

# Increase in the Apparent Rate Constant of the Reaction of Hydrogen Sulfide with Ozone upon the Treatment of the Reactor Surface with Reaction Products

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**Abstract**—The reaction of hydrogen sulfide with ozone at 343 K was studied in a flow reactor whose inner surface was coated with 32-L fluoroplastic both immediately after coating and after repeatedly treating with reaction products (sulfur compounds). In the latter case, the rate of hydrogen sulfide reaction with ozone increased by more than one order of magnitude.

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## INTRODUCTION

It is of importance to study chemical processes occurring in the Earth atmosphere because of the increasing role of anthropogenic factors related to the development of chemical industry, transport, power engineering, and other branches of world economy. As a result of intensive industrial activities, various chemicals enter the atmosphere to undergo chemical and photochemical transformations. These transformations are responsible for the importance of anthropogenic factors.

Hydrogen sulfide is released to the atmosphere both from natural sources (volcanic eruptions, organic matter degradation, and biomass combustion) and as a consequence of human activities, for example, as a result of the combustion of energy carriers and the operation of internal combustion engines [1–5]. Oxidation processes result in the rapid decomposition of hydrogen sulfide in the troposphere; however, the lifetime of the main hydrogen sulfide oxidation product— $\text{SO}_2$ —is as long as a few days and its concentration is as high as  $5 \times 10^{13}$  molecule/cm<sup>3</sup>. Approximately 10% of the sulfur dioxide reaches the stratosphere [6].

The reaction of hydrogen sulfide with ozone was studied by many researchers, who obtained a great body of data, which were sometimes contradictory. In the majority of publications, the rate constant of this reaction was no higher than  $2 \times 10^{-20}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (e.g., see [7, 8]). However, Glavas and Toby [9] reported much higher values from  $3.99 \times 10^{-16}$  at 298 K to  $1.26 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 343 K. Chain and even branched-chain mechanisms of the interaction of hydrogen sulfide with ozone have been proposed in a number of publications [7, 10].

In this work, to measure the rate constant of the reaction of hydrogen sulfide with ozone, we used an indirect method based on the measurement of the concentration of iodine atoms formed upon the interaction of  $\text{H}_2\text{S}$  with IO radicals in the presence of ozone. To detect iodine atoms, we used a resonance fluorescence method, which was described in detail elsewhere [11]. The procedure of measuring the rate constant of the reaction of  $\text{H}_2\text{S}$  with IO was considered previously [12]; therefore, in this work, we report only brief data on these experimental procedures.

## EXPERIMENTAL

The experiments were performed in a cylindrical reactor shown in Fig. 1 under jet conditions at 343 K. The reactor was placed in a thermostated jacket, which made it possible to maintain the preset temperature to within  $\pm 1$  K. The inner surface of the quartz reactor with an inner diameter of 2.2 cm was coated with 32-L fluoroplastic. Hydrogen sulfide was prepared under laboratory conditions by the interaction of  $\text{Na}_2\text{S}$  with sulfuric acid.

The concentrations of substances in the reactor were determined by measuring the outflow time of a certain amount of a substance from a calibrated volume. The pressure was monitored with a reference gage. In all of the experiments, chemically pure oxygen and high-purity helium were used. Ozone was prepared by passing a flow of oxygen through an Ozon-2 ozone generator. The concentration of  $\text{O}_3$  was measured using a Spectromom-204 spectrometer based on absorbance changes at a wavelength of 253.7 nm.

All of the lines for ozone supply to the reactor were made of glass and Teflon, and they did not contain grease.

