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Formation of Iodine Atoms in the Heterogeneous Reaction between Chlorine and Iodomethane

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Abstract—The rate constant of the reaction between iodomethane and chlorine atoms at 323 K, measured by the resonance florescence method under jet stream conditions as the iodine atom yield, is $k_1^{\mathrm{I}} = (2.9 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. It is demonstrated experimentally that this reaction takes place mainly on the reactor wall.

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The natural source of iodomethane is ocean biomass, which produces ~1.5 million tons of CH_3I per year [1]. Chlorine atoms in the marine atmosphere result from so-called halogen activation. The essence of this phenomenon is that heterogeneous processes involving marine aerosol particles cause fairly rapid conversion of chlorine reservoir species (NaCl, HCl, $ClONO_2$) into the weakly bonded molecules Cl_2 and HOCl. It was demonstrated that NaCl aerosol particles can react with $ClNO_3$ and N_2O_5 to form Cl_2 and $ClNO_2$ molecules [2], which decompose under the action of UV radiation to yield chlorine atoms:

$$ClNO_3(g) + NaCl(s) \rightarrow Cl_2(g) + NaNO_3(s),$$

$$N_2O_5(g) + NaCl(s) \rightarrow ClNO_2(g) + NaNO_3(s).$$

Tropospheric ozone also can participate in heterogeneous processes to transfer active chlorine from NaCl aerosol to the gas phase. There has been a report indicating Cl_2 formation from NaCl aerosol in the presence of O_3 [3]:

$$2Cl^- + O_3 \xrightarrow{H_2O} Cl_2 + 2OH^- + O_2.$$

The similar gaseous Cl_2 formation process in the heterogeneous reaction between ozone and hydrogen chloride was investigated in [4].

The reaction between iodomethane and chlorine atoms has been the subject of a number of studies [5–8]. The smallest value of the rate constant of this reaction is 9×10^{-13} cm^3 molecule^{-1} s^{-1} at 295 K [5], and the largest one is 1.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 273 K [6]. In none of these works is the iodine atom reported to be a reaction product. However, it was noted that marine aerosols are often depleted of sodium chloride as compared to seawater, while the NaI content of these aerosols is sometimes higher than that of ocean water by a factor of 1000 or even 10000 [9]. This fact possibly indicates that there is a chemical mechanism leading to this replacement of the chlorine atom by iodine in marine salt aerosols.

For the first time, the hypothesis that iodine atoms result from the reaction of chlorine atoms with iodomethane,

$$Cl + CH_3I \xrightarrow{k_1} I + \text{products} \qquad (I)$$

was used by us in an iodine atom resonance fluorescence (RF)study of the reaction between the $IO^{\bullet}$ and $ClO^{\bullet}$ radicals [10]. In that study, a chain process was organized in the reactor, whose main steps the following reactions:

$$I + O_3 \xrightarrow{k_2} IO^{\bullet} + O_2, \qquad (II)$$

$$IO^{\bullet} + ClO^{\bullet} \xrightarrow{k_3} I + \text{products}. \qquad (III)$$

If reactions (II) and (III) are the only reactions occurring in the reactor, then, if the reactant contact time is longer than the characteristic time of reaction (II), a steady-state iodine atom concentration ($[I]_{st}$) will be established, which is given by the equation

$$k_2[O_3][I]_{st} = k_3[ClO][IO]_{st}, \qquad (1)$$

where $[IO]_{st}$ is the steady-state concentration of $IO^{\bullet}$ radicals. When there are no chain termination reactions,

$$[I]_{st} + [IO]_{st} = [I]_0, \qquad (2)$$

where $[I]_0$ is the initial iodine atom concentration in the reactor. By combining expressions (1) and (2), we obtain

$$\frac{[I]_0}{[I]_{st}} = \frac{k_2[O_3]}{k_3[ClO]} + 1. \qquad (3)$$

Figure 1 plots the ratio of the initial RF signal from the iodine atoms ($J_0 - F$), which is proportional to the initial iodine atom concentration (F is the background signal recorded in the absence of iodine atoms), to the

