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Photocatalysis on atmospheric aerosols: Experimental studies and modeling

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Abstract

Photostimulated decomposition and oxidation of some ecologically significant volatile organic compounds (VOCs) on surfaces of natural aerosol constituents are taken as an example for demonstrating the importance of these processes as the tropospheric sink of organic pollutants. Oxidation rate constants of some halogenated hydrocarbons, isoprene and monoterpenes, as well as of aromatic hydrocarbons, on the surfaces of metal oxides, desert sand, volcanic ash, and sea salt are given. Comparison of the data obtained with the gas-phase homogeneous reaction rates proves the necessity for taking heterogeneous sinks into account in studying the atmospheric chemistry of radiative and photochemically active VOCs. © 1997 Elsevier Science B.V.

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1. Introduction

During the past 25 years considerable progress has been achieved in studying gas-phase homogeneous reactions of volatile organic compounds (VOCs) in the atmosphere [1–3]. However, one of the principal features of the Earth's atmosphere is its heterogeneity. According to different estimates, it absorbs annually vast amounts (2–2.5 billion tons) of solid particles [4] whose surface exceeds by far the total surface of our globe.

According to some authors, the presence in the atmosphere of a great amount of particles with a considerable variety of composition and a vast surface makes it possible to raise the question whether a purely homogeneous gas-phase model is suitable to the description of chemical processes taking place in the atmosphere [5]. In fact, it may be suggested that in some cases (urbanized regions with a high dust content, regions with the income of great masses of desert sand or finely disperse volcanic ash, etc.) heterogeneous destruction on the surface of solid aerosol particles is a considerable sink of chemically active gaseous atmospheric components.

The photostimulated sink of a gas constituent X with the molecular weight M_X taking place as a result of heterogeneous processes can be expressed in a general form by the equation

$$-\mathrm{d}[\mathrm{X}]/\mathrm{d}t = k(\lambda) \cdot S \cdot P_{\mathrm{X}}, \qquad (1)$$

where $k(\lambda)$ is the photostimulated reaction rate constant on the surface under irradiation with light at wavelength λ, S is the specific surface of aerosol particles, and P_X is the flux of the gas constituent X

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molecules onto the aerosol surface. In turn, the value of P_X can be expressed as a function

$$P_X = f\{C_X, \gamma(I,\lambda), D_X\}, \qquad (2)$$

where C_X is the VOC concentration, $\gamma(I,\lambda)$ is the (photo)sorption probability under the collision of the X molecule with the aerosol surface, $D_X = (1/3)L{\cdot}V = (1/3)L{\cdot}[8RT/(\pi{\cdot}M_X)]^{1/2}$ is the diffusion coefficient of the X molecule.

It is clear that the determination of a gas constituent's sink in the heterogeneous photostimulated reaction is a very difficult problem whose solution requires taking many factors into account. The multiphase nature of atmospheric aerosol particles and a great variety of atmospheric composition and properties variability involve additional complications. Therefore, the solution of Eq. (1) at first inevitably involves considerable simplifications and assumptions having different degrees of validity. We can hope, however, that in the course of data accumulation concerning aerosol composition and sorption characteristics, reaction rate constants under light irradiation in different spectral ranges, etc., and the correlation between homogeneous and heterogeneous physico-chemical transformations of ecologically significant radiative and photochemically active VOC in different atmospheric layers will be elucidated.

The aim of the present communication is to draw attention to the photostimulated heterogeneous reactions of organic pollutants of the atmosphere. This study started as far back as the 1970s [6–10] but has not been developed until recently. Taking a limited number of VOCs we attempted, following the authors of a recent review [11], to show the importance of these processes in the chemistry of the troposphere. The choice of the investigation objects was determined by their role in atmospheric chemistry. The first group consists of ozone destroying halocarbons including CFC and CFHC, the second one is composed of isoprene and terpenes belonging to principal biogenic constituents of the lower atmosphere. The third group comprises toxic aromatic hydrocarbons whose share in urban air organic pollution usually exceeds 30% [2,3]. We took as catalysts semiconductive metal oxides traditionally used in photocatalysis as well as natural materials forming part of the solid atmospheric aerosol: desert sand, volcanic ash, calcium carbonate and sea salt.

