# SOME PECULIARITIES IN THE INFLUENCE OF OZONE ON KINETICS OF PHOTONUCLEATION OF FORMALDEHYDE AND BENZALDEHYDE VAPOR

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*Received January 16, 1997*

*Kinetics of aerosol formation in the photolysis of benzaldehyde and formaldehyde vapor has been studied. The use of the excitation of reagents with light of different wavelengths makes it possible to conclude that aerosol formation is induced by free-radical photolysis of aldehydes. The nucleation in these systems is found to occur at high ozone concentration. The qualitative explanation to the experimental data obtained has been proposed.*

## INTRODUCTION

To gain a better understanding of a complex chemical dynamics of generation of an organic component of atmospheric aerosol the laboratory modeling is required of one of the key chemical mechanisms of generation and growth of aerosols, namely, a photochemical mechanism. During the past decades intensive experiments have been conducted in smog chambers and computer simulation has been developed with the use of the data obtained, which contributed to understanding of mechanisms leading to production of organic aerosols.[1,2]

The initial stage of gas components conversion to aerosols under exposure to light is poorly known. To investigate the kinetics of initial stages of aerosol formation in photolysis of a gas mixture in the particle flux we have developed a measuring complex whereby the photonucleation of phenyl halide and triethylamine is studied.[3–5] For these compounds, predecessors of production of ecotoxic compounds in the form of aerosol, the general kinetic regularities of the process were determined and its specific properties for every compound was shown. This paper describes aldehydes, the subject of investigation which present the products of incomplete oxidation of organic compounds in the atmosphere.[6]

The highest aldehydes concentrations (up to 200 ppb) are observed under photosmog conditions. Routinely in smog situations the increased ozone concentrations (> 150 ppb) are the necessary accompaniment of aldehydes. It is evident that under such conditions one of the unknown mechanisms of aldehydes transformation works, namely, formation of highly dispersed aerosols under exposure to light. Photoinduced polymerization of pure benzaldehyde (BA) vapor is described in Ref. 7. The ability of pure formaldehyde (FA) vapor to polymerize under different conditions is described in Ref. 8. However, physicochemical methods of observation of photochemistry of BA and FA never

dealt with the quantitative study of generation and growth of highly dispersed aerosols at early stages the process. This paper describes the investigation of kinetics of aerosol generation at photolysis of vapor of BA and FA in an inert gas and in the air. Particular attention has been paid to the involvement of ozone in the chemical mechanism of the process.

## EXPERIMENTAL PROCEDURE

Earlier[4] we have described the experimental technique measuring the concentration ($N_a$) and dimensions of highly dispersed aerosols resulting from photolysis of vapor of organic compounds. To reach the reproducibility of the results in the experiments with aldehydes some improved procedures have been developed. In the majority of experiments the light source was a mercury–vapor lamp DRT–220 instead of a lamp DRSh–500. To separate the light excitation band, at the wavelength above 330 nm, a glass filter was placed between the lamp and the quartz reactor. It has been known that ozone is generated in the air when the mercury–vapor lamps are in operation. The ozone concentration in the flux from the reactor was measured using an automated chemiluminescence ozonometer, developed at LGMI (for the concentrations lower than $1 \cdot 10^{13}$ cm$^{-3}$) or using the ozonometer «Tsiklon–1» (in the concentration range from $3 \cdot 10^{13}$ to $3 \cdot 10^{15}$ cm$^{-3}$) with the experimental error of ± 10%. The measurements revealed that in the case of air irradiation inside the reactor using the lamp DRSh–500 the O$_3$ content did not exceed 150 ppb ($< 8 \cdot 10^{12}$ cm$^{-3}$). For the lamp DRT–220 the O$_3$ content reached 3 ppm ($7 \cdot 10^{13}$ cm$^{-3}$). This amount of O$_3$ greatly exceeded the background level ($5.6 \cdot 10^{11}$ cm$^{-3}$). The measurements revealed that the O$_3$ concentration at the output of the reactor did not vary with the BA or FA vapor present in the air flux within the measurement error.

Before the experiments the liquid BA vapor source was purified using double distillation at low pressure, and then distilled in argon flow at atmospheric pressure

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($T_{boil} = 176° - 177°$C). The source of formaldehyde — paraformaldehyde (GERMED firm, Germany) was used without preliminary purification. The gas flow with different content of FA vapor was obtained when purging the carrier gas through a bubbler with paraformaldehyde powder located in a thermostat at temperatures from 37° to 60°C. In the case of BA the reagent vapor was created by passage the carrier gas through a $U$-shaped tube with silica gel saturated with liquid BA. The aldehydes concentrations in the flow were determined by purging the flow through the absorbing solution containing 2,4-dinitrophenylhyrazine. The generated hydrazines were measured by the method of High-Efficiency Chromatography of Liquids using a microcolumnchromatograph "Milichrom−1," with a column filled with a phase inverted sorbent LiChrosorb.[9] The mixture of acetonitrile and water, 3:1, served as an duant. Hydrazones were detected using UV-absorption at a wavelength of 354 nm (for formaldehyde) and 360 nm (for hydrazonebenzaldehyde).

