Photochemical formation of acid aerosols in the atmosphere as the factor determining its environmental status

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To study the processes of formation of acid aerosols in the atmosphere, we apply a complex approach, which combines the field measurements of the concentrations of reactive atmospheric admixtures with the laboratory modeling and numerical simulation of the photochemical mechanism of reactions and the aerosol-forming capability of some components (aldehydes, sulfur dioxide, ozone, alkanes). The data are obtained using high-sensitivity methods for analysis of secondary transformations of substances in the atmosphere and in the laboratory modeling. To interpret the results, we employ information databases on the kinetics of atmospheric reactions at the level of elementary chemical stages. The efficiency of this approach is demonstrated for the purpose of environmental forecast for the formation of acid components of atmospheric aerosol considered as an example.

Introduction

The hazard of irreversible environmental changes is most serious in large cities since those concentrate the main sources of air pollution like fuel-and-power production industry, transport, metallurgical industry. For prevention of ecological disasters, it is essential to predict, for instance, the degree of ecological stress occurring due to chemical conversion of the anthropogenically induced substances with the formation of acidic components. Due to secondary transformations of organic admixtures, submicron aerosols may form characterized by a higher biological availability in human beings. By now, physicochemical mechanisms of such processes have been poorly studied. This complicates making ecological predictions. In this study, we use a combined approach, which we have developed based on combining *in situ* measurements of the concentrations of reactive admixtures in the atmosphere with laboratory and numerical simulations of the photochemical reaction mechanism and capability of some components to form aerosols (aldehydes, sulfur dioxide, ozone, alkanes). All this data are based on the results obtained using highly sensitive methods of analysis of secondary transformations of the atmospheric substances. To interpret the data obtained, we refer to information databases on the atmospheric reaction kinetics yet at the level of elementary chemical stages. We demonstrate the effectiveness of this approach by applying it to ecological prediction of formation of acidic aerosol component as an example.

Experimental technique

In situ measurements of the content of hazardous substances in urban atmosphere were performed using the methods described in Ref. 1. The aldehyde and sulfur dioxide photooxidation mechanisms were studied in laboratory with a photochemical flow reactor assembled in a quartz cylinder. The light source was a DRSh-500 mercury lamp of medium pressure. Aerosol formation kinetics was studied with the use of a diffusion aerosol spectrometer capable of detecting 2 to 200-nm sized particles (Ref. 2). We studied the dependence of the photoaerosol yield on duration, intensity, and dose of radiation. The influence of some admixtures (oxygen, ozone, hydrocarbons, water) has been studied as well.

Chemical analysis of aerosol was performed upon selection of samples for the aerosol filters AFA-KhA. The presence in aerosol substance of organic compounds containing carbonyl and carboxyl groups was quantitatively determined by high-performance liquid chromatography (HPLC) using the witness method (Ref. 3). Besides, chemical composition of the reaction mixture and reaction products was determined by the methods of chemical semimicro- and microanalysis, liquid (HPLC) and thin-layer chromatography, chromatography-mass spectrometry, and UV and IR spectroscopy.

The sequences of supposed elementary stages for modeling the conversion mechanisms were correlated to the obtained results of chemical analysis of the reaction mixture and reaction products. Numerical modeling of reaction mechanisms was performed using the elementary reaction rate constants taken from the NIST database (Ref. 4).
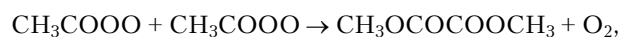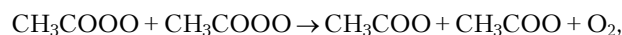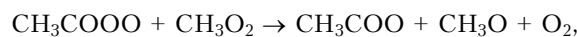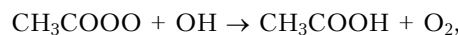
Results and discussion

Aldehydes

Concentration of aldehydes reaches high levels in urban smog. Our field measurements show that in Novosibirsk, on calm summer days, the concentration of formaldehyde in highways and near heat and power plants reaches 130—150 ppb. Under sunlight,

aldehydes undergo photolysis yielding short-lived free radicals ($RCHO + h\nu \rightarrow R^* + {}^*CHO$, $\lambda_{abs} = 290 - 350$ nm). This splits the chain of photo-oxidation processes of organic compounds and gives highly toxic components, such as peroxyacyl nitrates. Besides the gas phase products, photo-oxidation of aldehydes in the atmosphere also leads to formation of submicron aerosol particles, which are the most hazardous fraction of atmospheric aerosol. According to thermodynamic calculations, only low-volatile aldehydes were considered aerosol forming compounds. However, our laboratory investigations of photolysis of formaldehyde, acetaldehyde, and benzaldehyde performed with a flow generator of photolytic aerosol showed that even highly 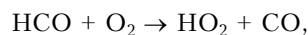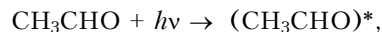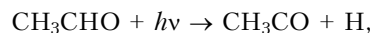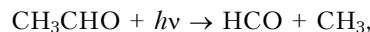volatile simple aliphatic aldehydes are comparable to aromatic aldehydes in their ability to form aerosols in photolysis if irradiated with light with the wavelengths near the absorption maximum of carbonyl group (298 − 330 nm). The resulting aerosol particles are of nanometer size (for example, 3−15 nm for acetaldehyde).

