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Destructive Photosorption of Halogen-Containing Organic Compounds by the Components of Solid Atmospheric Aerosol under Tropospheric Conditions

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Abstract

The results of investigation of the interaction of halogen-containing organic compoungs (HOCs) with magnesium, aluminium and silicon oxides of industrial and laboratory preparation in the dark and under the action of sunlight in the troposphere are presented. The chemical composition of these oxides corresponds to the main components of solid atmospheric aerosol. The experimental results are the evidence that fluorine- and chlorine-containing organic compounds containing also hydrogen atoms are destructively photosorbed on MgO exposed for a long time in the air, magnesium halides being formed as a result of photosorption. The rate of photosorption for fluorine-containing hydrocarbons is several times higher than that for chlorine-containing hydrocarbons. The amount of hydrochlorofluorocarbons (HCFCs) photosorbed at room temperature and pressure of 1 Pa can exceed 15 % of the monolayers of MgO surface. The interaction of magnesium oxide with HCFCs leads to their removal from the atmospheric air under tropospheric conditions till the residual HCFC pressure less than 10^{-6} Pa. The obtained results are the evidence of the substantial contribution of photoprocesses on MgO surface into the removal of the mentioned HCFCs from the gas phase of the troposphere.

INTRODUCTION

Chemical composition of the Earth's atmosphere can be stabilized at a life-safe level as a result of processes that occur on the surface of solid tropospheric aerosol particles under the action of sunlight [1]. In particular, these processes may result in a decrease in concentrations of gases able to deplete the ozone layer of the atmosphere, to cause the greenhouse effect, to worsen the quality of drinking water. It is extremely important to use those organic compounds in industry and for household purposes which would be efficiently transformed under the tropospheric conditions as a result of destruction, adsorption, or oxidation by the oxygen of the air into hazardless compounds, for example CO_2, H_2O or solid chlorine- or fluorine-containing metal compounds included in the particles of solid tropospheric aerosol [2]. It is an important problem to establish the list of organic compounds which undergo destruction on the surface of aerosol.

Solid aerosol of the continental part of Siberia is represented mainly by the continental aerosol composed of soil and rock particles. These particles are exposed to the action of the gas phase of the atmosphere, water, they coagulate with the solid particles emitted by the industry and transport, forest fire products, *etc.* As a result, the composition and state of the initial solid particles are transformed; the longer do they stay in the troposphere, the more substantial are these changes. The latter circumstance leads to more complications of the complicated phase composition of solid aerosol particles [3]. This makes difficulties for investigation of the interaction of the gas phase of the atmosphere with the solid aerosol of the troposphere, since aerosol particles contain large number of various chemical compounds.

The main initial components of continental aerosol particles are quartz and metal oxides, simple oxides such as iron, aluminium, magnesium, titanium oxides, as well as complex oxides, such as silicates or spinels [4]. Magnesium and aluminium oxides are formed in the troposphere also as a result of forest fires or spaceship launching [3, 5].

In the present work, we report the investigation of the interaction of magnesium, aluminium, and silicon oxides obtained in industry and under laboratory conditions, with halogen-containing organic compounds in the dark and under the action of light under conditions close to the atmospheric ones. These processes may occur in the troposphere and help removing halogen-containing organic pollutants.

EXPERIMENTAL

Commercial MgO of "ch.d.a." grade (analytically pure) (Reakhim, State Standard 4226−75), γ-Al_2O_3 (A_2 class, Technical Specifications 38.10190−80) and SiO_2 corresponding to the "os.ch." grade (specially pure) of laboratory preparation were used; the specific surface was 10, 150, and 500 m^2/g, respectively. The oxides were placed in water suspension onto the inner wall of a cylindrical quartz reactor and dried in the air at room temperature for one week.

The reactor with the oxide was soldered to a high-vacuum set-up through a U-tube which was cooled during experiments to 173 K, and evacuated at room temperature. Thus, conditions were created for water vapour to be always present in the reactor with oxide, and on the surface of oxide. Water vapour did not get into the high-vacuum (measuring) part of the set-up, which allowed us to measure small (in comparison with water vapour) concentration of HOCs and products desorbed from the surface of oxide during the dark and photo adsorption of HOCs.

