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Photoadsorption and Photocatalytic Processes Affecting the Composition of the Earth's Atmosphere: II. Dark and Photostimulated Adsorption of Freon 22 (CHF_2Cl) on MgO

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Abstract—The interaction of hydrogen-containing Freon 22 (CHF_2Cl) with the surface of MgO that was held in air both before and after heating at 620 K in the dark or under exposure to soft UV radiation, which corresponded to the solar spectrum in the troposphere, is examined. Up to 1% of a Freon 22 monolayer is adsorbed on the surface of MgO in the dark, and more than 10% of a monolayer was adsorbed under UV irradiation. The photoadsorption activity is not associated with the presence of nitrogen-containing compounds formed by the adsorption of nitrogen oxides from air on the surface of MgO. Magnesium oxide does not adsorb hydrogen-free Freon 12 (CF_2Cl_2) either in the dark or under exposure to UV radiation.

INTRODUCTION

Recently, it was found that freons can undergo destructive adsorption on the surface of magnesium or calcium oxide under exposure to soft UV radiation [1, 2]. Because these oxides, as well as silicon, aluminum, and iron oxides, are typical components of solid aerosols in the troposphere, such adsorption processes can be an effective channel for the removal of freons from the atmosphere under exposure to solar UV radiation.

It was found in [1–3] that Freon 134a (CF_3CH_2F) and Freon 12 (CF_2Cl_2) are not adsorbed on magnesium oxide in the dark. At the same time, preliminary data on the adsorbability of Freon 22 (CHF_2Cl) on magnesium oxide both in the dark and under exposure to UV light were obtained; the initial state of the surface corresponded to a long exposure of magnesium oxide to air [4].

In this work, we studied the dark and photostimulated adsorption of Freon 22 on the surface of dispersed magnesium oxide; this material was either held in air for a long time or treated by heating in a high vacuum for a long time. The experiments with samples exposed to air for a long time are of particular importance for the evaluation of the expected rate of freon adsorption on the surface of magnesium oxide under conditions similar to tropospheric ones.

EXPERIMENTAL

Magnesium oxide of analytical grade (Reakhim, GOST (State Standard) 4526-75) with a specific surface area of ~10 m^2/g was used in this study. According to technical specifications, this magnesium oxide was prepared from magnesium hydroxide and it was free of nitrogen-containing compounds. To perform the experiments, 1.6 g of MgO from an aqueous suspension was applied to half the inner wall of a cylindrical reactor of molybdenum glass [1]. Next, it was held in air for a long time and then in a vacuum at room temperature for several hours.

In operations with MgO that was held in air for longer than two weeks (henceforth, this state of a magnesium oxide surface is designated as MgO-I), water vapor was always present in the reactor volume.

To remove nitrogen-containing compounds from the surface of the magnesium oxide, MgO-I was heated at 620 K in a vacuum for several hours. The absence of nitrogen-containing compounds was confirmed by the absence of their photodesorption on exposure of the surface of heated magnesia to light. In this study, this was the main criterion for deciding on the absence of nitrogen-containing compounds on the surface of MgO. This state of the magnesia surface is designated here as MgO-II.

Freon 22 (CHF_2Cl) from Ural PO Galogen was additionally purified by freezing. The freon amount in the reaction volume was determined using a Pirani gauge or by mass spectrometry from the height of the most intense peak corresponding to the mass number 51; the freon was sampled with a leak valve.

The surface area of MgO applied to the reactor was 14 cm^2. The apparent quantum yields of photostimulated processes were determined as the ratios between the numbers of photoadsorbed or photodesorbed molecules and quanta passed through the front wall of the reactor. An OSL-1 illuminator with a DRSh 250 mercury lamp, a heat filter, and a UV light filter with the transmission band at 300–400 nm was used for the UV irradiation of MgO surfaces. Interference filters were used for separating monochromatic radiation; these filters were employed in the measurements of the action spectra of photostimulated processes. The experimental procedure was described in more detail elsewhere [1].

RESULTS AND DISCUSSION

In contrast to severe oxygen–vacuum treatment [5], heating in a vacuum at 620 K partially retained both molecules adsorbed under real atmospheric conditions and surface sites (defects), which are annealed upon treatment under more severe conditions. Nevertheless, most of the water adsorbed or formed by the decomposition of surface $Mg(OH)_2$ was removed on heating at 620 K [6]. Moreover, this heating partially removed adsorbed carbon dioxide and completely removed nitrogen oxides adsorbed from the air [6]. The presence of nitrogen oxides on the surface of MgO-I resulted in their desorption as a mixture of $2NO + N_2$ into a gas phase either on heating in the dark or on exposure to light in a vacuum. On heating of MgO-I to 620 K in the dark, the amount of released nitrogen-containing compounds corresponded to ~1% of a magnesium oxide monolayer [6].

