Contribution from Photooxidation of Aldehydes into the Formation of Atmospheric Organic Aerosol

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Abstract

The process of aerosol formation during the photolysis of aldehydes was investigated. It was shown that aldehydes in the atmosphere are an efficient source of organic aerosol. Environmental measurements of aldehydes concentrations in urban atmosphere were carried out; the scale of aerosol formation processes was estimated. It was established that the possibility of photochemical aerosol formation is to be taken into account in order to provide an adequate evaluation of the ecological consequences of the pollution of the atmosphere with organic compounds.

Key words: aldehydes, photochemical aerosol formation, minor gas components of the atmosphere

INTRODUCTION

The problem of air quality attracts attention of researchers due to the growth of industrial pollution and consequent worsening of the quality of life. The most complicated and less investigated processes are those participated by minor organic components of the atmosphere. At the same time, organic microimpurities play an important part in many global processes, for example in the formation of the radiative balance and oxidative capacity of the atmosphere.

The concentration of methane, the basic organic compound present in the atmosphere, is $4.8 \cdot 10^3$ Tg, the annual flux is estimated as approximately $0.5 \cdot 10^3$ Tg, or about 0.7 % of the total emission of volatile carbon-containing compounds [1]. The atmospheric concentration of nonmethane hydrocarbons in the troposphere reaches 1–2 ppm. A substantial part of these compounds is comprised by the products of incomplete oxidation of hydrocarbons – carbonyl compounds ($R_1R_2C=O$). Due to their ecotoxicity, carbonyls belong to priority pollutants requiring thorough investigation. Among carbonyls, the major attention is paid to the simplest aldehydes as the most widespread impurities prevailing in the emissions of heat and power engineering plants and motor vehicles. It is accepted that the motor vehicles account for 55–75 % of the total amount of emitted aldehydes. Formaldehyde and acetaldehyde are prevailing in the exhaust gases from diesel engines. The exhaust from engines operating with ethanol consists mainly of acetaldehyde [2]. The atmospheric concentrations of formaldehyde, a widespread and the most toxic carbonyl compound, vary from 0.02 to 100 ppb. In the air of background regions, the concentration of H_2CO is 0.02–3 ppb, while under the conditions of polluted urban atmosphere it may reach 200 ppb during photochemical smog [3, 4].

Aldehydes affect living organisms as toxicants in diverse manners. For example, permanent inhalation of formaldehyde causes asthma and other kinds of lung disturbance. Under the acute action of formaldehyde on an organism, such symptoms as eye irritation, headache, respiratory impairment, irritation of the upper air passages, purulent rhinitis, bronchopneumonia appear. The chronic action manifests itself as allergic reactions, disturbance of lung functioning, gene toxicity (teratogenic action), and carcinogenicity.

It is known that the toxic action of formaldehyde is enhanced substantially when it is combined with phenol, dimethyldioxane, carbophos, hydrogen peroxide, and with UV radiation. The combination of carcinogenic and immunosuppressive action brings formaldehyde to the top of substances that are especially dangerous for humans [5].

Aldehydes are photoactive compounds. Under the action of solar radiation, they are able to get decomposed into short-lived free radicals: RCHO + $h\nu \rightarrow R^{\bullet} + {}^{\bullet}CHO$ ($\lambda_{abs} = 290-330$ nm). As a consequence, branching of atmospheric photooxidation of organic compounds occurs and new highly toxic components are formed, for example peroxyacyl nitrates.

Investigations performed at the end of the past century showed that organic compounds of different classes generate aerosol under atmospheric conditions. These processes are initiated by sunlight. According to the data of thermodynamic calculations [3], highly volatile simple aldehydes are unable to form aerosol. However, our experiments showed that UV irradiation of aldehydes, in particular formaldehyde, acetaldehyde and benzaldehyde, stimulates the formation of aerosol [6–8]. It was discovered that under the action of light highly volatile aliphatic aldehydes are comparable with the representatives of aromatic aldehydes in the ability to form aerosol under photolysis within the region of maximal absorption of the carbonyl group (298–330 nm).

