=== **CHEMICAL PHYSICS OF ATMOSPHERIC PHENOMENA** ===

Modeling the Time-Dependent O_3 Uptake on a Methane Flame Soot Coating Under Conditions of Competitive O_3/NO_2 and O_3/N_2O_5 Adsorption

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Abstract—The uptake of O_3 (1×10^{12}–5×10^{13} cm^{-3}) on a methane soot coating preliminarily exposed to N_2O_5, is studied using a flow reactor with a movable insert. Based on the dependence of the ozone uptake coefficient on the exposure time and O_3 concentration, the uptake mechanism is established and a number of elementary parameters are obtained that describe the uptake process at arbitrary O_3 concentrations. Based on the Langmuir representation of adsorption, a model description of the uptake on soot under conditions of the competitive adsorption of O_3/NO_x, where $NO_x = NO_2$ and N_2O_5, taking into account the multistage uptake process, is proposed. Based on the developed model and elementary parameters describing the uptake of O_3, NO_2, and N_2O_5 on a fresh soot surface, as well as the uptake of ozone on a surface pretreated with NO_2 and N_2O_5, numerical estimates were made of the additional contributions to the ozone uptake for two real scenarios of the O_3/NO_x ratio. For an industrial region in winter, when the ozone concentration is minimal (10 ppb O_3, 17 ppb NO_2, and 4 ppb N_2O_5), the additional integral contribution to the uptake of O_3 on the reaction products of NO_2 with soot is 68%, and in the case of N_2O_5, it is 3.6%. For the same region in summer, at the maximum ozone concentration (36 ppb O_3, 17 ppb NO_2, and 4 ppb N_2O_5), the analogous contributions will be 20 and 1%, respectively. The reasons for this difference are discussed.

Keywords: chemistry of the troposphere, ozone, O_3, oxides of nitrogen, NO_2, N_2O_5, methane flame soot, uptake coefficient, competitive adsorption, Langmuir coefficient

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INTRODUCTION

Nitrogen oxides NO, NO_2, and N_2O_5, together with ozone O_3, play an important role in the oxidizing power of the Earth's atmosphere. One of these components, N_2O_5 is formed as an active night reagent by the reactions of $NO_2 + O_3 \rightarrow NO_3 + O_2$, $NO_3 + NO_2 + M \leftrightarrow N_2O_5$ [1] and participates in the branching scheme of ozone destruction in the upper atmosphere [2]. At the same time, the heterogeneous uptake of N_2O_5 on particles of atmospheric aerosol due to such a loss of N_2O_5 leads to an increase in the ozone concentration [3]. In general, the consumption of N_2O_5 is defined as the loss of reactants NO_2 and O_3, as well as the heterogeneous reactions on cloud droplets and aerosol particles of various nature [1, 4, 5]. Based on field measurements in the troposphere, the relative concentrations of N_2O_5 are 50–100 ppt over the Arctic in winter and up to 3.8 ppb over polluted regions [4]. The measured concentrations of O_3 in the troposphere give values of about 35–40 ppb [5, 6]. In the surface troposphere, ozone is formed in cycles of photochemical reactions involving OH, NO_x, and various organic compounds [6, 7]; an additional contribution is made by thunderstorms and partly by intrusion from the stratosphere. In field measurements of the relative concentrations of O_3, NO_2, and separately NO_x during the year in the surface troposphere of an industrialized region, it was found that the ozone content is maximum in summer (40 ppb) and minimum in winter (10 ppb) with a local minimum of 0.3 ppb. At the same time, the maximum of $[O_3]$ corresponds to the minimum of $[NO_x]$ (17 ppb), and the minimum of $[O_3]$ corresponds to the maximum of $[NO_x]$ (30 ppb). The NO_2 content varies slightly throughout the year and remains at the level of 15 to 20 ppb [8].

The average aerosol mass in the troposphere is 4.6 μg m^{-3}. At the same time, the organic fraction accounts for about 27%, most of which is carbon [9–11]. Carbon-containing aerosols are formed as a result of burning fuels and biomass, as well as forest fires. The global emission of the main soot component, carbon, is estimated as 6.6–11.6 Tg per year, and the concentration of submicron carbon particles in the air is ~0.6 μg m^{-3} [12–14].

The uptake of O$_3$ on the soot coating of hydrocarbon combustion has been studied in a large number of works using various techniques and methods for detecting both gas-phase reagents and products, and products of the condensed phase [15]. The dependence of the uptake coefficient γ on the time of exposure to the reagent gas and on its concentration is observed. The ozone uptake coefficients on soot coatings of various hydrocarbons, measured and calculated for the true BET surface (Brunnauer−Emmett−Teller) are $\gamma_{ini} \sim 10^{-3}$, the initial value, and $\gamma_{ss} \sim 10^{-4}$−10^{-5}, the average value over a long period of time. In many works, the complex multistage nature of the uptake is noted. Based on the temperature dependence of the uptake coefficient, in a number of works, the Langmuir coefficient K_L, heat of adsorption Q_{ad}, and activation energy E_a of the elementary O$_3$ uptake reactions on a soot coating were estimated [16−18].

The data on the temporal behavior of the uptake coefficient $\gamma(t)$ of ozone, its dependence on the concentration of O$_3$, according to the content of the resulting products, and the kinetic parameters of elementary reactions are necessary for a correct description of the process of such interaction and, ultimately, for modeling the global chemical processes occurring in the atmosphere. The uptake of ozone on aerosol particles in the troposphere occurs under conditions of competitive adsorption. On the one hand, due to the low concentrations of the competing reactant gases, the uptake of each of them should occur independently and practically should not affect each other. On the other hand, as a result of the uptake of the competing agent, a new reactive solid product can be formed, on which the additional uptake of ozone is possible. In particular, it was found that as a result of the uptake of NO$_2$, surface centers capable of such uptake are formed on the fresh soot coating [19].

