

IDENTIFICATION OF FREE RADICALS AND AEROSOL PRODUCTS OF THE PHOTONUCLEATION OF THRIETHYLAMINE AND BENZALDEHYDE

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Short-living radicals generated in photonucleation of thriethylamine and benzaldehyde vapor have been identified for the first time using the method of spin traps. Composition of aerosol products has been studied and a comparison is made of the mechanisms of aerosol formation assumed.

INTRODUCTION

Photonucleation of organic compounds vapor is an important stage of their transformation and removal from the atmosphere especially under conditions of anthropogenic pollution of the atmosphere. Chemical mechanisms of such processes are a complicated sequence of stages at which a great number of components are involved, including short-living free radicals.¹

Earlier we have studied the regularities of photonucleation kinetics in of haloibenzols vapor — the simplest analogs of pesticides²; thriethylamine — the compound modeling organic component of primary anthropogenic pollution of the atmosphere³; and benzaldehyde — the product of incomplete oxidation of organic (aromatic) impurities in the atmosphere.⁴ In a number of cases, physicochemical analysis of end products of aerosol formation have been done.⁵ In this paper we show, for the first time, using the method of spin traps that formation of short-living organic free radicals accompany the photonucleation. Composition of aerosol products generated in thriethylamine and benzaldehyde vapor has been analyzed and compared with the mechanisms supposed in order to reveal the stages giving rise to aerosol formation.

EXPERIMENT

Purification of initial reagents

Thriethylamine (chemically pure) was boiled with acetyl anhydride and distilled over zinc dust and then over metal sodium in the argon atmosphere. The TEA purity and concentration were controlled with Chrom-5 gas chromatograph with flame-ionization detector and 1.2 m long column with 5% OV-17 on a chromatrone. Benzaldehyde (pure) was purified by vacuum distillation under pressure of 20 mm Hg and then by distillation at atmospheric pressure in argon flow. Benzaldehyde purity and concentration were controlled by converting them into hydrazone using reaction with 2,4-dinitrophenylhydrazine. Hydrazone parameters were controlled with a Milichrom-1 microcolumn liquid chromatograph with column filled with LiChrosorb

phase inverted sorbent. Detection was done using UV absorption at 360 nm wavelength. To construct calibrated curves, benzaldehyde hydrazone was synthesized and purified by its recrystallization from isopropyl alcohol.

Experimental setup

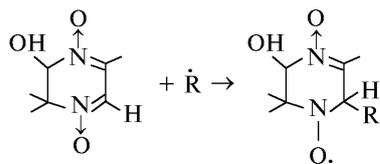
The continuous-flow setup⁷ consists of a block for gas mixture preparation, photochemical reactor, and an analytic unit. The carrier gas (air or argon) purified from aerosol impurities was passed through the source of vapor of organic compounds. Concentration of organic substance in the flow was controlled before and after the reactor. It remained constant (within $\pm 10\%$) during 5–7 hours. Experiment duration was 3–4 hours. For photolysis we used light from a DRT-220 mercury lamp. To exclude the influence of possible photochemically active gaseous impurities, flow of the carrier gas containing vapor of an organic compound was passed through a prereactor illuminated with UV radiation. At the prereactor output, the filter was placed for removal of generated aerosol particles. Then the flow entered the main reactor for photolysis. With the air as a carrier gas, illuminated flow always included ozone. Its concentration was controlled with an automated chemiluminescent ozonometer. Immediately after the photolysis we conducted aerosol sampling or concentrating of free radicals.