The addition of Freon 22 at a pressure of 1 Pa to MgO-II in the dark at 300 K resulted in rapid freon adsorption with a characteristic adsorption time of ~2 min (the time taken to almost complete freon adsorption from the reaction volume to a partial freon pressure of ~10^{-5} Pa). Simultaneously with freon adsorption, the formation of carbon monoxide in an amount approximately equal to that of adsorbed freon molecules was observed. Figure 1 shows kinetic curves for these processes. Note that, as detected by mass spectrometry, the initial rate of dark adsorption of the freon was lower than the initial rate of liberation of CO by a factor of 3 to 4. An increase in the sample temperature to 620 K after the low-temperature dark adsorption of the freon did not result in the desorption of the freon or other chlorine- and fluorine-containing products. Therefore, we believe that this dark adsorption of the freon is coupled with its irreversible destruction to form CO and surface magnesium fluorides and chlorides, for example, according to the reaction

$$\begin{aligned} &2CHF_2Cl + 3MgO \\ &= 2CO + 2MgF_2 + MgCl_2 + H_2O. \end{aligned} \qquad \text{(I)}$$

It is likely that the decomposition of surface CO clusters is responsible for additional liberation of carbon monoxide molecules at the beginning of the dark adsorption of Freon 22.

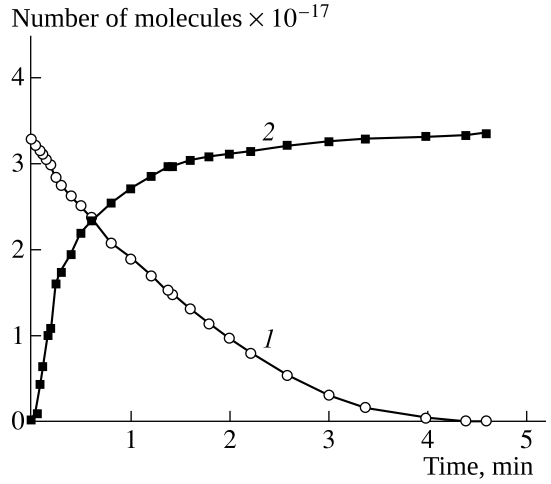

Fig. 1. Kinetic curves of (*1*) the dark adsorption of Freon 22 and (*2*) the accompanying liberation of CO for MgO-II, as found by measuring the amplitudes of peaks with the mass numbers 51 and 28 in the mass spectrum. The initial freon pressure was 1 Pa, and the temperature was 300 K.

Indeed, after the rapid liberation of CO in the dark (the characteristic time of liberation corresponds to the characteristic time of dark adsorption of Freon 22 in the order of magnitude), carbon monoxide underwent slow adsorption, which was accelerated under UV irradiation of the surface of MgO-II. Figure 2 (curve *1*) shows the efficiency spectrum for the apparent quantum yield of CO photoadsorption on MgO-II. The photoadsorption activity toward CO was observed in the spectral range $\lambda = 300$–400 nm, which is typical of the photoadsorption activity of MgO-I toward hydrogen-containing Freon 134a, which was examined previously [1]. The long-wave limit of the action spectrum of CO photoadsorption corresponds to the long-wave limit of the absorption of magnesium oxide held in air for a long time (Fig. 2, curve *2*). Because the above spectral range is inconsistent with the fundamental absorption band of MgO, this observation supports the conclusion that the treatment of MgO by heating at 620 K in a high vacuum incompletely removes an adsorbed layer and defect sites from the surface of magnesium oxide.

Nitrogen-containing compounds were for the most part removed from the adsorbed layer of MgO-II; however, MgO-II retained its activity toward the photoadsorption of CO and Freon 22. Therefore, we believe that the primary process of the absorption of UV photons is not associated with the presence of nitrogen-containing compounds on the surface of MgO.

This is supported by the following findings:

First, the absorption coefficient of NO_x compounds, which exhibit an absorption band at about 350 nm, is low in the absorption with the $n \longrightarrow \pi^*$ transition [7]. Kuznetsov *et al.* [8] interpreted the absorption at 300–400 nm that appeared after irradiation of MgO in an NO atmosphere as absorption by a complex of an adsorbed molecule with hole color centers induced by this radiation.