In the present work we report on the results obtained in the investigation of the kinetics of photonucleation of aldehydes and numerical modelling of this process, as well as the results of field measurements of aldehydes content of the air of the Novosibirsk Scientific Centre (NSC). The amount of atmospheric aerosol in the global scale is estimated on the basis of field measurement data and the yield of aerosol from photoodixation of aldehydes measured by us.

EXPERIMENTAL

The representatives of the class of aldehydes that are most abundant in the atmosphere – formaldehyde, acetaldehyde and benzaldehyde – were chosen as the objects of investigation. The aldehydes were purified before experiments by distillation in the inert atmosphere. Photolysis of aldehydes vapour at the partial pressure 3–4000 Pa was carried out in the flow of carrier gas at atmospheric pressure and room temperature in the photochemical quartz reactor. The source of light was the middle-pressure mercury lamp DRSh-500. Carrier gas was argon, air, artificial air (a mixture of nitrogen and oxygen). The kinetics of aerosol formation and the spectra of the distribution of the formed particles over sizes were studied using the set-up based on the diffusion spectrometer of aerosol (DSA). The range of recordable particle sizes was 2–100 nm [6]. The composition and properties of aerosol and gas products of photolysis were studied by means of UV, IR, EPR, NMR spectroscopy, liquid and gas chromatography, methods of qualitative chemical analysis. Short-lived free radicals (SFR) arising in reaction mixtures were identified by means of spin trapping using specially synthesized nitrone compounds [6]. Special attention was paid to revealing the effect of carboxylic acids that were detected in the gas products of photolysis on the efficiency of aerosol formation process.

Numerical modelling was carried out according to the coagulation model proposed by Smoluchowski in the approximation of the free molecular mode of cluster collisions using the experimentally measured concentrations and size distributions of the formed particles. The rate of generation of the condensable products (so-called monomers) was determined by comparing the experimental kinetic curves with the calculated ones [6]. To determine the yield of aerosol products, thus obtained monomer generation rates were compared with the measured rate of photolysis of the initial aldehydes. The kinetics of gas-phase transformations of aldehydes at the level of elementary stages was calculated using a special algorithm and the electronic kinetic database [9].

RESULTS AND DUSCUSSION

Laboratory investigation of aldehydes photonucleation

A common property of the studied aldehydes is their ability to generate aerosol only under the action of UV light in the region of radical decomposition ($\lambda < 330$ nm) both in the inert gas and in the air. The formation of aerosol

TABLE 1

Characteristics of the products of aldehyde photolysis in the air

Characteristics	Formaldehyde	Acetaldehyde	Benzaldehyde
Aerosol yield	10^{-7}	10^{-5}	10^{-3}
Particle size, nm	3–8	5–12	15–30
Gas products	HCOOH, HCOOOH	HCOOH, CH_3COOH, CH_3COOOH	$(CHO)_2$, $(C_6H_5)_2$, $C_6H_5COC_6H_5$
Aerosol products	–COOH	–COOH, –COOOH	$(C_6H_5CO)_n$
SFR*	HCO	CH_3O	C_6H_5O

*SFR – short-lived free radicals.

did not occur under irradiation with the longer-wavelength light or in the absence of irradiation.

The data on the concentrations and sizes of aerosol particles, composition of gas-phase and aerosol products, and the structure of SFR identified in the photolysis of aldehydes are presented in Table 1.

The detection of SFR (HCO, CH_3O, and C_6H_5O) during photolysis is the evidence of the free-radical mechanism of aerosol formation in aldehyde vapour.

It is necessary to stress that the formation of aerosol particles is characterized by very low yield (10^{-5}–10^{-7}) and small size (3–30 nm). Because of this, photonucleation of aldehydes may be studied only with the help of special instrumentation developed at the Institute of Chemical Kinetics and Combustion, SB RAS, based on the diffusion spectrometer of aerosol.