Analysis of a chemical composition of gaseous products of aldehyde photolysis shows that this process yields carbonic acids, which accompany formation of the disperse phase (Ref. 7). Our investigation of the chemical composition of gaseous and aerosol products of formaldehyde, acetaldehyde, and benzaldehyde photolysis showed that the compounds containing the carboxyl group can be found both in gas and aerosol phase. In the gas phase, we detected formic, acetic, and peracetic acids, and in benzaldehyde, the propionic and benzoic acids have also been found. In all the cases, aerosol products contained acetic and peracetic acids, and in the case of benzaldehyde, alloxy-substituted derivatives of benzoic acid were detected as well. Experiments with injections of small amounts of vapor of formic and acetic acids to gaseous aldehydes before photolysis showed that organic acids intensify aerosol formation in formaldehyde vapors, while for acetaldehyde they initiate additional photonucleation channels. The effectiveness of this initiation depends on the ratio between the acid-initiated form of aerosol generation and the polymerized aldehyde itself. For example, with acetaldehyde, which is effectively polymerized and forms aerosol in photolysis in an inert gas, injections of formic acid reduce the concentration of aerosol particles formed because of suppression of this effective channel and formation of the oxygen-containing products. In this case, aerosol does not contain formic acid, but the acids with the number of carbon atoms exceeding 3.

Kinetics of accumulation of carbonic acids (RCOOH) and peracids (RCOOOH) in the aerosol products of aldehyde photolysis is quite well described by a simple sequence of elementary chemical stages. Below, there are the stages describing photo-oxidation of acetaldehyde in the atmosphere; in the calculations, concentrations of free radicals were taken to be those typical of polluted urban atmosphere ([OH] ~ 10^5–10^6 and [HO$_2$] ~ 10^7–10^9 cm^{-3}).

$$CH_3CHO + h\nu \rightarrow HCO + CH_3,$$

$$CH_3CHO + h\nu \rightarrow CH_3CO + H,$$

$$CH_3CHO + h\nu \rightarrow (CH_3CHO)^*,$$

$$HCO + O_2 \rightarrow HO_2 + CO,$$

$$HCO + O_2 \rightarrow HC(O)O_2,$$

$$CH_3 + O_2 \rightarrow CH_3O_2,$$

$$2CH_3O_2 \rightarrow 2CH_3O + O_2,$$

$$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2,$$

$$CH_3CO + O_2 \rightarrow CH_3COOO,$$

$$CH_3COOO + HO_2 \rightarrow CH_3COOOH + O_2,$$

$$CH_3COOO + OH \rightarrow CH_3COOH + O_2,$$

$$CH_3COOO + CH_3O_2 \rightarrow CH_3COO + CH_3O + O_2,$$

$$CH_3COOO + CH_3COOO \rightarrow CH_3COO + CH_3COO + O_2,$$

$$CH_3COOO + CH_3COOO \rightarrow CH_3OCOCOOCH_3 + O_2,$$

$$(CH_3CHO)^* +$$

$$+ \{CH_3COOOH, CH_3COOH, CH_3OCOCOOCH_3) \rightarrow$$
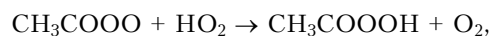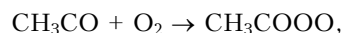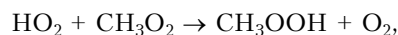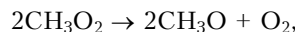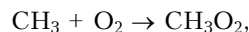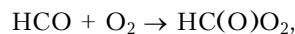
$$\rightarrow \text{aerosol.}$$

Below, we give the concentrations of acetic and peracetic acids found experimentally at the concentration of acetaldehyde in the original gas mixture of $5 \cdot 10^{18}$ cm^{-3} and, for comparison, the concentrations calculated by the method described above:

Compound	Concentration, cm^{-3}	
	measured	calculated
CH$_3$COOH	$2 \cdot 10^{17}$	$6 \cdot 10^{16}$
CH$_3$COOOH	$3 \cdot 10^{16}$	$7 \cdot 10^{16}$

The obtained ratio between experimental and calculated results can be characterized as semiquantitative. Thus, calculation and experiment show that the contribution of aldehydes to formation of nanodisperse organic aerosol with an acidic component must be given a due regard.