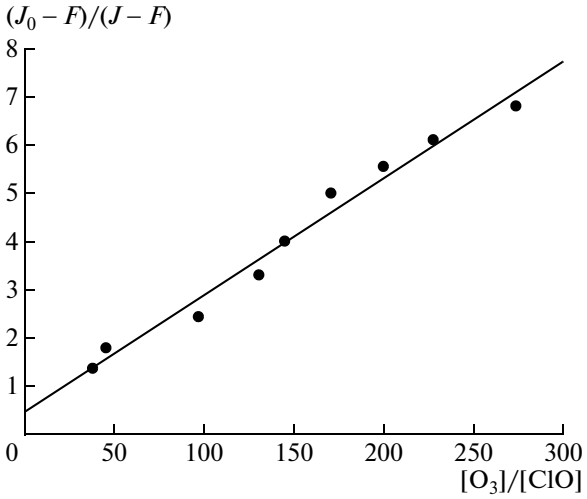

Fig. 1. Plot of $(J_0 - F)/(J - F)$ versus $[O_3]/[ClO]$ obtained at $T = (303 \pm 5)$ K, $P = 2.5$ Torr, $[ClO] = 1.4 \times 10^{12}$ molecule cm^{-3}, and ozone concentrations of 4.2×10^{13} to 3.9×10^{14} molecule cm^{-3}.

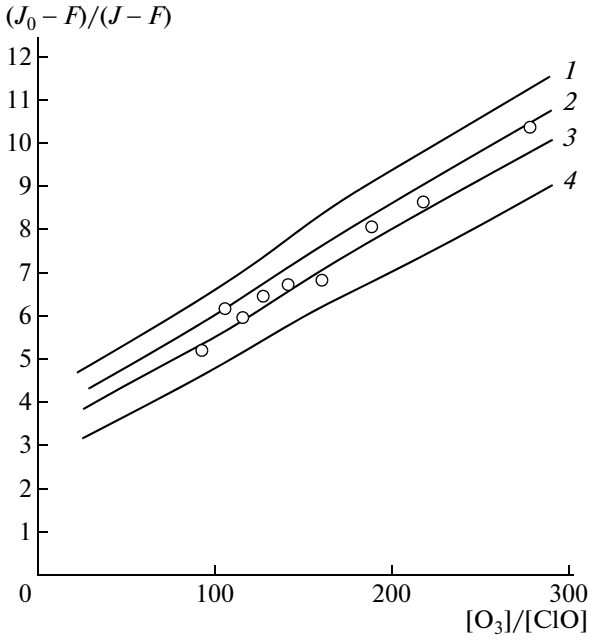

Fig. 2. Theoretical dependence of $(J_0 - F)/(J - F)$ on $[O_3]/[ClO]$ for various rate constants of reaction (I): $k_1 =$ (*1*) 0, (*2*) 2×10^{-12}, (*3*) 4×10^{-12}, and (*4*) 8×10^{-12} cm$^3 \times$ molecule^{-1} s^{-1}. The points represent experimental data obtained at a fixed ozone concentration of 4.1×10^{14} molecule cm^{-3} and [ClO] varied between 1.4×10^{12} and 4.2×10^{12} molecule cm^{-3}.

steady-state signal of the iodine atoms $(J - F)$ versus the $[O_3]/[ClO]$ ratio. At $[O_3]/[ClO] \to 0$, the straight line intersects the ordinate axis at some point below 1. Therefore, the steady-state signal from the iodine atoms exceeds the initial signal; that is, there is an extra source of iodine atoms in the system.

We assume that the chlorine atoms that were fed into the reactor for obtaining ClO$^\bullet$ reacted not only with ozone,

$$Cl + O_3 \xrightarrow{k_4} ClO^\bullet + O_2, \qquad \text{(IV)}$$

but also with iodomethane, which was used as the source of iodine atoms (reaction (I)).

At low ozone concentrations, reaction (I) dominated over reaction (IV) and there was an extra source of iodine atoms in the reactor.

We simulated the processes taking place in the reactor at various values of the rate constant of reaction (I). Figure 2 shows the results of this simulation and their comparison with experimental data obtained at an ozone concentration of 4.1×10^{14} molecule cm^{-3} and ClO$^\bullet$ concentrations between 1.4×10^{12} and 4.2×10^{12} molecule cm^{-3}. The best fit between the experimental data and theory is observed at rate constants of the reaction (k_1) in the $(2.0–4.0) \times 10^{-12}$ cm^3 molecule $^{-1}$ s^{-1} range.