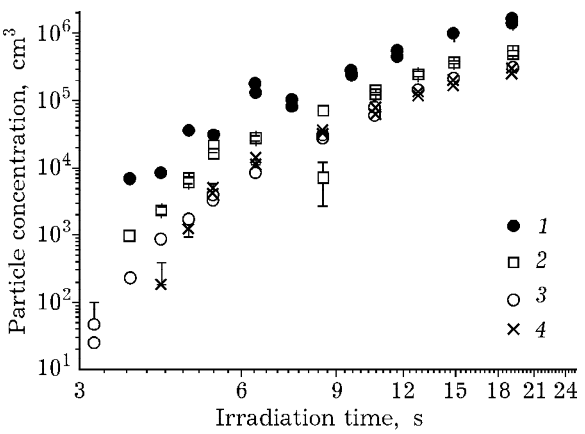


Fig. 1. Dependence of the concentration of aerosol particles on the time of benzaldehyde photolysis for different oxygen concentrations in mixture. Mixture composition: *1* – 100 % N_2, *2* – 72 % N_2 + 28 % O_2, *3* – 57 % N_2 + 43 % O_2, *4* – 44 % N_2 + 56 % O_2.

The dependence of the concentration of aerosol particles on the time of irradiation of benzaldehyde vapour for different oxygen concentrations in the mixture is shown in Fig. 1.

One can see that oxygen has only a weak effect on the kinetics of aerosol formation in benzaldehyde. However, the chemical composition of gas and aerosol products formed in the presence of oxygen is sharply different from that in the inert atmosphere [6]. Photodecomposition of aldehydes in the presence of oxygen leads to the formation of easily condensable products, first of all carboxylic acids, and the compounds of peroxide nature – peracids, hydroperoxides, peroxides of different composition. For the photolysis of acetaldehdye int eh air, these compounds serve as the direct precursors of aerosol. The experimental data on the yield of formic acid HCOOH and peracid HCOOOH in the reaction mixture during the photolysis of acetaldehyde *versus* the time of photolysis are shown in Fig. 2.

In the case of formaldehyde, the formation of aerosol was observed only during the photolysis of H_2CO in the air. Among gaseous products, we detected formic and acetic acid that are known to interact with many components of the reaction system and affect nucleation of the components. To reveal the role of these acids in aldehyde photonucleation, we carried out experiments with the addition of these acids to the reaction mixture flow before and after photolysis. It was established that the addition of formic acid vapour into the flow of reaction mixture of formaldehyde in argon before it enters the reactor causes the formation

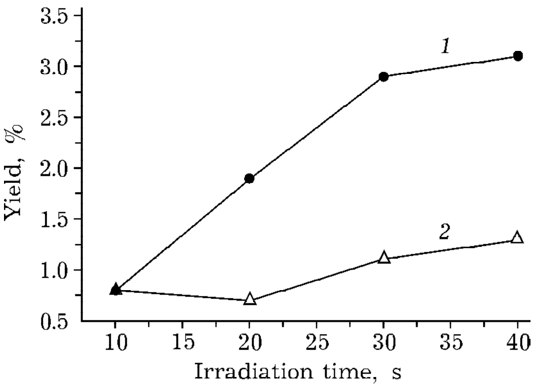


Fig. 2. Yield of HCOOH (*1*) and HCOOOH (*2*) in the reaction mixture depending on irradiation time during acetaldehyde photolysis.

of aerosol during photolysis. To remind, we did not observe the formation of the disperse phase in the photolysis of formaldehyde in argon without formic acid added. Therefore, formic acid participates in gas-phase reactions leading to the formation of aerosol. These reactions are likely to proceed after the decomposition of formaldehyde into free radicals because without photolysis of H_2CO formic acid does not cause the formation of aerosol. It cannot be excluded that formic acid serves as the source of additional oxygen atoms that promote a decrease in volatility of the products and thus the transformation into the disperse phase.