TABLE 1

Mass numbers of the most intensive peaks of the fragmentary cations of halogen-containing compounds used in the investigation

Compound	Mass	Fragmentary cation
$CHCl_3$ (chloroform)	35	Cl^{35}
$CHFCl_2$ (Freon 21)	67	$CHFCl^{35}$
CHF_2Cl (Freon 22)	51	CHF_2
CF_2Cl_2 (Freon 12)	50	CF_2
CHF_3 (Freon 23)	51	CHF_2
CF_4 (Freon 14)	69	CF_3
$CF_3{-}CH_2F$ (Freon 134a)	33	CH_2F
$CF_2Cl{-}CCl_2F$ (Freon 113)	31	CF
$CH_2Cl{-}CH_2Cl$ (dichloroethane)	28	C_2H_4
$CCl_3{-}CH_3$ (trichloroethane)	26	C_2H_2

The state of the oxide surface resulting from long-range exposure of the oxide to real atmospheric conditions at room temperature and the above-described treatment below will be referred to as the standard state of the oxide surface.

The amount of HOCs in the reaction volume was determined with Pirani gage and mass spectrometer using one of the most intensive peaks in the mass spectrum of HOCs. Masses of these peaks for all the HOCs used in the investigation are listed in Table 1.

The UV irradiation of the MgO surface was performed with an OSL-1 lighter for luminescence microscopes with DRSh-250 mercury lamp, water heat filter and UFS filter with transmittance band from 270 to 390 nm. To separate monochromatic radiation, interference filters were used.

The diffuse reflection spectra in the infrared region of the spectrum were recorded in the air with the FTIR-8300 PC spectrophotometer of Shimadzu company (Japan) and DRS-800 attachment before and after experiments with high-vacuum set-up.

RESULTS AND DISCUSSION

Magnesium oxide

Magnesium oxide naturally occurs in small amounts as periclase; its hydrated form brucite $Mg(OH)_2$ is more widespread [4].

TABLE 2

Amount of HOC molecules (*N*) adsorbed on 0.7 g MgO exposed under real atmospheric conditions for a long time, in the dark at 300 K and HOC pressure of 1 Pa

HOC	θ*, %	*N*	Products desorbed during dark adsorption of HOC
Methane series:			
$CHCl_3$ (chloroform)	0.1	10^{13}	CO_2, $\theta > 10$ %
$CHFCl_2$ (Freon 21)	1	10^{14}	CO, $\theta \sim 10^{-2}$ %
CF_2Cl_2 (Freon 12)	$<10^{-3}$	$<10^{11}$	–
CHF_2Cl (Freon 22)	1	10^{14}	CO, $\theta \sim 10^{-2}$ %
CHF_3 (Freon 23)	0.1	10^{13}	–
CF_4 (Freon 14)	$<10^{-3}$	$<10^{11}$	–
Ethane series:			
CCl_3-CH_3 (trichloroethane)	0.1	10^{13}	CO_2, $\theta \sim 0.1$ %
CH_2Cl-CH_2Cl (dichloroethane)	0.1	10^{13}	CO_2, $\theta \sim 0.1$ %
$CF_2Cl-CCl_2F$ (Freon 113)	$<10^{-3}$	$<10^{11}$	–
CF_3-CH_2F ((Freon 134a)	$<10^{-3}$	$<10^{11}$	–

*Coverage degree of the MgO surface.

Dark adsorption. It was reported in [6] that the surface of MgO exposed in the air (in troposphere) for a long time and deposited according to the above-described procedure onto reactor wall contains nearly a monolayer of hydrogen-containing compounds (water, hydroxyl groups), carbon-containing compounds (carbonates, CO_2 and CO) ~10 % of monolayer, and nitrogen-containing compounds up to 1 % of monolayer. The presence of the adsorbed layer of such a composition on the surface of magnesium oxide leads to changes in the adsorption ability of the surface with respect to HOCs.

According to our data, dark adsorption of HHCs on magnesium oxide with the surface state formed under tropospheric conditions is small and does not exceed 1 % of monolayer of magnesium oxide surface (Table 2). Hydrogen-containing Freon compounds of methane series (Freon 21 and 22) behave similarly both in covering the MgO surface by adsorbed molecules during the attainment of the equilibrium pressure of ~1 Pa, and in evolving a small amount of CO after the adsorption of these compounds in the dark.

