oxygen from a gas tank was introduced into a flowmeter. The downstream pressure of the flowmeter was 1 atm and did not change. Then, a flow of oxygen purified in a low temperature trap and cooled with dry ice was directed to an OZON-2 ozonizer (constructed at the Institute of Chemical Physics) through a control valve. Then the oxygen/ozone mixture passed through a glass spectrometer cell (10 cm in length) to measure the ozone concentration from a change in absorbance at 253.7 nm. The cell had quartz windows and a glass–Teflon adjustment valve positioned downstream of the cell. The valve enabled us to vary the pressure in the cell from 10 to100 torr without changing the mass flow. The membrane MACE-3M pressure gauge measured the pressure in the cell with an accuracy of 1%. The pressure adjustment allowed us to use a convenient absorbance range. Then, the mixture of O_2 and O_3 was introduced into the reactor. The amount of ozone admitted to the reactor was calculated according to the equation

$$Q_{O_3} = Q_{O_2}\frac{2.3D_{253.7}}{\sigma l P_{\text{cell}}(273/T)3.5 \times 10^{16}} \text{ cm}^3 \text{ torr s}^{-1},$$

where Q_{O_2} and Q_{O_3} are the total flow and the flow of ozone into the reactor, respectively, cm^3 torr s^{-1}; $D_{253.7}$ is absorbance; $\sigma = 1.15 \times 10^{-17}$ cm^2 is the absorption cross-section of ozone at $\lambda = 253.7$ nm; l is the length of the optical cell (10 cm); P_{cell} is pressure in the cell, torr; and T is temperature in the cell.

The flow of O_2 and O_3 contacted glass and Teflon surfaces only when it traveled from the cell to the reactor. Ozone does not decompose catalytically when it contacts these materials. We controlled the ozone concentration in the reactor by varying the voltage on the ozonizer under constant flow conditions.

Along with ozone, excited oxygen molecules in $^1\Delta_g$ and $^1\Sigma_g^+$ could be produced in the ozonizer. However, the molecules would disappear, completely reacting with ozone:

$$O_2(^1\Delta_g) + O_3 \longrightarrow 2O_2 + O,$$

$$k = 1.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ [18]};$$

$$O_2(^1\Sigma_g^+) + O_3 \longrightarrow 2O_2 + O,$$

$$k = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ [19]}.$$

About 1 s is needed for these reactions to occur. This time was equal to that necessary for the gas to pass through the communication lines at 760 torr before entering the flow-controlling lamp. The use of 99.98% purity or technical purity grade oxygen did not affect the results. CH_3I and C_2H_6 were chemically pure. Cl_2 was synthesized in the reaction of HCl oxidation with potassium permanganate and purified by low-temperature distillation.

PROCEDURE

The procedure used to study the $\mathrm{IO}^{\bullet} + \mathrm{ClO}^{\bullet}$ reaction was the same as that employed earlier for the reaction of $\mathrm{IO}^{\bullet}$ with NO [20]. This procedure is based on the process including propagation

$$\mathrm{I} + \mathrm{O_3} \xrightarrow{k_1} \mathrm{IO}^{\bullet} + \mathrm{O_2} \qquad \text{(I)}$$

and the reaction to be studied

$$\mathrm{IO}^{\bullet} + \mathrm{ClO} \xrightarrow{k_2} \mathrm{I} + \text{products}. \qquad \text{(II)}$$

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 contact time is longer than the characteristic time of reaction (I). The steady-state concentration can be found from the expression

$$k_1[\mathrm{I}]_{ss}[\mathrm{O_3}] = k_2[\mathrm{IO}^{\bullet}]_{ss}[\mathrm{ClO}^{\bullet}], \qquad (1)$$

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

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

where $[\mathrm{I}]_0$ is the initial concentration of iodine atoms in the reactor. Equations (1) and (2) give

$$\frac{[\mathrm{I}]_0}{[\mathrm{I}]} = \frac{k_1[\mathrm{O_3}]}{k_2[\mathrm{ClO}^{\bullet}]} + 1. \qquad (3)$$

As seen from (3), the $[\mathrm{I}]_0/[\mathrm{I}]$ ratio depends linearly on the $[\mathrm{O_3}]/[\mathrm{ClO}^{\bullet}]$ ratio, and the line intercepts the y-axis at $[\mathrm{I}]_0/[\mathrm{I}] = 1$. Using the known value of the rate constant for the reaction of I with ozone (k_1) in a wide temperature range [13], we find k_1/k_2 and calculate k_2.

