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Water as a Clustering Agent in Photolysis and Photonucleation of Benzaldehyde Vapor

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The role of water vapor in benzaldehyde photolysis and photonucleation is investigated experimentally as well as with the help of semiempirical estimation of reaction intermediates. It is shown that water molecules act as a clustering agent that brings together two benzaldehyde molecules. This mechanism may explain the experimental observation of glyoxal formation during photolysis in humid carrier gas even in the presence of oxygen, the dependence of the concentrations of glyoxal and diphenyl on water-vapor concentration, and some other unusual facts concerning minor products detected in the experiment.

Introduction

Nanoparticle formation is a process which is important both under natural conditions (e.g., in the atmosphere) and in technological applications (e.g. in the deposition of dielectric layers from the gas phase). Nucleation processes start with gas-to-particle conversion, which is often a chemical transformation, and proceed through particle growth. The latter stages may include not only chemical but also physical steps. In particular, when considering coagulation, one should take into account possible energy release due to the formation of liquid or solid particles. In the general case, the size of particles is affected not only by composition but also by pressure, temperature, and geometric parameters of the reaction arrangement. For many systems, it is convenient to simulate coagulation with the help of Smoluchowski equations,[1] but this method requires careful determination of the gaseous species, which is a monomer for aerosol formation. This makes it necessary to take into account the chemical nature of nucleation stages (especially initial ones), which is extremely important in the investigation of photonucleation in organic vapors, in particular aldehydes.

Benzaldehyde (BA), the simplest aromatic aldehyde, attracts the attention of researchers because of its significance in atmospheric chemistry of polluted urban air.[2] In addition to anthropogenic emission, aromatic aldehydes, including substituted ones, are emitted into the atmosphere by plants on a global scale. Although this process accounts for a relatively small amount of total atmospheric aromatics, it may affect the composition of fine particulate matter in the atmosphere, especially that within the breathable particle size range starting from several nanometers. It was shown in our previous investigations that the photolysis of BA vapor results in the formation of nanoparticles with a low yield ($\sim 10^{-3}-10^{-5}$). Until recently, investigations of BA photolysis focused on major gas-phase products.[3,4] As far as heterogeneous processes involved in BA photolysis were concerned, only the formation of a photopolymer was reported.[5,6] However, keeping in mind the low yield of particulate matter in BA photolysis, we see that, in order to study the intimate mechanisms of gas-to-particle conversion in BA vapor, one should inevitably pay prime attention to the analysis of minor gas products, the yield of which is comparable with that of the particulate matter. In particular, the role of short-lived free radicals formed in the primary steps of BA photodecomposition is to be studied. A recent investigation of the fate of HCO radical formed in BA photofragmentation under irradiation by light with different wavelengths outlined some links with atmospheric chemistry, but no detailed chemical analysis of the products was carried out.[7] In our previous investigations, we observed the dependence of BA photolysis and photonucleation rates on water-vapor concentration. However, it was unclear what elementary steps might be affected by the presence of water. The goal of the present study was to measure the dependencies of BA photolysis and photonucleation rates on water-vapor content, to analyze water-related changes in the concentrations of minor products, and to explain the mechanisms by which water affects the process in general.

Experimental Section

BA (chemically pure grade, 99.9%, containing water (<0.02%), benzoic acid (<0.05%), and benzonitrile (<0.05%) as impurities, as indicated by gas chromatography−mass spectrometry) was distilled under reduced pressure and then distilled in argon flow at atmospheric pressure ($T_{\text{boil.}} = 176-177$ °C). Compressed gases (high-purity grades, O_2 99.999% and N_2 99.999%) were used after purification by passing through a special gas-purification system with sorbents and molecular sieves. Aerosol impurities were removed with HEPA filters. Water vapor was removed from the carrier gas by passing through a gas-purification unit composed of columns filled with silica gel, active carbon, and molecular sieves NaX. Water-vapor concentration in the gas flow was measured with a PM CENTER 311 humidity and temperature meter; for thoroughly dried gas mixture, water-vapor content was estimated after long-term sampling with a cobalt chloride humidity indicator.