Here, we report direct determination of the rate constant of reaction (I) by measuring the resonance fluorescence from the iodine atoms resulting from this reaction.

EXPERIMENTAL

Reactor Design and Introduction of Reactants

Experiments were carried out under jet stream conditions in the reactor shown Fig. 3. The reactor was a cylindrical quartz tube 1.7 cm in diameter, whose inner surface was lined with F-32L fluoroplastic in order to reduce the heterogeneous loss of atoms and radicals. Helium or oxygen as the diluent gas and ethane were fed into the reactor through side inlets. The reactant gas lines, except the CH_3I line, had flow regulators, which allowed a constant gas flow rate to be maintained with an accuracy of 2–3% for 10–15 h. The mass flow rates of the reactants and carrier gases were measured as the amount of gas flowing out of a calibrated volume per unit time. Gas pressure was monitored using a standard pressure gage. High-purity grade helium and pure-grade oxygen were used in all runs. The molecular chlorine line had no vacuum grease throughout its length and was made of glass. Shutoff valves, designed at the Institute of Chemical Physics, Russian Academy of Sciences, were made of Teflon. Molecular chlorine was synthesized by oxidizing HCl with potassium permanganate. The product was purified by low-temperature distillation and was stored in glass cylinders. In experiments, chlorine was introduced via a capillary into the He stream passing through a resonance lamp and through a source of Cl

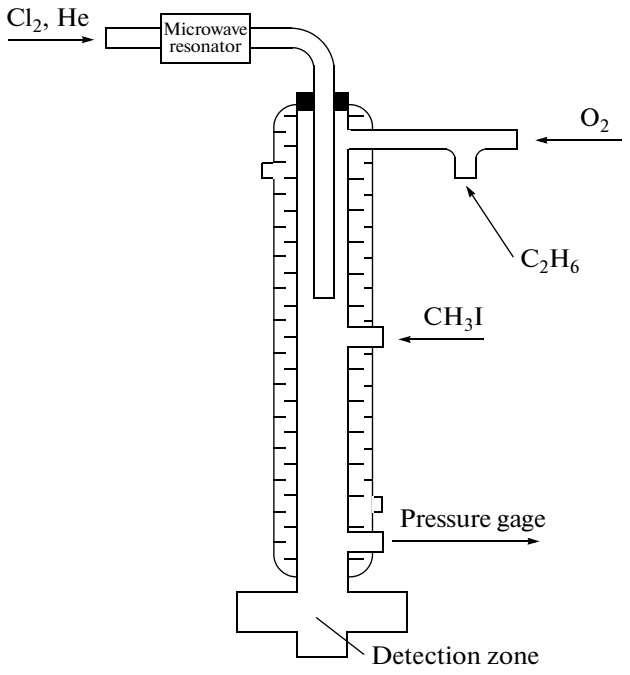

Fig. 3. Schematic of the reactor.

atoms. The molecular chlorine flow rate was controlled by varying the Cl_2 pressure at the inlet of the capillary.

Iodomethane was stored as a liquid in a glass cylinder protected from light in order to prevent its photodecomposition. During the run, this cylinder was immersed in melting ice. CH_3I vapor, mixed with helium or oxygen, was fed into the reactor through a metering valve. The flow rate was determined by measuring the pressure drop in a calibrated volume. CH_3I was reagent-grade. Reagent-grade ethane, which was used to calibrate 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

Iodine atoms were detected as their RF signal at 178.3 nm. The detection system consisted of an iodine resonance lamp, a photoionization counter sensitive in the 160–185 nm range for detection of photons reemitted by the iodine atoms, and a Ch3-63/1 frequency meter connected to a computer for signal recording and accumulation and subsequent data processing.

The iodine atom detection zone consisted of tubes ~10 mm in diameter and ~10 mm in length soldered crosswise into the reactor. The tubes ended with quartz sockets, in which the brass cones of a resonance lamp, photon counter, and Wood's horn were secured using a vacuum grease. The detection zone diameter was approximately 5 mm.

The flow-through resonance lamp operated at a wavelength of 178.3 nm, for which the resonance radiation absorption cross section of the iodine atom was 5×10^{-13} cm^2 [11]. The lamp was made of UF quartz with short-wavelength transmission cutoff at 160 nm. Vacuum sealing was achieved using an indium gasket. A He + molecular iodine mixture (~10000 : 1) was passed through the lamp. Discharges in the lamp were initiated with a Breid microwave resonator.