Sulfur dioxide

In the surface atmospheric air, the concentration of SO$_2$ is about 0.5 ppb. It grows in pollution, for example, by the products of sulfur-bearing fuel combustion. Along with SO$_2$, in urban air there are sulfonic and sulfinic acids (Ref. 8). Our *in situ* measurements show that though in general high SO$_2$ concentrations and acid precipitations are not typical of Siberian atmosphere, episodes of air pollution by sulfur dioxide often occur in the industrial regions. For example, in Novosibirsk, the

concentrations of $SO_2 \sim 30$ ppb were recorded. For laboratory simulation of aerosol formation in SO_2 photolysis, we used a raised concentration range (0.2–14 Torr), because lower concentrations complicated chemical analysis of the low-yield products (i.e., of the aerosol precursors).

It was demonstrated that size and concentration of aerosols generated due to photolysis of sulfur dioxide depend on the UV irradiation dose, on concentrations of not only the sulfur dioxide, but also of such ecologically important admixtures as ozone, alkanes (propane, *n*-butane, *n*-pentane), hydrogen peroxide, water, and oxygen. For example, dependence of aerosol concentration on the concentration of pentane in photolysis of the SO_2–pentane mixture in an inert gas and in the presence of oxygen is shown in Fig. 1.

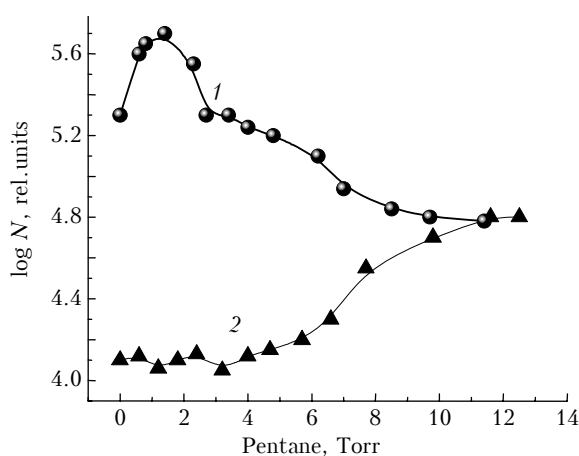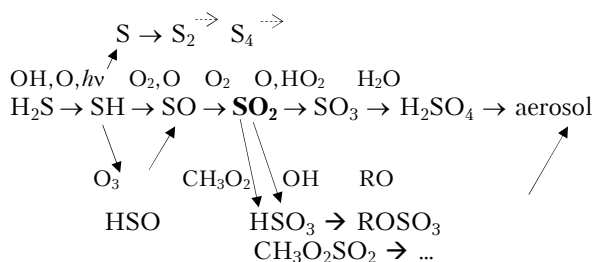**Fig. 1.** Concentration dependence of aerosols at photolysis of the SO_2-pentane mixture in helium (*1*) and air (*2*).
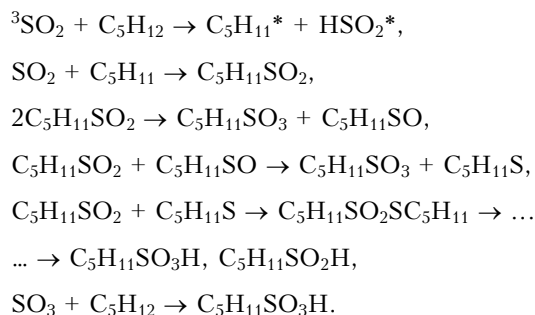
The study of the SO_2 aerosol formation dynamics in laboratory experiments, roughly simulating the photonucleation of *in situ* experiments, can be described by the Smolukhovsky coagulation model with a continuous source of condensing products ("monomers"). Kinetic curves feature two stages. At the first stage of photochemical formation of nuclei, we observe a strong power dependence of nanoparticle concentration on the intensity or duration of the UV irradiation of reagents (dose of radiation). The second stage (coagulation of existing photoaerosols) is characterized by a small tangent of the curve slopes. From kinetic dependences we have calculated particle generation rate and the number of monomers in the smallest detectable nanoparticles ($n_{min} = 5$–10). Measurements of acidity of the selected aerosol samples showed pH variations from 1.5 to 4.5 depending on the chemical composition of a gaseous mixture. Thus, a strong acid-forming power of sulfur dioxide at photonucleation was proved not only by *in situ* measurements, but by the laboratory experiments as well.

