

NUCLEATION OF TRIETHYLAMINE VAPOR UNDER UV IRRADIATION

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Kinetics of aerosol formation in the photolysis of triethylamine vapor has been studied for the first time. Based on the results obtained, we have concluded that this process involves free radicals. The chemical mechanism accompanying the aerosol formation has been proposed.

Formation of aerosol from the organic compounds vapors being exposed to UV radiation is of great scientific and practical interest, since just these processes make the basis for photochemical smog formation. To determine a role of primary photochemical processes and to clarify the mechanism of aerosol formation, studies of the fine aerosol fraction (particle diameter $D_p \sim 2\text{--}50$ nm) may be very informative. However, due to limited experimental possibilities, the studies mostly dealt with a relatively coarse-disperse aerosol ($D_p > 40$ nm). In addition, as a subject for studying photonucleation, the systems are usually used that contain nitrogen or sulfur oxides, while the aerosol formation from organic compound vapors is poorly studied.¹⁻⁴

When studying the photonucleation of organic compound vapors in different gaseous media, it is of interest to reveal in what way the properties of the initial reagents and aerosol products affect the concentration and the size of photochemically generated particles and their optical characteristics.

In our earlier works⁵⁻⁷ we have found, using the photolysis of benzol halides (PhHal) as an example, that the formation of centers is initiated by short-lived free radicals. It has been shown that the atom of substitute - halide - increases the efficiency of aerosol formation as is demonstrated by the following series $\text{PhCl} < \text{PhBr} < \text{PhI}$.

From the kinetic studies and analysis of the aerosol composition, the oxygen was shown to take part, at chemical stages, in the formation of condensing products thus sharply increasing the rate of the aerosol formation. It was discovered that ozone affects the PhHal photonucleation. From all the data obtained, we drew the conclusions about the chemical mechanism accompanying the gas-to-particle transition in the case of benzene halides photolysis.

In this work we chose the triethylamine (TEA) as a subject for study. It is interesting to reveal the common and specific features inherent in photochemical aerosol formation from amines as compared to that from benzene halides. Triethylamine is from the class of organic amines that are contained in the polluted atmosphere. In addition, the presence of unshared electronic pair in the nitrogen atom opens a possibility

of forming clusters and molecular complexes with other atmospheric pollutants.⁸⁻⁹

The kinetics of photochemical aerosol formation from TEA was studied using the device shown in Fig. 1 and described in detail in Ref. 7. TEA vapor underwent photolysis under the exposure to radiation with the wavelength longer than 254 nm. The initial reagent was carefully purified by boiling in acetic anhydride and further distillation. Before the kinetic measurements, the distillate was distilled over zinc dust and then over metallic sodium in the argon atmosphere. TEA purity and concentration were controlled with KhROM-5 gas chromatograph with a plasma-ionization detector and a column 1.2 m long with 5% OV-17 on a chromatron tube.

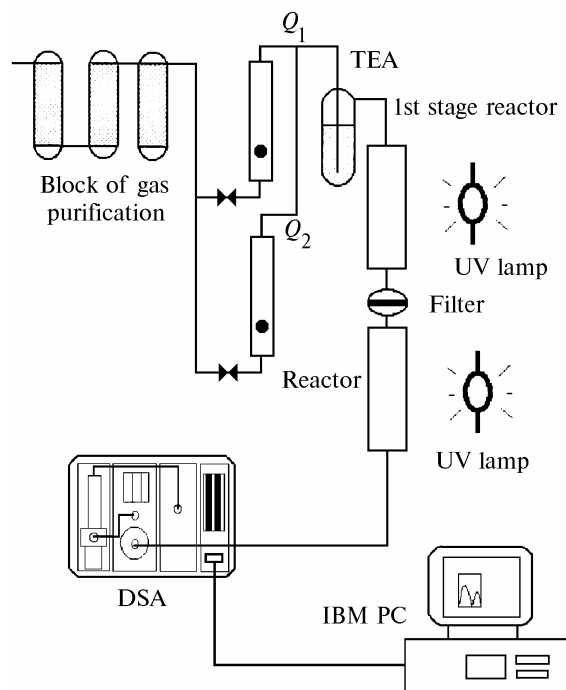


FIG. 1. Block diagram of the experimental setup for studying kinetics of triethylamine photonucleation.