The kinetics of dark adsorption of Freon 21 and 22 is shown in Fig. 1 when a mixture of these compounds at a molar ratio of 4 : 1. After the quasi-equilibrium pressure of these compounds is established in the gas phase, their slow adsorption occurs, accompanied by the evolution of CO and N_2O into the gas phase (see also [7]).

According to our data, trichloroethane in amount of about 1 % of monolayer is partially irreversibly adsorbed in the dark on MgO heated in vacuum at 750 K. However, on MgO with the standard surface state, trichloroethane

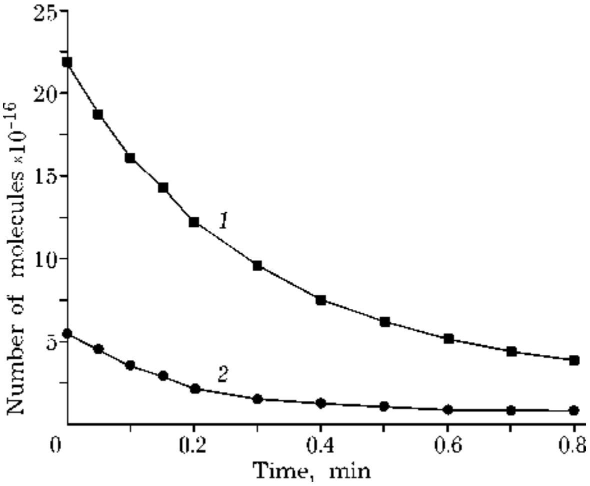

Fig. 1. Kinetics of dark adsorption of Freon 21 (*1*) and Freon 22 (*2*) on magnesium oxide from a mixture of these Freons at a temperature of ~300 K and total pressure 4 Pa (recorded by mass spectrometer using the changes in the amplitude of peaks of the 67 (Freon 21) and 51 (Freon 22) masses.

TABLE 3

Rates of HOC photoadsorption ($V_{p.a}$) and/or simultaneous photodesorption ($V_{p.d}$) from the surface of 0.7 g MgO exposed under real atmsopehric conditions at T = 300 K (irradiated through a UFS filter at the HOC pressure of ~1 Pa)

HOC	$V_{p.a}$, molecules/s	$V_{p.d}$, molecules/s	Compounds desorbed during irradiation
Methane series:			
$CHCl_3$ (chloroform)	$<2 \cdot 10^{13}$	10^{15}	NO, N_2
$CHFCl_2$ (Freon 21)	10^{14}	$6 \cdot 10^{14}$	N_2O, NO, N_2
CF_2Cl_2 (Freon 12)	$<10^{11}$	10^{14}	2NO + N_2
CHF_2Cl (Freon 22)	$8 \cdot 10^{13}$	$6 \cdot 10^{14}$	N_2O, NO, N_2
CHF_3 (Freon 23)	$6 \cdot 10^{13}$	$4 \cdot 10^{14}$	NO, N_2, CF_2O
CF_4 (Freon 14)	$<10^{11}$	–	2NO + N_2
Ethane series:			
CCl_3–CH_3 (trichloroethane)	$3 \cdot 10^{13}$	$4 \cdot 10^{14}$	N_2O, NO, N_2
CH_2Cl–CH_2Cl (dichloroethane)	~0	$3 \cdot 10^{14}$	NO, N_2
CF_2Cl–CCl_2F (Freon 113)	$<10^{11}$	–	2NO + N_2
CF_3–CH_2F (Freon 134a)	$4 \cdot 10^{14}$	–	NO, N_2, N_2O
Irradiation in vacuum	–	10^{14}	2NO + N_2

is adsorbed to a substantially smaller extent (~0.1 % of monolayer). Carbon dioxide is evolved into the gas phase in approximately equimolar amount with respect to the adsorbed trichloroethane.

Even larger amount of CO_2 is released in the dark adsorption of chloroform at room temperature. When chloroform is adsorbed at a level of ~0.1 % of monolayer, the amount of carbon dioxide evolved into the gas phase corresponds to more than 10 % of the monolayer of MgO surface.

