Chemical reactions in the troposphere

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Primary gas-phase chemical reactions initiated by the solar radiation in the troposphere are briefly reviewed. Besides, the paper reviews investigations of photo-induced heterogeneous chemical processes occurring on the surface of the main phase components of tropospheric solid aerosols. It is proposed to divide these processes into groups that differ by the absorption of radiation quanta. Based on this division it is possible to separate and define such experimentally observed processes as photoadsorption, photocatalytic reactions, interaction of gas-phase molecules with the solid-body surface under exposure to radiation quanta, and surface photochemical reactions.

Introduction

In spite of significant concentration of molecular oxygen in the gas phase in the troposphere, the tropospheric conditions, in the absence of solar radiation, do not favor oxidation of tropospheric trace gases (CO, SO_2, nitrogen oxides, H_2S, various hydrocarbons, etc.) even in the case that there are aerosol particles in the troposphere, which can serve catalysts in the oxidation process. In the presence of solar radiation, the situation drastically changes, since radiation quanta initiate many gas-phase and heterogeneous reactions. This paper reviews briefly the processes of initiation of tropospheric chemical reactions by the solar radiation.

Light-initiated gas-phase chemical reactions in the troposphere

The solar radiation is the driving force of chemical reactions in the troposphere. Transmitted through the stratospheric ozone layer is only solar radiation with the wavelength $\lambda > 300$ nm. Gases that are present in the troposphere in the largest amounts (see the Table) do not absorb such radiation and, consequently, cannot be activated. The effect of photochemical reactions in this spectral region of solar radiation in the troposphere for gases that are present in very low amounts (less than 1 ppb) on the chemistry of the troposphere is insignificant, and therefore it is not considered in this paper. Among the trace gases (concentrations ~10 ppb), photochemically active ones are the ozone and nitrogen dioxide (Table), and the concentration of the latter at air pollution can achieve 100 ppb (Ref. 1). The concentration profiles of O_3 in unpolluted areas are depicted in Fig. 1. The concentration profiles for other atmospheric gases can be found in the Internet (http://atmos.iao.ru).

Content of gases in unpolluted atmosphere, according to Refs. 1–9

Gas	Concentration, mol·cm^{-3}, % or fractions		Atmospheric lifetime
Gases present with the highest concentrations			
N_2	$2 \cdot 10^{19}$	78%	10^6 years
O_2	$5 \cdot 10^{18}$	21%	$5 \cdot 10^3$ years
H_2O	$<6 \cdot 10^{17}$	<2%	10 days
CO_2	$9 \cdot 10^{15}$	330 ppm	4 years
Gases absorbing solar radiation in the troposphere			
O_3	10^{11}	10 ppb	–
NO_2	$3 \cdot 10^9$	0.3 ppb	4 days
CH_2O	10^9–10^{10}	0.1–1 ppb	5–10 days
Gases causing acid rains			
NO	10^9	0.1 ppb	4 days
SO_2	10^8–10^9	0.01–0.1 ppb	3–7 days
Gases leading to formation of smog			
Hydrocarbons (without methane and formaldehyde)	$<10^{10}$	<1 ppb	–
CH_4	$4 \cdot 10^{13}$	1.5 ppb	3.6 years
Radicals			
OH	$7 \cdot 10^5$		–
HO_2	$2 \cdot 10^7$		–
$O(^1D)$	1 in 100 cm^3		–

Anthropogenic pollution of the troposphere with nitrogen dioxide is largely related to oxidation of molecular nitrogen and nitrogen monoxide by air oxygen in high-temperature processes (burning, volcanic activity, lightings). The background content of ozone in the troposphere, in its turn, is caused by its formation in the stratosphere and, probably, by the following slow diffusion into the troposphere. In the atmosphere polluted by nitrogen monoxide, the interaction of NO with ozone additionally increases the concentration of nitrogen dioxide. This reaction is the main one in the troposphere in the absence of solar radiation (nighttime). In the presence of solar radiation (daytime) photochemical reactions of ozone and nitrogen dioxide dissociation occur in the troposphere.