2. Experimental

2.1. Materials

Commercial metal oxides with the following specific surface (m^2/g) were used as photocatalysts: TiO_2 (rutile) – 35, ZnO – 6.5, and Fe_2O_3 – 17. According to data of X-ray fluorescent analysis, the fraction of the Kara-Kum desert sand (d<0.05 mm) with a specific surface of 20 m^2/g contained (in weight %): Fe – 3.3, Ti – 0.48, Mn – 0.08, Zn – 0.02, Ni – 0.01, Cu – 0.01. The volcanic ash (S=6.0 m^2/g) was supplied by the Volcanology Institute of Russian Academy of Sciences and collected in 1976 during an eruption of the Tolbachik volcano (Kamchatka) and the sea salt was obtained by evaporating sea water from the Pacific shore of the Kunashir island. Moreover, certain experiments were carried out with powdered technical chalk ($CaCO_3$, S=4.0 m^2/g).

Before carrying out the experiments, all materials (except the sea salt) were repeatedly washed with distilled water to negative reaction for chlorine ions and dried at 500–800°C and a pressure of 70–100 Torr.

Commercial halocarbons and aromatic hydrocarbons applied as standards in gas chromatography were also used. Isoprene was subjected to preliminary distillation with a dephlegmator, whereas terpene hydrocarbons were distilled on a rotor rectification column with an efficiency of 200 theoretical plates.

2.2. Experimental units

Experiments on photostimulated decomposition and oxidation of organic compounds were carried out under atmospheric pressure and at temperatures of 20–22°C in two types of units. The first of them were cylindrical flow pyrex glass reactors with an immersed burner. The light source in the reactor was a 250 W medium pressure mercury lamp immersed in a quartz "finger". The unit was cooled by water circulated in the space between the finger and the working chamber (530 cm^3) of the reactor [12]. In some experiments, liquid filters were used which transmitted only visible light (1 M $NaNO_2$) or the light in the range 310–390 nm (solution of $NiCl_2{\cdot}6H_2O$ and $CoCl_2{\cdot}H_2O$ acidified with HCl in a mixture of water and formamide).

Solid particles were applied to the inner reactor walls (800 cm^2) from an aqueous suspension and dried before experiment at 250°C for 5 h. After the reactor had been sealed, the organic compound under investigation was injected into it with a syringe, the reactor mixture was kept in the dark for 30 min, and subsequently the lamp was switched on.

The second reactor type (500 cm^3) had an external irradiation source: a 400 W mercury lamp. It was made from non-magnetic stainless steel and supplied with a jacket for introducing the thermostating liquid. Irradiation was carried out through a water filter absorbing the IR radiation and a quartz window in the sealed reactor lid. Moreover, light was passed through a glass filter cutting off radiation at wavelengths shorter than 290 nm or through a filter transmitting light at wavelengths of 300–400 nm. The photocatalyst purified by the above method was placed in the reactor and was stirred with the aid of a magnetic stirrer. Organic compounds were injected with a syringe through an inlet sealed with a silicon rubber gasket. According to data of actinometric measurements, the light flux in the first and second reactor types was about $1\cdot10^{17}$ and $5\cdot10^{17}$ quanta/s, respectively.

2.3. *Analysis*

The purity of initial reagents and the changes of gas-phase composition in the reactors in the course of experiments were controlled by gas chromatography. Samples for analysis (0.2–1 cm^3) were collected from the reactors with the aid of 1 cm^3 gas syringes.