Photosorption. Irradiation of MgO surface in the standard state in the presence of ~1 Pa of halogen-containing hydrocarbon in the gas phase, or in vacuum, is accompanied mainly by the desorption of nitrogen-containing compounds into the gas phase (Table 3). The initial presence of nitrogen-containing compounds on MgO surface after keeping magnesium oxide in the air is linked with adsorption of nitrogen oxides present in the atmospheric air. During irradiation in vacuum, mainly a mixture 2NO + N_2 is evolved from MgO surface (see also [6]); the same takes place when MgO is irradiated in the atmosphere containing HOCs which are not photosorbed on MgO surface in its standard state. These HOCs include Freons 12, 14, and 113 which do not contain hydrogen atoms. In the presence of halogen-containing hydrocarbons that are photosorbed on MgO surface, the rate of photodesorption of NO+N_2 mixture from MgO surface increases substantially. For example, when irradiated in the presence of Freon 22 (1 Pa), the effective quantum yield of photodesorption of the 2NO + N_2 mixture and N_2O from MgO surface at 365 nm increases by an order of magnitude, compared to the quantum yield of photodesorption of 2NO + N_2 mixture under irradiation in vacuum (Fig. 2). The amount of photodesorbing molecules also

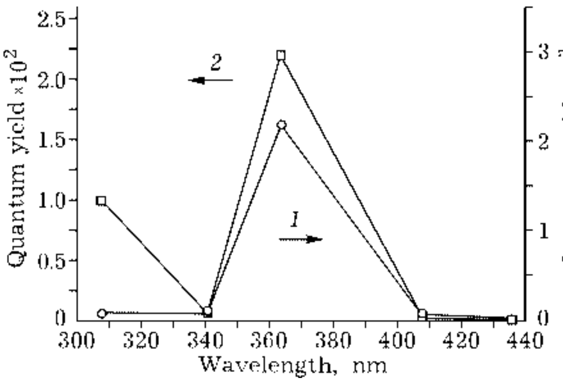

Fig. 2. Spectral dependence of effective quantum yield of photodesorption of 2NO + N_2 mixture on irradiation of magnesium oxide in vacuum (*1*), and a mixture of 2NO + N_2 with N_2O in the atmosphere of Freon 22 (*2*) (temperature: ~300 K; Freon 22 pressure: 1 Pa).

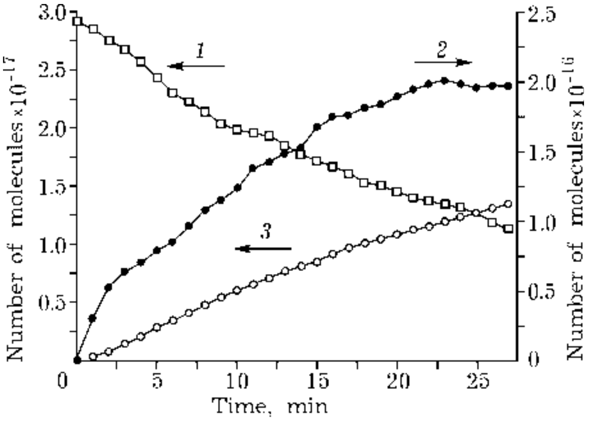

Fig. 3. Kinetics of photosorption of trichloroethane (*1*) on MgO surface, photodesorption of NO (*2*) and N_2O (*3*) from MgO surface, measured with the amplitudes of A_{26}, A_{30}, and A_{44} peaks in the mass spectrum, for trichloroethane, NO and N_2O, respectively (temperature: ~300 K; initial pressure of trichloroethane: 4.6 Pa).

increases more than by an order of magnitude, compared to their amount during magnesium oxide illumination in vacuum.