The aerosol particle number density (N_a) was measured with a diffusion aerosol spectrometer (DAS)¹⁰

which comprises a meshy-type eight-channel diffusion battery, a condenser enlarger, and a photoelectric counter. Accuracy of N_a measurement is $\pm 10\%$. DAS can be used to estimate not only the number density, but also the size distribution of aerosol particles within the range of 2–200 nm in diameter.

Kinetic measurements started after "training", which consisted in UV irradiation of the reactor during several hours with simultaneous passage of a reacting mixture through it. Reproducibility of the kinetic data after this procedure was $\pm 10\text{--}50\%$ during 4–6 hours. The results presented were obtained by averaging over 5–10 measurements.

To study the aerosol chemical composition, the aerosol was sampled from the air flow onto the vacuum impactor as well as the aerosol filters made of fiber glass material. The aerosol is a slightly colored yellowish substance, which melts and decomposes at the temperature of 63–69 °C. The aerosol is well soluble in acetonitrile and chloroform and somewhat worse in the hexane and water. Although the aerosol products have basic properties, they do not dissolve completely in acids. By studying the aerosol solutions in acetonitrile with the liCuid high-resolution chromatography with detection by UV light absorption, it was revealed that the aerosol is a mixture of at least five components.

In experiments on the UV photolysis of TEA vapor in argon and air, the formation of highly disperse aerosols ($D_p > 2$ nm) was discovered for the first time.¹² It was checked that in the dark aerosol formation and growth do not occur. Figure 2 shows the particle number density produced against the time of TEA irradiation in argon and air. It is seen that in air much more particles are produced than in argon. It was revealed that small air additions to argon ($< 1\%$) sharply increase N_a too. One should suppose that this is a result of oxygen participation, at the chemical stages, in formation of condensing products.

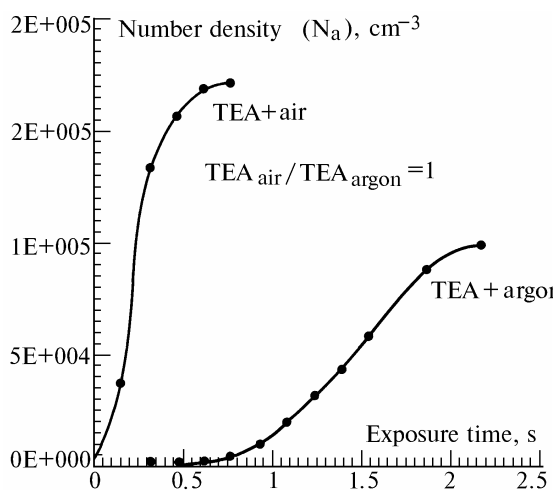


FIG. 2. Aerosol particle number density against the time of TEA irradiation in air and argon with the same TEA concentration.

Not only the number density, but also the particle size of aerosol produced from TEA in air and argon differ strongly. With the same time of photolysis and TEA concentrations, smaller-size particles are produced in argon than in air. The mean diameter of aerosol in argon is about 4 nm. In air the particle size distribution is bimodal with the mean mode diameters of 6 and 50 nm. The number density of particles of 6 nm diameter is much lower than that of particles 50 nm in diameter (see Fig. 3).

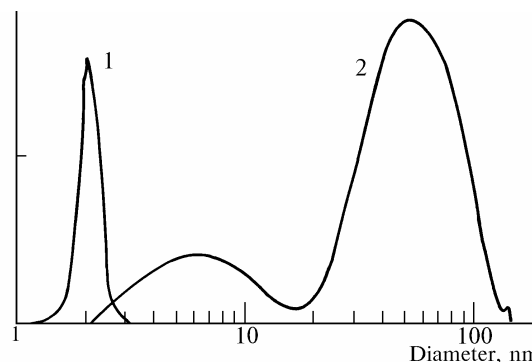


FIG. 3. Size distribution spectra for particles produced in TEA photolysis in argon (1) and air (2).