The reagent gas N$_2$O$_5$ is an important intermediate in the atmospheric chemistry of nitrogen oxides, and its concentration is thermodynamically related to the NO$_2$ and NO$_3$ concentrations. There are just a few laboratory studies of the interaction of N$_2$O$_5$ with soot of some hydrocarbons and they contain a wide range of values of the uptake coefficients γ, ranging from 0.33 to 4×10^{-5}, depending on the concentration of the reagent gas and taking into account the geometric or specific surface area of soot and the temporal factor of the process, when γ_{ini} of the initial uptake is an order of magnitude greater than γ_{ss} of the steady-state uptake [15, 20]. It is established that the uptake of N$_2$O$_5$ on such substrates occurs as a result of the combined action of physical sorption and redox reaction with the formation of the gas-phase product NO or NO$_2$ and a trace amount of HNO$_3$. The initial fast uptake is observed with an uptake coefficient $\gamma_{ini} \approx 0.1$ (based on the geometric surface of soot) and the subsequent decrease in the uptake coefficient to values $\gamma_{ss} \approx 5 \times 10^{-3}$.

Based on the real (BET) soot surface γ_{ss} is estimated to be 3×10^{-8} [21]. Based on dependence γ on the concentration of the reagent, the authors suggest a complex mechanism of the interaction of N$_2$O$_5$ with soot: N$_2$O$_5$ + {C} → N$_2$O$_3$(ads) + Product, N$_2$O$_3$(ads) → NO + NO$_2$. Such a process is not catalytic; carbon centers are consumed in these capture processes, which leads to modification of the substrate surface and the formation of new functional groups.

The aim of this study is to establish additional ozone sink channels on the surface centers formed as a result of the uptake of a competing gas-reagent. N$_2$O$_5$ and NO$_2$ (the latter was studied by us earlier) are considered as such a competitive agent. Based on the Langmuir representation of competitive adsorption, a model description of the process of the ozone uptake on a fresh soot coating in the presence of these reagent gases is proposed. Quantitative estimates of the additional ozone uptake channel for a number of its characteristic tropospheric concentrations are obtained.

EXPERIMENTAL

Chemical reactor. The uptake of O$_3$ and N$_2$O$_5$ was studied in a flow reactor with a movable insert and a soot film coating deposited on it [18]. The reactor was coupled to a high resolution mass spectrometer with electron ionization. The energy range of ionizing electrons can be varied from 50 to several eV with a spread of 0.1 eV.

When studying the uptake of N$_2$O$_5$ the main flow of helium (of the special purity grade) flows through a thermostated ampule filled with pieces of Teflon capillaries and N$_2$O$_5$ frozen, and then through a cylindrical glass reactor with an inner diameter $d_R = 1.3$ cm with linear velocity $u = 100-250$ cm s^{-1} at a total pressure in the reactor of $p = 1-3$ Torr. A thin carbon black coated stainless steel central rod with diameter $d_r = 0.2$ cm and maximum length $L = 50$ cm can be moved with an external magnet along the axis of the reactor's tube from the compensating volume to the zone of contact with the reagent gas. An additional flow of helium is supplied through the compensating volume to avoid an uncontrolled diffuse flow of the reagent gas from the reaction zone into this volume. Sampling in to the mass spectrometer is carried out in the form of a molecular beam through a hole with a diameter of 0.35 mm at the top of the inlet cone located coaxially with the outer tube of the reactor.

In the study of the ozone uptake, an additional flow of the O$_3$/He mixture with the given ozone concentration was fed through a side inlet to the main helium flux. This mixture was prepared in advance in a stainless steel tank. The tank and all tubes for supplying the mixture to the reactor were prepassivated with molecular fluorine.

Reagent N_2O_5 was prepared in advance under static conditions by the reaction $O_3 + NO_2 \rightarrow NO_3 + O_2$, $NO_3 + NO_2 \rightarrow N_2O_5$, then refrozen into a cryostat ampule with the slow pumping of helium and stored at the temperature of the ampule of 178 K. The main side reactant was nitrogen dioxide whose contribution of the flux of which to the flux of N_2O_5 was about 5%.

A laboratory burner connected to a gas main was used as the source of the soot. The metal rod was placed at a distance of 15 to 17 cm from the base of the flame with the constant manual rotation of the rod. The specific surface area of the soot was determined experimentally by the BET method. In the diffusion combustion of methane and under our deposition conditions, the specific surface area of soot is $S_{spec} = (40 \pm 10)$ m^2 g^{-1}.

Measurement procedure. The experimental dependences of the uptake coefficient O_3 on the soot coating from the time of its exposure was determined by the relative change in the ozone concentration on the mass spectral line I_{48} ($m/z = 48$) when the coated rod was introduced into the zone of its contact with ozone and then removed from this zone. The intensity of the ion current was measured in the mode of mechanical modulation of the molecular beam and synchronous ion counting. The initial ozone concentration was measured in the absence of a coated rod. A section of the rod was introduced into the contact zone (usually 5−10 cm), while simultaneously switching on the mode of multiple measurements for several hundred seconds. The rod was removed and the level of the ozone concentration was remeasured. The rod was reintroduced and the multiple measurement mode was repeated until the complete cessation of the ozone uptake. We changed the initial ozone concentration and repeated the entire measurement procedure with the introduction of the next section of the coated rod.

At our flow rates and pressure in the reactor, the kinetics of ozone consumption during its uptake on the soot coating is described by the first order equation:

$$-d[O_3(t_c,t)]/dt_c = k_w(t)[O_3(t_c,t)], \qquad (1)$$

where $[O_3]$ is the ozone concentration; $t_c = [0, \Delta L/u]$ is the contact time of ozone with the coating on the rod introduced into the reactor into the contact zone up to length ΔL; u is the average flow rate of the helium carrier gas; and t is the exposure time of the coating to the reagent gas flow. The rate constant of a heterogeneous reaction $k_w(t)$ is expressed through the kinetic, $k_w^k(t) = [\gamma(t)c_{O_3}/4](S_{eff}/V_R)$, and diffusion, $k_w^d \approx 4D_{O_3}/d_R^2$, limits: $1/k_w(t) = 1/k_w^k(t) + 1/k_w^d$. Here $c_{O_3} = 3.61 \times 10^4$ cm s^{-1} is the average molecular speed O_3 at temperature $T = 295$ K; $pD_{O_3} = 394$ Torr cm^2 s^{-1} [22] is the diffusion coefficient of O_3 molecules in helium; S_{eff} is the effective coverage area in the reaction zone when the rod is inserted up to length ΔL; and

V_R is the volume of the reactor corresponding to the same length. In our case, even in the initial stage of a fast uptake, the condition $k_w^d \gg k_w^k$, was met and it could be assumed that $k_w \approx k_w^k$.