Separation was carried out on columns (3 m×2 mm) packed with 10% tris-cyanethoxypropane (TCEP) on Celite-545 and with activated carbon (for CO_2 determination with a TCD detector). After carrying out experiments with aromatic hydrocarbons, aqueous extracts of the photocatalyst particles were analyzed for phenol content on a column packed with SP-1000. In addition, ether extracts of the catalysts were treated with an acidified solution of 2,4-dinitrophenylhydrazine and analyzed on a glass capillary column (45 m×0.26 mm) packed with SE-30 for carbonyl compounds content. The composition of products of incomplete oxidation of isoprene, aromatic and terpene hydrocarbons contained on the photocatalysts surface was determined by GC/MS (LKB-2091, Sweden) with cryofocusing on a capillary column (45 m×0.25 mm) packed with dinonylphtalate. For this purpose the photocatalyst was transferred from the reactor into the glass sorption tube and subjected to mild thermodesorption by heating it gradually to 120°C in helium flow for 25–30 min. The products were identified from mass spectra and gas chromatographic retention parameters.

The determination of chlorine ions accumulated on particle surface in experiments involving halocarbons was made by potentiometric titration of aqueous extracts. The diffuse reflection spectra of photocatalyst samples were recorded on a Perkin-Elmer FTIR-1700 instrument.

3. Halocarbons

A series of experiments on light irradiation in the near UV and visible spectral ranges of halocarbons adsorbed on various materials showed that they all undergo intensive oxidation with the formation of CO_2 as the only gaseous product. It was found, however, that particles of different materials used as photocatalysts behave differently. Special experiments have shown that on dark sorption and decomposition of halocarbons take place on ZnO and TiO_2. For example, the analysis of ZnO aqueous extracts showed the presence of Cl^- ions in amounts equivalent to 10% of total chlorine contained in CCl_4 adsorbed in dark experiments. Irradiation with light at wavelength greater than 300 nm resulted in greatly accelerated decomposition of the adsorbed halocarbon. At the same time it was detected that photostimulated decomposition takes place only during the first 1.5–2 h of irradiation, the chlorine ions yield being reproducible and averaging 35±5% with respect to the adsorbed reagent quantity.

The inhibition of photostimulated decomposition is evidently caused by the fact that the sites previously occupied by the halocarbon molecules do not become free but adsorb reaction products, i.e. surface chlorides and carbonates. Carbonate accumulation was confirmed by experiments on acid and thermal treatment of ZnO taking part in the reaction. The CO_2 evolution began only upon heating above 300°C, i.e. above the $ZnCO_3$ decomposition temperature. It may be assumed that the chloride and carbonate formation during the photostimulated decomposition of CCl_4 takes place with an intermediate participation of phosgene:

$$\begin{array}{l} ZnO + CCl_4 \rightarrow Cl_2C{=}O + ZnCl_2 \\ 2\,ZnO + Cl_2C{=}O \rightarrow ZnCO_3 + ZnCl_2 \\ \hline 3\,ZnO + CCl_4 \rightarrow ZnCO_3 + 2\,ZnCl_2 \end{array}$$

The presence of phosgene and CO_2 on surfaces of various materials irradiated in the presence of CCl_4 and $CHCl_3$ has been recorded by Pozdnyakov et al. [9] and confirmed by our IR diffuse reflection spectroscopy data. It has been ascertained [12] that in this reaction TiO_2 behaves like ZnO: the photostimulated decomposition of adsorbed halocarbons results in Cl^- ion accumulation and surface deactivation. The photostimulated decomposition of halocarbons on Fe_2O_3, particles of desert sand, volcanic ash, and chalk forming part of the atmospheric aerosol are of special interest. In contrast to ZnO and TiO_2, in the decomposition of halocarbons on these materials, reaction inhibition was not observed throughout the irradiation time. Table 1 gives the reaction rate constants calculated from reagent consumption in the reactor gas phase and Cl^- ion accumulation on the catalyst surface. These data show that on the surface of natural materials irradiated by light in the near UV and visible spectral ranges at 20°C, the decomposition of various halocarbons takes place. The rate constants for these processes are in the $(1.3–6.0)\cdot 10^{-6}\ s^{-1}$ range [12]. These values are in good agreement with those obtained by Kutzuna et al. [13] for natural alumosilicate materials and some soil types.