Photodesorption kinetics for various HCFCs in the atmosphere is shown in Figs. 3 and 4. Under the conditions when a Freon to be photoadsorbed is present in the gas phase, the gas products evolved from MgO surface are observed to contain N_2O (it is not evolved during irradiation in vacuum). In addition, photodesorption of NO and N_2 is characterized by more rapid decrease in the process rate than photodesorption of N_2O; photosorption of HCFCs proceeds till it is completely consumed from the gas phase. So, this is the evidence that NO and N_2 are the products of N_2O decomposition during the photosorption HCFCs. This decomposition occurs at higher rate than the decomposition of N_2O under irradiation of MgO in vacuum or in the atmosphere of HOCs containing no hydrogen atoms (Freons 12, 14, and 113).

Photoinduced evolution of a mixture of nitrogen (II) oxide and molecular nitrogen at a constant ratio of 2 : 1 is the evidence of the presence of adsorbed nitrogen (I) oxide on MgO surface. This is due to prolonged contact of MgO with air in which a small amount of N_2O is always present (under stationary conditions, partial pressure of N_2O in the atmosphere is 0.1 Pa). The formation of nitrogen (I) oxide in the layer adsorbed on MgO is also possible as a result of adsorption of nitrogen (II) and (IV) oxides from the air. This allows assuming that the decompostion of nitrogen (I) oxide adsorbed on MgO surface occurs during its irradiation.

Similarly to the case of destructive photoadsorption of Freon 134a on magnesium oxide exposed to the atmospheric air for a long time [1], the spectrum of the action of photoinduced formation of nitrogen (II) oxide (see Fig. 2) and molecular nitrogen is also shifted to longer wavelengths, compared to the spectrum of the action of decomposition of N_2O on magnesium oxide subjected to rigid oxygen-vacuum treatment [8]. In the latter case, N_2O photodecomposition on MgO is observed at the wavelengths $\lambda < 260$ nm.

It is known that in the dark the decomposition of N_2O on a surface centre (for example, anionic vacancy) with captured electron (electron centre of the surface) occurs with the formation of N_2 in the gas phase and the adsorbed atomic oxygen. Electron centres on MgO surface, in turn, can be formed either by its chemical reduction or by irradiation with the light of wavelengths $\lambda < 260$ nm [9].

One can assume that photosorption of hydrogen-containing HCFCs leads to additional formation of the surface vacancies, most probably oxygen, in addition to those present on the surface of magnesium oxide in the standard state formed under tropospheric conditions, before UV irradiation. Additional oxygen vacan-

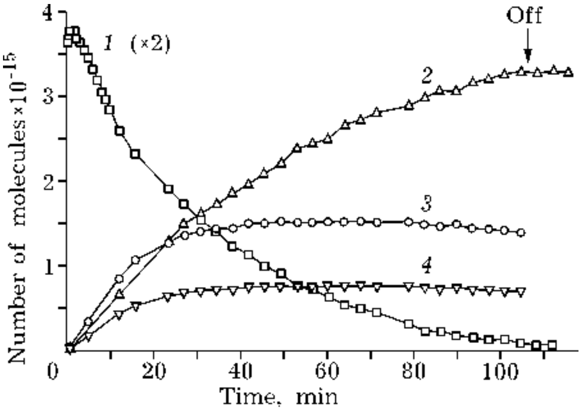

Fig. 4. Kinetics of photosorption of Freon 22 (*1*) and photodesorption of N_2O (*2*), NO (*3*) and N_2 (*4*) from MgO surface, measured with the amplitudes of A_{51}, A_{44}, A_{30}, and A_{28} peaks in the mass spectrum, for Freon 22, N_2O, NO and N_2, respectively (temperature: ~300 K; initial pressure of Freon 22: 4.6 Pa).

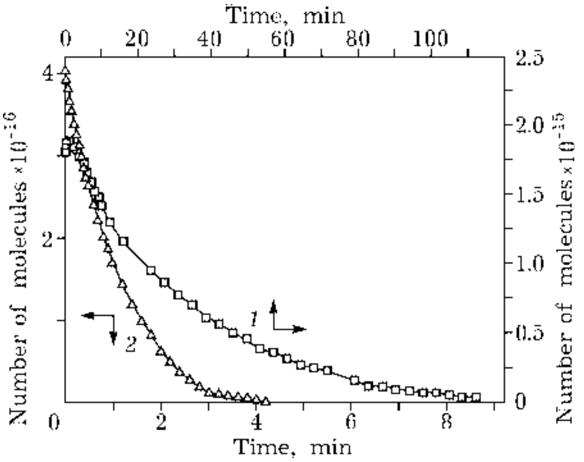

Fig. 5. Kinetics of photoadsorption of Freon 22 (*1*) and Freon 134a (*2*) on MgO (temperature: ~300 K; initial pressure of Freon 22: 1 Pa, Freon 134a: 2 Pa).

cies form additional number of surface centres on which nitrogen (I) oxide is decomposed and nitrogen (II) oxide is formed, for example according to the scheme reported in [6].

