

Chemical processes photoinduced on solid tropospheric aerosols

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Received November 27, 2001

Experimental results obtained indicate that organofluorine and organochlorine compounds containing hydrogen atoms experience destructive photosorption on MgO aged for a long time in air under conditions close to the tropospheric ones. The photosorption rate is higher for halogen-containing hydrocarbons (HCH) including fluorine while being several times lower for chlorine-containing hydrocarbons. The amount of photosorbed HCH at room temperature and at the pressure of 1 Pa can exceed 15% of MgO surface, that confirms the hypothesis of a substantial contribution of the photoprocesses on the MgO surface to removal of these HCH from the troposphere. The absence of photosorption activity with respect to HCH on γ -Al₂O₃ ($S_{sp} = 150 \text{ m}^2/\text{g}$) and SiO₂ ($S_{sp} = 500 \text{ m}^2/\text{g}$) is connected with the difference in crystallinity of the studied oxide powders.

The Earth's atmosphere can withstand numerous technogenic effects due to natural chemical processes in it.^{1,2} In particular, the chemical state of the atmosphere can stabilize at the biospherically safe level due to processes proceeding on the surface of aerosol particles in the troposphere under the exposure to solar radiation.³

Solid tropospheric aerosols in Central Siberia are mostly the continental aerosol consisting of soil and rock particles. These particles are subject to the effect of atmospheric gases and water; they coagulate with solid particles of industrial emissions, motor car exhausts, forest burning products, etc. As a result, the state and composition of the initial solid particles transform, and the longer they stay in the atmosphere, the stronger is this transformation.

This circumstance additionally complicates the complex phase composition of solid aerosol particles.⁴ This hampers the study of interaction between the gas phase of the atmosphere and the solid tropospheric aerosol, since aerosol particles contain large amount of different chemical compounds.

It is thought that the initial components of continental aerosol particles were formed under conditions of their long mineralization from high-temperature melts at high pressure in the process of the Earth's crust formation. For this reason, some main components of the solid aerosol are in the form of microcrystals of various minerals, such as quartz, corundum, silicates, etc.⁵

Under laboratory conditions, compounds with the chemical composition corresponding to some minerals, for example, quartz SiO₂ and corundum Al₂O₃ can be obtained and their effect on removal of gas pollutants from the atmosphere can be assessed.

In this paper, we present the results of studying the interaction of halogen-containing hydrocarbons

(HCH) with the surface of magnesium, silicon, and aluminum oxide powders having specific surface from 10 to 500 m²/g under conditions close to tropospheric during dark time and under the exposure to radiation with the spectrum corresponding to solar radiation in the troposphere.

Experimental technique

In the experiments we used industrial preparations of magnesium oxide qualified as p.f.a. (pure for analysis) and γ -Al₂O₃ of A-2 sort with the specific surface (S_{sp}) of, respectively, 10 and 150 m²/g. The silicon oxide was obtained at the Laboratory of Catalyst Preparation of the Institute of Catalysis SB RAS. The preparation corresponded to the qualification h.p. (high purity) and had the specific surface of 500 m²/g. All oxides from water suspension were applied on an inner wall of a cylindrical quartz reactor and dried in air at room temperature during a week.

After soldering to a high-vacuum setup, the reactor with a sample was pumped out at room temperature through a trap with a cooling mixture to decrease the rate of CO₂ emission from the oxide surface. After the oxide was aged for a long time under conditions of the actual atmosphere and subjected to the above processing, its surface acquired the state, which can be called the standard state of the oxide surface.

The amounts of HCH, dried air, oxygen, nitrogen oxides, and products of their interaction with the adsorbent surface in the reaction volume were determined by a Pirani manometer and a mass-spectrometer from the value of one of the most intense peaks at gas sampling through a leak valve.

Dark adsorption was conducted until establishment of the equilibrium pressure ~1 Pa in the reaction volume and then light was turned on. To irradiate the

MgO surface by UV, we used a light for OSL-1 luminescent microscopes with a DRSh-250 mercury lamp, a heat water filter, and an UFS filter (pass band from 270 to 390 nm). The total density of the radiation flux measured by an RTN-20S thermoelement was $\sim 1 \text{ mW/cm}^2$ with this filter.