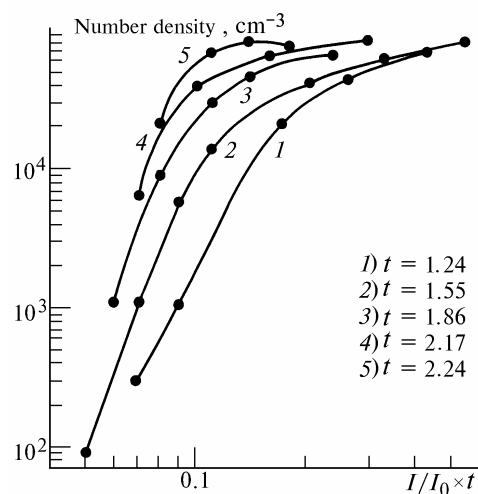
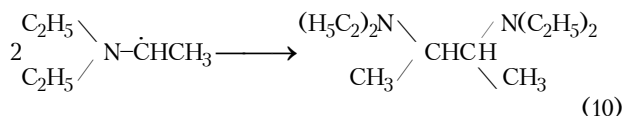
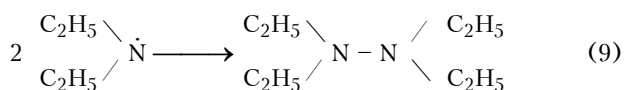
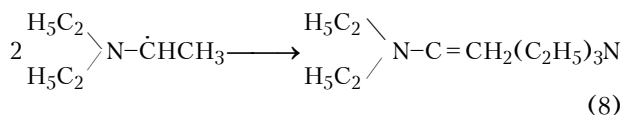
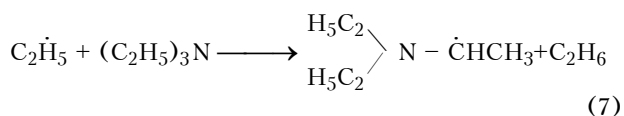
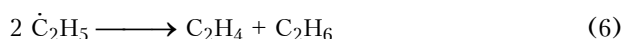
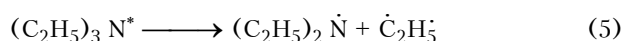
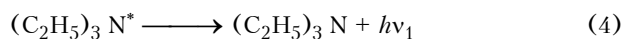
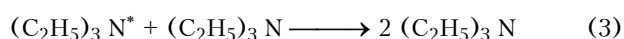
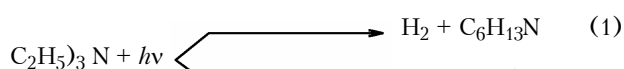


FIG. 4. Aerosol particle number density against the irradiation rate ($I/I_0 \times t$). Different kinetic curves correspond to different values of irradiation time. The value of t was fixed in each experiment, whereas the irradiation intensity I/I_0 varied.

Intensity (I) and time (t) of the irradiation affect the number density of aerosols generated from TEA. The strongest dependence is observed at the initial section ($N_a \leq 2 \cdot 10^4$ cm^{-3}) where even slight changes in I result in great changes in N_a (Fig. 4). As I increases ($N_a > 2 \cdot 10^4$ cm^{-3}), the slope of curves decreases. Such a shape of curves is typical for the kinetics of photochemical aerosol formation, and it is usually described within the scope of the Smolukhovskii coagulation model in the mode of molecular collisions.³

¹³ Earlier in Ref. 13 it was shown that the slope of the kinetic curves at the initial section is connected with the value of minimum detectable cluster (j^*), i.e. the size of minimal cluster that can be detected experimentally, for the value $j^* \leq 10$. For greater j^* , the initial slope of curves is practically the same for any j^* . Since the curve slope at the initial interval is practically the same for different t (see Fig. 4), one can conclude, by comparing with the numerical results, that minimum detectable clusters generated in TEA photonucleation contain more than 10 monomeric units.

