Simplest aldehydes as efficient precursors of atmospheric photoaerosols

G.I. Skubnevskaya, G.G. Dul'tseva, and S.N. Dubtsov

Institute of Chemical Kinetics and Combustion,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk

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The results of investigation into photolysis and photonucleation of simple aldehydes, most typical of car exhausts and emissions of power plants, are generalized. It is shown how the secondary phototransformations of aldehydes (formaldehyde, acetaldehyde, and benzaldehyde) lead to formation of organic acids, peroxyl compounds, and aerosols as secondary pollutants. The application of experimental kinetic and analytical methods along with numerical simulation of phototransformation and photonucleation processes allowed us to study short-lived free radicals, gas products, and photoaerosols generated from the aldehydes. The data obtained in our studies along with the literature data allowed us to propose and validate physicochemical mechanism of the aldehyde photonucleation at the level of elementary stages from the primary event of photolysis to the gas-to-particle phase. This transition is followed by growth via adsorption of other species from air including aldehydes and accompanying water vapor, as well as other optically active compounds.

Introduction

The dynamic equilibrium between sources and sinks of chemical compounds in the atmosphere is now significantly distorted because of anthropogenic impact and fast growth of the number of artificial substances emitted into the ground atmospheric layer. Aldehydes, which are the products of incomplete oxidation of organic compounds in the processes of combustion and photooxidation under exposure to sunlight, occupy a particular place among these substances.

The high chemical activity of aldehydes in the environment is caused, first of all, by the presence of CHO fragment. Thanks to this, the lowest aldehydes in solutions can be easily polymerized and oxidized by the air oxygen to acids which are catalysts of polymerization. The polarization of the $C^{(+)} = O^{(-)}$ bond of aldehydes causes active addition of such nucleophile as water, what is especially important under conditions of the ground atmospheric layer.

Aldehydes fall in the category of photochemically active admixtures in the troposphere, since the aldehyde group CHO is characterized by intense absorption bands in the IR and UV regions. In the ground atmospheric layer, aldehydes easily disintegrate under the exposure to sunlight, since the maximum in the electronic absorption spectra ($n \rightarrow \pi^*$) of aldehydes lies in the region from 290 to 350 nm with the energy sufficient to break chemical bonds. As a result, the lifetime of the aldehydes is relatively short (two to three hours for the simplest aldehyde – formaldehyde).[1–5] The background concentrations of aldehydes at the level of ppb are formed in the process of oxidation of their precursors – the corresponding hydrocarbons.[1,3,4]

With growing anthropogenic pollution of the atmosphere, the concentration of artificial organic components increases. The chemical balance of the atmosphere between sources and sinks is thus distorted under the growing anthropogenic impact.

The air of heavily populated industrial regions includes hydrocarbons not typical of the background atmosphere and often toxic. Under the initiating effect of sunlight, ecologically dangerous situations of photochemical smog occur with active participation of aldehydes and, in the first turn, formaldehyde, which is a very strong mutagen.[6,7]

The high chemical activity of aldehydes connected with the presence of the carbonyl group C = O in the molecule determine their particular role in organic chemistry of the atmosphere.[1] Aldehydes easily react with various atmospheric constituents. Especially complex chemical transformations take place under conditions of smog in which the concentration of aldehydes can achieve 150–200 ppb, provoking stress ecological situations. Under exposure to sunlight, the aldehydes photolyze with high yield forming long-lived free radicals ($RCHO + h\nu \rightarrow R^* + {}^*CHO$, $\lambda_{abs} = 290 - 360$ nm) (Ref. 8). The chain processes of the organic compounds photooxidation are thus branched with formation of new highly toxic components, for example, peroxilacylnitrates.

The urgency of the problem of aldehydes in the atmosphere has initiated our works involving field measurements,[12,13] analysis of possible sources and sinks of aldehydes, study of kinetics of gas-phase reactions under action of UV radiation with the following photonucleation[9,11] and in the combustion processes,[13] and numerical simulation on different scales.[3,11,13]

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The available data on the aldehyde content and dynamics in the atmosphere of Siberia, as well as participation at various stages of global biogeochemical and geophysical cycles are insufficient for evaluating the global influence of aldehydes. That is why we have conducted field measurements of aldehydes typical of car exhausts (formaldehyde, acetaldehyde, and benzaldehyde) in the air of Novosibirsk and its suburbs, numerically simulated the photochemical mechanism of the aldehyde generation in the atmosphere, and modeled the photochemical processes with participation of aldehydes under laboratory conditions.[12,13]

We have shown that in addition to gas-phase products, photooxidation of aldehydes results in formation of aerosol particles with size <0.1 μm, for the first time studied their chemical composition, and proved the participation of free radicals in kinetics of the process. Thus, the most ecologically dangerous fraction of the atmospheric aerosol has been thoroughly studied by us.[9–11] Until now it was believed, according to thermodynamic calculations,[3] that only low-volatile aldehydes are capable of forming aerosols. Our studies of photochemistry of formaldehyde, acetaldehyde, and benzaldehyde have shown that even the highly volatile lowest aliphatic aldehydes are comparable with representatives of the class of low-volatile aromatic aldehydes in their capability of forming aerosols at photolysis in the region of maximum absorption of the carbonyl group (290–330 nm), i.e., in the lower troposphere.

Content of aldehydes in the urban air

Aldehydes in air were analyzed by concentrating them in the form of 2,4-dinitrophenylhydrazones and then evaluating by the method of high-performance liquid chromatography (HPLC) on the Milikhrom–1 chromatograph, as was described in detail in Refs. 7 and 11. The measurements have shown that the content of H_2CO in the air varies, on average, from 0.2 to 105 ppb. The highest content of H_2CO (160–338 ppb) was observed near highways and objects of the power supply system. The content of acetaldehyde and benzaldehyde on the whole is proportional to the level of H_2CO and varies synchronously with it making up 8–13% (acetaldehyde) and 3–5% (benzaldehyde) of the H_2CO content. It should be noted that in some summer fine windless days we observed situations typical of photosmog with high content of formaldehyde and ozone[12] (see Fig. 1).