The irradiation geometry, radiation intensity, and the area of the irradiated surface were kept constant for all the studied compounds. Interference filters were used to separate monochromatic radiation.

Spectra of diffuse reflection in the IR region were recorded in air using Shimadzu FTIR-8300 spectrometers with a DRS-8000 attachment before and after experiments in the high-vacuum setup.

Results and discussion

Magnesium oxide MgO

Natural magnesium oxide exists in small amounts as periclase mineral.⁵ It is produced in considerable amounts at forest fires.³ We have studied dark adsorption and photoadsorption of HCH on MgO with $S_{\text{sp}} = 10 \text{ m}^2/\text{g}$.

Dark adsorption of HCH

The presence of an adsorbed layer⁶ formed under the tropospheric conditions on the magnesium oxide surface leads to the change of the surface adsorptivity with respect to HCH as compared with MgO after high-temperature oxygen-vacuum processing. According to data from Table 1, methane hydrocarbons including no hydrogen atoms (CF_2Cl_2 and CF_4 – freons 12 and 14) are not adsorbed on the MgO surface at room temperature. Among ethane halogen-containing hydrocarbons, trifluorotrchloroethane containing no hydrogen and asymmetric tetrafluoroethane (freon 134a) do not adsorb.

Water-containing freons of the methane series: freons 21 and 22 (their chemical composition is given in Table 1) behave similarly in both coverage of the MgO surface by adsorbed molecules at establishment of the equilibrium pressure of 1 Pa and in emission of a small amount of CO after adsorption of these freons in the

dark. The amounts of chloroform and freon 23 adsorbed are ten times smaller.

According to our data, trichloroethane in the amount of $\sim 1\%$ of a surface layer is adsorbed on MgO heated in vacuum up to 750 K in the dark. However, much smaller amount of trichloroethane ($\sim 0.1\%$ of the surface layer) is adsorbed on MgO in the states standard for these experiments. As this occurs, carbon dioxide in the amount equimolar to the adsorbed trichloroethane is emitted in the gas phase.

Even larger amount of CO_2 is emitted at dark adsorption of chloroform at room temperature. At adsorption of $\sim 0.1\%$ of surface layer of chloroform, carbon dioxide in the amount corresponding to the surface coverage larger than 10% of the MgO surface layer is emitted in the gas phase.

Thus, dark adsorption of HCH on magnesium oxide with the surface state formed by the tropospheric conditions is small and does not exceed 1% of the MgO surface layer.

HCH photosorption

Irradiation of the MgO surface in the standard state in vacuum or in the presence of $\sim 1 \text{ Pa}$ gas-phase halogen-containing hydrocarbon is accompanied by desorption of mostly nitrogen-containing compounds into the gas phase (Table 2). At MgO irradiation in vacuum, its surface emits mostly the mixture $2\text{NO} + \text{N}_2$; the same occurs at MgO irradiation in the atmosphere of HCH not subject to photosorption on the MgO surface in the standard state. Such HCH include freons 12, 14, and 113 (see Table 1) including no hydrogen atoms. In the presence of halogen-containing hydrocarbons subject to photosorption on MgO, the rate of photodesorption of NO and N_2 from the MgO surface increases significantly. Thus, at irradiation of magnesium oxide in the presence of 1 Pa of freon 22, the effective quantum yield of photodesorption of the mixture $2\text{NO} + \text{N}_2$ at 365 nm increases by ten times as compared with the quantum yield of this mixture under irradiation in vacuum. The number of photodesorbed molecules also increases by more than ten times as compared with that at magnesium oxide irradiation in vacuum.