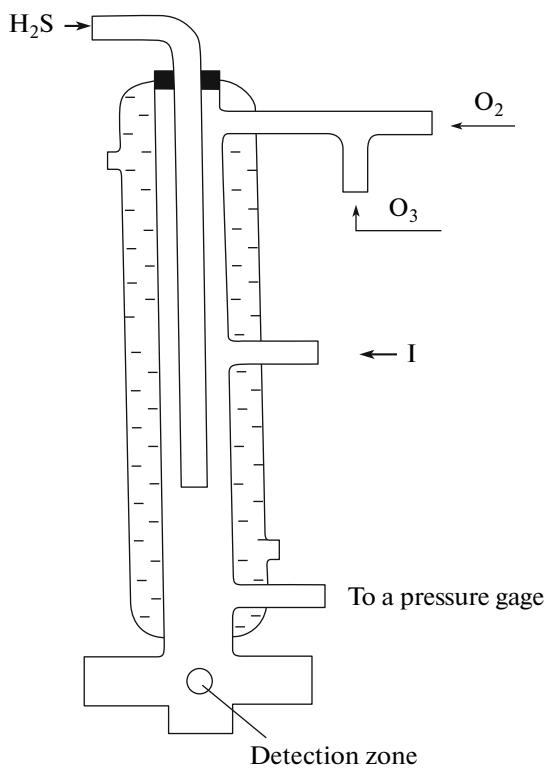


Fig. 1. Schematic of the reactor.

The source of iodine atoms was a quartz tube with an inner diameter of 8–10 mm joined to the reactor with a quartz capillary 1 mm in diameter and 10 mm in length. This tube was illuminated with a DRB-8 bactericide low-pressure quartz mercury lamp (power of 6 W), which emitted a resonance line with the wavelength  $\lambda = 253.7$  nm. A mixture of helium with gaseous methyl iodide was passed through the tube, and iodine atoms in the states  $^2P_{1/2}$  and  $^2P_{3/2}$  were formed from this compound under the action of radiation (20% atoms were formed in the ground state  $^2P_{3/2}$  [13]). The deactivation of iodine atoms, that is, the transition from the state  $^2P_{1/2}$  to the state  $^2P_{3/2}$  partially occurred in the source at  $\text{CH}_3\text{I}$  and helium molecules and partially in the reactor on oxygen molecules. Analytical-grade  $\text{CH}_3\text{I}$  was used. Ampoules with  $\text{CH}_3\text{I}$  were kept at  $0^\circ\text{C}$  (thawing ice).

The flow resonance lamp, which generated resonance emission with a wavelength of 178.3 nm, was made of quartz. The inner diameter of the working zone was 3 mm. The windows were made of UV quartz with the short-wavelength limit of 160 nm. A mixture of He with molecular iodine in a ratio of about 10000 : 1 was passed through the lamp. A Broida microwave resonator was used to excite a discharge in the lamp. A LUCh-3M generator with an output power of 2.5 W was used as a source of microwave radiation.

The light photons reemitted by iodine atoms were detected with a photoionization counter. The signal

from the counter was directed to a ChZ-63/1 frequency meter and simultaneously to an S-107 oscilloscope through a 470-pF blocking capacitor. The accumulation of signals was performed using a computer through the ChZ-63/1 frequency meter. From  $500$  to  $10^4$  pulses were accumulated at each experimental point. The end window of the counter was made of UV quartz with the short-wavelength limit of 160 nm. Initially, the counter was evacuated with a diffusion pump to a pressure of  $5 \times 10^{-5}$  Torr and then filled with a mixture of NO (10 Torr) and Ar (230 Torr). A drop of diethylferrocene was placed in a special glass finger; in this case, equilibrium was established between the vapor and liquid phases of diethylferrocene. The long-wavelength limit of the counter was  $\sim 185$  nm, which was determined by the ionization potential of diethylferrocene (6.3 eV). Thus, the photoionization counter simultaneously served as a monochromator, which separated a spectral region from  $\sim 160$  to  $\sim 185$  nm.

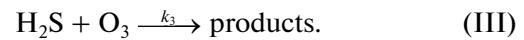
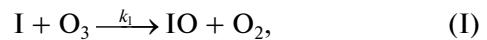
To calibrate the absolute sensitivity of the system to iodine atoms, molecular iodine was added to an excess of oxygen atoms for the complete conversion of  $\text{I}_2$  into I atoms.

Oxygen atoms were obtained by the action of a microwave discharge on a mixture of 4%  $\text{O}_2$  and 96% He, and their concentration was determined by chemiluminescence titration with the use of  $\text{NO}_2$  [14]. The concentration of O atoms was  $\sim 10^{14} \text{ cm}^{-3}$ , which was higher than the concentration of I atoms by three orders of magnitude; therefore, heterogeneous decay was the main cause of the consumption of oxygen atoms.