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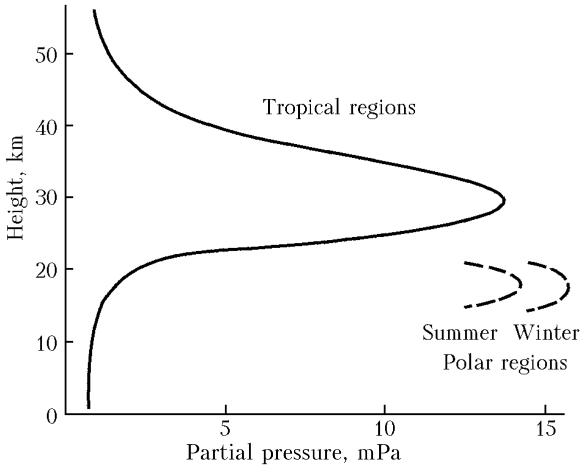

Fig. 1. The profile of ozone concentration in an unpolluted atmosphere according to the data from Ref. 3.

Under the effect of radiation having different wavelength from the solar spectrum in the troposphere the following ozone photodissociation reactions take place[2]:

$$O_3 \rightarrow O(^3P) + O_2(^3\Sigma_g^-),\ \lambda < 1180\ \text{nm} \quad (1)$$

$$\rightarrow O(^3P) + O_2(^1\Delta_g),\ \lambda < 611\ \text{nm} \quad (2)$$

$$\rightarrow O(^3P) + O_2(^1\Sigma_g^+),\ \lambda < 463\ \text{nm} \quad (3)$$

$$\rightarrow O(^1D) + O_2(^3\Sigma_g^-),\ \lambda < 411\ \text{nm} \quad (4)$$

$$\rightarrow O(^1D) + O_2(^1\Delta_g),\ \lambda < 310\ \text{nm}. \quad (5)$$

The maximum absorption cross section in the region near 600 nm is equal to $4.89 \cdot 10^{-21}\ \text{cm}^2$, and the quantum yield for reaction (5) is 0.90.

Photodissociation of nitrogen dioxide in the troposphere occurs under the effect of quanta with the wavelengths $300 < \lambda < 398$ nm by the sole reaction[2]:

$$NO_2 \rightarrow NO + O(^3P),\ \lambda < 398\ \text{nm}. \quad (6)$$

The maximum absorption cross section at 400 nm is $6.76 \cdot 10^{-19}\ \text{cm}^2$ and the quantum yield is about 0.69.

Formation of oxygen atoms at photodissociation of ozone and nitrogen dioxide leads to secondary reactions and production of radicals, whose concentration in an unpolluted atmosphere is given in the Table. The main secondary reaction is the interaction of atomic oxygen in the singlet D state, which is the product of reactions (4) and (5), with the water molecule yielding formation of the hydroxyls:

$$O(^1D) + H_2O \rightarrow 2\ OH. \quad (7)$$

The effect of hydroxyls on the chemistry of the troposphere is significant[3–7] and can be illustrated by the following reactions:

(a) formation of the nitric acid:

$$OH + NO_2 \rightarrow HNO_3, \quad (8)$$

(b) formation of sulfuric acid (oxidation of SO_2):

$$2OH + SO_2 \rightarrow H_2SO_4, \quad (9)$$

(c) interaction with methane:

$$OH + CH_4 \rightarrow CH_3 + H_2O, \quad (10)$$

(d) formation of hydroperoxide radical:

$$OH + O \rightarrow HO_2, \quad (11)$$

(e) formation of a strong oxidizer – hydrogen peroxide:

$$OH + OH \rightarrow H_2O_2, \quad (12)$$

(f) formation of hydrogen atoms:

$$OH + CO \rightarrow CO_2 + H. \quad (13)$$

Formation of strong oxidizers (H_2O_2 and HO_2) in reactions (11) and (12) leads to oxidation of hydrocarbons with the following production of peroxide compounds in the troposphere polluted with car exhausts and to formation of smog.[3,7,8] Besides, peroxide compounds oxidize nitrogen monoxide, and the ozone concentration increases, since ozone is no longer consumed for oxidation of nitrogen monoxide.

Thus, initiation of the gas-phase chemical reactions in the troposphere is caused by the effect of solar radiation on ozone (unpolluted troposphere) and ozone and nitrogen dioxide (polluted troposphere).