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

Figure 5 shows the schematic of the measurement procedure.

Measurement of the initial resonance fluorescence signal of iodine atoms in the reactor. Iodine atoms were produced by the photodissociation of $\mathrm{CH_3I}$ in the iodine atom source and admitted into the reactor. The flows of $\mathrm{O_2}$ and He through the source were equal to those during the experiment itself. The pressure in the reactor was 2.5 torr, the linear flow rate was 450–500 cm/s. The concentration of iodine atoms was ~3×10^{10} molecule/cm^3 and virtually invariable along the reactor. We measured the rate constant for the heterogeneous decay of iodine atoms in special experiments and found it equal to $k \leq 1$ s^{-1}. The contact time was at most 2×10^{-2} s; thus, the concentration of iodine atoms in the registration zone was equal to the initial concentration within 2%. The initial resonance fluorescence signal of iodine atoms (J_0) was from 500 to 1000 counts per 10 s in different experiments. Figure 5a presents the schematic of the J_0 signal measurement.

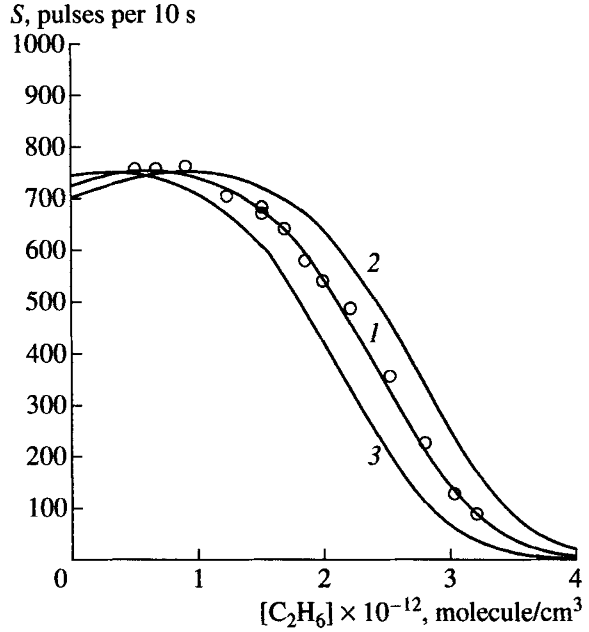

Fig. 4. The resonance fluorescence signal of chlorine atoms versus $\mathrm{C_2H_6}$ concentration. Symbols are experimental data; solid curves were calculated at $[\mathrm{Cl}]_0$ of (*1*) 2.9×10^{12}, (*2*) $(2.9 + 0.29) \times 10^{12}$, and (*3*) $(2.9 - 0.29) \times 10^{12}$ molecule/cm^3.

Measurement of the background signal. Upon measuring and recording the J_0 signal, we introduced more than 4×10^{14} molecule/cm^3 of ozone into the reactor without changing the parameters of the flow. As a result, fast reaction (I) occurred. The rate constant for reaction (I) is 1.1×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K 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 $\mathrm{IO}^{\bullet}$ radicals under the experimental conditions.

The background signal is largely associated with the light scattering on the molecules, which were present in the reactor, mainly on $\mathrm{CH_3I}$. Figure 5b shows the schematic of the measurement of background signal F.

Measurement of the steady-state resonance fluorescence signal of iodine atoms. When the initial signal disappeared, that is, almost all iodine atoms in the reactor transformed into $\mathrm{IO}^{\bullet}$ radicals, chlorine atoms were introduced into the reactor. The flow parameters were kept constant. Chlorine atoms transformed into $\mathrm{ClO}^{\bullet}$ radicals in the fast reaction

$$\mathrm{Cl} + \mathrm{O_3} \longrightarrow \mathrm{ClO}^{\bullet} + \mathrm{O_2}. \qquad \text{(III)}$$

