Carboxylic acids as the key molecules in photonucleation of aldehydes in the gas phase

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The conditions for photochemical generation of aerosol particles were studied using, as an example, photolysis of some aldehydes (acetaldehyde, formaldehyde, and benzaldehyde). Results of laboratory experiments have been confirmed by calculations. Evidences were obtained on the existence of competing mechanisms of aerosol generation depending on the chemical nature of a substance subject to photolysis.

Atmospheric photooxidation of organic substances is accompanied by generation of intermediate products: aldehydes, ketones, carboxylic acids, and peroxides. All these products are photoactive and take part in transformations of atmospheric constituents. To understand the mechanisms of photochemical processes in such complex multicomponent systems as the polluted atmosphere of industrial regions, one can perform laboratory modeling, i.e., limiting the number of components and studying their photochemical transformations separately.

In our studies of photolysis of aldehydes, which are indispensable participants of the photochemical smog formation, we have found that, besides the gas-phase products, the disperse phase, namely submicron aerosol, is generated.[1,2] Carboxylic acids were found among the gas products of photolysis. As known, aldehydes are subject to acid-catalyzed polymerization; therefore, we decided to study the role of carboxylic acids in photonucleation of aldehydes.

Experiment

For our study, we have selected the most abundant atmospheric aldehydes: formaldehyde and acetaldehyde that are generated in photooxidation of aliphatic compounds, as well as benzaldehyde being the intermediate product of oxidation of aromatic hydrocarbons. The aldehyde vapor (at the partial pressure of 0.1–8 Torr) was subjected to photolysis in a flow of a carrier gas at the atmospheric pressure and room temperature in a quartz photochemical reactor under the action of radiation of a medium-pressure mercury lamp. As a carrier gas, we used argon, air, and artificial air (mixture of nitrogen and oxygen). The spectral regions needed for photolysis were selected using glass filters.

The kinetics of aerosol formation and the size spectra of generated aerosol particles were studied with a setup based on a diffusion aerosol spectrometer (DAS) capable of detecting aerosol particles with the size from 2 to 100 nm (Ref. 2). The composition and properties of the aerosol and gas products of photolysis were studied by the methods of UV and IR spectroscopy, liquid chromatography, photocolorimetry, and qualitative chemical analysis.

Results and discussion

Generation of aerosol particles was observed at photolysis of acetaldehyde and benzaldehyde in the region of radical decomposition ($\lambda < 330$ nm) in both an inert gas and air. Generation of aerosol with the participation of formaldehyde was observed only in air. Generation of formic and acetic acids as gaseous products of photolysis was observed only in the cases when the carrier gas was air. It was found that the concentration of the generated acids depends on concentration of the initial aldehyde, as well as on the time of irradiation in the reactor. The formic acid was present in gaseous products of photolysis of all the aldehydes studied. The dependence of concentration of formic acid on the time of irradiation of aldehyde vapor is given in Table 1. The acetic acid was detected only at photolysis of acetaldehyde; its concentration in the flow coming from the reactor outlet was no more than 10% of the formic acid concentration.

Table 1. Concentration of formic acid in mixture at the reactor outlet for the case of aldehyde photolysis in the airflow

Aldehyde, Torr	HCOOH, mol · cm^{-3}		
	t = 1 min	t = 10 min	t = 100 min
HCHO, 1.2	$4.3 \cdot 10^{14}$	$7.2 \cdot 10^{14}$	$9.8 \cdot 10^{14}$
CH_3CHO, 1.2	$1.5 \cdot 10^{15}$	$6.8 \cdot 10^{15}$	$7.5 \cdot 10^{15}$
C_6H_5CHO, 0.5	$< 1 \cdot 10^{14}$	$1.3 \cdot 10^{14}$	–

To elucidate role the carboxylic acids plays in the photonucleation of aldehydes, we have conducted experiments with addition of acetic and formic acids to the flow of the reacting mixture in the inert gas and in air before and after the photolysis.

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Formaldehyde. No disperse phase was observed at photolysis of formaldehyde in argon. In the case that the vapor of formic acid was added to the flow of the reacting mixture (formaldehyde + argon) before it entered the reactor, aerosol was generated at photolysis. As the vapor of the acetic acid was added to the same mixture, no aerosol was observed. When the acids were added to the flow of the reacting mixture after it left the reactor, both the concentration of aerosol particles and their size spectrum remained the same as in the case of photolysis without any additions.

