INVESTIGATION OF AEROSOL FORMATION DURING ALDEHYDES PHOTOLYSIS

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Photochemically induced nucleation of nanosized aerosol-particle formation is one of the effective removal channels for the large number of gaseous pollutants from the atmosphere.

Photochemically induced nucleation has been widely observed in the polluted urban atmosphere and in the rural sites [1]. An organic component of the submicrometer fraction of atmospheric aerosols contributes to about 10%–60% from the total mass, but despite a large number of laboratory studies of photochemically induced aerosol formation (e.g., [2–5]), many its features are still unclear and need further investigation. This results from the complexity of the particle's chemical composition and from the complexity of the chemical reactions leading to aerosol formation. Therefore, the research of the chemical mechanisms leading to organic nanoparticles formation and estimation of aerosol yield during photochemical decomposition of individual compounds is an important and timely problem in atmospheric chemistry.

Benzaldehyde (BA) and acetaldehyde (AA) are important intermediates of organic compounds photooxidation and are present in detectable amounts (along with formaldehyde) in the polluted urban atmosphere. They can be photolyzed by the sun ultraviolet (UV) light with rather high efficiency [6], while some of the products can undergo gas-to-particle conversion. The present paper deals with the investigation of the aerosol particles formation and growth during BA and AA photolyses, as well as with the estimation of the aerosol yield and chemical composition of gaseous and aerosol products.

Experimental Studies

Photochemically induced aerosol formation kinetics has been studied using the experimental setup similar to that described elsewhere [7]. The setup consists of the quartz flow reactor (internal diameter is 22 mm, length is 300 mm), low-pressure Hg lamp DRT-240 and Novosibirsk Automated Diffusion Battery (NADB). The setup is shown schematically in Fig. 1.
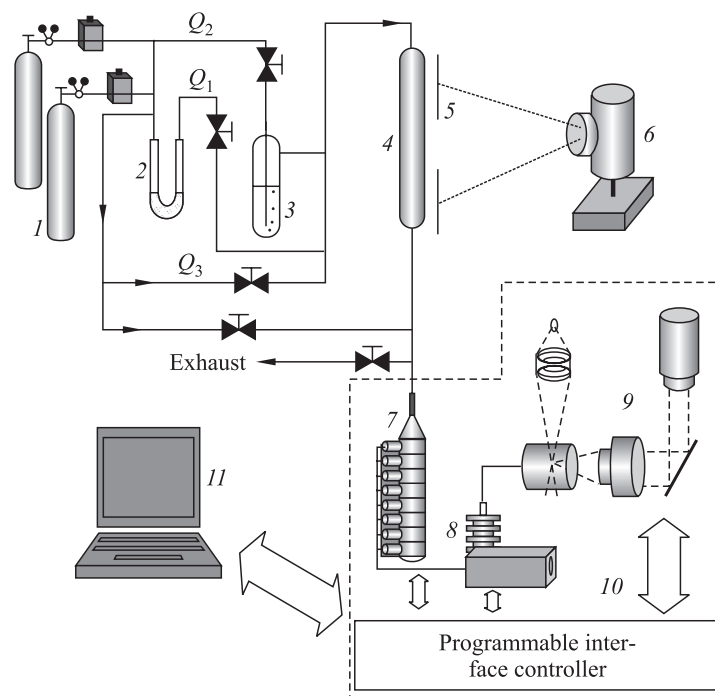

Figure 1 Schematic of the experimental setup: *1* — cylinders with compressed N_2 and O_2 with flow controllers; *2* — U-shaped tube with the aldehyde; *3* — bubbler with H_2O; *4* — flow reactor; *5* — slit; *6* — UV-lamp; *7* — diffusion battery; *8* — condensation enlarger; *9* — photoelectric particle counter; *10* — PIC controller; and *11* — PC