Reemitted quanta were detected with a photoionization counter. For each data point, 500 to 10^4 pulses were coadded. The counter was pumped with a diffusion pump to a residual pressure of 5×10^{-5} Torr and was then filled with a mixture of NO (10 Torr) and Ar (230 Torr). A drop of diethylferrocene was placed in the glass appendix of the counter to establish the equilibrium vapor pressure. The long-wavelength cutoff of the counter was determined by the ionization potential of diethylferrocene (6.3 eV [12]) and was ~185 nm. Thus, the photoionization counter served as a kind of monochromator as well, selecting the spectral range of 160–185 nm. Before measurements, the iodine atom sensitivity of the system was calibrated as described in our earlier work [13].

Calibrating the Sensitivity of the System to Chlorine Atoms

For calibrating the chlorine atom sensitivity of the system, it was necessary to produce a known concentration of chlorine atoms in the reactor. Chlorine atoms were generated by a 254-MHz discharge with a power of 2.5 W in a helium-diluted Cl_2 stream and were titrated with ethane. Ethane was used as the titrating agent for the reason that it reacts with chlorine at a high rate:

$$Cl + C_2H_6 \xrightarrow{k_5} HCl + C_2H_5^{\bullet}. \qquad (V)$$

The rate constant of reaction (V) at 298 K is $k_5 = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [14].

Chlorine atoms were titrated by introducing C_2H_6 at a known low flow rate through a capillary into the oxygen stream. The C_2H_6 flow rate was measured as the pressure drop in a calibrated vessel, which contained ethylene at a pressure of 700 Torr and was placed at the capillary inlet. The other flow rates were calculated under the assumption that the flow rate is proportional to the square of the pressure drop at the inlet of the capillary. Ethane was added to the chlorine atom stream until the RF signal from the chlorine atoms was zero. The titration of chlorine atoms is detailed in our earlier publication [15].

Determining the Rate Constant of the Reaction between CH_3I and Cl Atoms by Detection of I atoms

Under the assumption that chlorine atoms are lost on the wall of the reactor, we obtain the following

expression for the disappearance of chlorine atoms during reaction (I):

$$d[\mathrm{Cl}]/dt = -k_1[\mathrm{CH_3I}][\mathrm{Cl}] - k_{\mathrm{loss}}[\mathrm{Cl}], \quad (4)$$

where k_{loss} is the chlorine atom loss rate constant.

Expression (4) can be rearranged into

$$d[\mathrm{Cl}]/[\mathrm{Cl}] = -k_1[\mathrm{CH_3I}]dz/v_0 - k_{\mathrm{loss}}dz/v_0, \quad (5)$$

where z is the longitudinal coordinate of the reaction and v_0 is the velocity of the reactants.

The RF signal from iodine atoms (J) is directly proportional to the iodine atom concentration: $[\mathrm{I}] = \alpha J$. If reaction (I) is the only source of iodine atoms, the number of the resulting iodine atoms is equal to the number of reacted chlorine atoms:

$$[\mathrm{Cl}]_0 - [\mathrm{Cl}] = [\mathrm{I}], \quad (6)$$

where $[\mathrm{Cl}]_0$ is the initial concentration of chlorine atoms.

Hence,

$$[\mathrm{Cl}] = [\mathrm{Cl}]_0 - \alpha J, \quad (7)$$

and the maximum iodine yield and, accordingly, the maximum iodine atom RF signal are proportional to $[\mathrm{Cl}]_0$:

$$\alpha J_{\max} = [\mathrm{Cl}]_0. \quad (8)$$

Integrating expression (5) with expressions (6)–(8) taken into account, we arrive at

$$\ln(J_{\max}/J_{\max} - J) = k_1[\mathrm{CH_3I}]\tau + k_{\mathrm{loss}}\tau, \quad (9)$$

where τ is the reactant contact time, which is equal to z/v_0.