A communication from Lovelock [14], who has observed a decrease in CCl_4 concentration in air near the Atlantic coast of Africa during intensive transport of fine-grained sand from Sahara desert, may serve as a confirmation of the photocatalytic decomposition of halocarbons extremely stable under tropospheric conditions. Thus, taking into account the above results as well as data concerning soil sink of halocarbons including CCl_4 and $CFCl_3$ [15] we must evidently reconsider the prevailing concept of the non-existence of tropospheric sink for these ecologically significant VOCs.

4. Isoprene and monoterpene hydrocarbons

The data available now suggest that the bulk of C_{org} is emitted into the atmosphere in the form of these hydrocarbons [2,16]. No wonder that in the past 15 years many investigations of transformation of phytogenic VOCs in the atmosphere were carried out. However, all of them with few exceptions [17,18] concerned gas-phase homogeneous reactions with the participation of various active particles (HO, O_3, NO_3) and did not make any allowance for the possibility of heterogeneous oxidation on the atmospheric aerosol surface.

Our experiments showed that the surfaces of metal oxides and natural materials actively adsorb isoprene

Table 1
Photostimulated decomposition of halocarbons on the surface of various materials

Material	Mass (g)	Irradiation time (h)	Halocarbon		$k\cdot 10^6\ (s^{-1})$
			Formula	Quantity (10^{-4} M)	
ZnO	3.7	240	CCl_4	50	26
ZnO	3.6	240	CC_4	0.12	29
ZnO	6.5	300	$C_2F_4Br_2$	3.0	16
Fe_2O_3	1.6	540	CCl_4	2.0	6.0
Volcanic ash	13.1	1080	CCl_4	3.0	1.5
Chalk	5.0	600	CCl_4	2.0	2.0
Kara-Kum Desert sand	1.0	240	CCl_4	2.0	10.0
Kara-Kum Desert sand	6.9	240	$CHCl_3$	3.8	6.0
Kara-Kum Desert sand	1.0	360	$CFCl_3$	1.2	4.4
Kara-Kum Desert sand	10	960	CF_2Cl_2	2.5	1.3
Kara-Kum Desert sand	5.0	510	$C_2F_3Cl_3$	2.2	4.4
Kara-Kum Desert sand	5.0	360	CH_3CCl_3	2.2	15.0

and terpenes. Upon light irradiation in the near UV and visible spectral ranges, these hydrocarbons rapidly disappear from the reactor gas phase.

Isoprene and terpene concentrations decrease in experiments with particles of different kinds allows linearization in the first order reaction coordinates. In experiments with ZnO irradiated by light at $\lambda \geq 300$ nm the only gaseous product was CO_2 (in the case of isoprene, acetone traces were also detected). The quantum yield in isoprene oxidation amounted to 0.1. Upon irradiation through a filter transmitting only visible light, isoprene oxidation was also observed but the composition of gaseous products was different. Besides CO_2 (which was still the main product) and acetone we observed small amounts of formaldehyde, acetaldehyde, α-methylacrolein, methyl vinyl ketone, butanone-2, 3-methylbutanone-2, 3-methylbuten-2-one, and 3-methylfuran.

The same products were found in the gas-phase isoprene oxidation in the reactions with HO radicals, but their ratio was drastically different. For instance, according to Gu Chee-Ilang et al. [19], gas-phase reactions at ambient temperature and atmospheric pressure result in a mixture of compounds where 3-methyl furan, methyl vinyl ketone and α-methylacrolein account for 44–52% of the total yield, CO_2 being observed only as an insignificant admixture. Hence, the comparison of our results with the literature data shows that the distinctive feature of isoprene photocatalytic reactions is its more extensive oxidation resulting in the formation of CO_2 as the main gaseous product.