Sampling and concentrating

Aerosols for analysis were sampled and concentrated at the output of photochemical reactor using filters of different materials (filtering paper of different marks, glass fiber material, Teflon filter), as well as using vacuum impactor. Gas flow rate through the sampler was 40–200 ml/min. Average aerosol particle size, as was shown earlier in kinetic measurements, was about 50 nm. Aerosol particle number density in the flow measured with an aerosol counter was about 10^6 cm^{-3} . An impactor provides for higher rate of aerosol sampling, but physicochemical properties of aerosol sampled onto the impactor markedly differ from properties of the

aerosol sampled onto filters (T_{pl} , solubility) while all filters give similar results and only differ in the rate of product collection. Therefore for sampling we have selected the most efficient aerosol filter of AFA–HA type. To make sure that solvent introduces no distortions into the product composition, the product was washed out from the filter by different solvents: isopropanol, acetonitril, chloroform. Obtained solutions were evaporated to dryness. Bottoms were dried up to constant weight and the dissolved in media suitable for physicochemical analysis. We employed the methods of quality chemical analysis, as well as High Efficiency Liquid Chromatography (HELCh) (in solution acetonitril – water 3:1) with the UV detection, UV (in chloroform) and IR spectroscopy (in ethanol and butanol).

To identify short–living free radicals, we used the method of spin traps. Twelve compounds were tested as spin traps, namely, nitrones of dihydropyrazine and imidazoline.¹ It proves that only one of them: 3–hydroxi–2,3–dihydro–2;2,5–thrimethylpyrasine–1,4 dioxide (HDPDO) allows the EPR spectra of spin adducts to be observed in the systems under study. Trapping of short–living radicals was done by reaction



The EPR spectrum of spin adduct of this trap is a triplet of doublets characterized by STS constants on nitrogen atom (a_N) and hydrogen atom (a_H). Cyclic structure of the trap provides for large value of a_H (7–29 E) that allows determination of structure of the trapped short–living radical by the value of a_H . In independent experiments it was shown that spin adduct HDPDO with alkyl radical \dot{R} is characterized by $a_H \sim 25$ –29 E, with alkoxy radical $RO\cdot$ – 14–21 E, alkylperoxy radical $RO_2\cdot$ – 7–10 E, and hydroxyl OH – 19.9 E.

At the output of photochemical reactor a thin–wall glass tube–concentrator (output diameter 5 mm) was placed. The tube contained quartz powder covered with water solution of HDPDO (0.1 M, 0.3 ml solution). To prevent photolysis of the spin trap itself, the photosafe cover was put on the tube. The flow of the reaction mixture after photolysis was passed through the tube–concentrator at a rate of 40–100 ml/min during 10–30 min, and the spin adducts generated and nonreacted trap were washed out with a small amount of water and placed into a standard plane quartz cell for recording EPR spectra. The EPR spectra were recorded with a Bruker ER–200 spectrometer. Microwave power was below 10 mw, modulation amplitude was within 0.8–1.2 E. The absence of background signal and trap inertness to ozone being in the flow in such cases when the air was used as a carrier gas were proved in special experiments

when the carrier gas was illuminated in the absence of vapor of an organic compound. It was shown that no EPR spectra are observed under such conditions.

In some experiments, on generation of hydroxyl radical, the standard reaction was used, namely, the photolysis of hydrogen peroxide vapor (0.3–5 Torr). Under dark conditions in the presence of hydrogen peroxide, generation of spin adduct of HDPDO) trap with OH was not observed.

RESULTS AND DISCUSSION

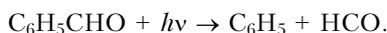
Benzaldehyde. Free–radical stages.

At photolysis of benzaldehyde vapor in argon flow, superposition of three signals is observed in the EPR spectrum (Table I): two of them are triplets of doublets and the third one is a triplet. In air only one weak signal is observed, the triplet of doublets, with $a_N = 14.7$ E, $a_H = 15.1$ E.

TABLE I. Spin adducts observed at the benzaldehyde vapor photolysis.