BA concentration in the gaseous mixture under static conditions was measured with a HP 8354 spectrophotometer by absorption at 233 nm in the cylindrical cell ($l = 82$ mm) and also chromatographically after passing the flow with BA vapor through a solution with 2,4-dinitrophenylhydrazine. The concentration of the formed hydrazone was measured with HPLC on a Milikhrom-1 chromatograph with a LiChrosorb (reverse phase) column. An acetonitrile−water (3:1) mixture was used as an eluent. The hydrazone was detected by UV absorption at 360 nm.

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The BA photolysis under the static conditions (for spectrophotometric examination) was performed in a cylindrical cell (i.d. = 18 mm, l = 82 mm) with Suprasil windows by using the same light source as in aerosol experiments described in detail previously.[8] Photolysis of BA flow in the carrier gas (for chemical analysis of gas and aerosol products) was performed in a quartz cylindrical cell, 240 mm long with an i.d. of 22 mm. The cell was irradiated with the unfocused light of a middle-pressure Hg lamp DRSh-500 through the side wall; the irradiation time was varied by changing the irradiated volume of the cell with the help of a black screen. The length of irradiated side wall varied from 0 to 220 mm. The distance from the lamp to the cell was 270 mm. Gas and aerosol products were collected for analysis at the outlet of the reaction cell.

The IR transmission spectra were recorded with a Fourier Bruker IFS-113V spectrometer within the wavenumber range 400−2500 cm^{-1} with a resolution of 1 cm^{-1}. We used a specially constructed cell with optical windows made of NaCl.

The analysis of aerosol products was carried out by using GC−MS (HP6890N/5973N). Aerosol particles were collected on a glass-fiber aerosol filter. Aerosol material was extracted with acetone (high purity grade) in an ultrasonic bath. NMR analysis of aerosol products dissolved in CD_3CN was carried out with a Bruker DFX200 spectrometer.

EPR spectra of spin adducts were recorded with a Bruker EMX spectrometer in a standard quartz cell. The stability of the magnetic field was 2 mT/h. The microwave power was not higher than 10 mW, and the modulation amplitude was 0.03−0.10 mT. The modulation frequency was 100 kHz, and the receiver gain was $1 \times 10^4 - 6.32 \times 10^5$. The time constant was 0.2 s, and the scan rate was 10 mT/200 s. The microwave frequency was 9.6 GHz (X-band). The instrumental error of measuring the constants of hyperfine splitting was 0.004 mT.

Products were also analyzed by means of thin-layer chromatography with Silufol plates and by using the procedures of qualitative microanalysis.

Results and Discussion

The yield of aerosol versus irradiation time (irradiation dose) and BA-vapor concentration was investigated by us previously.[8] We noticed that humidity affects the rate of BA photolysis and the yield of particulate matter in different manners: water vapor enhances photolysis and hinders aerosol formation. The chemical nature of this phenomenon remained unclear because of the lack of data on the corresponding changes in the composition of minor gas products. In the present investigation, we obtained these data.

The yield of aerosol as a function of irradiation time for different water-vapor content in the reaction mixture is shown in Figure 1. One can see that the concentration of aerosol particles in the mixture after photolysis decreases with an increase in water-vapor concentration.

To explain such an effect of water vapor on photonucleation, we calculated changes of energy accompanying the interactions between species at the initial stage of BA photolysis in the presence and in the absence of water. The effect of oxygen was also simulated. It was shown that water, in contrast to oxygen, plays an essential part in the association of gaseous BA. The method applied for these estimations, and the results are described below in the Calculations section.

Calculation results allowed us to assume that the presence of water vapor in a concentration comparable with or somewhat lower than that of BA (about 3.5×10^{16} cm^{-3}) should manifest itself in the kinetic characteristics of BA photolysis and photonucleation. In order to obtain the experimental data within a broader range of water-vapor concentrations, we performed BA photolysis in the carrier gas specially purified to $[H_2O] \leq 3.5 \times 10^{13}$ cm^{-3} by passing through the gas-purification unit.