The volatility of terpene hydrocarbons is much lower than that of isoprene, and they have a strong tendency to be adsorbed on the aerosol surface. Therefore, we may assume that in the atmospheric chemistry of terpenes the role of photocatalytic reactions is still greater. Table 2 gives some results of our investigation of photocatalytic reactions of isoprene and terpenes. It should be noted that throughout irradiation

Table 2
Rate constants for photostimulated oxidation of isoprene and monoterpenes on the surface of oxides and natural aerosol components

Compound	Photocatalyst	Irradiation time (min)	CO_2 yield (%)	$k \cdot 10^4$ s^{-1}	$k' \cdot [HO] \cdot 10^4$ s^{-1}
Isoprene	ZnO	45	—	20	0.39
	TiO_2	30	—	20	
	Desert sand	1000	—	1.1	
	Volcanic ash	810	—	0.1	
	Chalk	920	—	0.2	
	Sea salt	700	—	0.2	
	Soot	560	—	0.5	
α-Pinene	ZnO	480	12.0	3.0	0.30
	TiO_2	480	—	4.0	
	Desert sand	2530	3.0	0.2	
	Chalk	560	2.0	0.2	
β-Pinene	ZnO	120	7.5	3.7	0.39
Limonene	ZnO	120	30.0	8.0	
	Desert sand	2330	3.8	0.06	
Myrcene	ZnO	240	30.0	1.5	0.95
	TiO_2	60	1.0	4.0	
	Chalk	140	3.0	3.0	
	Desert sand	1020	4.0	0.5	
	Volcanic ash	1850	0.8	0.2	
γ-Terpinene	ZnO	40	7.0	1.2	1.00
	TiO_2	45	10.0	1.0	
	Chalk	100	4.6	2.2	
	Desert sand	300	0.9	0.05	
β-Phellandrene	ZnO	400	13.0	5.0	0.70
Sabinene	ZnO	265	12.0	4.0	

Note: k is the rate constant for photocatalytic oxidation, k' is the pseudo-first rate constant for homogeneous oxidation in the reaction with the HO radical. Concentration of this radical is taken to be $5 \cdot 10^5$ cm^{-3}.

a regular decrease in hydrocarbons amount in the gas phase took place, and no "poisoning" of the photocatalysts was observed. The last column in Table 2 gives for comparison calculated specific rates of gas-phase reactions with the HO radical [20] whose concentration is taken to be equal to $5 \cdot 10^5$ cm^{-3}. It can be seen that the rates of photocatalytic oxidation of C_5H_8 and $C_{10}H_{16}$ hydrocarbons are close to and in some cases even exceed those of homogeneous reactions.

In our experiments we observed very fast disappearance of terpenes from the gas phase and the evolution of CO_2 as the only gaseous product (it is surprising that in contrast to gas-phase oxidation, in our experiments absolutely no CO evolution was observed). The yield of CO_2 in experiments with ZnO and TiO_2 was 10–30% and in those with natural materials it did not exceed 5% of theory for complete oxidation of $C_{10}H_{16}$ molecules. This suggests that a considerable part of carbon in the initial terpenes is bonded to photocatalyst particles in the form of partially oxidized intermediates. In fact, GC/MS investigation of gaseous and liquid extracts of photocatalysts obtained from reactors made it possible to identify a great number of C_2–C_{10} organic compounds, the products of isomerization, ring cleavage, and incomplete terpene oxidation [21]. The final sink of these products from the atmosphere is, without doubt, their precipitation on the underlying surface in the composition of aerosols and subsequent microbiological oxidation.