BA – Argon	BA – Air
1) triplet of doublets $a_N = 16.8$ E $a_H = 25.7$ E $t_{1/2} = 24$ min	triplet of doublets $a_N = 14.7$ E $a_H = 15.1$ E $t_{1/2} = 48$ min
2) triplet of doublets $a_N = 16.5$ E $a_H = 20.8$ E $t_{1/2} = 35$ min	
3) triplet $a_N = 16.5$ E $t_{1/2} = 31$ min	

As is seen from Table I, at BA photolysis in an inert gas and air, different free radicals are generated. At photolysis of benzaldehyde, one of the possible primary processes is decomposition into HCO and C_6H_5 radical:



Based on a_H values of spin adducts generated at photolysis in argon, we can propose that (1) is the adduct with phenyl radical and (2) is the adduct with HCO . The triplet (3) is indicative of the hydrogen β -atom removal from the trap molecule with the formation of nitroxyl radical, and interpretation of this signal is now impossible. The adduct generated at photolysis in air is characterized by a_H , value typical for oxiradicals $RO\cdot$. Thus, in air the primary radical generated at benzaldehyde photolysis are then transformed.

Aerosol products

Aerosol products generated at benzaldehyde nucleation in air (AB) and argon (AA) are amorphous slightly colored solid substances with the melting

point about 80°C, well solvable in acetonitrile and partially solvable in benzene. Qualitative analysis of the presence of double bonds (interaction with bromine water) gave negative result for both AA and AB cases. Both products are insoluble in dilute acids (sulfur and hydrochloric). Analysis by HELCh method with the detection using UV absorption at 310 nm wavelength has shown that there are three compounds in AA and two in AB. All of them absorb radiation in 306–328 nm range. Analysis by HELCh methods after reaction with 2,4-dinitrophenylhydrazine, standard reagent for detection of carbonyl compounds in the form of hydrazines, has shown that neither AA nor AB contains carbonyl groups (Table II).

TABLE II. Properties of aerosols generated at C₆H₅CHO photolysis.

Property	C ₆ H ₅ CHO—argon	C ₆ H ₅ CHO—air
State, color	solid, light-gray	solid, white
Melting point, °C	78–84	78–81
Soluble in:	C ₆ H ₆ , CHCl ₃	CHCl ₃ , CH ₃ CN
HELCh, number of components (306–328 nm)	3	2

Triethylamine. Study of free-radical stages

When studying photonucleation of triethylamine (TEA) by the method of spin traps, it was discovered that both in the atmosphere of an inert gas and in air the same spin adduct is generated. This adduct is characterized by the following parameters: $a_N = 16.9$ E, $a_H = 17.8$ E, $t_{1/2} = 38$ min (see Fig. 1). Taking into account the scheme of TEA photolysis proposed earlier,⁶ from the value of the a_H constant observed we can assume that the radical (C₂H₅)₂N–C•HCH₃ has been trapped. It is known that the same radical is generated in the reaction of triethylamine with OH•: (C₂H₅)₃N + OH → (C₂H₅)₂N–CH•–CH₃.⁷ In the test experiments on photolysis of mixture of triethylamine vapor (10 Torr) and hydrogen peroxide (3 Torr) the spin adduct obtained was characterized by the same values of STV constants that supports our assumption about the structure of the radical trapped.

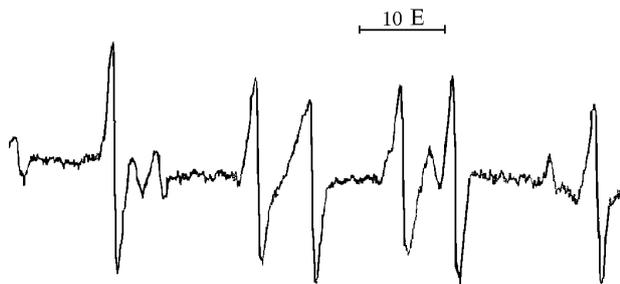


FIG. 1. EPR spectrum of the spin adduct of HDPDO trap in photolysis of triethylamine vapor.