Table 1. Amount of HCH molecules (N) adsorbed in the dark at 300 K and HCH pressure of 1 Pa

HCH	θ , %	N , molecule	Products of dark adsorption
<i>Methane:</i>			
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)	$< 10^{-3}$	$< 10^{11}$	–
<i>Ethane:</i>			
$\text{CCl}_3\text{-CH}_3$ (trichloroethane)	0.1	10^{13}	CO_2 , $\theta \sim 0.1$
$\text{CH}_2\text{Cl-CH}_2\text{Cl}$ (dichloroethane)	0.1	10^{13}	CO_2 , $\theta \sim 0.1$
$\text{CF}_2\text{Cl-CCl}_2\text{F}$ (freon 113)	$< 10^{-3}$	$< 10^{11}$	–
$\text{CF}_3\text{-CH}_2\text{F}$ (freon 134a)	$< 10^{-3}$	$< 10^{11}$	–

Note. θ is the estimated coverage of the MgO surface.

Table 2. Rates of photoadsorption (v_{phad}) for HCH and (or) simultaneous photodesorption (v_{phd}) from the MgO surface at $T \sim 300$ K. Irradiation through UFS filter at HCH pressure ~ 1 Pa

HCH	v_{phad} , molecule·s ⁻¹	v_{phd} , molecule·s ⁻¹	Irradiation induced products
<i>Methane:</i>			
CHCl ₃ (chloroform)	$<2 \cdot 10^{13}$	10^{15}	NO; N ₂
CHFCl ₂ (freon 21)	10^{14}	$6 \cdot 10^{14}$	N ₂ O; NO; N ₂
CF ₂ Cl ₂ (freon 12)	$< 10^{11}$	10^{14}	2NO + N ₂
CHF ₂ Cl (freon 22)	$8 \cdot 10^{13}$	$6 \cdot 10^{14}$	N ₂ O; NO; N ₂
CHF ₃ (freon 23)	$6 \cdot 10^{13}$	$4 \cdot 10^{14}$	NO; N ₂ ; CF ₂ O
CF ₄ (freon 14)	$<10^{11}$	–	2NO + N ₂
<i>Ethane:</i>			
CCl ₃ –CH ₃ (trichloroethane)	$3 \cdot 10^{13}$	$4 \cdot 10^{14}$	N ₂ O; NO; N ₂
CH ₂ Cl–CH ₂ Cl (dichloroethane)	~ 0	$3 \cdot 10^{14}$	NO; N ₂
CF ₂ Cl–CCl ₂ F (freon 113)	$<10^{11}$	–	2NO + N ₂
CF ₃ –CH ₂ F (freon 134a)	$4 \cdot 10^{14}$	–	NO; N ₂ ; N ₂ O
<i>Irradiation in vacuum</i>	–	10^{14}	2NO + N ₂

The products of gas emission from the MgO surface under conditions that a photosorbing freon is in the gas phase include N₂O, which is not emitted at irradiation in vacuum. Besides, photodesorption of NO and N₂ is characterized by a faster decrease in the rate of the process than photodesorption of N₂O, and photosorption of HCH proceeds until its complete consumption from the gas phase. Consequently, NO and N₂ are the products of N₂O decomposition at photosorption of water-containing HCH. This decomposition occurs with higher rate than decomposition of N₂O at MgO irradiation in vacuum or in the atmosphere of HCH containing no hydrogen atoms (freons 12, 14, and 113).

It can be assumed that photosorption of water-containing HCH leads to the additional formation of surface vacancies (most probably, for oxygen) besides the existing ones on the magnesium oxide surface in the standard state formed by tropospheric conditions before the irradiation with the UV in vacuum.

Additional oxygen vacancies form extra surface centers, at which nitrous oxide is decomposed and nitrogen oxide is formed, for example, by the scheme given in Ref. 6.

Irradiation of the MgO surface with soft UV radiation in the atmosphere of freons containing hydrogen and fluorine atoms (freons 21–23 and 134a) leads to their almost complete photosorption down to the freon partial pressure of lower than 10^{-5} Pa. If freons 21–24 are repeatedly let in after their complete photosorption at a constant intensity of UV irradiation, then the total amount of irreversibly photosorbed freons can reach 10% of the MgO surface layer.