On the basis of the rate constants [9] of elementary processes of the interaction of photolytically generated free radicals with the components of the reaction mixture, we can calculate the yields of many products including condensable ones that act as the source of aerosol. A generalized scheme of the transformations of organic compounds during photooxidation of hydrocarbons in the atmosphere is presented in Fig. 1. One can see that the photooxidation of hydrocarbons is an important source of aldehydes in the atmosphere. Below we present the sequence of stages for formaldehyde as an example:

$HCHO + h\nu \rightarrow H + HCO$ $\quad w_0$

$HCO + O_2 \rightarrow CO + HO_2$ $\quad 5.6 \cdot 10^{-12}\ cm^3/s$

$HO_2 + HCHO \rightarrow HOCH_2OO$ $\quad 7.5 \cdot 10^{-14}\ cm^3/s$

$HOCH_2OO \rightarrow HO_2 + HCHO$ $\quad 151\ s^{-1}$

$HOCH_2OO + HOCH_2OO \rightarrow H_2O + HCO$ $\quad 1.0 \cdot 10^{-11}\ cm^3/s$

$HOCH_2OO + HOCH_2OO \rightarrow HCOOH + CH_2(OH)_2 + O_2$ $\quad 7.0 \cdot 10^{-13}\ cm^3/s$

$HOCH_2OO + HOCH_2OO \rightarrow HOCH_2O + HOCH_2O + O_2$ $\quad 5.5 \cdot 10^{-12}\ cm^3/s$

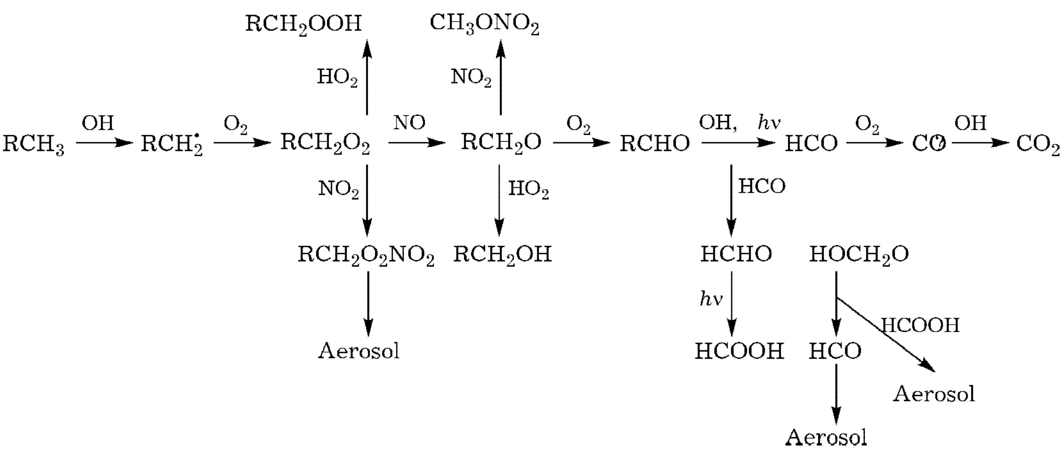
$HOCH_2O + O_2 \rightarrow HCOOH$ $\quad 3.5 \cdot 10^{-14}\ cm^3/s$

$HOCH_2O \rightarrow H + HCOOH$ $\quad 1.17 \cdot 10^3\ s^{-1}$

Calculations showed that the rate of formation of condensable products sharply increases with the accumulation of formic acid, so the reaction becomes autocatalytic in its character.

In the case of acetaldehyde photolyzed in argon, the concentration of aerosol particles turned out to be 100 times larger than that for photolysis in the air. Using HPLC and IR spectroscopy, we established that the aerosol obtained in argon is composed of the tetramers of acetaldehyde, while that obtained in the air contains oxygen-containing components with carboxylic groups, and an admixture of peracids.

The addition of the vapour of formic or acetic acid (~$10^{15}\ cm^{-1}$) into the flow of CH_3CHO + Ar



Scheme 1.

before photolysis leads to the decrease of the concentration of formed particles by a factor of 2.5–4 in comparison with the concentration of particles formed during photolysis without acids. In addition, the composition of aerosol products changes. The addition of the acid into the flow of CH_3CHO in the air does not affect the concentration of aerosol formed during photolysis. This fact suggests that carboxylic acids affect photooxidation of formaldehyde and acetaldehyde in different manners. In the case of formaldehyde in argon, acids act as additional polymerization initiators. Quite contrary, for acetaldehyde in argon, the acids serve as an alternative reagent routing the reaction to the formation of volatile peroxy compounds.