At $(d_r/d_R) \ll 1$ for a soot coating, whose surface is determined by the effective area S_{eff}, expressed through the mass of the sample ρ_m per unit surface and specific surface area of soot S_{spec}, the value $k_w^k(t)$ is determined by the equation

$$k_w^k(t) \cong (\gamma(t)c_{O_3}S_{spec}\rho_m/d_R)(d_r/d_R). \qquad (2)$$

The typical contact time t_c is not more than 0.1 s, which is significantly less than the minimum time ($t = 5$ s) of the integration of the signal intensity of the mass spectral peak. Based on this, it is possible to integrate Eq. (1) with respect to t_c, and taking into account (2), the dependence of the uptake coefficient γ in Eq. (1) on the exposure time t during the uptake on a soot coating, taking into account the BET surface, is

$$\gamma(t) = \frac{\ln\left(I_{48}^0/I_{48}(t)\right)}{t_c} \frac{d_R^2}{c_{O_3}S_{spec}\rho_m d_r}, \qquad (3)$$

where $I_{48}^0(t)$ and $I_{48}(t)$ are the intensities of the ozone ion currents without the introduction of the coated rod and with the inserted rod, respectively.

Time-dependent uptake of N_2O_5 and O_3 on a soot coating previously exposed to a competitive reagent gas. Figure 1 shows the temporal profile of the N_2O_5 concentration when introducing a soot-coated rod, which was previously exposed to ozone, into the reaction zone. With the periodic introduction of the rod, a reproducible uptake of N_2O_5 molecules and the reproducible desorption of these molecules after the rod is removed from the reaction zone are observed. The reproducibility of the uptake upon repeated insertion of the rod indicates the uptake mechanism through the decomposition of molecules on surface centers without changing the chemical activity of these centers. Otherwise, recapturing on a chemically inert coating would be less effective. In addition, the temporal profile $[N_2O_5]$ cannot be explained only by adsorption, since the latter occurs during the characteristic time of achieving dynamic equilibrium in the reaction

$$N_2O_5(g) + z(s) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} N_2O_5\ldots z$$
$$\overset{k_r}{\longrightarrow} z(s) + M(g), \qquad (R1)$$
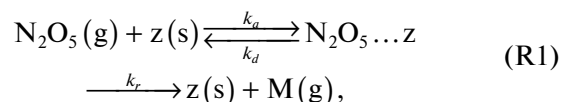
This time is determined by the relation $\tau = [z]/k_a = 4[z]/c_{N_2O_5}[N_2O_5]$ and under our conditions for $[N_2O_5] = 3 \times 10^{12}$ cm^{-3}, $c_{N_2O_5} = 2.4 \times 10^4$ cm s^{-1}, and $[z] = 2 \times 10^{14}$ cm^{-2} [18], it is only 10 ms.

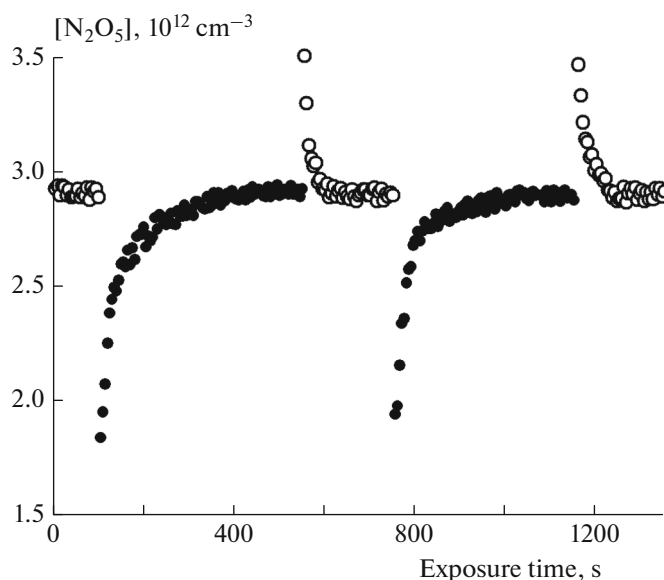On a soot coating previously exposed to N_2O_5, the uptake of ozone is observed. Unlike the previous case,

Fig. 1. Change in concentration of reagent N_2O_5 in the reactor with the introduction of a movable rod coated with methane soot, previously exposed to ozone. Conditions of uptake of N_2O_5: $[N_2O_5] = 2.9 \times 10^{12}$ cm^{-3}, $T = 295$ K, pressure $p = 2.3$ Torr, $\Delta L = 10$ cm, average helium flow velocity $u = 147$ cm s^{-1}, mass of soot sample per unit surface of the rod $\rho_m = 130$ µg cm^{-2}. Hollow symbols are measured concentration of N_2O_5 with periodic removal of the coated rod from the contact zone; solid symbols are the concentration N_2O_5 when the rod is introduced into the reaction zone.

the uptake is irreversible. Figure 2 shows an example of the temporal profile of the ozone concentration upon the periodic introduction of an exposed soot coating
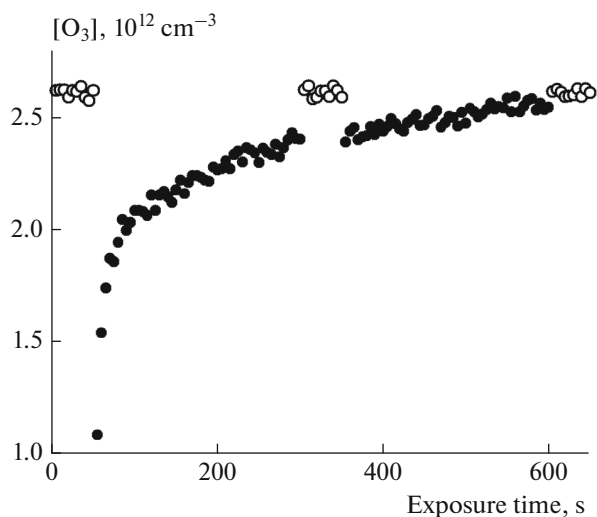