The irradiation of MgO surface with soft UV in the atmosphere of Freons containing hydrogen and fluorine atoms (Freons 21, 22, 23, and 134a) leads to their almost complete photosorption till the partial pressure of Freons less than 10^{-6} Pa. The kinetics of photoadsorption of Freon 22 and Freon 134a is shown in Fig. 5. If the Freons are repeatedly admitted after complete photoadsorption of Freons 21, 22, 23, and 24 under constant intensity of UV radiation, the total amount of photosorbed Freons can reach 15 % of monolayer of MgO surface.

It is interesting that HOCs containing hydrogen and chlorine atoms but not fluorine (chloroform, trichloroethane, dichloroethane) are photosorbed at lower rate than the HOCs containing fluorine and hydrogen. Photoadsorption of chlorine- and fluorine-containing organic compounds having no hydrogen atoms (Freons 12, 14, 113) is not observed.

It is necessary to note that during photosorption of trifluoromethane (CHF_3) in the gas phase CF_2O is formed. The latter fact is an additional confirmation that at the irreversible photosorption of HCFCs the oxygen of magnesium oxide lattice is substituted by fluorine atoms of Freon, in consistency with the initial assumption of [3, 10] for the photosorption of Freon 134a on magnesium oxide. An evidence of this fact is also the formation of C=O bonds (according to the data of IR spectroscopy, an increase in the intensity of the absorption band at 1715 cm^{-1} is observed) during photosorption of Freon 134a on MgO surface. In addition, after photosorption of Freon 134a on MgO in amount exceeding 10 % of the monolayer of its surface, the intensity of the IR absorption band of C−F bonds is very weak (absorption bands in the spectral regions 1823−1866 cm^{-1} and 2540−2641 cm^{-1}). This can also be the evidence in favour of the fact that C−F bonds on MgO surface are broken under the action of light, and Mg−F bonds are formed instead.

It was assumed in [1, 3] that a substantial coverage of MgO by photosorbed Freon 134a is conditioned by the formation of surface vacancies of oxygen during photosorption. These vacancies can be formed after the interaction of HCFCs with the surface oxygen of MgO lattice at the moment of its discharge by a free hole of the valence band. Because of this, the interaction of a halogen-containing hydrocarbon with magnesium oxide surface is not limited only by the interaction with the initial surface vacancies of oxygen in which an electron is transferred from the valence band of magnesium oxide after light absorption.

If photosorption of HCFs is performed after irradiating the MgO surface before HCFCs admission (conditions to observe the memory effect [11]), in spite of large initial rate of HCFCs photoadsorption (for Freon 134a, 10^{15} molecules/s), total amount of photoadsorbed HCFCs does not exceed ~0.1 % of monolayer, similarly to usual processes of photoadsorption of simple gases (O_2, H_2, CH_4) on MgO after rigid oxygen-vacuum treatment [12]. It is essential that in [11, 12], photoadsorption was performed after high-temperature oxygen and vacuum treatment of magnesium oxide. This causes the difference of the spectra of action of simple gas photoadsorption on MgO (radiation with $\lambda < 260$ nm is active) from the spectra of action of HCFs photoadsorption of MgO with standard state of surface formed under tropospheric conditions (radiation with $\lambda < 400$ nm is active) [10].

Thus, we can state that the real atmospheric conditions form specific state of magnesium oxide surface which is exhibited in broadening the spectrum of action of photoprocesses into the soft UV region corresponding to the sunlight spectrum in troposphere (λ > 300 nm).

Aluminium oxide (γ-Al_2O_3)

Aluminium oxide naturally occurs as corundum (α-Al_2O_3); its hydrated forms are also widespread: diaspore ($HAlO_2$), boehmite ($AlO(OH)$), and gibbsite ($Al(OH)_3$) [4].