Typical time of kinetic experiments was three or four hours. In the experiments with FA methodical difficulties were found when obtaining a stable FA vapor flow during this period. Some methods of preparation of reaction mixture were tested. The use of a thermostated vapor source enabled us to reach the necessary stability of the system parameters (the constancy of FA concentration in the flow was not worse than $10-15\%$) as well as to obtain the reproducible kinetic pattern of the process. It should be noted that under stable conditions of the experiment (the thermostat temperature, intensity, exposure time, etc.) after 5 or 6 hours of continuous work of the FA vapor source the gradual decrease of the aerosol particle concentration occurred and in 8 hours we observed its complete disappearance. Termination of gas passage through paraform for 10 or 12 hours and subsequent restoration of irradiation of a reagent flow under the same conditions reconstructed the aerosol concentration within the limits of reproducibility, which did not differ from the preceding concentration. These data well agree with data showing that there exists equilibrium in solid paraform between the forms with different molecular weight as well as that gas formaldehyde, may be generated from low-molecular forms[8] more easily. Kinetic measurements were repeated more than once day after day with the use of different samples of solid paraform. The reproducibility of $N_a$ was in the case of formaldehyde $\pm 100\%$ and $\pm 50\%$ for benzaldehyde.

## THE RESULTS AND DISCUSSION

It was revealed that the formation of highly dispersed aerosols from BA and FA only occurred when irradiating the carrier gas flow containing the BA and FA vapor with light. In darkness generation and growth of aerosols particles were not observed.

Thus, photolysis is necessary for initiating the formation of aerosol from aldehydes.

## Benzaldehyde

Figure 1 presents typical results of photolysis of BA vapor by DRT lamp in the inert gas and in air. The particle concentration ($N_a$) depends nonlinearly on time and intensity of irradiation that is specific of the photonucleation kinetics. From a comparison of the curves obtained in argon and air it is evident that the efficiency of the process in air is lower than in argon. It should be noted that chemical composition of accompanying carrier gas is scarcely affected by the aerosol concentration from BA as compared with the previously studied phenyl halides (PA) and triethylamine (TEA).[2, 3] As compared with the argon concentration in air, the $N_a$ aerosol concentration in the case of BA decreases approximately by an order of magnitude, and in the case of phenyl halides, the $N_a$ aerosol concentration increases by a factor of a thousand.
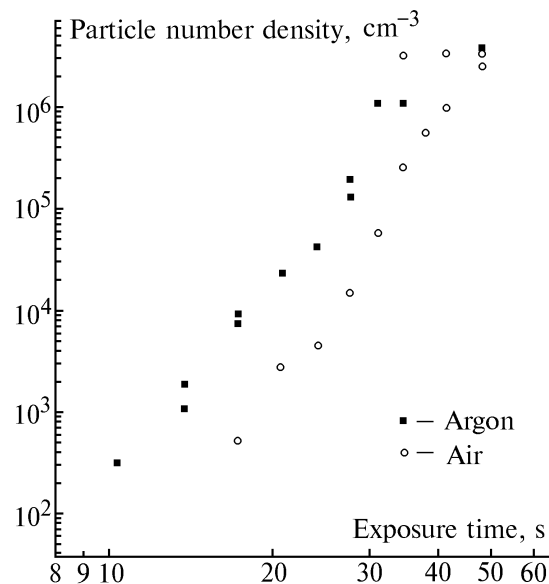


FIG. 1. *Dependences of the aerosol particle number density on the exposure time of benzaldehyde vapor in air and argon*; [PhCHO] = $1.1 \cdot 10^{16}$ mol/cm$^3$.

Note that in the system studied the photonucleation of BA in air occurs in the presence of an enhanced ozone content capable of strongly affecting the process efficiency and leveling the oxygen effect. When exciting BA with a long-wave light (>300 nm) no generation of highly dispersed aerosol in air and argon occurred. These experiments are in a good agreement with the known fact that photochemical reactions of BA strongly depend on the electron excitation energy.[10] Since in the photolysis in this area the excitation to a singlet state does not occur, we can draw a conclusion that the direct excitation of triplet state

is ineffective for the process activation due to low radiation intensity or a lack of energy.