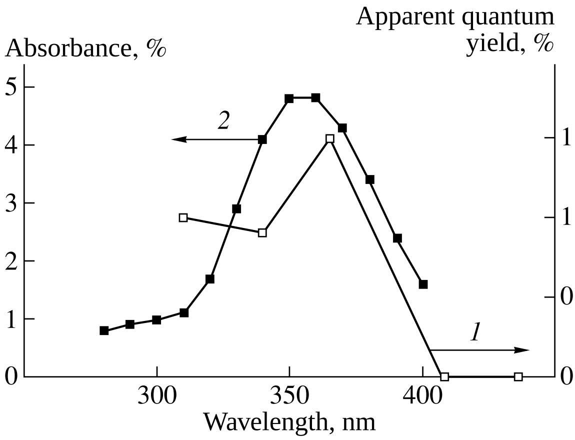

Fig. 2. (*1*) Efficiency spectrum of the photoadsorption of CO on MgO-II and (*2*) the absorption spectrum of MgO-I measured in air. The CO pressure was 1 Pa, and the temperature was 300 K.

Second, we found that the removal of nitrogen-containing compounds by desorption at experimental temperatures results in a decrease in the quantum efficiency of photostimulated processes in the spectral range 300–400 nm.

Third, the high apparent quantum yield of freon photoadsorption in the above spectral range is indicative of a high efficiency of the primary absorption of light quanta [1].

Yet we do not know what kind of species in the adsorbed layer on MgO is responsible for the absorption of UV radiation in the spectral range 300–400 nm. However, findings that the initial rate of CO desorption on MgO-II is more than three times as high as the initial rate of dark desorption of Freon 22 are likely indicative of the presence of CO clusters on the surface of magnesium oxide. The formation of such clusters, which absorb at 300–400 nm, on the surface of magnesium oxide was observed previously by Morris and Klabunde [9].

The dark adsorption of Freon 22 with a characteristic time of ~2 min was also observed on MgO in the initial state (MgO-I). However, in this case, the freon adsorption resulted in the liberation of only a small amount of CO into the gas phase, and a quasi-equilibrium pressure of the freon was attained in the gas phase. Note that long exposure (for tens of hours) of MgO-I to an atmosphere of the freon that remained after rapid adsorption resulted in the complete adsorption of freon with the formation of CO and N_2O. In this case, the total amount of the products (CO and N_2O) depended on the MgO surface coverage by the freon, whereas the ratio of the number of desorbed CO molecules to the number of desorbed N_2O molecules was independent of this parameter (see the table). The MgO-I surface coverage by the freon adsorbed in the dark was as high as 1% of a surface monolayer.

Dependence of $\frac{[CO] + [N_2O]}{[CHF_2Cl]_s}$ and $\frac{[CO]}{[N_2O]}$ on the MgO-I surface coverage (θ_s) with Freon 22*

θ_s, % of a monolayer	$\frac{[CO] + [N_2O]}{[CHF_2Cl]_s}$	$\frac{[CO]}{[N_2O]}$
10^{-3}	1 : 1	1 : 1
5×10^{-3}	2 : 1	1 : 1
10^{-2}	3 : 1	1 : 1

* [CO] and [N_2O] are the total numbers of CO and N_2O molecules released into the gas phase, respectively, and $[CHF_2Cl]_s$ is the total number of Freon 22 molecules adsorbed on the surface.

We believe that, after long exposure of the MgO sample to air, N_2O molecules adsorbed from the air [6] block sites that are required for the destructive adsorption of the freon. Indeed, the thermal removal of N_2O molecules that were adsorbed under native conditions, from the surface of MgO (the preparation of MgO-II) as N_2O decomposition products (a mixture of 2NO + N_2) resulted in dark freon adsorption with the formation of only CO. The amount of CO was much greater than that in the case when N_2O occupied adsorption sites on the surface of MgO-I.

The formation of N_2O decomposition products, which was observed upon UV irradiation of the surface of MgO-I in a vacuum, is indicative of the presence of N_2O (~1% of a monolayer) on the surface of initial MgO-I, whereas CO is formed by only the photoadsorption or dark adsorption of the freon; CO is not formed in detectable amounts upon irradiation of MgO-I in a vacuum.

The UV irradiation of the surface of MgO-I after the saturation of the dark freon adsorption in a Freon 22 atmosphere (the freon pressure of 1 Pa) resulted in almost complete photoadsorption of Freon 22 from the reaction volume to a partial pressure of the freon lower than 10^{-5} Pa. Figure 3 (curve *1*) demonstrates the kinetics of photoadsorption of Freon 22 as found by measuring changes in the amplitude of a peak with the mass number 51.

When Freon 22 was repeatedly added after the complete photoadsorption of Freon 22 on MgO-I from the reaction volume at a constant intensity of UV irradiation, the total amount of the photoadsorbed Freon 22 was as high as 10% of a monolayer on the surface of MgO-I. At the end of this photoadsorption of Freon 22, the rate of photoadsorption decreased several times compared with the initial rate.