The study of the effect of ozone concentration on photoaerosol generation dynamics demonstrated

the complexity of ozone effect on SO_2 photonucleation. There were cases of both inhibiting and promoting effects the photonucleation by ozone depending on the presence of other admixtures in the reactor. Sulfur dioxide is injected into the atmosphere not only by primary emissions. It is also formed at atmospheric oxidation of hydrogen sulfides and organic sulfides that are available in the atmosphere as admixtures of natural gas. Therefore, we studied the influence of alkanes, the analogs of gas fuel (propane, butane, pentane) on SO_2 photonucleation. It was found that the effectiveness of SO_2 photonucleation in the presence of alkanes increases by 10–100 times depending on other parameters of the reacting system. The order of alkane reactivity is as follows: propane<*n*-butane<*n*-pentane. This agrees with the expected effect of alkanes owing to their reactivity and volatility of photolysis products in the aerosol phase (detected sulfinic and sulfo-acids). We composed a scheme of photochemical mechanism of SO_2 photonucleation at elementary stages, beginning with electronic excitation state SO_2^* and ending up with the photoproducts: sulfuric, propanesulfinic, and sulfonic acids. Using the calculated results, we composed schemes to illustrate the mechanisms of SO_2 and acid formation in this system:

$$S \rightarrow S_2 \dashrightarrow S_4 \dashrightarrow$$
$$OH,O,h\nu \quad O_2,O \quad O_2 \quad O,HO_2 \quad H_2O$$
$$H_2S \rightarrow SH \rightarrow SO \rightarrow \mathbf{SO_2} \rightarrow SO_3 \rightarrow H_2SO_4 \rightarrow aerosol$$
$$O_3 \quad\quad CH_3O_2 \quad OH \quad RO$$
$$HSO \quad\quad HSO_3 \rightarrow ROSO_3$$
$$CH_3O_2SO_2 \rightarrow ...$$

Chemical analysis of aerosol formed at photolysis of the SO_2–pentane mixture proved the presence of sulfonic and sulfinic acids and thioethers. Formation of these sulfur-containing organic compounds is qualitatively correctly described by the above scheme. Similar schemes were composed for transformations with propane, butane, and pentane involved. The first stage of interaction of sulfur dioxide with the hydrocarbons must be the reaction of the electronic-excited triplet sulfur dioxide $^3SO_2$ that is formed at SO_2 photolysis. Interaction with pentane can be described by the following stages:

$$^3SO_2 + C_5H_{12} \rightarrow C_5H_{11}{}^* + HSO_2{}^*,$$
$$SO_2 + C_5H_{11} \rightarrow C_5H_{11}SO_2,$$
$$2C_5H_{11}SO_2 \rightarrow C_5H_{11}SO_3 + C_5H_{11}SO,$$
$$C_5H_{11}SO_2 + C_5H_{11}SO \rightarrow C_5H_{11}SO_3 + C_5H_{11}S,$$
$$C_5H_{11}SO_2 + C_5H_{11}S \rightarrow C_5H_{11}SO_2SC_5H_{11} \rightarrow ...$$
$$... \rightarrow C_5H_{11}SO_3H, \; C_5H_{11}SO_2H,$$
$$SO_3 + C_5H_{12} \rightarrow C_5H_{11}SO_3H.$$

Numerical calculation by the suggested model shows that at the concentration of $SO_2 \sim 10^{15}$ cm^{-3}, the concentration of sulfonic acids in reaction products reaches 10^{12} cm^{-3}.

A qualitative agreement between the calculated and experimental results proves the effectiveness of this approach in interpreting both the *in situ* and laboratory experiments.

Conclusion

The monitoring of aldehyde and sulfur dioxide contents in the urban air of Novosibirsk has been performed. In laboratory experiments and numerical calculations, the regularities of aerosol generation from gaseous precursors, air-polluting sulfur dioxide, and aldehydes are studied under exposure to UV radiation. The composition of resulting aerosols is studied, where the nucleation favoring acids have been detected.

Based on the laboratory and numerical simulations, we have proposed the photochemical mechanism of acid aerosol component formation from sulfur dioxide, acetaldehyde, and benzaldehyde with participation of free radicals. It has been demonstrated that high chemical activity of aldehydes follows from photoactivity of the carbonyl group C=O, which promotes formation of organic aerosol in the atmosphere. In the case of sulfur dioxide, excitation by light causes a chain of transformations up to formation of sulfuric acid and sulfo-acids. The concentrations of acids obtained from numerical calculations qualitatively agree with the *in situ* measured acid content in the atmospheric aerosols.

Thus, the combination of *in situ* measurements, model experiments, and calculations has made it possible to elucidate the cause of appearance of acid component in aerosols that are formed under conditions of photosmog with excess of aldehyde and sulfur dioxide content. This work has expanded the fundamental knowledge on the acid precipitation formation mechanisms, which will allow prediction of the consequences of the anthropogenic load from aldehydes and sulfur-containing admixtures. The account of the photochemical factor of interaction of emissions in the urban atmosphere will improve the effectiveness of this approach in application to seeking the factors determining the level of urban aerosols. It gives out the hope of quality upgrade in ecological prediction.

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