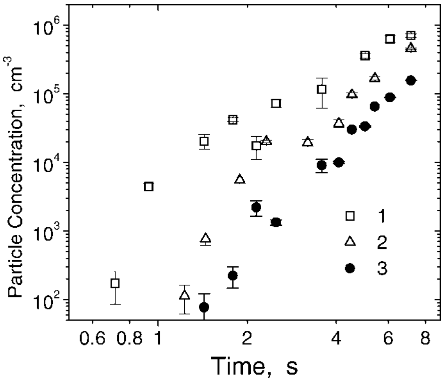

Figure 1. Aerosol yield from BA photolysis in air versus irradiation time for different water-vapor concentrations. $[H_2O]$, cm^{-3}: (1) 3.5×10^{16}, (2) 2.2×10^{17}, and (3) 3.3×10^{17}. [BA] = 1.25×10^{16} cm^{-3}, T = 22 °C.

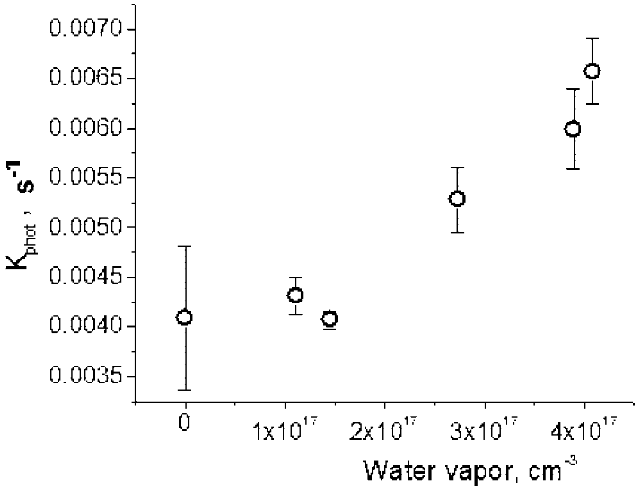

Figure 2. Dependence of BA photolysis rate in air on water-vapor concentration in the reaction mixture.

The rate of BA photolysis was measured in the presence of water vapor in a quartz cell under static conditions. The BA concentration was measured as UV absorption at 233 nm. The photolysis rate was observed to increase with an increase in water-vapor concentration, as shown in Figure 2. Oxygen did not affect the rate of BA consumption.

In addition, chromatographic analysis of the flow of the reaction mixture after photolysis showed that an increase in water-vapor content causes changes in the composition of photolysis products. The concentrations of some minor products, namely, glyoxal and diphenyl, exhibited the most noticeable changes: glyoxal yield increased from 0.08% (of the reacted BA) to 0.62% with an increase in water-vapor concentration from 1.4×10^{16} to 1.8×10^{17} cm^{-3}. The yield of diphenyl increased too (from 0.01 to 0.46%). Dependencies of glyoxal and diphenyl yields on water-vapor concentration are shown in Figure 3.

Among carbonyl compounds, formaldehyde and benzophenone are also present in the products of BA photolysis. The concentrations of these compounds were measured by means of HPLC in the form of hydrazones (after the interaction with 2,4-dinitrophenylhydrazine). The yields of H_2CO and

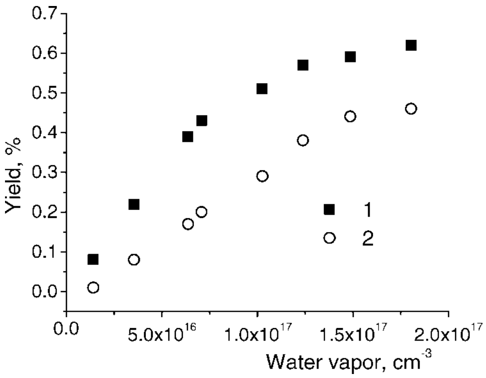

Figure 3. Dependence of glyoxal (1) and diphenyl (2) yields from BA photolysis on water-vapor concentration in the reaction mixture. [BA] = 3.54×10^{16} cm^{-3}.