For more justified interpretation of the observations, the data of the formaldehyde monitoring were compared with the data of scenario calculations of pollution in the Novosibirsk Scientific Center and impurity transport from Novosibirsk. These calculations were performed by the research team headed by Professor V.V. Penenko (Computer Center SB RAS). The comparison has shown that the concentrations of aldehydes in the air are formed both by local sources and in the process of intense photochemical oxidation of organic admixtures at the air mass transport at the regional scale.[3,13]

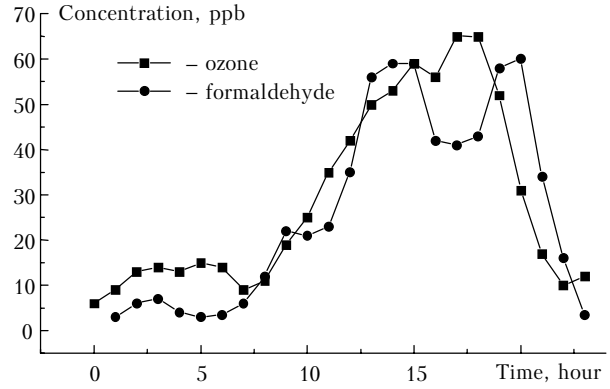

Fig. 1. Typical example of the situation of photosmog with highly elevated concentrations of ozone and formaldehyde in the Novosibirsk Scientific Center.

Aldehydes as initiators of aerosol formation in air

Aldehydes are photochemically active substances and can break down into free radicals under exposure to sunlight $RCHO \rightarrow R + HCO$ thus providing their atmospheric sink. Besides, aldehydes are the sources of peroxide radicals $H,HCO + O_2 \rightarrow HO_2$. As the result, the concentration of HO_2 in the polluted atmosphere can achieve 10^9 cm^{-3}, what is sufficient to make them competitive in smog-formation chemistry with the most active hydroxyl radical OH, because the quasistationary concentration of OH in the atmosphere does not exceed $6 \cdot 10^6$ cm^{-3} (Refs. 3 and 4).

The situations of photosmog with high content of aldehydes and ozone set the prerequisites for formation of fine-disperse aerosols in the process of numerous photochemical transformations. The key aspect of the problem of photosmog – formation of fine-disperse aerosols from gaseous precursors – is still poorly studied. The complex chemical dynamics of the organic aerosol formation provide the most information on participation of gaseous precursors and the role of active intermediate products at the initial stages of nucleation. However, because of the experimental limitations, most researches into photonucleation deal with aerosol particles of more than 50 nm in diameter, for which the process of coagulation smoothes, to a great degree, the specific chemical character of initial stages of the gas-to-particle transition.

Because of toxic properties of the organic component grouped in the fine (nanometer particle size) fraction of the atmospheric aerosol, we studied the photonucleation of aldehydes under laboratory conditions on a flow-through setup with photolytic generation of the aerosol.[9] Submicron aerosols were detected with a diffusion aerosol spectrometer designed at the Institute of Chemical Kinetics and Combustion,

SB RAS (Ecos Group headed by A.N. Ankilov). It was found that in the photolysis of aldehydes, the generation of aerosols is more intense at the elevated ozone concentration typical of the conditions of photosmog. The study of the kinetic characteristics of this process has shown that although the yield of aerosol products is low (only 10^{-7}–10^{-9} of the yield of gaseous products of photolysis), the appearance of the disperse phase has a marked influence on the processes of photochemical transformation.[13]

The anthropogenic emission of organic compounds into the atmosphere is estimated, as a whole, as (in terms of hydrocarbons) 100 Tg/year (Refs. 1 and 4). Formation of carbonyl compounds at photooxidation of such amount of hydrocarbons can be estimated based on the relation between the background concentrations of methane ($3 \cdot 10^{13}$ cm^{-3}) and formaldehyde – the intermediate product of its photooxidation ($2 \cdot 10^{11}$ cm^{-3}). This estimation gives the rate of generation of secondary aldehydes due to the phototransformation as 0.8 Tg/year. The application of the obtained characteristics of the aldehyde photonucleation process, in particular, the quantum yield of photonucleation, allows us to estimate the contribution of aldehydes into the organic aerosol generation in the atmosphere as $5 \cdot 10^{-6}$ Tg/year.

It should be noted that the aldehydes can react with other pollutants, producing adducts, which transit into the solid phase. Thus, for example, in the presence of sulfur dioxide, the sulfate derivative of formaldehyde is produced. As a result, the concentration of formaldehyde in aerosols somewhat exceeds the equilibrium value determined by the Henry law.[4] Our measurements of the formaldehyde, acetaldehyde, and benzaldehyde content in car exhausts, separately in the gas phase and in aerosol particles, have shown that up to 25% of formaldehyde is in the disperse phase, when it is adsorbed on foreign particles or reversibly produces the adducts with aerosol; the corresponding value for acetaldehyde is 3–7%, and the benzaldehyde is almost equally distributed between the both phases.

Thus, the thorough investigation into photochemistry and photonucleation of simple aldehydes, most typical of car exhausts and emissions of power stations, at the current level of basic knowledge has allowed us to propose the scheme (at the level of elementary stages) of photochemical aerosol formation of formaldehyde, acetaldehyde, and benzaldehyde from the primary event of the aldehydes photoexcitation to the primary stage of their nucleation in the gas-to-particle transition.

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