We measured the RF signal from iodine atoms at various iodomethane concentrations, a pressure of 2.1 Torr in the reactor, $T = 303$ K, and $[\mathrm{Cl}_0] = 3.1 \times 10^{11}$ molecule cm^{-3}, using helium as the diluent gas. A plot of $\ln(J_{\max}/(J_{\max} - J))$ versus the CH_3I concentration was constructed (Fig. 4), and the rate constant of reaction (I) was derived from the slope of the straight line: $k_1^{\mathrm{I}} = (2.9 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

This rate constant is larger than anyone hitherto reported for the reaction of chlorine atoms with iodomethane. We assumed that reaction (I) might take place on the reactor wall. To see whether the reaction occurs in the gas phase or on the reactor surface, we used the method suggested by Orkin et al. [16]. With this method, it is unnecessary to perform experiments at different ratios of the reactor surface area to the reactor volume or with walls coated with various substances. This method enables one to identify the heterogeneous processes whose rate depends on the concentrations of the initial reactants in the same way as the rate of the homogeneous reaction. It is in this case that the kinetic regularities derived from the jet stream experiment under conditions allowing one-dimensional description are the same for the homogeneous and heterogeneous reactions. The diffusion transfer processes (axial and radial diffusion) under experimental conditions such that the reactant diffusion times are longer than the reaction time lead to the fact that the rate constant determined under these conditions (k_{eff}) is smaller than the true rate constant (k). This effect is particularly strong when the measured rate constant pertains to a heterogeneous process.

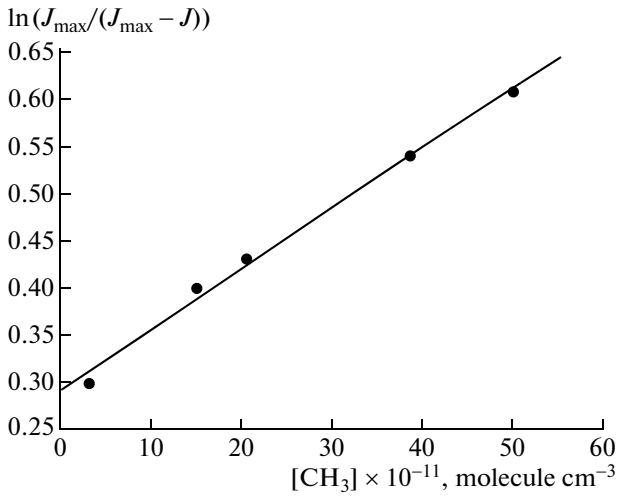

Fig. 4. $\ln(J_{\max}/(J_{\max} - J))$ versus the CH_3I concentration. $P = 2.1$ Torr, $T = 303$ K, and $[\mathrm{Cl}_0] = 3.1 \times 10^{11}$ molecule × cm^{-3}. The diluent gas is helium.

For a reaction similar to reaction (I), the concentration profile of the active reactant was obtained in the form of a convergent series [17]. It was demonstrated that, downstream of the concentration profile formation zone, the decline of the reactant R concentration along the reactor is describable in terms of a single exponentially decreasing function:

$$[\mathrm{R}(z)] \sim \exp(-(\lambda^2/V)(z/r_0)), \quad (10)$$

where $V = 2v_0r_0/D$, r_0 is the reactor radius, z is the coordinate along the path of the reaction, and λ is the smallest positive root of the transcendental equation

$$\frac{[1/2 - \lambda/4 + (k - \mu^2)/4\lambda]\Phi[3/2 - \lambda/4 + (k - \mu^2)/4\lambda; 2; \lambda]}{\Phi[1/2 - \lambda/4 + (k - \mu^2)/4\lambda; 1; \lambda]} = \frac{\lambda - (k_{\mathrm{het}}r_0)/D}{2D}. \quad (11)$$

Here, $\Phi[...]$ is Kummer's function [18], r is the radial coordinate of the reactor, D is the diffusion coefficient of active species, $\mu = \lambda^2 D/2v_{\mathrm{mean}}r_0$, $k = k_{\mathrm{hom}}r_0/D$, k_{hom} (s^{-1}) is the rate constant of the homogeneous reaction, and k_{het} (s^{-1}) is the rate constant of the heterogeneous reaction.