$C_6H_5COC_6H_5$ were found to be independent of water-vapor content at the accuracy of measurement error (15% for formaldehyde and 10% for benzophenone). We showed in a previous investigation that the yields of H_2CO and $C_6H_5COC_6H_5$ increase almost linearly with an increase in BA concentration in the reaction mixture, whereas the yields of glyoxal and diphenyl only weakly depend on BA concentration within the range $3.5 \times 10^{15}-2.8 \times 10^{17}$ cm^{-3}. On the contrary, the yields of formaldehyde and benzophenone depend on BA concentration and only weakly change with an increase in water-vapor concentration. Such a behavior of these minor products allows us to assume that water participates in the formation of glyoxal and diphenyl, whereas formaldehyde and benzophenone formation is unaffected by water.

In order to explain these features, it was necessary to understand how water interacts with the components of the reaction mixture under investigation. The experimental data allowed us to assume that water somehow participates in the formation of clusters (possibly dimers) of BA. In particular, the formation of glyoxal in approximately the same amounts in the absence and in the presence of oxygen (other conditions being kept constant) suggests that the formyl radical HCO generated in the primary photolysis step is incorporated into a complex (possibly participated by water); otherwise, it would react with oxygen (e.g., $HCO + O_2 \rightarrow HO_2 + CO$, $k = 5.6 \times 10^{-12}$),[9] and glyoxal concentration would be less than that in the absence of oxygen. In addition, if HO_2 were formed, it could be recorded in the form of a spin adduct. We searched for HO_2 in the reaction mixture by using spin traps that proved to be sensitive to peroxy radicals in the gas phase[10] but failed to observe the spin adducts of HO_2.[10] The calculations described below had to answer these questions concerning the mechanism of water effect on BA photolysis and photonucleation.

Calculations

Calculations were based on the idea of a hypothetical adsorption complex (AC) defined and described by us previously.[11,12] An AC is, in this case, some intermediate state formed when the reagents approach each other to a distance of about 1.5−2 times the length of the expected chemical bond. We assume that the formation of reaction products occurs through this state. Modeling involving AC allows us to suppose what products can be formed from the AC and to decide whether the reaction is possible. AC is a model state in which the molecules are held together by weak bonding (e.g., hydrogen bonds or Van der Waals interactions). In the case under consideration, AC is a kind of Van der Waals complex formed by several BA molecules.

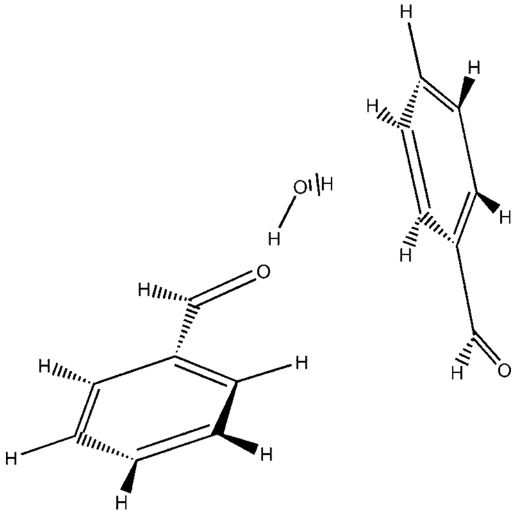

Figure 4. Calculated structure of AC formed by two BA molecules and one water molecule.

TABLE 1: Energy of Formation (ΔE) and Shortest Distance (r_{min}) between Two BA Molecules (Atoms O···C) for the Formation of AC Composed of Two BA Molecules with a Third Partner Molecule and without Any Partner[a]

	no partner	O_2	H_2O
ΔE, kcal/mol	1.38	2.87	20.11
r_{min}, Å	3.42	3.46	2.83

[a] Calculated by using semi-empirical MNDO, AM1, and PM3 methods and molecular mechanics MM2.