Fig. 2. Change in the ozone concentration in the reactor when a movable rod coated with methane soot, previously exposed to reagent N_2O_5, is introduced into it. Conditions of uptake of O_3: $[O_3] = 2.6 \times 10^{12}$ cm^{-3}, $T = 295$ K, pressure $p = 1.4$ Torr, $\Delta L = 10$ cm, average helium flow velocity $u = 200$ cm s^{-1}, mass of soot sample per unit surface of the rod $\rho_m = 130$ µg cm^{-2}. Hollow symbols are the measured concentration of O_3 in the absence of a coated rod; solid symbols, O_3 concentration with the rod introduced into the O_3 flow.

into its flow. The corresponding temporal dependence of the uptake coefficient $\gamma(t)$ is shown in Fig. 3. For comparison, the inset in the same figure shows a similar dependence of the ozone uptake coefficient under the same conditions on a fresh soot coating. The shapes of the temporal profiles of the uptake coefficients are similar. Based on the similarity of the profiles, we concluded that the uptake mechanisms are similar and that the temporal dependences can be approximated by the analytical formula

$$\gamma(t) = \gamma_r \exp(-a_r t) + \gamma_s \exp(-a_s t)[1 - \exp(-a_r t)]. \quad (4)$$

This formula follows from the description of the uptake of the reagent gas by a two-stage reaction mechanism with the adsorbed molecule on the surface [18]. Here, the terms on the right side of formula (4) are the contributions to the uptake coefficient of its rapid and slow stages. The parameters γ_r and γ_s determine the dependence of the uptake coefficient on the concentration of the reagent gas, and the parameters a_r and a_s characterize their temporal dependence.

The dependences of the ozone uptake coefficient on the soot coating on the exposure time, similar to those shown in Fig. 3, were obtained in the concentration range $1 \times 10^{12} - 5 \times 10^{13}$ cm^{-3}. The results of approximation of these dependencies by formula (4) are given in Table 1, and the dependences of the corresponding parameters on the ozone concentration are shown in Figs. 4 and 5.
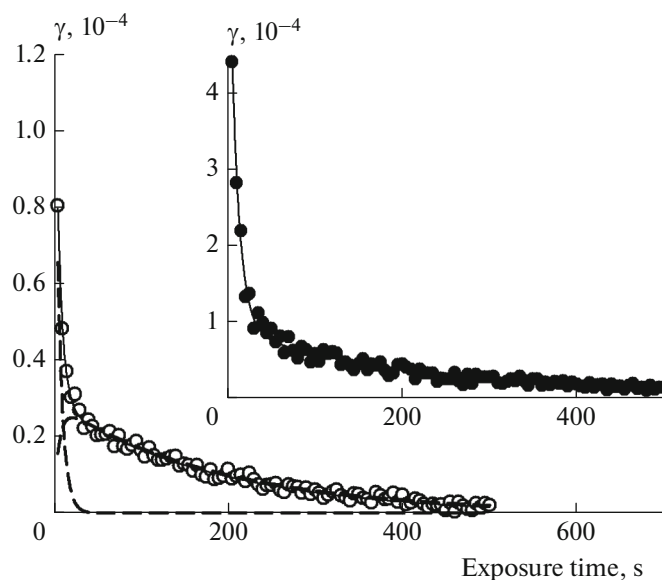
Fig. 3. Time dependence of the coefficient of uptake O_3 (hollow symbols) calculated from the data in Fig. 2 according to formula (3); solid curve, approximation according to formula (4) with parameters from Table 1; dashed curves are the contributions of the first rapid and subsequent slow uptake stages. In the inset for comparison, the time dependence of the uptake coefficient O_3 on a fresh methane soot coating under similar conditions [18].

RESULTS AND DISCUSSION

The dependences of parameters γ_r and γ_s, as well as a_r and a_s, on the ozone concentration given in Fig. 4 and 5 are analogous in form to similar dependences for the ozone uptake on a fresh soot coating [18]. This form of the dependence corresponds to the uptake mechanism via the reaction on the surface with an adsorbed particle [23, 24]. The parameters that define this dependence are a combination of elementary constants that describe the uptake process:

$$\gamma_r = \gamma_{r,max}/(1 + K_{L,r}[O_3]),$$
$$\gamma_s = \gamma_{s,max}/(1 + K_{L,s}[O_3]), \tag{5}$$

$$a_r = k_r\theta, \quad a_s = k_s\theta, \tag{6}$$

$$\theta = K_L[O_3]/(1 + K_L[O_3]), \tag{7}$$

where $\gamma_{r,\,max}$ and $\gamma_{s,\,max}$ are the amplitude values of the uptake coefficient; k_r and k_s are the rate constants of the monomolecular decomposition of complexes formed at the first and second stages of the uptake; K_L is the Langmuir constant, which determines the fraction of the surface θ occupied by the adsorbed molecules.

The results of the approximation of the dependences in Figs. 4 and 5 according to formulas (5)–(7) are given in Table 2. The results of the approximation of the data obtained earlier on the uptake of O_3, N_2O_5, and NO_2 on a fresh soot surface, as well as on the uptake of O_3 on a surface previously exposed to NO_2, are given here. Based on the combination of these parameters, it is possible to simulate the process of the ozone uptake under conditions of the competitive

adsorption of O_3/N_2O_5 and O_3/NO_2, taking into account the additional ozone sink channel on the products of the uptake of N_2O_5 and NO_2.

Table 1. Approximation parameters according to formula (4) of the uptake coefficient $\gamma(t)$ of the ozone at $T = 295$ K on a coating of methane soot preliminarily exposed to reagent N_2O_5