Starting from the experimental results and the literature data,^{14,15} the chemical scheme of the products formation in photolysis of TEA in Ar under the exposure to radiation with $\lambda > 254$ nm can be proposed to be as follows



Reactions (1) and (8)–(10) produce low-volatile nitrogen-containing products: NNN'N'-tetraethyl-2,3-diamino-butane, tetraethylhydrazine, NN'-diethyl-2,3-diamino-butane, which can transform into the disperse phase. For example, diethyldiamino-butane is a crystal substance. The product of reaction (1), $\text{C}_6\text{H}_{13}\text{N}$, can be diethylvinylamine (DEVA) capable of polymerization. It is not improbable that the formation of such products in the irradiation zone is accompanied by further copolymerization, that results in aerosol formation. For example, DEVA and ethylene can take part in this process.

In air one should expect the oxygen to add to the radicals $\text{C}_2\text{H}_5\dot{\text{C}}\text{H}_2$, $(\text{C}_2\text{H}_5)_2\dot{\text{N}}$, $(\text{C}_2\text{H}_5)_2\text{NC}\dot{\text{N}}\text{CH}_3$ with the formation of peroxide radicals. This changes the

capability of intermediate particles to enter into reactions, the scheme of reactions, and the products composition. Since the TEA photolysis in air yields high number density of aerosols, the peroxide radicals RO_2 should be assumed to more efficiently participate in the process of formation of products – centers of the disperse phase.

It should be noted that the IR analysis of aerosol products revealed the presence of nitrile groups (in air) and double bonds $\text{C}=\text{C}$ (in argon). The UV absorption spectra of the initial reagent – triethylamine – and the aerosol products differ radically. In addition, different accompanying carrier gases (argon or air) also results in different optical characteristics of the aerosol products (Fig. 5).

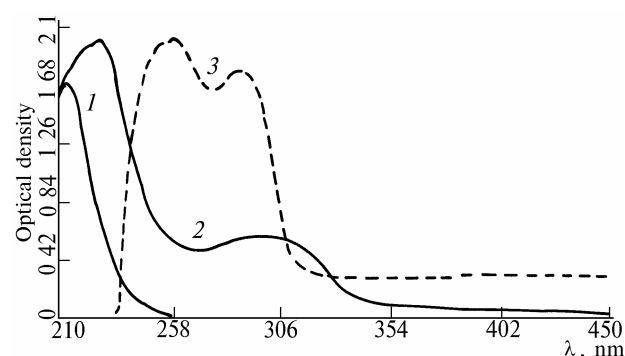


FIG. 5. UV absorption spectra of the initial triethylamine (1) and aerosol produced as a result of TEA vapor irradiation in argon (2) and air (3).

By comparing the photonucleation of TEA and previously studied PhHal, one can notice that common for both these classes of organic molecules are the aerosol formation and growth only under the exposure to radiation. Irradiation duration and intensity affect the number density of centers produced. It is indicative of a free-radical mechanism of their photonucleation. The similarity of TEA and PhHal to one another is also the higher efficiency of the process in air than in an inert gas, that is connected with the oxygen participation at the chemical stages of nucleation. In both cases, the size distribution of highly disperse particles produced in air is bimodal. These modes probably correspond to different channels of aerosol formation.

It should be noted in addition that the photonucleation of TEA differs from that of PhHal by the following facts: TEA produces smaller-size particles. Initial aerosol particle number density in TEA depends on the radiation intensity more strongly than in PhHal. The dynamics of particle formation in TEA has different t and I dependences. For PhHal t and I dependences of N_a are similar.

Thus, in this work we have studied kinetic regularities of formation of highly disperse aerosols in the photolysis of TEA vapor. Particle size spectra have been measured. The data obtained for triethylamine

photonucleation have been compared with that obtained earlier for halidebenzenes under similar conditions. Physico-chemical characteristics of aerosol products are listed. It is shown to what extent the resultant spectra differ from those for the initial reagent. The results obtained allow us to conclude that photoexcitation of TEA initiates the chemical transformations and results in formation of the compound aerosol products.

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