5. Aromatic hydrocarbons

Experiments on photostimulated oxidation of aromatic hydrocarbons were carried out in sealed pyrex reactors with an immersed burner as well as in a stainless steel reactor with external irradiation. The aim of most experiments in these series was to elucidate the dependence of reactivity of aromatic hydrocarbons on their structure. Just as we expected, they were found to be less reactive in photostimulated oxidation than isoprene and monoterpenes. The data given in Table 3 show that the reaction rate depends on the nature of substitution in the aromatic nucleus: it increases on passing from mono- to di- and trialkyl substituted benzene homologs. The few experiments on toluene oxidation on natural materials (Kara-Kum desert sand, volcanic ash, and sea salt) show that the rate of this process is almost two orders of magnitude higher than the specific rate of gas-phase reaction with the hydroxyl radical. As was in the case of other organic compounds, the only gaseous oxidation product of aromatic hydrocarbons was CO_2 whose yield after 2–3 h of irradiation did not exceed 10% of theory.

Table 3
Rate constants for photostimulated oxidation of some aromatic hydrocarbons

Hydrocarbon	Photocatalyst	$k_{het} \cdot 10^5$ s^{-1}		$k' \cdot 10^5$
		Reactor with an immersed burner	External irradiation	
Benzene	TiO_2	2.4±0.5	1.4±0.2	0.06
Benzene	ZnO	—	6.1±0.7	
Toluene	TiO_2	4.0±0.5	—	0.29
Toluene	ZnO	4.0±0.8	6.7±1.9	
Toluene	$CaCO_3$	0.6±0.1	—	
Toluene	Volcaic ash	—	2.1±0.3	
Toluene	Sea salt	—	1.4±0.4	
Toluene	Fe_2O_3	—	1.4±0.4	
Toluene	Desert sand	—	2.1±0.3	
Ethyl benzene	TiO_2	3.9±2.4	—	0.39
Cumene	TiO_2	4.5±0.7	—	0.39
o-Xylene	TiO_2	51.6±9.4	—	0.77
1,3,5-Trimethylbenzene	TiO_2	96.4±68.3	—	1.32

Note: k' is the pseudo-first rate constant of gas-phase reaction for interaction of arene with the OH radical and $[OH]=5 \cdot 10^5$ cm^{-3}. The weight of solid photocatalyst particles ranged from 3 to 4 g.

However, upon thermal desorption, a great number of products of incomplete oxidation and structural degradation of initial compounds was found on the catalyst particles' surface [22]. Phenol and cresols were detected in aqueous extracts of zincoxide which had taken part in the reactions with toluene.

These data show that the photocatalytic oxidation of such ecologically significant pollutants as aromatic hydrocarbons can be very important under the conditions of high solid aerosol content in large modern cities as well as in the transport of large amounts of mineral dust from arid regions. A simple one-dimensional model is shown below for demonstrating the importance of this sink taking toluene and isoprene as examples.

6. Homogeneous and heterogeneous photostimulated hydrocarbons oxidation: One-dimensional model

As a result of simulation we hope to obtain answers to two questions:

First, what is the contribution of the photocatalytic decomposition of hydrocarbons to the total value of their tropospheric sink.

Second, what are the criteria making it possible to determine that photocatalytic processes are significant for a particular class of atmospheric pollutants under the conditions of a specific atmospheric basin.

The dependence of the photostimulated oxidation rate will be written in the following form [23]:

$$V_1 = k_1 \cdot S \cdot I \cdot C, \tag{3}$$

where k_1 is the specific rate constant for the photostimulated destruction of hydrocarbons referred to intensity of radiation in 1 W/m^2, S the aerosol surface area in unit air volume, I the intensity of radiation incident on aerosol surface, and C is the hydrocarbon concentration. The following expression will be considered valid for homogeneous oxidation:

$$V_2 = k_2 \cdot [\mathrm{OH}] \cdot C, \tag{4}$$

where k_2 is the rate constant for the interaction of hydrocarbon with hydroxyl, and [OH] is the concentration of hydroxyl radicals, which will be taken equal to $5 \cdot 10^5$ cm^{-3} for diurnal conditions. For simplicity it is assumed that the OH radicals provide the main contribution to the homogeneous oxidation of hydrocarbons in the lower troposphere.