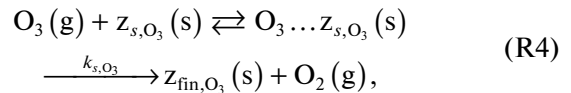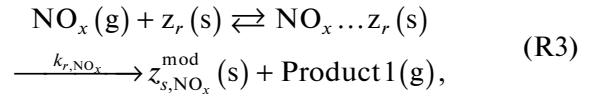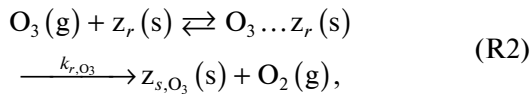| $[O_3]$, 10^{12} cm^{-3}	γ_r, 10^{-4}	a_r, s^{-1}	γ_s, 10^{-5}	a_s, 10^{-2} s^{-1}
1.1	1.32 ± 0.5	0.1 ± 0.05	3 ± 1.1	0.9 ± 0.5
2.6	1.4 ± 0.15	0.15 ± 0.02	2.9 ± 0.2	0.5 ± 0.1
3.4	1.2 ± 0.14	0.12 ± 0.02	2.3 ± 0.4	1.2 ± 0.3
5.7	0.94 ± 0.1	0.12 ± 0.02	1.7 ± 0.2	1 ± 0.2
6.9	1.05 ± 0.1	0.13 ± 0.02	2.6 ± 0.2	0.6 ± 0.2
9.2	0.63 ± 0.3	0.15 ± 0.05	2 ± 0.6	0.4 ± 0.2
11	0.81 ± 0.1	0.09 ± 0.02	1.5 ± 0.3	0.7 ± 0.3
11	0.71 ± 0.07	0.13 ± 0.02	1.4 ± 0.1	0.5 ± 0.1
12	0.84 ± 0.1	0.16 ± 0.03	1.6 ± 0.3	1.8 ± 0.3
12	0.9 ± 0.15	0.18 ± 0.04	2 ± 0.3	1.4 ± 0.2
14	0.65 ± 0.08	0.15 ± 0.03	2.2 ± 0.4	0.2 ± 0.1
20	0.64 ± 0.09	0.17 ± 0.02	1.3 ± 0.2	0.8 ± 0.2
22	0.52 ± 0.06	0.12 ± 0.02	1 ± 0.1	0.8 ± 0.2
24	0.5 ± 0.08	0.14 ± 0.03	1.5 ± 0.6	1 ± 0.3
27	0.56 ± 0.17	0.23 ± 0.07	1.1 ± 0.1	1.3 ± 0.4
40	0.35 ± 0.07	0.23 ± 0.1	0.9 ± 0.2	–
49	0.33 ± 0.08	0.24 ± 0.04	0.87 ± 0.2	–
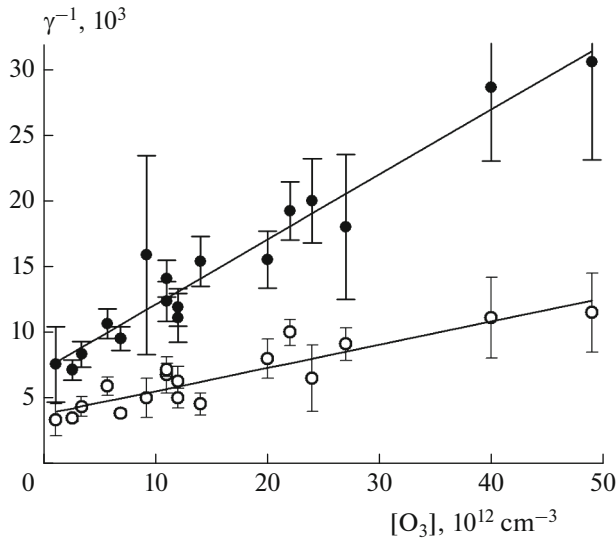
Fig. 4. Dependence of parameters γ_r and γ_s of the time-dependent uptake coefficient of O$_3$ on a methane soot coating preexposed to N$_2$O$_5$ on [O$_3$]: solid characters, γ_r, rapid uptake stage (scale 1 : 1); hollow symbols, γ_s, the subsequent slow stage (vertical scale 1 : 10). Solid straight lines are approximations by formula (5) with parameters $\gamma_{r,\,max}$, $K_{L,\,r}$, $\gamma_{s,\,max}$, $K_{L,\,s}$ from Table 2.

Ozone consumption under the conditions of the competitive adsorption of O$_3$/NO$_x$, taking into account the two-stage uptake process, will be determined by the set of reactions

$$O_3\,(g) + z_r\,(s) \rightleftarrows O_3 \ldots z_r\,(s)$$
$$\xrightarrow{k_{r,O_3}} z_{s,O_3}\,(s) + O_2\,(g), \tag{R2}$$

$$NO_x\,(g) + z_r\,(s) \rightleftarrows NO_x \ldots z_r\,(s)$$
$$\xrightarrow{k_{r,NO_x}} z_{s,NO_x}^{mod}\,(s) + Product\,1\,(g), \tag{R3}$$

$$O_3\,(g) + z_{s,O_3}\,(s) \rightleftarrows O_3 \ldots z_{s,O_3}\,(s)$$
$$\xrightarrow{k_{s,O_3}} z_{fin,O_3}\,(s) + O_2\,(g), \tag{R4}$$

$$O_3\,(g) + z_{s,NO_x}^{mod}\,(s) \rightleftarrows O_3 \ldots z_{s,NO_x}^{mod}\,(s)$$
$$\xrightarrow{k_{r,O_3}^{mod}} z_{s,O_3}^{mod}\,(s) + O_2\,(g), \tag{R5}$$

$$O_3\,(g) + z_{s,O_3}^{mod}\,(s) \rightleftarrows O_3 \ldots z_{s,O_3}^{mod}\,(s)$$
$$\xrightarrow{k_{s,O_3}^{mod}} z_{fin,O_3}^{mod}\,(s) + O_2\,(g), \tag{R6}$$

$$NO_x\,(g) + z_{s,NO_x}^{mod}\,(s)$$
$$\rightleftarrows NO_x \ldots z_{s,NO_x}^{mod}\,(s) \tag{R7}$$
$$\xrightarrow{k_{s,NO_x}} z_{fin,NO_x}^{mod} + Product\,2\,(g),$$

$$O_3\,(g) + z_{fin,NO_x}^{mod}\,(s)$$
$$\rightleftarrows O_3 \ldots z_{fin,NO_x}^{mod}\,(s) \tag{R8}$$
$$\xrightarrow{k_{r,O_3}^{mod}} z_{s,O_3,NO_x}^{mod}\,(s) + O_2\,(g),$$

$$O_3\,(g) + z_{s,O_3,NO_x}^{mod}\,(s)$$
$$\rightleftarrows O_3 \ldots z_{s,O_3,NO_x}^{mod}\,(s) \tag{R9}$$
$$\xrightarrow{k_{s,O_3}^{mod}} z_{fin,O_3,NO_x}^{mod}\,(s) + O_2\,(g).$$