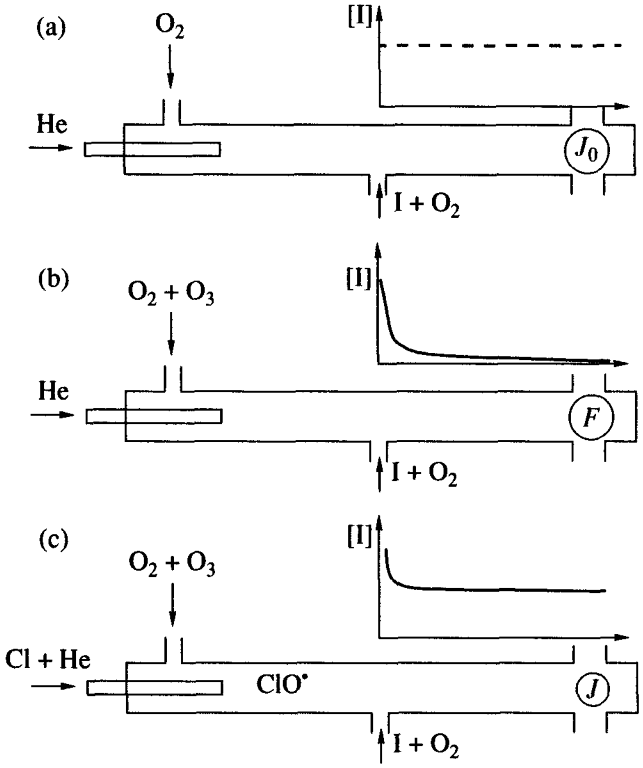

Fig. 5. Determination of the (a) initial resonance fluorescence signal of iodine atoms, (b) background signal, and (c) steady-state signal of iodine atom measurements.

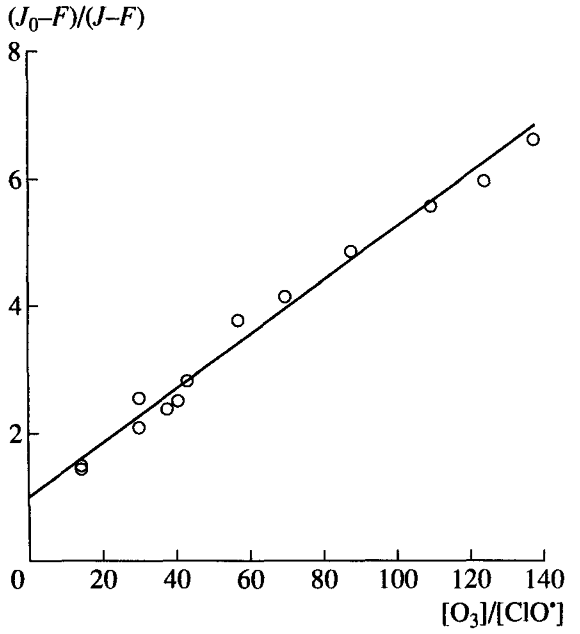

Fig. 6. Measured values of $(J_0-F)/(J-F)$ versus $[O_3]/[ClO^\bullet]$.

The rate constant for this reaction is 1.2×10^{-11} cm^3 molecule^{-1} s^{-1} at 295 K. Therefore, the $ClO^\bullet$ concentration was equal to the concentration of chlorine atoms. The latter changed from 1×10^{12} to 1×10^{13} molecule/cm^3. The measurement of the chlorine atom concentration is described above. The reaction (II) of $IO^\bullet$ and $ClO^\bullet$ radicals resulted in the formation of the steady-state concentration of iodine atoms. Figure 5c outlines the measurement of the steady-state resonance fluorescence signal of iodine atoms.

RESULTS AND DISCUSSION

As the initial concentration of iodine atoms in the reactor was proportional to the measured difference between signals $J_0 - F$ and the steady-state concentration was proportional to the difference $J - F$, equation (3) can be rearranged as

$$(J_0 - F)/(J - F) = (k_1[O_3]/k_2[ClO^\bullet]) + 1. \qquad (4)$$

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

Figure 6 shows the results of experiments performed at 295 K; the concentrations of chlorine atoms and $ClO^\bullet$ radicals were 2.1×10^{12} molecule/cm^3; the pressure in the reactor, the flow rate, and the ozone concentration were $P = 2.5$ torr, $v = 473$ cm/s, and 4×10^{14}–3×10^{15} molecule/cm^3, respectively. The linear dependence

$$Y = BX + A$$

with coefficients $A = 1$ and $B = 0.042$ fits the experimental points.

The slope of the line gives the value k_1/k_2. A number of measurements of k_1 are in good agreement. $k_1 = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 K [21]. The slope of the line in Fig. 6 gives the rate constant

$$k_2 = (2.62 \pm 0.57) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

This value is twice as high as the rate constant for the reaction of $IO^\bullet$ with $ClO^\bullet$ measured in [10] and 2.5 times as high as the similar value measured in [11].

Finding the reason for this discrepancy will be the subject of our further research.

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