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Benzaldehyde and acetaldehyde vapors in the flow Q_1 were produced by passing career-gas $(O_2 + N_2)$ from the cylinders *1* through the thermostated U-shaped tube *2*, filled with silica, impregnated with a liquid aldehyde. Q_2 and Q_3 were used for dilution and for adding water vapors *3* into the reagents flow. The resulting flow was then delivered to the reactor *4*. Aerosol particles were formed in the reactor under UV-light from the lamp *6*. The irradiation time was varied from 1 to 20 s with a slit *5*. Novosibirsk automated diffusion battery consists of the condensation enlarger *8*, 8-stage screen-type diffusion battery *7*, photoelectric particle counter *9*, and a programmable interface controller *10* for NADB operation and data transfer to the PC *11*. Novosibirsk automated diffusion battery allows one to measure aerosol particles' concentration (from 10^1 to 10^7 cm^{-3}) and size distribution from 2 to 200 nm in diameter.

Aldehyde concentration was measured with HP8354 spectrophotometer by absorption on 233 nm for BA and 290 nm for AA in a cylindrical cell ($l = 82$ mm). Aerosol products were analyzed by Gas Chromatography$-$Mass Spectrometry (GC-MS) (HP6890N/5973N) and Nuclear Magnetic Resonance (NMR) (Bruker DFX200). Aerosol particles were collected on a glass-fiber aerosol filter. Free radicals formed during photolysis were detected and identified using spin-traps [8]. Electron Magnetic Resonance (ESR) spectra of the spin adducts were recorded with BRUKER ER-200 D-SRC spectrometer.

RESULTS AND DISCUSSION

ALDEHYDES PHOTOLYSIS KINETICS

First, to estimate the aerosol yield, the aldehydes' photolysis kinetics has been studied in nitrogen and in N_2–O_2 mixture. The decrease of aldehydes concentration has been found to follow the first-order kinetics. The influence of oxygen and water vapors on BA and AA photolysis has been studied. The effective photolysis constants (k_{eff}) were measured from the initial slope of the kinetic curves. These values were further used to calculate the BA and AA photolysis rate in aerosol experiments and for the evaluation of the aerosol yield.

AEROSOL FORMATION KINETICS

The aerosol formation during aldehydes photolysis is observed during the photolysis in the region of free-radical decomposition only ($\lambda <$ 290 nm). This indicates the free-radical initiation of the aerosol formation. The dependencies of the particles number concentration and size on the irradiation time, reagents concentration, and the composition of the career-gas has been studied.

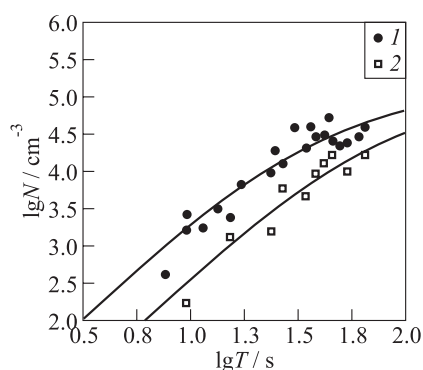### Acetaldehyde Aerosol Formation Kinetics

Figure 2 Aerosol formation kinetics of acetaldehyde in N_2 (1) and in air (2). Symbols represent the experimental data, curves correspond to numerical simulation

The aerosol formation kinetics of AA in N_2 and in synthetic air is shown in Fig. 2. It follows from Fig. 2 that the aerosol formation rate in the nitrogen is approximately 10 times higher than in the air. N_a–t_0 dependencies are typical for the aerosol formation kinetics in the free-molecular region with the constant source of condensing products, the so-called "monomers." The particles' mean diameter increases from 3 to 12 nm with the irradiation time (t_0). The particle size distribution has a single mode. At equal t_0 values, the formed particles' size is almost the same in air and in nitrogen. The increase of H_2O concentration in the career-gas results in increasing the aerosol formation rate both in N_2 and in the air. If H_2O_2 is added to the reagents mixture, the aerosol formation rate increases by a factor of 2–3, if compared with dry nitrogen. The particle size is almost the same in all these three cases.