Here the subscripts r and s denote the rapid and slow uptake stages, respectively. The subscripts O$_3$ and NO$_x$ for the symbol z denote the surface density of centers z
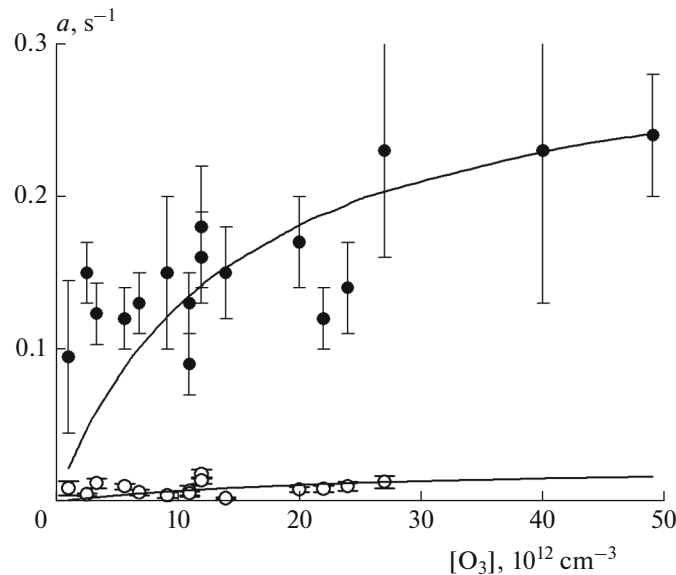

Fig. 5. Dependence of parameters a_r and a_s of time-dependent uptake coefficient O$_3$ on a methane soot coating preexposed to N$_2$O$_5$ on [O$_3$]: solid characters, a_r, rapid uptake stage; hollow symbols, a_s, the subsequent slow stage. Solid curves are approximation by formula (6) with parameters k_r, k_s, $K_{L,\,r}$, and $K_{L,\,s}$ from Table 2.

Table 2. Elementary parameters that determine by formulas (5), (6) the time-dependent uptake coefficient of O_3, N_2O_5 and NO_2 on methane soot

Adsorbate/Adsorbent	First, rapid stage			Second, slow stage		
	$K_{L,r}$, 10^{-14} cm^3	k_r, s^{-1}	$\gamma_{r,\,max}$, 10^{-4}	$K_{L,s}$, 10^{-14} cm^3	k_s, 10^{-2} s^{-1}	$\gamma_{s,\,max}$, 10^{-5}
O_3/fresh soot [18]	7 ± 1	0.39 ± 0.05	6.6 ± 0.4	11 ± 2	2.8 ± 0.1	13 ± 2
N_2O_5/fresh soot [20]	0.66 ± 0.15	0.84 ± 0.05	0.55 ± 0.1	0.7 ± 0.4	10 ± 0.6	1.4 ± 0.1
NO_2/fresh soot [19]	5.7 ± 0.7	0.22 ± 0.02	1.6 ± 0.2	6.3 ± 1.7	2.6 ± 0.3	2.1 ± 0.3
O_3/soot after treatment of N_2O_5	6.9 ± 1	0.3 ± 0.02	1.4 ± 0.2	4.7 ± 1	2.5 ± 0.4	2.7 ± 0.3
O_3/soot after treatment of NO_2 [19]	3.5 ± 1	0.2 ± 0.06	1.5 ± 0.2	3.0 ± 0.8	2.0 ± 0.5	2.2 ± 0.5

occupied by the adsorbed O_3 or NO_x molecules. The subscripts O_3 and NO_x for parameter k denote the rate constant of the monomolecular decomposition of the corresponding surface center z containing the adsorbed O_3 or NO_x molecule. The superscript *mod* denotes the process that occurs on the modified surface as a result of treatment with a competing reagent. Reaction (R1) is not included in the scheme presented above, since it proceeds without changing the chemical activity of the adsorption centers and does not affect the additional uptake of ozone.

The consumption of ozone from the gas phase is determined by its uptake on the surface

$$-V_R \frac{d}{dt}[O_3] = \frac{\gamma(t)c_{O_3}}{4}[O_3]S_{ef},$$

with the uptake coefficient $\gamma(t)$ expressed in terms of the reaction flows,

$$\gamma_{O_3}(t) = 4[J_{R2}(t) + J_{R4}(t) + J_{R5}(t) \\ + J_{R6}(t) + J_{R8}(t) + J_{R9}(t)]/c_{O_3}[O_3]. \quad (8)$$

The reaction flows $J_{R2}(t)$ and $J_{R4}(t)$ represent the sink of ozone in reactions (R2) and (R4) according to the mechanism of the monomolecular decomposition of the corresponding surface complex

$$J_{R2}(t) = k_{r,O_3}\theta_{r,O_3}[z_r(t)], \\ J_{R4}(t) = k_{s,O_3}\theta_{s,O_3}[z_{s,O_3}(t)], \quad (9)$$

taking into account the fraction of the surface occupied by adsorbed ozone molecules under conditions of competitive adsorption. An expanded representation of these surface fractions is given in the Appendices.

The reactive flows $J_{R5}(t)$, $J_{R6}(t)$, $J_{R8}(t)$, and $J_{R9}(t)$ are responsible for the additional sink of ozone in the corresponding reactions on the heterogeneous uptake products of the competing reagent gas. In this case, the sink channel according to reactions (R5) and (R8) is the rapid uptake stage, and the sink channel according to reactions (R6) and (R9) is the repeated slow stage of the ozone uptake at the same adsorption centers:

$$J_{R5}(t) = k_{r,O_3}^{mod}\theta_{r,O_3}^{mod}\left[z_{s,NO_x}^{mod}(t)\right], \\ J_{R6}(t) = k_{s,O_3}^{mod}\theta_{s,O_3}^{mod}\left[z_{s,O_3}^{mod}(t)\right], \\ J_{R8}(t) = k_{r,O_3}^{mod}\theta_{r,O_3}^{mod}\left[z_{fin,NOx}^{mod}(t)\right], \\ J_{R9}(t) = k_{s,O_3}^{mod}\theta_{s,O_3}^{mod}\left[z_{s,O_3,NO_x}^{mod}(t)\right]. \quad (10)$$