It is interesting that HCH containing hydrogen and chlorine, rather than fluorine, atoms (chloroform, trichloroethane, dichloroethane) are photosorbed at a lower rate as compared with that for HCH containing fluorine and hydrogen. Photoadsorption of fluorine-containing HCH including no hydrogen atoms (freons 12, 14, and 113) is not observed.

It should be noted that CF₂O is produced at photosorption of trifluoromethane (CHF₃) in the gas phase. This is an additional confirmation of the fact that oxygen of the MgO lattice is substituted, at irreversible adsorption of HCH, by fluorine atoms of freons, as was first supposed in Ref. 7 for photosorption of freon 134a on magnesium oxide. The formation of C=O bonds (according to the data of IR spectroscopy, the intensity of the absorption band in the region of 1715 cm^{-1} increases) at photosorption of freon 134a on the MgO surface also indicates this fact.

At the same time it was found that after photosorption of freon 134a on MgO in the amount exceeding 10% of its surface layer, the intensity of IR absorption lines from C–F bonds (absorption bands in the regions $1823\text{--}1866$ and $2540\text{--}2641\text{ cm}^{-1}$) becomes very low. This also may be an evidence that C–F bonds on the MgO surface destruct under the irradiation and Mg–F bonds are formed in their place.

In Refs. 3 and 4 it was assumed that significant coverage of MgO by photosorbed freon 134a is caused by the formation of surface oxygen vacancies in the process of photosorption. These vacancies can be formed after HCH interaction with surface oxygen of the MgO lattice during its discharge by a movable free vacancy of the valence band. Therefore, interaction of halogen-containing hydrocarbon with the MgO surface is not limited only to the interaction with the initial amount of surface oxygen vacancies, which are occupied by the electrons from the valence band of magnesium oxide at radiation absorption.

If HCH photosorption is conducted after irradiation of the MgO surface before HCH is let in (conditions for observation of the memory effect⁸), then, in spite of high initial rate of HCH photoadsorption (for freon 134a – 10^{15} molecule/s), the total amount of photoadsorbed HCH does not exceed $\sim 0.1\%$ of the surface layer, as for ordinary processes of photoadsorption of simple gases (O₂, H₂, CH₄) on MgO after hard oxygen-vacuum processing.⁹ It

is important that in Refs. 8 and 9 photoadsorption was conducted after high-temperature oxygen-vacuum processing of magnesium oxide. This leads to the difference in the action spectra of photoadsorption of simple gases on MgO (active radiation has $\lambda < 260$ nm) as compared with the action spectra of HCH photoadsorption on MgO with the standard state of the surface formed under the tropospheric conditions (active radiation has $\lambda < 400$ nm) (Ref. 7). Photoadsorption of NO is also observed on the MgO surface formed under the tropospheric conditions starting from the wavelength of 400 nm (Fig. 1).

Aluminum oxide γ -Al₂O₃

Aluminum oxide exists in the nature in the form of corundum mineral (α = Al₂O₃), and its hydrated forms diaspore (HAlO₂), boemite (AlO(OH)), and gibbsite (Al(OH)₃) are abundant as well.⁴

When studying γ -Al₂O₃ with $S_{sp} = 150$ m²/g, we found the absence of marked dark adsorption of NO. At the same time, photoadsorption of NO was observed, and its action spectrum is shown in Fig. 1. It is worth noting that the same, as for MgO, shift occurs of the red boundary of the action spectrum of NO photoadsorption toward longer waves as compared with NO photoadsorption on γ -Al₂O₃ after oxygen-vacuum processing (active radiation has $\lambda < 370$ nm) (Ref. 10).

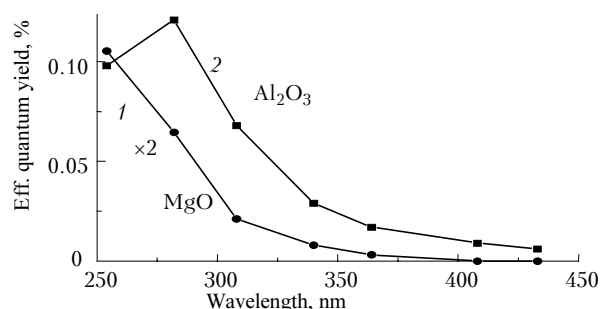


Fig. 1. Spectral dependence of the effective quantum yield of NO photoadsorption on MgO (1) and on γ -Al₂O₃ (2) after long effect of the actual atmosphere.