Quantum-chemical semiempirical methods (MNDO, AM1, and PM3) and molecular mechanics (MM2) were used in the calculations within CS Chem 3D Pro, Version 5.0 (Cambridge Soft Corporation, U.S.A.). The structure of each complex was optimized by using MNDO, AM1, and PM3. Then, the MNDO- and AM1-optimized structures were each optimized further on by using MM2. The algorithm involved in calculations was similar to that described in refs 13 and 14.

Considering the interaction between BA molecules through the formation of AC, we modeled AC with the participation of other kinds of molecules, for example, O_2 and H_2O. The energies of Van der Waals complexes formed by a foreign molecule with one, two, three, or more BA molecules were calculated.

At first, the interaction between two BA molecules without a third participant was calculated in order to choose the relative positions which would be optimal from the viewpoint of energy; after that, a third partner was added. Finally, it was found that the most advantageous AC configuration is a complex (cluster) formed by an H_2O molecule with BA molecules surrounding it.

The structure of the most favorable AC is shown in Figure 4. Two BA molecules surround a water molecule in such a manner that the oxygen of carbonyl group of one of the BA molecules forms a hydrogen bond with one of the hydrogen atoms of water (the bond length is about 1.87 Å), while another hydrogen of the water molecule approaches the aromatic ring on the second BA molecule; the mean distance between hydrogen and any of the carbon atoms of the aromatic ring is about 2.90 Å. The estimated energy of formation and the minimal distance in such a complex composed of two BA molecules and O_2 or H_2O as the third partner are listed in Table 1.

The formation of a Van der Waals complex is also possible with the participation of more than two BA molecules. The

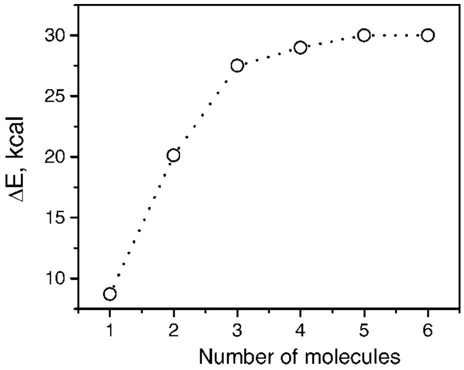

Figure 5. Dependence of the energy of formation of AC with water on the number of BA molecules in the complex.

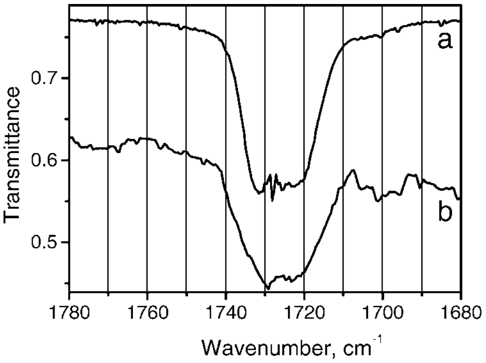

Figure 6. IR Fourier transform spectra of BA vapor (10^{16} molecule/cm^3) in the presence of water vapor. (a) [H_2O] ≈ 3.5×10^{13} molecule/cm^3 and (b) [H_2O] ≈ 2.1×10^{17} molecule/cm^3. For convenience, the spectra are shifted with respect to each other along the ordinate axis.

dependence of energy of formation of AC with one water molecule on the number of aldehyde molecules is shown in Figure 5.

One can see that the AC providing the largest energy gain includes two or three aldehyde molecules. Now, let us consider photodissociation of BA in a complex composed of two BA molecules and one H_2O molecule. The photolytic decomposition of one BA molecule results in the formation of two short-lived radicals, HCO and C_6H_5. Calculation of the energy of a thus formed AC, which includes a BA molecule, water, and the formed phenyl radical, shows that the energy level of this complex is about 25 kcal/mol, which is lower (by ca. 5 kcal/mol) than that of the complex formed by two BA molecules with water (20 kcal/mol). In other words, this radical complex is more favorable from the energy viewpoint than the AC composed of two BA molecules and water. This may somewhat stabilize the cluster and hence increase its lifetime; because the molecules are bound into a complex, pair recombination goes on more easily ($2HCO^\bullet \rightarrow (CHO)_2$ and $2C_6H_5^\bullet \rightarrow (C_6H_5)_2$). In other words, this reaction route is more essential in the cluster, even with low reagent concentrations, than in the case of unbound molecules. Therefore, because of the presence of water, BA dimerization becomes advantageous from the viewpoint of energy; that is why we observe the formation of glyoxal and diphenyl as minor products of BA photolysis, even in the presence of oxygen.