Light-induced heterogeneous chemical reactions in the troposphere

The troposphere is polluted not only with various gaseous compounds, but also with particles of solid-state and liquid-droplet aerosol. Chemical reactions in the volume of liquid-droplet aerosol particles are similar to gas-phase reactions, differing only by the concentrations of liquid-phase reagents because of their different solubility in liquids.[9,10] In the presence of aerosol particles having a well-developed surface[11] and nearby the Earth's surface, chemical reactions by the radical mechanism become unlikely.[12] In the presence of solid particles of tropospheric aerosol, photoinduced reactions under the effect of solar radiation are possible on the particle surface.[13]

Photoinduced processes can be divided into groups with different radiation absorption processes determining the direction of chemical reactions on the surface of particles of solid-state tropospheric aerosol. This division allows us to separate and characterize experimentally observed photoinduced processes: photoadsorption, photocatalytic reactions, reactions of interaction of gas-phase molecules with the surface of solid-state aerosol under the effect of radiation, and surface photochemical reactions.

Photoadsorption

Photoadsorption is characterized by the formation of surface electron or hole centers after electron transport in a solid particle under the effect of radiation. The maximum coverage of the surface by photoadsorbed molecules does not exceed 0.1% of the surface monolayer.[14]

Photocatalysis

Photocatalytic reactions are characterized by the formation of free mobile electrons in the conduction band of solid particles and, simultaneously, free mobile holes in the valence band after absorption of radiation with the energy exceeding the width of the solid-body forbidden zone. Thus, at photocatalytic reaction of oxidation, the oxidized gas-phase tropospheric molecule (H_2, CO, NO, SO_2, hydrocarbons) interacts with surface lattice oxygen at the moment of its discharge by a free mobile hole.[15] In Ref. 16 it was confirmed experimentally that photocatalytic activity is inherent in metal oxides, the top level of whose valence zone is formed by 2*p* orbitals of oxygen (TiO_2, ZnO, SnO_2, PbO_2, etc.).

Particles of tropospheric aerosol may include, as a phase, metal oxides[17–19] that are photocatalysts for reaction of oxidation of various chemical compounds, including organic ones, by oxygen. Such catalysts include ZnO, SnO_2, TiO_2, In_2O_3, V_2O_5, MoO_3, WO_3, and ZrO_2 (Refs. 16, 20, and 21). In these reactions, hydrocarbons are oxidized to water and CO_2, while halogenhydrocarbons are oxidized to water, CO_2, and the corresponding acids (reaction of mineralization).

The tropospheric conditions (temperature, pressure, high oxygen concentration, solar radiation) favor photocatalytic reactions. Photocatalytic reactions have low activation energy, they proceed at low partial pressure of the oxidized gas, and quantum yields of the photocatalytic reactions can achieve 30% (Refs. 16, 20, and 21). As a result of these reactions, organic and halogenorganic substances are removed from the gas-phase troposphere, and CO, SO_2, and nitrogen oxides are oxidized.

Let us consider in a more detail some phase components of solid-state atmospheric aerosols that are semiconductor metals oxides.

ZnO

It is well-known that ZnO is the most active photoadsorbent and photocatalyst among all other metal oxides. Photoadsorption of oxygen and methane was observed under irradiation in the ZnO surface absorption band,[22] while photocatalytic oxidation of organic compounds and carbon monoxide was observed under irradiation in the intrinsic absorption band (see, for example, Refs. 16, 20, 21, and 23). The results in these papers were obtained after hard oxygen-vacuum treatment of oxides. Without such treatment, long consumption of oxygen from the gas phase was observed. This consumption was likely associated with oxidation of adsorbed organic compounds.[24] In such a state (untreated), a large amount of water and carbon dioxide is present on the oxide surface.[25]

According to Ref. 25, the maximum amount of oxygen and methane photoadsorbed on the surface of zinc oxide and making up 0.01% of the surface monolayer was obtained at mixing of powdery zinc oxide.