Adsorption of oxygen from the dried air on aluminum oxide occurs in the dark at a high rate: at the initial gas-phase oxygen pressure of 0.6 Pa the adsorption rate achieved $1.6 \cdot 10^6$ molecule·s⁻¹·cm⁻². The spectral dependence of the effective quantum yield of oxygen photoadsorption on γ -Al₂O₃ is shown in Fig. 2 (curve 1).

Adsorption of pure oxygen obtained from decomposition of potassium permanganate in vacuum was also observed in the dark. At the gas-phase oxygen pressure of 1.5 Pa, the rate of dark adsorption of O₂ was $3.2 \cdot 10^7$ molecule·s⁻¹·cm⁻². The spectral dependence of the effective quantum yield of oxygen photoadsorption on γ -Al₂O₃ is shown in Fig. 2 (curve 2) and Fig. 3 (curve 1) for the oxygen pressure of 1.5 and 2.5 Pa, respectively. The result of oxygen

photoadsorption is its complete removal from the gas phase down to the pressure $< 10^{-6}$ Pa.

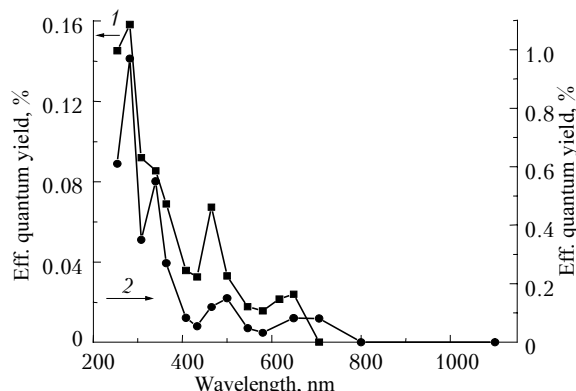


Fig. 2. Spectral dependence of the effective quantum yield of photoadsorption of oxygen from dried air (1) and oxygen (O₂ pressure of 1.5 Pa) obtained from decomposition of potassium permanganate (2) on γ -Al₂O₃ after long effect of the actual atmosphere.

For a comparison, Fig. 3 (curve 2) shows the action spectrum of O₂ photoadsorption on the γ -Al₂O₃ surface in the state obtained as a result of high-temperature oxygen-vacuum processing (the data are borrowed from Ref. 10).

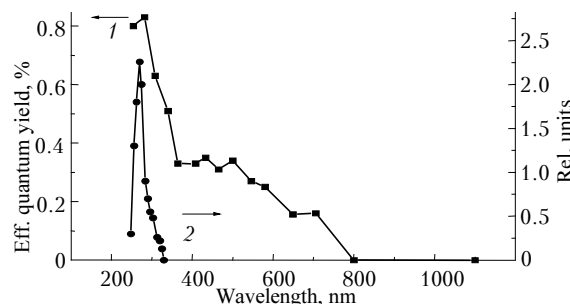


Fig. 3. Spectral dependence of the effective quantum yield of photoadsorption of oxygen (O₂ pressure of 2.5 Pa) obtained from decomposition of potassium permanganate on γ -Al₂O₃, aged in air for a long time (1) and on γ -Al₂O₃ after high-temperature oxygen-vacuum processing (2). The data for curve 2 were taken from Ref. 10.

Silicon oxide SiO₂

Natural continental aerosol contains much more silicon oxide in the form of quartz mineral than aluminum oxide in the form of corundum mineral. The study of dark and photoinduced processes on silicon oxide with $S_{sp} = 500$ m²/g gave the following results.