Under the conditions of our experiments, the signal-to-noise ratio was 1 at the concentration  $[\text{I}] \approx 3 \times 10^7 \text{ atom/cm}^3$ .

## RESULTS

In the reactor shown in Fig. 1, conditions for the occurrence of the following reactions were provided:

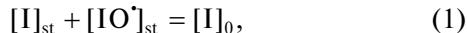


Because the rate of reaction (III) should affect the rate of reaction (II) and, consequently, the concentration of iodine atoms formed in this reaction, the rate constant  $k_3$  of the reaction of hydrogen sulfide with ozone can be measured by observing changes in the concentration of iodine atoms.

Hydrogen sulfide was supplied to a specified point in the reactor at a certain distance from the detection zone through a mobile nozzle coated with 32-L fluoroplastic from the outside. Ozone was supplied to the top part of the reactor. The concentration of ozone in the reactor was much higher than the concentration of hydrogen sulfide. Iodine atoms obtained by the photolysis of methyl iodide were introduced into the reac-

tor at an 8-cm distance from the detection zone. This distance was sufficient for the mixing of reactants and reaching a steady-state concentration of iodine atoms. Under the experimental conditions, the contact time of iodine atoms with hydrogen sulfide and ozone was  $4 \times 10^{-2}$  s, and the characteristic time of establishing a steady-state concentration of I atoms was shorter than  $1 \times 10^{-2}$  s. The concentration of hydrogen sulfide was  $1.2 \times 10^{14}$  molecule/cm<sup>3</sup>, and the concentration of ozone varied from  $6 \times 10^{14}$  to  $3.0 \times 10^{15}$  molecule/cm<sup>3</sup>. The experiments were performed at a reactor pressure of 1.8 Torr.

If the rates of decay of I atoms and  $\text{IO}^{\cdot}$  radicals are low and processes affecting the concentrations of I and  $\text{IO}^{\cdot}$  other than the above reactions do not occur in the reactor,



where  $[\text{I}]_{\text{st}}$  and  $[\text{IO}^{\cdot}]_{\text{st}}$  are the steady-state concentrations of I and  $\text{IO}^{\cdot}$ , respectively, and  $[\text{I}]_0$  is the initial concentration of iodine atoms. The steady-state condition is



Hence, using expression (1), we obtain the simple relationship

$$\frac{[\text{I}]_0}{[\text{I}]_{\text{st}}} = \frac{k_1}{k_2} \frac{[\text{O}_3]}{[\text{H}_2\text{S}]} + 1. \quad (3)$$

Note that the dependence of the rate of reaction (II) on the concentration of  $\text{H}_2\text{S}$  does not ensure the occurrence of the reaction in the bulk. Thus, we proposed a procedure in order to determine whether the test reaction occurs at the wall of the reactor or in the bulk [12].

On the assumption that reaction (II) can occur both in the bulk and at the wall of the reaction vessel, expression (3) changes to

$$\frac{[\text{I}]_0}{[\text{I}]_{\text{st}}} = \frac{[\text{O}_3]}{[\text{H}_2\text{S}]} \times \frac{k_1}{k_2^{\text{hom}} + k_2^{\text{het}}} \frac{k_{\text{dif}}}{k_2^{\text{het}} [\text{H}_2\text{S}] + k_{\text{dif}}} + 1, \quad (4)$$

where  $k_2^{\text{hom}}$  and  $k_2^{\text{het}}$  are the rate constants of homogeneous and heterogeneous reactions, respectively;  $k_{\text{dif}} = 23D/4R^2$  ( $D$  is the diffusion coefficient of  $\text{IO}^{\cdot}$  radicals, and  $R$  is the reactor radius). The coefficient  $D$  can be found from the equation  $D = D_0 \frac{760}{P}$ , where  $D_0$  is the diffusion coefficient of  $\text{IO}^{\cdot}$  radicals at a pressure of 760 Torr, and  $P$  is the reactor pressure ( $D_0 = 0.18 \text{ cm}^2/\text{s}$  for a 1 : 10 mixture of helium and oxygen at 343 K).