The reactive flows depend on the surface density $[z_i(t)]$ of these centers. The surface density of the latter is determined from the solution of a system of differential equations describing their temporal evolution

$$-\frac{d}{dt}[z_r] = (k_{r,O_3}\theta_{r,O_3} + k_{r,NO_x}\theta_{r,NO_x})[z_r],$$

$$-\frac{d}{dt}[z_{s,O_3}] = k_{s,O_3}\theta_{s,O_3}[z_{s,O_3}] - k_{r,O_3}\theta_{r,O_3}[z_r],$$

$$-\frac{d}{dt}\left[z_{s,NO_x}^{mod}\right] = (k_{r,O_3}^{mod}\theta_{r,O_3}^{mod} + k_{s,NO_x}\theta_{s,NO_x}^{mod})\left[z_{s,NO_x}^{mod}\right] \\ - k_{r,NO_x}\theta_{r,NO_x}[z_r],$$

$$-\frac{d}{dt}\left[z_{s,O_3}^{mod}\right] = k_{s,O_3}^{mod}\theta_{s,O_3}^{mod}\left[z_{s,O_3}^{mod}\right] - k_{r,O_3}^{mod}\theta_{r,O_3}^{mod}\left[z_{s,NO_x}^{mod}\right],$$

$$-\frac{d}{dt}\left[z_{fin,NO_x}^{mod}\right] \\ = k_{r,O_3}^{mod}\theta_{r,O_3}^{mod}\left[z_{fin,NO_x}^{mod}\right] - k_{s,NO_x}\theta_{s,NO_x}^{mod}\left[z_{s,NO_x}^{mod}\right],$$

$$-\frac{d}{dt}\left[z_{s,O_3,NO_x}^{mod}\right] \\ = k_{s,O_3}^{mod}\theta_{s,O_3}^{mod}\left[z_{s,O_3,NO_x}^{mod}\right] - k_{r,O_3}^{mod}\theta_{r,O_3}^{mod}\left[z_{fin,NO_x}^{mod}\right],$$

with the initial conditions

$$[z_r(t=0)] = [z_0], \, [z_{s,O_3}(t=0)] = [z_{s,NO_x}^{mod}(t=0)] = \\ [z_{s,O_3}^{mod}(t=0)] = [z_{fin,NO_x}^{mod}(t=0)] = [z_{s,O_3,NO_x}^{mod}(t=0)] = 0.$$

Here $[z_0]$ is the maximum surface density of the active centers for the given type of surface.

After solving this system of equations and substituting the obtained values $[z_i(t)]$ into expression (8), we obtain an explicit form of the ozone uptake coefficient for the entire set of adsorption centers. The uptake coefficient $\gamma(t)$ of ozone without taking into account its uptake on the heterogeneous reaction products of a
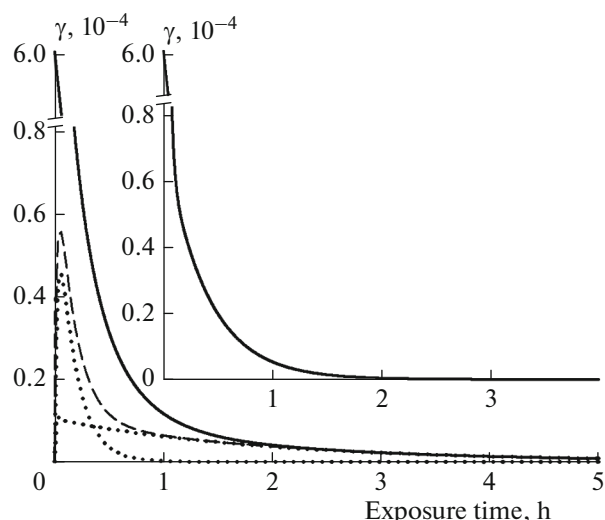
Fig. 6. Time dependence of the uptake coefficient of O$_3$ on a methane soot coating, modeled under conditions of competitive adsorption of O$_3$ and NO$_2$ at their typical concentrations in the troposphere: [O$_3$] = 10 ppb, [NO$_2$] = 17 ppb. The solid curve is the total uptake rate $\gamma(t)$ taking into account competitive adsorption; the dashed curve is the contribution due to the uptake of O$_3$ only on centers z_{s,NO_2}, formed during the uptake of the competing agent NO$_2$; dotted curves are the contributions of the primary and secondary stages of O$_3$ uptake at these centres. The inset shows the time dependence of the uptake coefficient O$_3$ without taking into account its uptake on the centers z_{s,NO_2}.

competing reagent is expressed by formula (4) with the parameters

$$\gamma_r = \frac{\gamma_{r,max}}{1 + K_{L,r,O_3}[O_3] + K_{L,r,NO_x}[NO_x]},$$

$$\gamma_s = \frac{\gamma_{s,max}}{1 + K_{L,s,O_3}[O_3] + K_{L,s,NO_x}[NO_x]}$$

$$\times \frac{k_{r,O_3}\theta_{r,O_3}}{k_{r,O_3}\theta_{r,O_3} + k_{r,NO_x}\theta_{r,NO_x}},$$

$$a_r = k_{r,O_3}\theta_{r,O_3} + k_{r,NO_x}\theta_{r,NO_x}, \quad a_s = k_{s,O_3}\theta_{s,O_3}.$$

The analytical expressions for the contributions to the uptake coefficient, taking into account reactions (R5), (R6), (R8), and (R9), are quite cumbersome and are presented in the Appendices.

An example of modeling the value of the time-dependent ozone uptake coefficient under the conditions of the competitive adsorption of O$_3$/NO$_2$ is shown in Fig. 6. The dependence corresponds to the ratio of the average monthly concentrations of these reagent gases measured in the lower troposphere of an industrialized region in winter, when the ozone concentration is minimal [8]. As can be seen from Fig. 6, taking into account the additional ozone sink channel increases the processing time of the soot substrate. The integral contribution of this channel under conditions specified in the caption to Fig. 6 is 68% of the main sink channel according to reactions (R2) and (R4). At the typical summer monthly averages, 36 ppb O$_3$ and 17 ppb NO$_2$ measured in the same region, the

contribution of additional ozone sink channels will be about 20%.