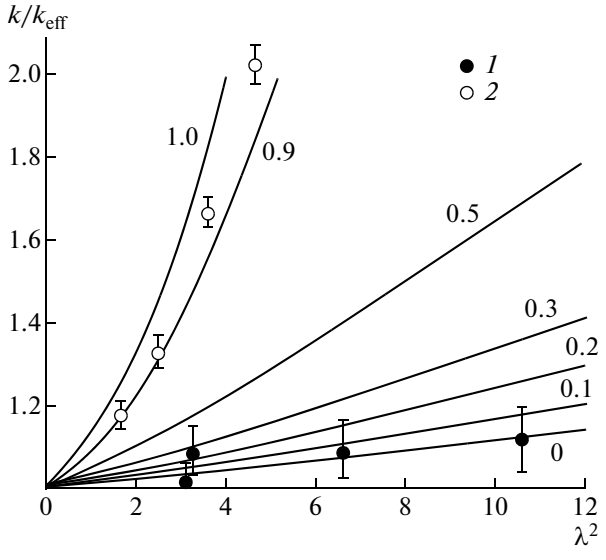

Fig. 5. Theoretical dependence of k/k_{eff} on λ^2 for various fractions of the heterogeneous component in the rate constant of the reaction; experimental data for the reactions of (*1*) iodine atoms with ozone and (*2*) chlorine atoms with iodomethane.

By comparing expressions (5) and (10) and taking into account that, in our system, $[R(z)] = [Cl(z)]$, it is possible to relate λ^2 to the characteristic lifetime of active species in the reactor:

$$\lambda^2 = 2\tau_{eff}^{-1} r_0^2 / D, \quad (12)$$

$$\tau_{eff}^{-1} = (-v_0 d\ln[R(z)]/dz). \quad (13)$$

Here, τ_{eff}^{-1} is determined experimentally.

Using an earlier reported program [16], we calculated k/k_{eff} as a function of λ^2 for the homogeneous and heterogeneous reactions of active species occurring simultaneously. Figure 5 shows the theoretical dependence of k/k_{eff} on λ^2 for the purely homogeneous reaction (lower curve), for the purely heterogeneous reaction (upper curve), and for $k_{het}/(k_{het} + k_{hom}) = 0.1$, 0.2, 0.3, 0.5, and 0.9. For experiments conducted under conditions of $\lambda^2 \ll 1$ (as in our k_1 measurements, in which λ^2 did not exceed 0.07), k_{eff} is close to k both the heterogeneous and homogeneous reactions. Thus, we obtained the true value of the rate constant of the reaction examined, but it remains unclear whether this reaction takes place in the bulk or on the reactor surface.

This issue was elucidated by experiment in which k_{eff} differed significantly from k (at large λ^2 values). These conditions were established by replacing helium with oxygen as the diluent gas (the iodine atom diffusion coefficients in oxygen and helium are 0.135 and 0.564, respectively) and by conducting experiments at higher pressures in the reactor. By measuring k_{eff} at large λ^2 values and plotting the resulting data points together with theoretical dependences of k/k_{eff} on λ^2, it is possible to determine the locus of the reaction. Figure 5 shows experimental data for the reaction of iodine atoms with ozone [19] (points *1*) superimposed on the theoretical dependences of k/k_{eff} on λ^2. At large λ^2 values, the data points lie near the curve corresponding to the homogeneous reaction. The contribution from the heterogeneous reaction does not exceed 10%. Figure 5 also plots experimental data obtained at large λ^2 for reaction (I) (points *2*). Evidently, the reaction of chlorine atoms with iodomethane, which yields iodine atoms, is largely heterogeneous. The contribution from the homogeneous reaction does not exceed 10%. Our data do not allow the mechanism of this reaction to be determined, so the rate constant that we measured should be considered to be the effective constant of the process, whose rate-limiting step is the reaction occurring on the reactor wall. The above evidence that the iodine atoms resulting from reaction (I) form via a heterogeneous mechanism is also valid when the reaction proceeds in several steps since this evidence is based on the strong distortion of the radial iodine atom concentration profile at long active species diffusion times.

Note that heterogeneous reactions in the atmosphere are currently attracting keen interest from researchers of tropospheric and stratospheric phenomena. It is heterogeneous processes that cause the ozone depletion over Antarctica and the spring ozone decline in the northern hemisphere. It is investigated how the ozone concentration in the atmosphere is affected by heterogeneous reactions taking place on solid particles erupted by volcanoes and raised by dust storms [20, 21]. Heterogeneous reactions on solid and liquid components of the atmosphere, which proceed more rapidly than homogeneous reactions, are still insufficiently understood, but their significant contribution to atmospheric chemistry is beyond any doubt.

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