N_2O (Fig. 3, curve *2*), NO + N_2 (Fig. 3, curves *3* and *4*), and a small amount of CO released into the gas phase in the photoadsorption of Freon 22 on MgO-I. In this case, after the complete freon consumption, three product molecules per molecule of adsorbed Freon 22 were liberated into the gas phase.

Thus, it is likely that the decomposition of N_2O to $2NO + N_2$ also takes place under exposure to light in addition to the photodesorption of N_2O and the release of CO, which was also detected upon the dark adsorption of the freon. Due to decomposition, adsorption sites are freed as in the case of the MgO-I surface exposure to light in a vacuum [6]. The action spectra of the photoadsorption of Freon 22 and of the photodesorption of nitrous oxide decomposition products in the wavelength range from 300 to 400 nm are similar to the spectrum of the photoadsorption of Freon 134a, which was observed earlier for MgO-I [1], and to the absorption spectrum of MgO-I [10]. Note that in MgO-I after preliminary severe treatment with oxygen in a vacuum the decomposition of adsorbed N_2O began on irradiation with quanta at $\lambda < 260$ nm. Molecular nitrogen and oxygen, which remains bound to the surface of MgO [5], rather than the $2NO + N_2$ mixture are the products of N_2O decomposition.

At the instant the photoadsorption of Freon 22 on MgO-I took place, the overall rate of liberation of N_2O, NO, and N_2 molecules and the total number of molecules were considerably higher than the rate of liberation and the total number of molecules released under UV irradiation of the surface of MgO-I in a vacuum, respectively [6].

Thus, the dark or photostimulated destructive adsorption of Freon 22 was observed on magnesia in both the initial form (MgO-I) and the form obtained by heating in a high vacuum (MgO-II). The dark destructive adsorption of Freon 22 on the surface of MgO-I was accompanied by the desorption of N_2O and CO, whereas the photoadsorption of Freon 22 onto the same magnesia species was accompanied by the decomposition of N_2O to NO and N_2.

Note that the dark or photostimulated adsorption on the surface of MgO was not observed with another freon from the methane series, Freon 12 (CF_2Cl_2), which contains no hydrogen atoms in contrast to Freon 22.

In this study, we failed to detect the effect of water vapor on the efficiency of photostimulated processes, whereas the effect of a hydroxyl cover on the efficiency was not examined because the hydroxyl cover can be removed only at high temperatures. The latter results in a MgO surface state at which photostimulated processes in the spectral range 300–400 nm do not occur.

In conclusion, we note that only at the initial period of irradiation time the photoadsorption of Freon 22 was accompanied by the release of nitrogen compounds (N_2O, NO, and N_2) and, in a smaller amount, carbon monoxide. The amount of nitrogen-containing compounds on the surface of MgO exposed to air for a long time was ~1% of the surface monolayer, and a small fraction of these compounds released into a gas phase upon exposure to light. In contrast, the total amount of Freon 22 photoadsorbed on MgO exposed to air for a long time was as high as 10% of a surface monolayer. Thus, it is evident that MgO as a solid aerosol component of the troposphere makes a valuable contribution to the removal of Freon 22 from a gas phase.

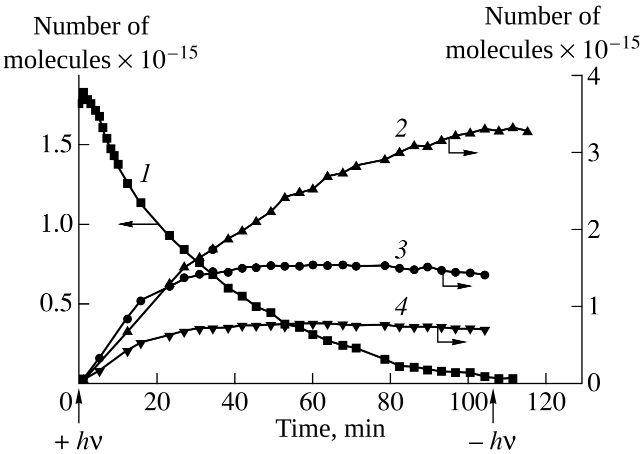

Fig. 3. Kinetic curves of (*1*) the photoadsorption of Freon 22 and the photodesorption of (*2*) N_2O, (*3*) NO, and (*4*) N_2 for MgO-I, as found by measuring the intensities of peaks with the mass numbers 51, 44, 30, and 28, respectively. The initial freon pressure was 1 Pa, and the temperature was 300 K. UV irradiation was performed using an OSL-1 illuminator with a UV light filter. The points in time at which light was turned on and off are indicated by arrows.

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