At the average monthly concentration of NO$_2$ of 17 ppb, the equilibrium of NO$_3$ + NO$_2$ $\leftrightarrow$ N$_2$O$_5$ shifts to the right. At the same time, [N$_2$O$_5$]/[NO$_3$] $\approx$ 20; i.e., the N$_2$O$_5$ concentration compared to NO$_3$ is maximum and is ~4 ppb [4]. Even at this maximum concentration of N$_2$O$_5$ and its minimum monthly average of 10 ppb [O$_3$], the additional ozone sink channel under the conditions of the competitive adsorption of [O$_3$]/[N$_2$O$_5$] turns out to be just 3.6%. The main reason for such a small effect of the N$_2$O$_5$ reagent is the small fraction of the surface occupied by its adsorbed molecules. At low concentrations of N$_2$O$_5$, this fraction, $\theta_{N_2O_5}$, is just equal to K_{L,N_2O_5}[N$_2$O$_5$], based on its definition by formula (A.1). Table 2 shows that K_{L,N_2O_5} is an order of magnitude smaller than the similar parameters for the other reagent gases.

CONCLUSIONS

The uptake of a reactive gas on the surface is due to a chemical reaction involving its adsorbed molecules. The fraction of the surface occupied by adsorbed molecules under conditions of competitive adsorption in the Langmuir representation is determined below by formulas (A.1). Under the conditions of a troposphere at low concentrations of O$_3$ and NO$_x$, i.e., at K_{L,O_3}[O$_3$] $\ll$ 1 and K_{L,NO_x}[NO$_x$] $\ll$ 1, this fraction is equal to K_{L,O_3}[O$_3$] and does not depend on the presence of a competing reagent gas.

In fact, it turns out that as a result of the uptake of the competing reagent gas, a chemically active surface is formed, on which the uptake of ozone is also possible. Thus, there is an additional channel of its runoff, which was not previously taken into account. In order to quantify the contribution of this channel, we studied the uptake of ozone on the surface of soot pretreated with N_2O_5 until the complete cessation of the uptake of the latter. The uptake mechanism is established and a number of elementary parameters are obtained, which make it possible to model the value of the uptake coefficient at arbitrary ozone concentrations.

Based on the Langmuir representation of adsorption, a model description of the uptake on a soot coating under conditions of the competitive adsorption of O_3/NO_x, $NO_x = NO_2$, and N_2O_5, taking into account the multistage uptake process, is proposed. Based on the developed model and elementary parameters describing the uptake of O_3, NO_2, and N_2O_5 on a fresh soot coating, as well as the ozone uptake on a surface pretreated with NO_2 or N_2O_5, additional ozone uptake channels were numerically estimated for two real tropospheric scenarios of the O_3/NO_2 and O_3/N_2O_5 concentration ratios. In the lower troposphere of an industrialized region during winter, when the ozone concentration is minimal (10 ppb O_3, 17 ppb NO_2, and 4 ppb N_2O_5), the additional integral contribution to the uptake of O_3 on reaction products NO_2 is 68%; and in the case of N_2O_5, 3.6%. For the same region in summer, at the maximum ozone concentration (36 ppb O_3, 17 ppb NO_2, and 4ppbN_2O_5), the analogous contributions will be 20 and 1%, respectively. The estimates obtained show that for a number of scenarios, an additional runoff channel, which was not previously taken into account, can be significant.

APPENDIX A

Fractions of the surface occupied by the adsorbed ozone and NO_x molecules under the conditions of their competitive adsorption are expressed by the formulas

$$\theta_{r,O_3}$$
$$= K_{L,r,O_3}[O_3]/(1 + K_{L,r,O_3}[O_3] + K_{L,r,NO_x}[NO_x]),$$
$$\theta_{s,O_3}$$
$$= K_{L,s,O_3}[O_3]/(1 + K_{L,s,O_3}[O_3] + K_{L,s,NO_x}[NO_x]),$$
$$\theta_{r,O_3}^{mod}$$
$$= K_{L,r,O_3}^{mod}[O_3]/\left(1 + K_{L,r,O_3}^{mod}[O_3] + K_{L,s,NO_x}[NO_x]\right),$$
$$\theta_{s,O_3}^{mod} \hspace{3cm} (A.1)$$
$$= K_{L,s,O_3}^{mod}[O_3]/\left(1 + K_{L,s,O_3}^{mod}[O_3] + K_{L,s,NO_x}[NO_x]\right),$$
$$\theta_{r,NO_x} = K_{L,r,NO_x}[NO_x]/(1 + K_{L,r,O_3}[O_3]$$
$$+ K_{L,r,NO_x}[NO_x]),$$
$$\theta_{s,NO_x}^{mod} = K_{L,s,NO_x}[NO_x]/(1 + K_{L,s,O_3}^{mod}[O_3]$$
$$+ K_{L,s,NO_x}[NO_x]).$$

Here the Langmuir coefficients K_L with subscripts r and s for the respective reagent gas O_3 or NO_x, and with the superscript character mod, are taken from Table 2.

APPENDIX B

The explicit form of the contributions to the ozone uptake coefficient on the soot coating under conditions of the competitive adsorption of O_3/NO_x on the reaction products of the competing gas-reagent is determined by the expressions

$$\gamma_{R5}(t) = \frac{\gamma_{r,max}^{mod}}{1 + K_{L,r,O_3}^{mod}[O_3] + K_{L,s,NO_x}[NO_x]} \frac{\left[z_{s,NO_x}^{mod}(t)\right]}{[z_0]},$$

$$\gamma_{R6}(t) = \frac{\gamma_{s,max}^{mod}}{1 + K_{L,s,O_3}^{mod}[O_3] + K_{L,s,NO_x}[NO_x]} \frac{\left[z_{s,O_3}^{mod}(t)\right]}{[z_0]},$$

$$\gamma_{R8}(t) = \frac{\gamma_{r,max}^{mod}}{1 + K_{L,r,O_3}^{mod}[O_3] + K_{L,s,NO_x}[NO_x]} \frac{\left[z_{fin,NO_x}^{mod}(t)\right]}{[z_0]},$$

$$\gamma_{R9}(t) = \frac{\gamma_{s,max}^{mod}}{1 + K_{L,s,O_3}^{mod}[O_3] + K_{L,s,NO_x}[NO_x]} \frac{\left[z_{s,O_3,NO_x}^{mod}(t)\right]}{[z_0]}.$$

Here $\gamma_{r,max}^{mod}$ and $\gamma_{s,max}^{mod}$ are the initial values of the ozone uptake coefficient from Table 2 for the rapid (index r) and slow (index s) uptake stage on the modified surface. Surface densities $[z_i(t)]$ are substituted either from the analytical solution of the system of differential equations given above or from its numerical solution in the Mathcad environment at the given concentrations of the competing reagent gases.

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