Such a behavior of the formic acid means that it takes part in gas-phase reactions of generation of low-volatile products. These reactions follow photodecomposition of formaldehyde in the reactor. The formic acid serves a source of additional oxygen atoms for the products of formaldehyde photooxidation, and this leads to the decrease in the volatility of the products down to their transition into the disperse phase.

Acetaldehyde. At photolysis of acetaldehyde in argon, we observed the concentration of aerosol particles 100 times higher than at photolysis in air. It was shown, using the methods of HPLC and IR spectroscopy, that the aerosol generated in argon consisted of tetramers of acetaldehyde, while the aerosol generated in air consisted of oxygen-containing components, including the carboxyl group as well. Addition of vapor of the formic acid ($\sim 10^{15}$ cm^{-3}) to the flow (in argon) before photolysis caused the four to five times decrease in the concentration of generated particles as compared to photolysis without any HCOOH additions. At the same time, addition of the formic acid to the flow at photolysis in air had no effect on the concentration of generated particles.

When adding the vapor of the acetic acid to the flow of acetaldehyde in argon, the concentration of aerosol particles decreased by 2 to 2.5 times as compared with their concentration at photolysis without any additions. In the case of acetaldehyde photolysis in air, the addition of acetic acid did not change the concentration of generated aerosol particles.

Thus, carboxylic acids take part in transformations of aldehydes, causing formation of less volatile products than aldehydes themselves in the case that carboxylic acids make up the sole source of extra oxygen. Decreasing the volatility of the products, they serve as additional initiators of polymerization, for example, at photolysis of formaldehyde in argon. At photolysis of acetaldehyde in argon (generation of tetramers), when a more efficient channel of aerosol formation exists that does not need in an enhanced oxygen containing fraction, adding the formic acid causes a decrease in the concentration of aerosol particles which approaches the value observed at the photolysis in air.

To explain the regularities observed, we have performed numerical simulation of the formic acid generation at formaldehyde photooxidation and evaluated the part of the acid itself and the products of its transformation in the initiation of gas-to-particle conversion. The efficiency of the conversion channel was characterized by the relative increase in the boiling point of a reaction product as compared with that of the most high-boiling reagent. Simulation was performed by use of the NICK iteration algorithm.[3] The rate constants of the elementary stages were chosen according to NIST recommendations (USA).[4] The simplified scheme of the gas-phase stages of transformation of aldehydes (with formaldehyde as an example) with generation of the formic acid can be represented as follows:

$HCHO + h\nu \rightarrow H + HCO$	w_0
$HCO + O_2 \rightarrow CO + HO_2$	$5.6\cdot10^{-12}$ cm^3/s
$HO_2 + HCHO \rightarrow HOCH_2OO$	$7.5\cdot10^{-14}$ cm^3/s
$HOCH_2OO \rightarrow HO_2 + HCHO$	151 s^{-1}
$HOCH_2OO + HOCH_2OO \rightarrow$ $\rightarrow HCOOH + CH_2(OH)_2 + O_2$	$7.0\cdot10^{-13}$ cm^3/s
$HOCH_2OO + HOCH_2OO \rightarrow$ $\rightarrow HOCH_2O + HOCH_2O + O_2$	$5.5\cdot10^{-12}$ cm^3/s
$HOCH_2O + O_2 \rightarrow HCOOH + HO_2$	$3.5\cdot10^{-14}$ cm^3/s
$HOCH_2O \rightarrow H + HCOOH$	$1.17\cdot10^3$ s^{-1}

As to the stages of initiation of the gas-to-particle conversion with the participation of formic acid, there is some uncertainty in the values of the constants because of incompleteness of the database (in particular, no data on the acid-initiated polymerization of aldehydes can be found in it) and insufficient data on the chemical mechanism of the process. For the tentative estimates, we used the following assumption: in the case that formation of aerosol is possible in the absence of air (at photolysis of acetaldehyde in argon), polymerization initiated by carboxylic acids competes with the process of formation of the disperse phase at polymerization of aldehyde itself. In the case that aerosol is not generated in the absence of air (formaldehyde), additions of carboxylic acids initiate its generation following just the mechanism, which takes place at photolysis in the presence of air.

Conclusions

Carboxylic acids generated in the gas phase at photolysis of aldehydes in air initiate their polymerization by the acid mechanism. If another way – polymerization of aldehyde itself – exists (as in the case of acetaldehyde), competition between these two mechanisms is observed, and the resulting effect depends on the ratio between their efficiencies.

References

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