Photoadsorption of CO and CO_2 on ZnO is observed as well, but it is too low.[26]

TiO_2

Powdery titanium dioxide is the most stable and most studied photocatalyst for both liquid- and gas-phase photocatalytic oxidation. Note that for TiO_2 the photoadsorption and photocatalysis processes are observed mostly in the intrinsic absorption band of titanium dioxide, and the quantum yield of these processes can be 1% and higher.[27–29] The maximum amount of photoadsorbed molecules achieves 0.01% of the TiO_2 surface monolayer.[25] In the initial state (before oxygen-vacuum treatment) the adsorbed layer of TiO_2 contains both carbon dioxide and significant amount of water.[30,31] Without oxygen-vacuum treatment and under irradiation in the oxygen atmosphere, oxygen consumption from the gas phase to oxidation of adsorbed organic compounds is observed.[16] The presence of such compounds on the TiO_2 surface with platinum leads to their dehydrogenation and emission of hydrogen (observed, for example, in Pt/TiO_2 suspended in 1N H_2SO_4, Ref. 32).

Sensitizing TiO_2 to the visible light in water-organic suspensions of TiO_2 after adsorption of organic or metal-complex dyes on its surface is known quite well. For example, on TiO_2 with platinum such sensitizing leads to photocatalytic dehydrogenation of organic compounds in the visible spectral region.[33–35]

SnO_2

In the initial state, the SnO_2 surface contains adsorbed water, which can be completely removed after warming at 473 K, as well as hydroxyl groups and carbonates.[36] After hard oxygen-vacuum treatment, photoadsorption of O_2, as well as H_2 and CH_4, is observed on stannic dioxide.[27] Photoadsorption activity is observed in the intrinsic absorption band of stannic dioxide along with the photocatalytic oxidation of carbon monoxide[16,37] and ammonia.[38] The quantum yields of these processes achieve 4% for O_2 photoadsorption and 10% for the photocatalytic oxidation of CO.[14,16]

For metal oxides that do not absorb the tropospheric solar radiation, the possibility of taking part in photoadsorption and photocatalytic processes is connected with the possibility of sensitizing of such metal oxides due to the formation of adsorption or surface layers under tropospheric conditions. Such sensitizing by adsorbed or surface compounds was observed for stannic dioxide at photoadsorption of oxygen and nitrogen monoxide on the surface of SnO_2 (Ref. 39). In Ref. 39 it was shown that stannic dioxide is sensitized by surface carbonates formed after adsorption of carbon monoxide.

Fe_2O_3

Among the oxides considered in this paper, ferric oxide is the only oxide having the catalytic activity already at the temperature of 373 K, for example, in the reaction of oxidation of carbon monoxide.[40] However, ferric oxide has no photocatalytic properties, at least, in photocatalytic oxidation of carbon monoxide, hydrocarbons, and ammonia.[16,38] The absence of photocatalytic activity of ferric oxide in the reactions of oxidation is connected with the fact that the upper level of the valence band is formed by $3d$-orbitals of Fe, rather than by $2p$-orbitals of oxygen, as in photocatalysts – semiconductor metal oxides.[15,16]

Photoinduced processes on dielectric oxides – main components of solid particles of the tropospheric aerosol

Destructive photosorption of halogen containing organic compounds observed in Refs. 15 and 41 is likely an example of a photoinduced reaction from the group of reactions, in which the gas-phase molecules interact with the surface of metal oxides. As a result, such an interaction causes replacement of the lattice oxygen of metal oxide by the halogen atom of the gas-phase halogenhydrocarbon molecule.

Dielectric oxides (SiO_2, Al_2O_3, MgO, CaO) have no photocatalytic activity in the spectral region of solar radiation in the troposphere.[37,38,42] Their intrinsic absorption bands are in the wavelength range shorter than 200 nm (Ref. 13), while the photocatalytic activity is connected with the formation of mobile electrons and, simultaneously, mobile holes at absorption of radiation by a solid body (intrinsic absorption of a solid body). This gives grounds to believe that when the photocatalytic activity is observed for natural materials, such as sand, chalk, volcanic ash, etc., this means that natural materials contain trace amounts of metal oxides being good photocatalysts in the visible region of solar radiation (for example, TiO_2, ZnO, SnO_2) (Refs. 7 and 41).