Comparing experimental data with the theoretical dependence of the ratio between the initial and steady-state intensities of resonance fluorescence signals due to iodine atoms, which corresponds to the  $[\text{I}]_0/[\text{I}]_{\text{st}}$  ratio, on the concentrations of reactants, we can evaluate the contribution of the heterogeneous reaction component [12].

At low concentrations of  $\text{H}_2\text{S}$ , when

$$\frac{k_{\text{dif}}}{k_2^{\text{het}} [\text{H}_2\text{S}] + k_{\text{dif}}} \approx 1, \quad (5)$$

expression (4) takes the form

$$\frac{[\text{I}]_0}{[\text{I}]_{\text{st}}} = \frac{[\text{O}_3]}{[\text{H}_2\text{S}]} \times \frac{k_1}{k_2^{\text{hom}} + k_2^{\text{het}}} + 1 \quad (6)$$

and becomes almost identical to expression (3) with the only difference that here  $k_2 = k_2^{\text{het}} + k_2^{\text{hom}}$ . Note that the introduced value of  $k_2^{\text{het}}$  is constant only for the given reaction configuration and the particular surface at which the reaction occurs.

Before each series of experiments, we measured the rate constants of decay of I atoms and  $\text{IO}^{\cdot}$  radicals at the reactor surface in order to determine that they are small and expression (2) is valid. Under the conditions of our experiments, the constants of both of these reactions were no higher than  $5 \text{ s}^{-1}$ . In addition, we determined the value of  $k_2$  before each series of experiments. As found by Larin et al. [12], reaction (II) mainly occurs at the reactor surface; therefore, the constant  $k_2$  could depend on the state of the surface. Under the conditions of our experiments,  $k_2 = (2.3 \pm 0.6) \times 10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ .

The apparent rate constant of reaction (III) was measured as follows: Iodine atoms were introduced into a flow of molecular oxygen containing ozone at a fixed distance from the detection zone. They were converted into  $\text{IO}^{\cdot}$  radicals in reaction (I). Their concentration rapidly decreased as a result of both this reaction and the decay of iodine atoms on the walls. The preliminarily measured constant of decay of iodine atoms on the walls was negligibly small, as compared with the rate constant of reaction (I). At a distance of 1 cm from the site of introduction, 98% iodine atoms were converted into  $\text{IO}^{\cdot}$  radicals. At a fixed distance ( $\sim 8$  cm) from the detection zone, hydrogen sulfide supplied to the reactor entered into the reaction with  $\text{IO}^{\cdot}$  radicals. As a result of reactions (I) and (II), a steady-state concentration of iodine atoms was established in the reactor. If the combustion of hydrogen sulfide by the interaction with ozone were not the case, the resonance fluorescence signal corresponding to the given concentration of iodine atoms would remain unchanged regardless the distance from the detection zone at which hydrogen sulfide arrived at the reactor. As a sufficiently high rate of reaction (III), the resonance fluorescence signal intensity will depend on the distance between the point of  $\text{H}_2\text{S}$  injection and the detection zone.

Then, the following dependence of the concentration of hydrogen sulfide on the time of contact with ozone ( $\tau$ ) should be additionally introduced into Eq. (6):

$$\frac{[\text{I}]_0}{[\text{I}]_{\text{st}}} = \frac{[\text{O}_3]}{[\text{H}_2\text{S}]_0 \exp(-k_2[\text{O}_3] \tau)} \times \frac{k_1}{k_2^{\text{hom}} + k_2^{\text{het}}} + 1. \quad (7)$$

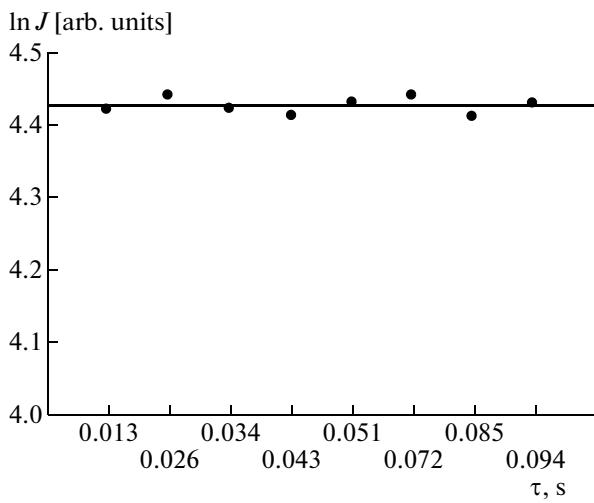


Fig. 2. Dependence of  $\ln J$  on  $\tau$  in the reactor untreated with reaction products.