The mean size of particles, originating in argon, varies from 20 to 50 nm, depending on the exposure time duration. The increase in aerosol concentration is accompanied by a growth of the mean aerosol size. From this it follows that simultaneously with the stages of aerosol generation from the gas phase the process of their further growth takes place. Some versions of the generation of larger particles are possible. Special experiments with variation of time of termination of particle generation and their detection have shown that the stages of dark growth do not contribute essentially to the particle concentration and size. To clear up a question on whether the BA molecules participate only in photoinitiation process or they are in addition involved in the subsequent stages of heterogeneous growth, it is necessary to accumulate various results and to supplement those by the data on physicochemical composition of aerosol.

### Formaldehyde

At photolysis of FA vapor in argon no aerosol formation was detected. At photolysis performed in air we managed to select the conditions of aerosol formation. The dependence of aerosol concentration on the exposure time is depicted in Fig. 2.
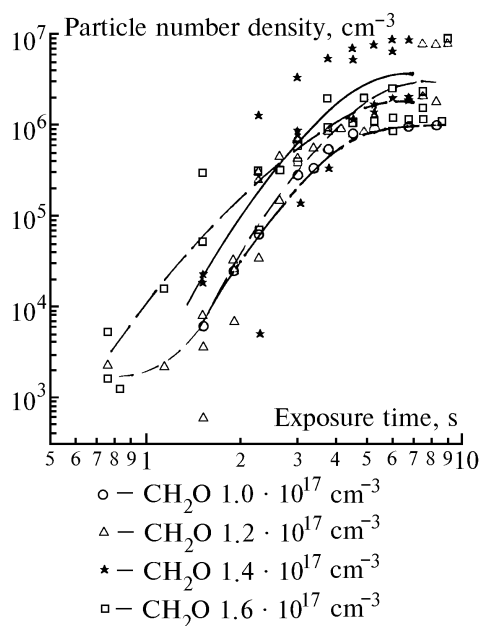


$\circ$ — $CH_2O$ $1.0 \cdot 10^{17}$ cm$^{-3}$
$\triangle$ — $CH_2O$ $1.2 \cdot 10^{17}$ cm$^{-3}$
$\star$ — $CH_2O$ $1.4 \cdot 10^{17}$ cm$^{-3}$
$\square$ — $CH_2O$ $1.6 \cdot 10^{17}$ cm$^{-3}$

*FIG. 2. Dependences of the aerosol particle number density on exposure time for formaldehyde vapor in air at different concentrations of* $CH_2O$ *vapor.*

Kinetic curves have the shape typical for aerosol generation initiated photochemically. With the increase of exposure time of reagents not only the particle number density increases but also the mean diameter of aerosol grows from ~ 3 to 15 nm.

Since the composition of primary products of FA photochemical dissociation depends on the energy of electron excitation, we have carried out an extensive investigation into the influence of the photolyzing light wavelength on the nucleation efficiency. The aerosol formation turned out to be observed only in the region of complete dissociation $H_2CO \rightarrow H + HCO$ ($\lambda < 330$ nm). At the molecular dissociation $H_2CO \rightarrow H_2 + CO$ ($\lambda < 330$ nm) the aerosol formation does not occur. These results enable us to draw the conclusion that the FA photonucleation takes place with participation of free radicals appearing due to interaction between the primary products of FA photolysis. There is another version, namely, the initiating effect of $HO_2$ radicals generated during the interaction of H and HCO with oxygen in air.

Note that the photonucleation of formaldehyde was observed only in the presence of enhanced ozone concentration ($5 \cdot 10^{13}$ cm$^{-3}$).

The estimates done show that several ways of the process initiation by ozone are possible. The first way is the $O_3$ involving in the reactions with radicals appearing at photolysis of FA. The second way is through the atoms $O(^1D)$ and $O(^3P)$, generated at photodissociation of $O_3$, which at these ozone concentrations becomes essential. Involving in the process of high-reactive particles, occurring at $O_3$ photolysis, can additionally initiate aerosol formation in the reactions with unexcited molecules of FA. Since apart from O atoms the singlet excited oxygen molecules occur, their reactions with aldehydes can also result in aerosols.

The experimental data obtained and their analysis do not enable us to determine uniquely the main way of aerosol generation (electron excitation and photolysis of formaldehyde or reactions of products of ozone photolysis with unexcited formaldehyde).

### CONCLUSIONS

Kinetics of aerosol formation at photolysis of benzaldehyde and formaldehyde vapor was investigated. The use of light with different wavelengths (in the range of molecular and radical dissociation) for the excitation has made it possible to draw the conclusion that aerosols are generated at the free radical aldehyde photolysis. It was determined that the nucleation in these systems takes place at high ozone concentrations. Therefore it is necessary to consider the participation of $O_3$ in the process of aerosol formation of aldehydes both due to the $O_3$ photolysis (in the case of formaldehyde) and due to the $O_3$ interaction with the primary radicals arising from the aldehyde photolysis.

### ACKNOWLEDGMENTS

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