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Benzaldehyde Aerosol Formation Kinetics

The aerosol formation kinetics during BA photolysis in N_2–O_2 mixture is presented in Fig. 3. At t_0 increase from 3 to 6 s, the formed aerosol particle concentration N_a has a 300-fold increase. When the t_0 value is higher than 10 s, the aerosol concentration is almost constant with time. The average particle diameter increases with the irradiation time of the BA vapors. It follows from Fig. 3 that increase of O_2 concentration decreases the aerosol formation rate. The particle mass concentration is linear with t_0; at the same time, oxygen-concentration increase results in the decrease of the particle's mass generation rate. Water and oxygen exhibit no significant influence on the particle size distribution. The particle size distribution has two modes, the small one from 5 to 8 nm, and the large one from 50 to 80 nm. There are no particles with the intermediate size. Such type of size distribution is typical for the coagulation driven particle growth in the presence of essential evaporation. The increase of the mean particle diameter with the irradiation time results from the decrease of the small mode fraction, while the
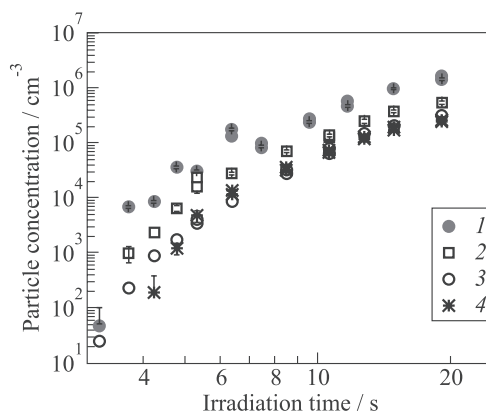

Figure 3 Oxygen influence on the aerosol formation kinetics during BA photolysis, $[\text{PhCHO}] = 1.56 \cdot 10^{16}$ cm^{-3}, $[\text{H}_2\text{O}] = 1.41 \cdot 10^{15}$ cm^{-3}: 1 — pure N_2; 2 — $[\text{O}] = 7.52 \cdot 10^{18}$ cm^{-3}; 3 — $[\text{O}] = 1.15 \cdot 10^{19}$ cm^{-3}; and 4 — $[\text{O}] = 1.51 \cdot 10^{19}$ cm^{-3}

modal diameter of the large mode is almost constant with time. The influence of water on the aerosol formation kinetics during BA photolysis in N_2 has been also investigated. Despite the fact that the increase in the H_2O concentration results in increasing the BA photolysis rate, the aerosol formation rate decreases with water concentration. The aerosol mass generation rate also decreases with water concentration.

Aerosol Yield

The aerosol formation yield φ_{aer} was calculated as the ratio of the aerosol mass formation rate W_{aer} to the benzaldehyde photolysis rate W_{phot}:

$$\varphi_{aer} = \frac{W_{aer}}{W_{phot}} = \frac{d(1/6\pi N d_m^3 \rho)/dt}{k_{phot}[\text{PhCHO}]}$$

where N is the particle concentration (cm^{-3}), d_m is the particle mean mass diameter, and k_{phot} is the aldehydes photolysis constant. The aldehydes photolyzed mass was calculated from the photolysis kinetics, and the aerosol particles mass was calculated by integrating the particle size distribution assuming that the particle's specific density is 1 g/cm^3. The aerosol-formation yield values determined for various experimental conditions are presented in Table 1. It follows from Table 1 that BA aerosol products yield in N_2 decreases with the oxygen and water concentration. Rough estimate of aerosol yield during BA photolysis [3] (5 μg/m^{3}ppm^{-1}, or about 1 mg/cm^{3}g^{-1}, that is 10^{-3}) is very close to that obtained in this study. The similar estimate for AA photolysis equals to zero. The decrease of the yield with the oxygen concentration can be qualitatively explained by the growing importance of photooxidation reactions. The photooxidation reactions result in production of gaseous products, rather than low-volatile compounds forming aerosol particles. The chemical composition of aerosol gas products also changes with the increase of O_2 concentration in the reaction mixture. The decrease of the φ_{aer} value with water concentration is opposite to that observed for acetaldehyde photochemical aerosol formation. This can be probably explained by the fact that aerosol particles formed during acetaldehyde photolysis exhibit hydrophilic properties, while for BA photolysis they are hydrophobic.