Analysis of aerosol products

Aerosol products generated in the TEA photolysis in both argon (AA) and air (AB) are solid substances. Melting point is 67–92°C for AB and 124–127°C for AA. Melting behavior of AB is different. The AA being heated up to 63°C darkens, and at a melting point it becomes oily and partially sublimates. AB being heated does not change color and break down. There are also some differences in product solubility. The AB is soluble in chloroform, acetonitril, and butanole; partially soluble in sulfur ether and benzene (insoluble fraction remains, yellow colored). The AA is only partially soluble in chloroform and benzene and better soluble in sulfur ether. It was shown by the method of thin-layer chromatography on silicagel (eluent-chloroform) that AB composition includes at least three compounds, while AA comprises four ones. We failed in separation of each fraction and its separate analysis because of little total yield of the aerosol product.

The AA and AB reacts with acids in different way. AB is fully soluble in sulfur acid without residue, while in hydrochloric acid only colored component is soluble, uncolored component remains in precipitation. Washing of this residue by hydrochloric acid yields uncolored crystal plates. The AA is in soluble in sulfur and hydrochloric acid, but it reacts with nitrogen acid yielding resintificated residue (Table III).

TABLE III. Properties of aerosols generated in TEA vapor photolysis.

Property	TEA + argon	TEA + air
State, color	solid, light-yellow	solid, yellow-brown
Melting point, °C	124–127	67–92
Soluble in:	CH ₃ OCH ₃ , CH ₃ COCH ₃	CHCl ₃ , CH ₃ CN, <i>i</i> -PrOH, <i>t</i> -BuOH
TSKh, number of components:	4	3
Solubility in acid	partially soluble	soluble
H ₂ SO ₄	soluble	colored fraction soluble
HCl	— " —	soluble
HNO ₃	becomes resintificated	uncolored one insoluble
		insoluble

The qualitative reaction of saponification is indicative of the presence of nitrile in the AB composition. Qualitative reaction with the bromine water has shown that AA decolorize bromine water, while AB does not. It is indicative of the presence of multiple bonds in the AA product. In air, the aging of AA is observed. After one month, melting point of the AA sample is already 124–125°C; in addition, the product stops to decolorize bromine water. The

AB sample does not change its properties in time. The obtained samples were studied by the method of IR spectroscopy (Table IV).

TABLE IV. IR spectra of aerosols generated in TEA photolysis

Wavenumber, cm^{-1}	Bonds	TEA initial	AB	AA fresh	AA "aged"
3430	N-H amid	—	—	—	3
3170		—	3	—	—
3000–2800	C-H (sp^3)	10	4	8	7
2240	nitril, C = C	—	10	—	—
1800–1780		—	3	—	10
1700–1600	C = H, C = C, N = N	—	4	10	—
1500–1450	C-H (sp^3)	6	6	4	4
1380	C-H, N-C	7	6	—	—
1290–1280		5	—	—	4
1190	C-N	7	—	5	3
1100	C-N val.	—	5	—	—
1080–1060	C-N	7	—	2	—
910–900		1	—	10	—

Note: presented are relative intensities of the peaks in the IR the spectrum. 10 corresponds to the most intense line in a spectrum.

Comparison of the data of qualitative analysis and IR spectroscopy shows that the presence of nitril group in the AB product and double bonds in AA can be considered proved. Comparison of these data with the proposed scheme of triethylamine photolysis,⁶ allows the conclusion to be drawn that the scheme of TEA photochemical aerosol formation should be completed by the due regard of the functional groups discovered.

CONCLUSION

Our study has shown that aerosol formation at photolysis of TEA and BA vapor is accompanied by

stages where free radicals participate. The results of the product analysis enabled identification of separate functional groups. Their presence in aerosol supports that in aerosol formation chemical transformation of initial organic compound takes place. The results of analysis were compared with the mechanism of aerosol formation in photolysis of triethylamine vapor proposed earlier. The existence of some stages were supported, while some functional groups missing in the scheme were discovered. Based on this, we can conclude that the real mechanism of photolysis is more complicated, and consideration of additional stages is needed.

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