So, the gas products of aldehdye photolysis – carboxylic acids – are able to affect in two manners: by initiating polymerization and by enhancing the photooxidation of aldehydes to the formation of more volatile products.

Aldehydes in the emission from power plants and automobile engines

In addition to laboratory experiments that allowed us to study the photochemical formation of aerosol from aldehydes, we also carried out field measurements of the concentrations of aldehydes in the air of NSC in order to determine the scales of air pollution with aldehydes [7].

The concentration of formaldehyde serves as the criterion of air quality on the global, regional and local scale [5]. According to the data of perennial observations, the concentration of formaldehyde is often above the maximum permissible level in the air of Novosibirsk; thus, ecologically unfavourable situations arise [7].

As we have mentioned above, combustion of hydrocarbon fuel (at power engineering plants and in vehicle motors) play the part of the major sources of the primary admission of aldehydes into the atmosphere. For example, the heat and electric power plant working to supply energy to Novosibirsk

Akademgorodok was transferred in early 1990-es for gas fuel, so it was necessary to measure the concentrations of aldehydes in its emissions. It is known that passing from coal or black oil to gas one should optimize the combustion mode; otherwise the emission of aldehydes may increase. According to the data of [11], under the conditions of incomplete combustion of fuel, the relative yield of aldehydes in hydrocarbon flame can reach 0.4–0.5. Indeed, our measurements showed that even after purification the gas released from the heat power plant operating on gas fuel contained high formaldehyde concentration (up to 1.6 mg/m^3).

In addition, we measured the concentrations of aldehydes in the exhaust gases of motor transport to evaluate this source of air pollution with aldehydes in NSC. Together with the Institute of Catalysis, SB RAS, within the Ecological Programme of the Novosibirsk Scientific Centre, we carried out the measurements of aldehyde concentrations in the exhaust gases of buses during different engine operation modes: idling, half-load, and normal load. The data on the aldehyde concentrations depending on engine operation modes are presented in Fig. 3. Measurement was carried out using the data obtained in 170 measurements in which the concentrations of hydrocarbons, aldehydes and nitrogen oxides in the exhaust gases of 55 vehicles were measured. It was detected that the largest amount of aldehydes is formed while the engine operation in the idle mode and during braking. This agrees with the data obtained previously: high concentrations of aldehydes in urban atmosphere arise near bus stops, crossings, and during the accumulation of a large number of cars (traffic jams).

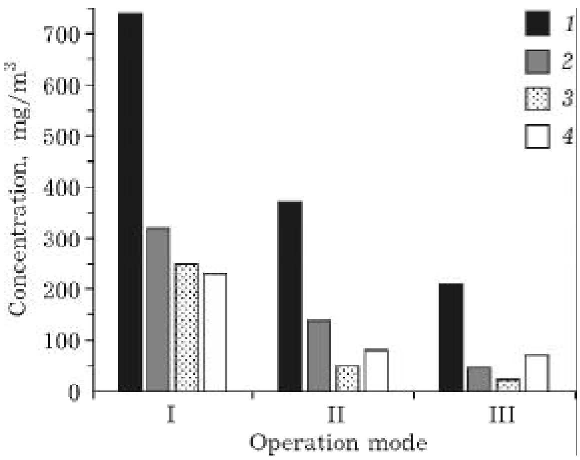


Fig. 3. Aldehyde concentrations in the exhaust gases of engines for different engine operation modes: I – idle, II – braking, III – normal motion; *1* – formaldehyde, *2* – acetaldehyde, *3* – benzaldehyde, *4* – acrolein..