It can be easily seen that both processes are first order in reagent concentration. This fact implies that the ratio of their contributions to the total hydrocarbon sink does not depend on its distribution in the atmospheric region under consideration and is given by the following expression:

$$V_1/V_2 = (k_1 \cdot S \cdot I)/(k_2 \cdot [\mathrm{OH}]). \tag{5}$$

It is appropriate to call the product of surface density S by light intensity I the photocatalytic activity of atmosphere (PCA) and to operate with it just as with the concentration of other active oxidants. PCA has the dimensionality (W/m^3) and characterizes the concentration of photocatalytically active centers in one cubic meter of the atmosphere. Note that PCA has no relation whatever to the concepts of quantum yield and energy expenditures of the photocatalytic process.

Toluene and α-pinene were chosen as simulation objects. The former is a typical representative of the alkylbenzene class in the urban atmosphere, and the latter is one of the main components in volatile emission of many species of higher plants. The kinetic parameters of these compounds necessary for calculations are given in Table 4. Other values used in the model are given below:

	Parameter, dimensionality	Value	Comment
1	Intensity of UV radiation (<400 nm) at latitudes at the Earth's surface 50–60° (W/m^2)	28	Average for July
2	Aerosol density in the atmosphere at the Earth's surface (m^2/m^3)	0.01	Pure atmosphere of the background region
		100	Dust cloud over a desert or an antropogenic source
3	Transparency of the atmosphere	0.6	

Table 4
Mean values of pseudo-first order rate constants for the interaction of toluene and α-pinene with the hydroxyl radical and specific rate constants for photostimulated oxidation of these compounds on the surface of desert sand

	k_2·[OH] (s^{-1})	k_1 ($s\ W\ m^2)^{-1}$
α-Pinene	$5 \cdot 10^{-5}$	$2.0 \cdot 10^{-3}$
Toluene	$2.9 \cdot 10^{-6}$	$2.1 \cdot 10^{-5}$

Table 5
Contribution (%) of photocatalytic oxidation of toluene and α-pinene to the total atmospheric sink of these compounds depending on the near-ground density of tropospheric aerosol

S (m^2/m^3), H=0	Contribution of photo-catalytic oxidation to the total sink (%)	PCA (W/m^3), H=0
Toluene		
0.01	0.037	0.28
0.1	0.36	2.8
1.0	3.53	28.0
10.0	26.80	279.9
100.0	78.55	2798.9
α-Pinene		
0.01	0.5	0.28
0.1	4.6	2.8
1.0	32.7	28.0
10.0	82.9	279.9
100.0	98.0	2798.9

To evaluate the decrease in aerosol density with altitude, an empirical dependence [4] of the following type was used:

$$S(H) = S_0 \cdot \exp(-\alpha_1 \cdot H) \qquad (6)$$

where α_1 is the empirical parameter for the lower troposphere, which is approximately equal to 0.5 km^{-1}. The evaluation of the increase in UV radiation intensity with altitude was based on a simple model for non-specific absorption [24] according to which extinction of the atmosphere at an altitude H is proportional to the mass of the atmospheric residue situated above this altitude. According to the Laplas barometric equation, the mass of this residue is proportional to the $\exp(-\alpha_2 \cdot H)$, and the dependence of UV radiation intensity on altitude is given by

$$W(H) = W_0 \cdot P^{(\exp(-\alpha_2 \cdot H)-1)} \qquad (7)$$

where W_0 is the UV radiation intensity at the earth's surface and α_2=0.125 km^{-1}. Calculation was carried out for the lower atmospheric layer with a height of 2.5 km, the rates of homo- and heterogeneous oxidation were calculated from Eqs. (3) and (4), and the specific weight of the processes of photostimulated decomposition was calculated from the following equation:

$$U = v_{s1}/(v_{s1} + v_{s2}), \qquad (8)$$

where v_{s1} and v_{s2} are the rates of heterogeneous oxidation obtained by the summation of the corresponding values of v_1 and v_2 through the height of the simulated region of the atmosphere. Simulation results for α-pinene and toluene are listed in Table 5.