Taking the logarithm and combining the constants, we obtain the expression

$$\ln[I]_{\text{st}} = \text{const} - k_3[\text{O}_3]\tau. \quad (8)$$

Figure 2 shows the dependence of the logarithm of the resonance fluorescence signal intensity ( $\ln J$ ), which is proportional to the logarithm of the steady-state concentration of iodine atoms ( $\ln[I]_{\text{st}}$ ), on time  $\tau$  in the reactor whose surface was immediately coated with 32-L fluoroplastic and not treated with the reaction products. As can be seen, the concentration of iodine atoms remained unchanged. The experiments were performed at a hydrogen sulfide concentration of  $6.3 \times 10^{14} \text{ molecule/cm}^3$ , and the concentration of ozone was  $3.0 \times 10^{15} \text{ molecule/cm}^3$ . This was a maximum concentration of ozone in our experiments. The

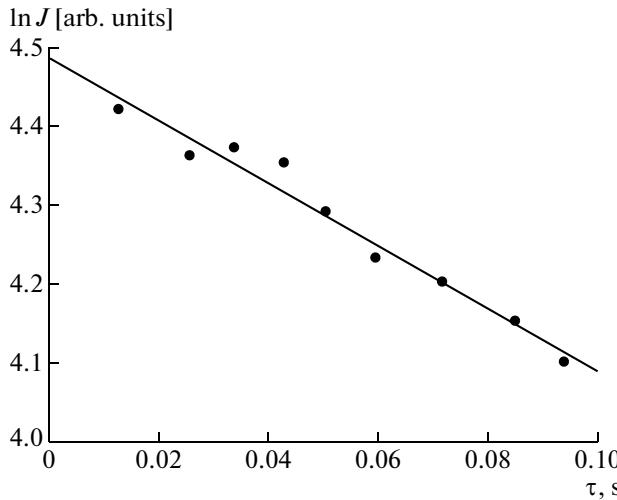


Fig. 3. Dependence of  $\ln J$  on  $\tau$  in the reactor treated with reaction products.

apparent rate constant of the reaction of hydrogen sulfide with ozone ( $k_3$ ), which was estimated from the slope of the straight line in Fig. 2, was no higher than  $4 \times 10^{-17} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$  under these conditions.

Figure 3 shows an analogous dependence obtained at the same concentrations of ozone and hydrogen sulfide after the repeated treatment of the reactor with reaction products. In this case, a decrease in the concentration of iodine atoms was observed as the time of the reaction between hydrogen sulfide and ozone was increased. Another series of experiments was performed at a lower concentration of hydrogen sulfide to fulfill relationship (5). Figure 4 shows the results of experiments performed at various ozone concentrations.

The apparent rate constant of reaction (III) was found from the slope of the straight line in Fig. 4:  $k_3 = (7.9 \pm 3) \times 10^{-16} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ .

Thus, the treatment of the reactor surface with reaction products increased the apparent rate constant of the reaction of hydrogen sulfide with ozone by more than one order of magnitude. Note that this constant corresponds to only the rate of hydrogen sulfide combustion in an excess of ozone under the conditions of our experiments. It suggests that the rate of the reaction of hydrogen sulfide with ozone increased many-fold in the case of the participation of heterogeneous processes in the reaction.