Monitoring of formaldehyde concentrations in the air at the roads of NSC revealed the correlation of these data with field observations. The highest concentrations of formaldehyde were recorded at crossings and near traffic lights where the engines operate in unfavourable modes. Aldehyde monitoring allowed us to determine the most unfavourable situations during a day in different seasons of the year. The most dangerous days turned out to be summer windless days when photochemical smog is formed above NSC [7, 8]. Under these conditions, when the concentrations of aldehydes reach 150–200 ppb, aldehydes easily enter the reactions with various components of the atmosphere, which leads to the formation of extremely toxic products, for example peroxyacyl nitrates that are able to produce lung damage and cause respiratory diseases.

Comparison of the obtained results with the data of medical observations showed that the continuous increase in the concentration of formaldehyde that was observed in Novosibirsk since 1984 caused an increase in the occurrence of lung cancer by a factor of about two, and in 1987 lung cancer occupied the first position among cancer diseases [4].

It should be noted that a decrease in the concentrations of pollutants in engine exhaust gases is a substantial technological and ecological problem. The attempts to reduce the concentration of carbon monoxide in exhaust gases may lead to an increase in the concentrations of the products of incomplete combustion of fuel (formaldehyde, organic peroxides). The use of catalytic afterburners allows one to decrease the yield of carbonyls, but only if the engine operation mode is optimized. To minimize the emission of carbonyls, it is necessary to monitor the excess air, combustion temperature, and optimize the design of burning chambers to ensure close contact of fuel with oxidizer [12].

The yield of products in the form of aerosol during photonucleation was determined on the basis of the aldehyde content of engine exhaust gases. In spite of the prevalence of formaldehyde and acetaldehyde, the major contribution into aerosol formation is made by aromatic aldehydes because the yield of aerosol from their photolysis turned out to be several orders of magnitude larger than that for aliphatic aldehydes. So, benzaldehyde is the most dangerous source of aerosol in urban air under the action of sunlight.

Aldehydes in atmosphere as the precursors of aerosol

The quantitative data on the transition of the products of aldehyde photolysis into the aerosol phase allow us to evaluate the possible contribution from this process to the formation of aerosol on the global scale. Total flux of hydrocarbons in the atmosphere from natural and anthropogenic sources is 460–1110 Mt/y (calculated for methane) [10]. The amount of aldehydes that may be formed from these hydrocarbons during photooxidation in the atmosphere is 14–330 Mt/y (calculated for formaldehyde). Taking into account the yield of photochemical aerosol from aldehydes, the mass of the formed aerosol particles will be 140–3300 t/y. In addition, the emission of aldehydes as primary pollutants of the atmosphere increases from year to year because aldehydes are present in the exhaust gases from engines and power stations. The total capacity of these sources can hardly be measured; however, because formaldehyde content in air column above the Northern Hemisphere is estimated to be $1 \cdot 10^{15}$ molecules/cm^2, the amount of aldehydes entering the atmosphere is several ten times larger than the amount of formaldehyde formed as the intermediate product of hydrocarbon oxidation. So, it is evident that aldehydes in the atmosphere are a powerful source of organic aerosol on the global scale. In the presence of oxygen-containing functional groups in a molecule of aromatic aldehyde, the formation of volatile complexes of these aldehydes with heavy metals entering the plants from soil under anthropogenic pollution is possible. Investigation of the mechanisms of aerosol formation during the photooxidation of these complexes will allow us to estimate the ecological danger connected with the formation of metal-containing organic aerosol with nanometer-sized particles.

CONCLUSION

It was shown that formaldehyde, acetaldehyde and benzaldehyde are able to form aerosol with the nanometer-sized particles under the action of the ultraviolet radiation of the Sun. The yield of aerosol is 10^{-3}–10^{-7} of the amount of photolyzed aldehyde. The composition of gaseous and aerosol products was studied; the effect of the products of aldehyde photooxidation – formic, acetic, performic and other acids – on the efficiency of photonucleation was studied. A mechanism of aerosol formation at the level of elementary stages was proposed; numerical calculations of the process kinetics were carried out, the yield of aerosol was estimated.

Field observations of aldehyde concentrations in the emissions from power plants and automobile engines showed that the transition from coal to gas fuel may lead to the enhancement of aldehyde content in emissions. On the basis of laboratory and field studies, the aerosol-forming ability of aldehydes on the global scale was evaluated.

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