The formation of such a complex may be an explanation of (i) experimentally observed dependencies of the yields of products (glyoxal and diphenyl) on water-vapor concentration, (ii) the effect of water on photolysis and photonucleation rates, and (iii) changes in the chemical composition of products depending on water-vapor content.

Because the calculation showed that the formation of a cluster with the participation of the carbonyl group of one BA molecule and the aromatic ring of another BA molecule is advantageous from the viewpoint of energy, it was interesting to check how the association of other aldehyde molecules (including those having no aromatic groups) could be predicted by the above-described calculation procedure. A detailed chemical analysis of the gaseous and aerosol products of the photolysis of CH_3CHO carried out previously[15] exhibited no dependence of glyoxal yield on water-vapor content. To test the adequacy of the theoretical approach proposed here, we calculated the energy of a similar clustering process in acetaldehyde. If was found that the depth of the potential well accompanying the formation of a cluster composed of two acetaldehyde molecules and one water molecule is only about 4 kcal/mol; with an increase in the number of aldehyde molecules, this parameter decreases to 3 kcal/mol. Therefore, the calculation shows that the formation of complexes with water is unessential in the case of acetaldehyde. This agrees with the experimental data,[15] in particular with the fact that the rate of acetaldehyde photolysis is independent of water-vapor concentration, although the aerosol yield somewhat increases in the presence of water, whereas the glyoxal yield is independent of water.

For another test, we chose a compound for which dimerization in the gas phase is a well-established experimental fact. This compound is formic acid; similarly to all volatile carboxylic acids, it forms dimers in the gas phase.[16] Our calculation of AC energy showed that the formation of a dimeric AC gives about 16 kcal/mol.

If we correctly determine the role of water as a clustering agent for BA photolysis, the presence of water vapor causes clearly observable changes in the IR spectrum of gaseous BA in comparison with the spectrum of dry BA. We recorded IR absorption spectra of gaseous BA (10^{16} cm^{-3}) with lower and higher water-vapor concentrations. The spectral regions exhibiting characteristic frequencies are shown in Figure 6.

One can see that an increase in water-vapor content causes broadening of the band in the region 1720−1740 cm^{-1}, which corresponds to the vibrations of the C=O (carbonyl) group. In addition, the maximum is slightly shifted to lower frequencies, which points to the participation of the carbonyl group in the formation of an intermolecular hydrogen bond.[17] The appearance of a new band (1700 cm^{-1}) is another evidence of dimerization. Similar changes in the IR spectra of formic acid are known to be caused by dimerization;[17,18] unlike for BA, water molecules do not participate in the dimerization of formic acid. Therefore, our assumption concerning the existence of clusters in gaseous BA in the presence of water is also confirmed by the IR spectroscopic data.

Conclusions

It was established that the rate of BA photolysis increases with an increase in water-vapor concentration in the gas mixture, whereas the yield of aerosol products decreases. The yields of glyoxal and diphenyl (products of pair recombination) increase with water-vapor concentration, whereas the yields of benzophenone and formaldehyde are independent of water-vapor concentration.

A mechanism proposed on the basis of semiempirical calculation allowed us to assume that the observed regularities are due to the formation of BA−water complexes in the gas phase. The initial stages of photochemical decomposition of gaseous BA proceed through the formation of these complexes composed of several BA molecules; water plays the role of a clustering agent. According to calculation, the formation of such a complex involving water is accompanied by energy release (about 20 kcal/mol), which means the formation of two rather strong intermolecular hydrogen bonds.

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