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Table 1 Aldehydes' photolysis and aerosol formation rates, and aerosol yields for various experimental conditions

$[N_2] \cdot 10^{-19}$, cm^{-3}	$[O_2] \cdot 10^{-19}$, cm^{-3}	$[H_2O] \cdot 10^{-15}$, cm^{-3}	$W_{phot} \cdot 10^{10}$, g/(cm^{3}s)	$W_{aer} \cdot 10^{15}$, g/cm^{3}s	$\varphi_{aer} \cdot 10^6$
Benzaldehyde					
2.69	0	< 2.36	18.1	228	1260
2.69	0	148	22.5	1980	880
2.69	0	206	30.2	1630	540
1.94	0.752	< 2.36	18.9	1010	580
1.53	1.15	< 2.36	17.0	970	570
1.18	1.51	< 2.36	21.1	730	350
Acetaldehyde					
2.69	0	< 2.36	4.87	1.07	2.2
1.94	0.752	< 2.36	6.53	0.522	0.80
1.94	0.750	40	6.53	0.522	0.75
1.94	0.738	120	4.50	0.585	1.3
1.94	0.727	240	3.23	0.808	2.5

**Chemical Analysis of Gaseous and Aerosol Products
of BA and AA Photolysis**

Carbonyl-containing gas products of aldehydes photolysis were analyzed using the high-performance liquid chromatography (HPLC) technique. Free radicals formed at aldehydes photolysis were identified using the spin-trapping method [8]. The qualitative physico-chemical analysis of aerosol products properties has been carried out. The aerosol composition was shown to change in the presence of oxygen in the career-gas. The aerosol products formed during AA photolysis in N_2 consist, most probably, of the polymeric form of acetaldehyde $(CH_3CHO)_n$. This is confirmed by the elemental analysis. The aerosol formed from AA in the presence of O_2 differs in chemical composition and includes oxygen-containing compounds with peroxy- O–O) bonds. The infrared (IR) absorption spectrum of the aerosol product formed under BA photolysis in nitrogen contains characteristic bands related to benzaldehyde. This allows one to assume that the aerosol product contains fragments of photopolymer $(C_6H_5CHO)_n$, which is known to form under photol-

ysis at 366 nm. The IR spectrum of the aerosol product formed under photolysis in air contains bands related to benzaldehyde as well, but they are much weaker than those observed for the product formed in N_2. In air, the predominant fraction is sharply different in solubility from the initial benzaldehyde; it does not contain phenyl fragment. This may be the product of oxidative opening of the cycle. These results are conformed by the data of ^{1}H NMR spectroscopy and GC–MS analysis. Based on the literature data and experimental results from this study, the possible chemical mechanism of aerosol formation during BA and AA photolysis in nitrogen and in air has been proposed.

Concluding Remarks

The investigation of aerosol formation kinetics during BA and AA photolysis showed that aerosol yield varies from 10^{-3} to $3 \cdot 10^{-4}$ for BA, and from $8 \cdot 10^{-7}$ to $2.5 \cdot 10^{-6}$ for AA, depending on the composition of the career-gas and humidity. The chemical composition of aerosol products changes in the presence of oxygen. The data on chemical composition of gas and aerosol products of benzaldehyde photolysis allow one to assume that the aerosol formation is initiated by two types of chemical processes: photochemical polymerization and opening of the cycle. In inert gas, phenyl radical formed in the primary photochemical step acts as an initiator of polymerization. The aerosol product is a mixture of fractions with different molecular mass, conserving the phenyl fragment in the structure of oligomeric molecules. In air, competition between two mechanisms is likely to take place, since, in addition to the fraction containing phenyl fragment, also a product of oxidative opening of the cycle is observed in the aerosol products. The aerosol products of AA photolysis in N_2 are polymeric products $(CH_3CHO)_n$. Chemical mechanisms, leading to the aerosol formations in the systems under investigation have been proposed.

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