As oxygen is let in the reaction volume, its dark adsorption on the SiO₂ surface is observed. This dark adsorption terminates 12 min later. At the initial gas-phase oxygen pressure of 1.5 Pa, the initial rate of the dark adsorption was $1.5 \cdot 10^6$ molecule·s⁻¹·cm⁻².

As in the case with the aluminum oxide, we did not observe marked HCH photoadsorption on SiO₂ under the exposure to radiation in the entire studied wavelength range from 200 to 1100 nm. Photoinduced

oxygen adsorption on the silicon oxide surface at the gas-phase oxygen pressure of 2.5 Pa had rather high rate equal to $2 \cdot 10^{12}$ molecule \cdot s $^{-1}$ at irradiation by quanta with $\lambda = 254$ nm. The action spectrum of oxygen photoadsorption on SiO $_2$ is shown in Fig. 4.

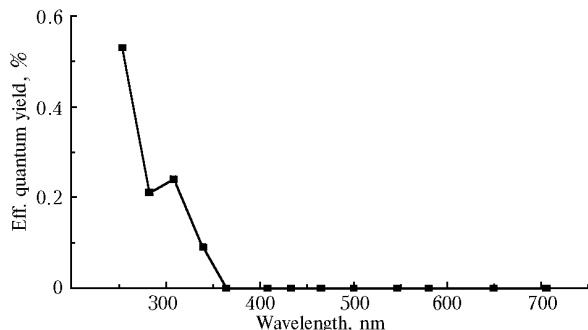


Fig. 4. Spectral dependence of the effective quantum yield of oxygen photoadsorption on fine SiO $_2$ after long effect of the actual atmosphere.

Thus, we can assert that the actual atmospheric conditions form a specific state of the surface of magnesium, aluminum, and silicon oxides, which manifests itself in broadening of the action spectrum of photoprocesses into the region of soft UV radiation corresponding to the solar radiation spectrum in the troposphere ($\lambda > 300$ nm). The absence of photoadsorption activity of γ -Al $_2$ O $_3$ and SiO $_2$ with respect to HCH photoadsorbed on magnesium oxide aged for a long time under actual atmospheric conditions can be explained within the framework of the mechanism proposed for photoadsorption of HCH containing hydrogen atoms.

According to the mechanism of freon photosorption proposed in Refs. 3 and 4, irradiation in the absorption region of the adsorbed layer leads to formation of a primary movable vacancy in the valence band of magnesium oxide. At a rather large size of insulator oxide microcrystals, a valence band with a continuous spectrum of occupied energy states is formed in it,¹¹ and, consequently, a vacancy formed at photoinduced electron transfer in the valence band can have the properties of a free movable vacancy. Magnesium oxide with the specific surface of 10 m 2 /g consists of rather large microcrystals ($> 1 \mu\text{m}$), and free vacancies are formed in its valence band. Quartz with the specific surface of 500 m 2 /g has no crystalline particles (according to the data of X-ray phase analysis). The main part of γ -Al $_2$ O $_3$ with the specific surface of 150 m 2 /g also does not consist of microcrystals with linear dimensions sufficient for the formation of a valence

band favoring formation of free vacancies. Hence, it follows that the observed considerable differences in the destructive photoadsorption activity with respect to halogen-containing organic compounds for the studied samples are likely connected not only with the chemical nature of the oxide, but also with different degree of crystallinity, that is, the amount and dimensions of microcrystals in oxide powders.

A considerable part of the continental aerosol in the troposphere consists largely of crystalline silicate and quartz microparticles. It can be thought that in this case the photoadsorption activity with respect to, at least, water-containing HCH should be observed. The literature data^{12–14} show that effective photoinduced processes with participation of organic, in particular, halogen-containing compounds are actually observed on particles of coastal or desert sand. Thus, for example, TiO $_2$, ZnO, and Fe $_2$ O $_3$ oxides contained in sand particles^{3,4} have pronounced photocatalytic properties in reactions of oxidation of organic compounds in the region of solar radiation spectrum in the troposphere. This increases the probability that such natural materials can be active in photoinduced processes with the participation of HCH.

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