Significant photoadsorption of different gases on the dielectric oxides after hard oxygen-vacuum treatment was observed at irradiation by light with the wavelengths shorter than 300 nm. This follows from the spectral dependence of photoadsorption of O_2, H_2 and CH_4 and photodecomposition of N_2O on SiO_2, Al_2O_3, MgO, and CaO (Refs. 14 and 43). However, the amount of photoadsorbed molecules for dielectric oxides, as well as for semiconductor metal oxides, does not exceed 0.1% of the surface monolayer.[14]

Note that the processes of photoadsorption on oxide components of solid-state tropospheric aerosols, as well as photocatalytic oxidation, not only affect the concentration of the main components, but also can lead to clearing of the atmosphere from polluting halogen-containing hydrocarbons, such as freons.

Photoadsorption of some freons on the surface of MgO without oxygen-vacuum treatment was studied in Refs. 41 and 44. The oxide surface in this state contains largely water, carbon dioxide, and nitrogen oxides.[45] The studies were conducted with halogen-containing hydrocarbons of the methane and ethane series under conditions close to the tropospheric ones.

Irradiation of the MgO surface in this state leads to complete photoadsorption of halogen-containing organic compounds up to the hydrocarbon partial pressure of less than 10^{-6} Torr. At photoadsorption of freons by small portions (initial pressure of 10^{-2} Torr), the total amount of photoadsorbed halogen-containing hydrocarbon exceeds 10% of the surface monolayer of magnesium oxide. This is a significant difference between photoadsorption (from here on, photosorption) of halogen-containing hydrocarbons and photosorption of oxygen, hydrogen, and methane on magnesium oxide after oxygen-vacuum treatment. As a result of such a treatment, the coverage by photoadsorbed molecules does not exceed 0.1% of the magnesium oxide surface monolayer.[46]

Calcium oxide after residence in the atmospheric air (under tropospheric conditions) transforms into calcium hydroxidecarbonate, whose characteristics with respect to halogen-containing organic compounds are similar to the characteristics for magnesium oxides stored under tropospheric conditions for a long time. As an example, Figs. 2 and 3 show the spectral dependences of the effective quantum yield of photosorption of 134a freon on MgO and CaO stored in air for a long time. The photosorption activity of such oxides with respect to freon 134a is observed for radiation at wavelengths shorter than 400 nm, as well as the absorption of MgO and CaO stored in air for a long time.

Conducting freon photosorption in the presence of dried (by blowing through a trap cooled by fluid nitrogen) air only slightly changes the quantum yield of photoadsorption of freon on CaO and the shape of the action spectrum (Fig. 4). It is interesting to note that photoadsorption of oxygen from air in this case has a red boundary of the action spectrum near 360 nm (Fig. 4), as well as photoadsorption of oxygen on CaO after hard oxygen-vacuum treatment.[43]

Photosorption (photodestruction) of halogen containing organic compounds on magnesium and calcium oxides after long storage in air has an irreversible character: photosorbed compounds cannot be desorbed at heating of sorbents up to 620 K. Halogen containing products of decomposition of photosorbent compounds are not observed in the gas phase as well.

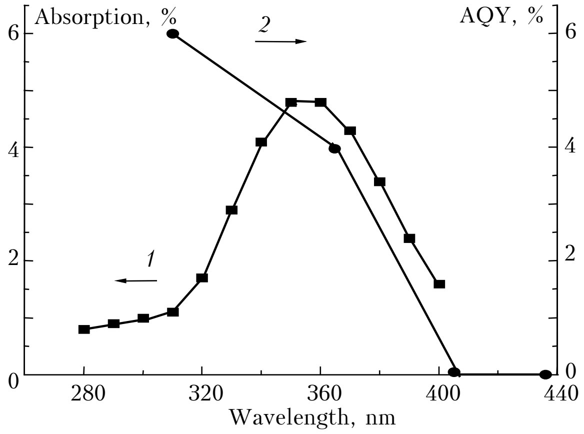

Fig. 2. Spectra of diffuse reflection (*1*) and absolute quantum yield (AQY) of photosorption of freon 134a on MgO stored in air for a long time (*2*) according to the data of Ref. 15.