It can be seen that specific weight of processes of photostimulated decomposition is profoundly affected by tropospheric aerosol density and at average illumination conditions can attain 70–90% of the total sink. To evaluate qualitatively the contribution of these processes, the value of catalytic activity of the atmosphere may be used. Let us determine the PCA value at which the contribution of heterogeneous processes to the total sink of hydrocarbons begins to exceed 1%. According to Eq. (8) we have

$$0.01 = k_1 \cdot F/(k_2 \cdot [\mathrm{OH}] + k_1 \cdot F), \qquad (9)$$

where F=$S \cdot I$ is the photocatalytic activity. Then

$$F(1\%) = 1/99 \cdot (k_2/k_1) \cdot [\mathrm{OH}]. \qquad (10)$$

Computer simulation shows that at [OH]= $5 \cdot 10^5$ cm^{-3}, the values of k_2=$1 \cdot 10^{-11}$ cm^3/(molecules s) and k_1=$1 \cdot 10^{-8}$ ($s\ m^2\ W)^{-1}$, the contribution of photostimulated heterogeneous processes becomes considerable when the PCA value begins to exceed 8 W/m^3. Under the conditions of the real atmosphere, the PCA values in the near-ground layer can attain 3000–5000 W/m^3. For most non-methane hydrocarbons these values imply that the processes of heterogeneous oxidation greatly predominate over homogeneous sinks. This certainly does not mean that the role of homogeneous processes is small as compared to heterogeneous processes, because under conditions of the lower troposphere the contribution of the photocatalytic processes undergoes abrupt changes as a result of changes in illumination and aerosol concentration. The data of laboratory experiments can only indicate the local significance of photocatalytic processes.

7. Conclusion

The experimental data on the oxidation rate and products of selected representative atmospheric pollutants on the surface of semiconductive metal oxides and natural material particles indicate that all of them can undergo various transformations due to the action of light penetrating into the lower atmosphere. A simple 1D model demonstrates the competitiveness of photostimulated heterogeneous and gas-phase homogeneous reactions, in particular when the aerosol particles content in the atmosphere is high.

Field observations show that in different regions of the globe great masses of fine-disperse sand rise episodically or even almost continuously and are transported for many hundreds and even thousands of miles. It has been repeatedly reported, for example, that sand from the Sahara desert is precipitated in central Europe [25]. Other regions characterized by great sand emission are the Namib (Africa) and Kara-Kum (central Asia) deserts and semi-desert regions around the Aral sea. The results of recent observations of Russian authors have shown that the Aral region during a few days up to 2 million tons of sand rises into the atmosphere. Dust trains exhibit layer structure and are hundreds of miles long [26].

A part of atmospheric aerosol initially contains water; the other part became covered with a water shell during atmospheric transport. The formation of this shell must evidently affect sorption intensity and subsequent photodecomposition of organic components. However, there is no reason to suppose that the water shell makes photocatalytic reactions impossible; numerous papers on the photocatalytic purification of water from persistent pollutants demonstrate that these processes are highly effective (see, for example, [27]).

In our opinion, all these facts show that further investigations of photostimulated heterogeneous processes in the lower atmosphere are very promising. Of particular interest may be the study of relatively long-lived chlorofluorohydrocarbons which replaced CFC-11 and -12, because the concentrations of these radiative active gases in the atmosphere is increasing very rapidly.

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