We investigated the oxide form γ-Al_2O_3 with S_{sp} = 150 m^2/g obtained by thermal dehydration of gibbsite. A noticeable dark adsorption of HOCs and photoadsorption of HOCs on this aluminium oxide under irradiation with light in the spectral region 1100–200 nm are absent; so is the dark adsorption of NO.

Nevertheless, on this aluminium oxide in the dark, the adsorption of oxygen from dried air occurs: at the initial oxygen pressure in the gas phase 0.6 Pa, adsorption rate reached 1.6 10^6 molecules/(s cm^2). In the dark, also the adsorption of pure oxygen obtained by the decomposition of potassium permanganate in vacuum occurs. At the oxygen pressure in the gas phase 1.5 Pa, the rate of adsorption of this O_2 was 3.2 10^7 molecules/(s cm^2).

Under the action of irradiation on γ-A_2lO_3, the photoadsorption of oxygen is observed. The kinetics of oxygen photoadsorption from the dried air is shown in Fig. 6 (curve *1*). Photoadsorption of oxygen results in its complete removal from the gas phase till the pressure of <10^{-6} Pa.

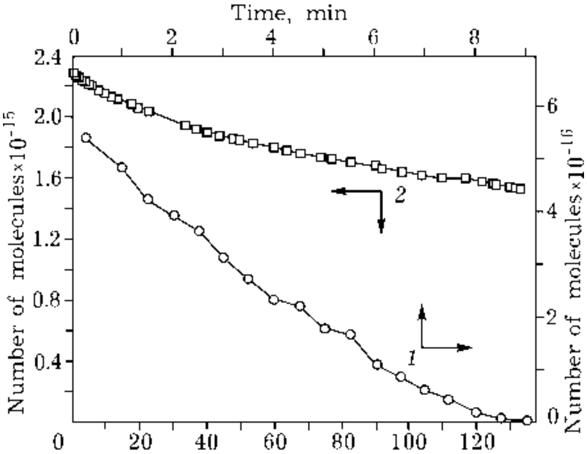

Fig. 6. Kinetics of oxygen photoadsorption under irradiation through a UFS filter: on γ-Al_2O_3 (*1*) and on SiO_2 (*2*): temperature, ~300 K; initial oxygen pressure: 0.6 (*1*) and 1 Pa (*2*).

Silicon oxide

In the continental natural aerosol, silicon oxide is present as quartz even more than aluminium oxide as corundum. The investigation of dark and photoinduced processes on silicon oxide with S_{sp} = 500 m^2/g gave the following results.

On admitting oxygen into the reaction volume, its dark adsorption on the surface of SiO_2 is observed; it stops after 12 min. At the initial oxygen pressure in the gas phase 1.5 Pa, the initial rate of dark adsorption was 1.5 10^6 molecules/(s cm^2).

Similarly to aluminium oxide, no noticeable photoadsorption of HHCs occurs on irradiation with the light within the whole investigated wavelength region from 1100 to 200 nm. Photoinduced adsorption of oxygen on the surface of silicon oxide at the oxygen pressure in the gas phase 2.5 Pa occurs at a noticeable rate which is $2 \cdot 10^{12}$ molecules/s under irradiation with the wavelength λ = 254 nm. Oxygen photoadsorption kinetics is shown in Fig. 6 (curve *2*).

CONCLUSIONS

The obtained experimental results show that fluorine- and chlorine-containing hydrocarbons possessing hydrogen atoms are destructively photo-adsorbed on MgO exposed for a long time in the air under the conditions close to those of the troposphere. Photoadsorption activity in this process is higher for the HCFCs containing fluorine; for chlorine-containing HCFCs, it is several times lower. The amount of photoadsorbed HCFCs can exceed 15 % of the monolayer of MgO surface. The interaction of magnesium oxide with HCFCs leads to their removal from the atmospheric air under tropospheric conditions till the residual pressure of less than 10^{-6} Pa (0.01 ppb). The obtained results are the evidence of a substantial contribution from photo-processes on MgO surface into the removal of the mentioned HCFCs from the gas phase of the troposphere.

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