## DISCUSSION

The observed dependence of the rate of reaction of hydrogen sulfide with ozone on the state of the reactor surface, as well as a large scatter of published experimental data on the rate constant of this reaction, allowed us to hypothesize that this reaction belongs to the class of chain reactions, in which chain initiation

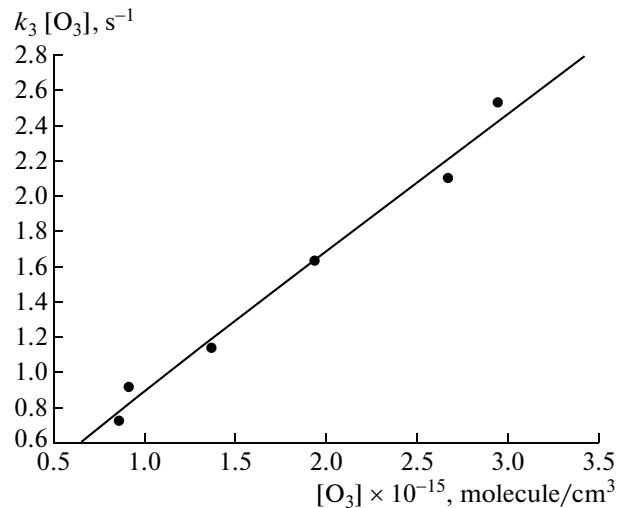
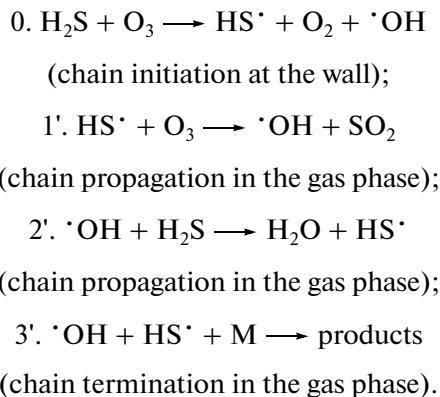


Fig. 4. Dependence of the concentrations of  $k_3[\text{O}_3]$  on  $[\text{O}_3]$  in the reactor treated with reaction products.

can occur at the walls of the reaction vessel. Therefore, the measured constant is an apparent rate constant of a complex process, which can be described by the following simplified reaction scheme:



Reaction 1' can involve several intermediate steps with the participation of  $\text{HS}^\cdot$  and  $\text{HSO}^\cdot$  radicals.

The complex mechanism of the interaction of hydrogen sulfide with ozone was supported by the results of our experiments: upon mixing hydrogen sulfide with ozone under batch conditions at a pressure of  $\sim 1$  Torr, a bright flare was observed, whose spectrum corresponded to the excited state of the  $\text{SO}_2$  molecule, and ozone, which was detected by its absorption at a wavelength of 253.7 nm, disappeared in less than 10 s.

The experimentally observed dependence of the rate of the reaction on the state of the reactor surface may suggest that chain initiation occurs at a detectable rate only at certain surfaces, in particular, at a surface treated with reaction products, one of which is sulfurous acid. Because the rate of a chain reaction is determined as the product of the rate of chain initiation and the chain length, it is clear why the rate of the interaction of hydrogen sulfide with ozone increased as the rate of chain initiation was increased.

The results obtained in this study are of considerable importance for troposphere chemistry. Indeed, because sulfur-containing aerosols occur in the troposphere, the rate of the interaction of hydrogen sulfide with ozone resulting in the formation of sulfur dioxide can be higher than in a gas phase. Note that sulfur dioxide is the most important atmospheric pollutant whose accumulation in the troposphere causes acid rains, which adversely affect living organisms. This substance also plays an important role in the formation of clouds to exert a serious effect on climate.

The hypothesis that a vast release of hydrogen sulfide to the atmosphere was responsible for a global catastrophe that resulted in the extinction of dinosaurs and the appearance of misshapen plant species similar to those resulting from the action of hard UV radiation

has been actively described in the current scientific literature [15]. This release might result from either giant volcanic eruptions or the entry of a large meteorite into a body of water, for example, Black Sea, the depths of which contain vast amounts of hydrogen sulfide. Any of these events would be accompanied by the release of a large amount of solid particles into the atmosphere to facilitate the catastrophic decrease in the ozone layer because of the occurrence of a fast heterogeneous reaction between hydrogen sulfide and ozone and hence the penetration of destructive hard UV radiation to the Earth surface.

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