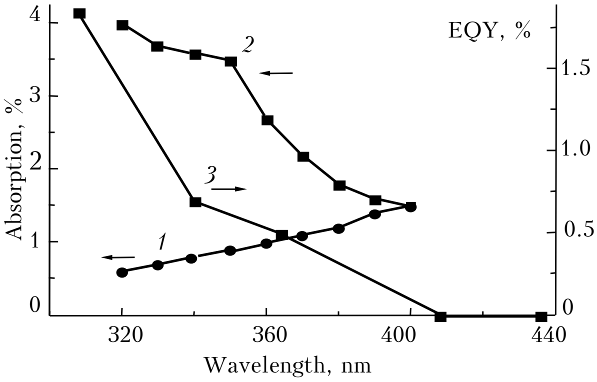

Fig. 3. Spectrum of diffuse reflection of CaO after high-temperature oxygen-vacuum treatment (*1*) and spectra of diffuse reflection (*2*) and effective quantum yield (EQY) of photosorption of freon 134a (*3*) for CaO after long air storage (according to the data of Ref. 15).

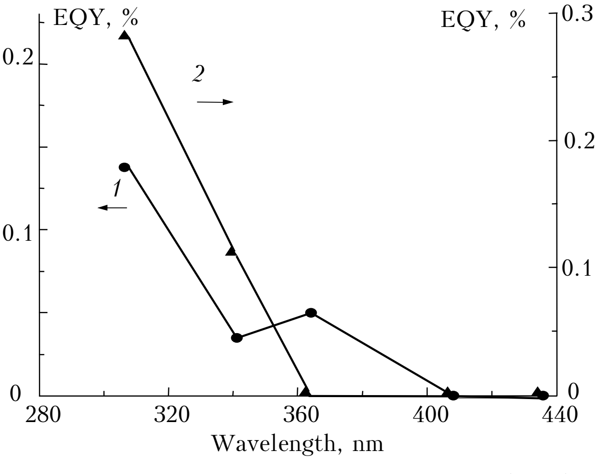

Fig. 4. Spectra of effective quantum yield (EQY) of photosorption of freon 134a in the presence of air (*1*) and photoadsorption of oxygen (*2*) for CaO stored in air for a long time (according to the data of Ref. 47).

To estimate quantitatively the efficiency of photosorption in clearing of the atmosphere from organic and halogen containing organic compounds under the effect of solar radiation in the troposphere, it is needed to determine spectral dependences of the quantum yield of photosorption under close-to-tropospheric conditions. By now, such experiments were conducted for magnesium and calcium oxides.[44,45,47] For natural materials (sand, chalk, dust, soot, volcanic ash) the activity in destruction (degradation) of organic compounds was studied under the exposure to nonmonochromatic radiation.[48–50] The activity in these photoinduced processes on natural materials was far lower than that for magnesium and calcium oxides, as well as for the reactions of photocatalytic oxidation on semiconductor metal oxides.

Surface photochemical reactions

Surface photochemical reactions occur after absorption of radiation by compounds adsorbed on the surface of solid-body particles as they transform into the excited reactive state.[51] An example of such a reaction is photodecomposition of nitrous oxide adsorbed on the surface of magnesium oxide.[14,52] The surface in this case plays the role of a “carrier” (substrate), changing the energy of excited state of the adsorbed compound, or the role of a stabilizer of the adsorbed compound in the state different from the state of molecules in the gas phase, for example, for such compounds as CO_3 complex, OH groups, etc.

Conclusion

The solar radiation has an initiative effect on the main chemical reactions in the troposphere. The solar radiation with $\lambda < 300$ nm in the ozone layer of the atmosphere initiates the reaction of photodissociation of molecular oxygen with the following formation of longer-lived, but reactive (first of all, with respect to nitrogen monoxide) ozone. The solar radiation with wavelength longer than 300 nm initiates ozone decomposition with production of highly reactive, with respect to water, atomic oxygen in the $O(^1D)$ state and photodissociation of ozone and nitrogen dioxide producing atomic oxygen in the ground state $O(^3P)$.

Another important effect of solar radiation in the troposphere is the initiation of heterogeneous chemical reactions caused by absorption of radiation by some phase components of solid-body aerosol particles: dielectric oxides (main components of the tropospheric aerosol) and semiconductor metal oxides. Photoinduced heterogeneous reactions favor clearing of the gas phase of the troposphere from many polluting chemical compounds.

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