Dynamics of aerosol formation at hydrolysis of uranium hexafluoride of low concentration

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Some results of experimental investigation into the dynamics of aerosol formation in the process of hydrolysis of uranium hexafluoride of low concentration under controlled conditions are presented. It has been found that at relatively high concentrations of UF_6 (20 g/m^3 and higher) the process of active hydrolysis with formation of uranyl fluoride aerosol particles completes for the first 20 to 25 minutes, and the particles formed have the size much smaller than the He–Ne laser wavelength and have no time to grow during the gravitational sedimentation. As the hexafluoride concentration decreases, the process of hydrolysis of residual (free) UF_6 with formation of aerosol particles still goes on for a long time. The results obtained contradict the common opinion that hydrolysis of uranium hexafluoride of low concentration occurs only on surfaces.

Introduction

As is known,[1–3] uranium hexafluoride actively interacts with water vapor and water droplets in atmospheric air with formation of solid-state and liquid aerosols, as well as gaseous hydrogen fluoride. Chemical and physical transformations can yield the following compounds containing uranium fluoride in the form of solid-state and liquid aerosols and clusters:

1. Uranyl fluorides in the form of solutions, solid particles, and two-layer particles with a solid nucleus and a shell (H_2O or HF): UO_2F_2; $UO_2F_2 \cdot H_2O$; $UF_6 \cdot H_2O \cdot HF$; $H(UF_4(H_2O))$.
2. Uranyls and uranyl fluorides in the form of molecular complexes (clusters): UO_2^{+2}; $U_2O_3^{+2}$; $U_3O_8^{+2}$; $U_3O_8F_2$; $U_2O_5F_2$.
3. Liquid particles: HF + H_2O.

Although the number of papers devoted to hydrolysis is rather large, there are no quantitative data on the characteristics of hydrolysis under atmospheric conditions. In Ref. 4 it is stated that for hydrolysis to proceed, tenfold excess of water is needed. However, the data on constants of chemical reactions for these conditions are not given in this paper. So, we can conclude that the dynamics of hydrolysis of uranium hexafluoride under atmospheric conditions is studied insufficiently and special experiments are to be conducted.

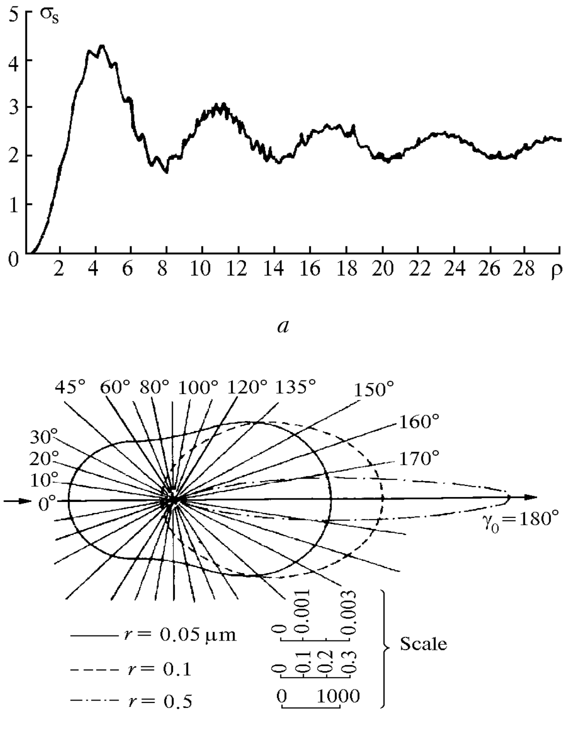
On the other hand, the problems of monitoring of toxic and radioactive emissions from nuclear reprocessing plants both indoors and outdoors require development of new methods enabling one to determine concentrations of chemical and radioactive pollutants in real time. Uranium hexafluoride, which is subject to hydrolysis by atmospheric moisture, can play a significant part in formation of aerosol fraction in emissions from nuclear reprocessing plants.

The currently available methods for evaluation of the radioactive situation in plants are based on the data of radiometry and analysis of precipitated aerosols. Therefore, they often are inefficient and even useless. In this connection, it is rather interesting to consider the potentialities of the methods of remote, in particular, laser sounding in application to analysis of chemical composition of emissions in real time. The size of aerosol particles formed at hydrolysis of uranium hexafluoride is 0.02 to 0.2 μm according to data from Refs. 2 and 3. So, they form an aerosol which is detectable by optical sounding methods.

This paper generalizes the results of our experimental studies[5,6] of the dynamics of uranium hexafluoride hydrolysis under controlled conditions close to the atmospheric ones. The studies were performed using optical methods.

Background

Scattering and absorption coefficients are the principal parameters which can be used to study the process of aerosol formation at UF_6 interaction with gaseous and aerosol components of the atmosphere by laser sounding methods. Let us consider them separately. As known, molecular (Rayleigh) scattering is characterized by a simple angular distribution of intensity, that is, intensity of scattered radiation is symmetric with respect to the normal to the initial direction. Amounts of energy scattered in the forward and backward hemispheres are equal. The Rayleigh scattering coefficient is proportional to λ^{-4} (where λ is the wavelength of light). However, if the radius of scattering particles is comparable with the radiation wavelength or exceeds it, the scattering is described by the Mie theory and determined by the function depending on the refractive index (its real part) and the parameter $\rho = 2\pi r/\lambda$ (r is the particle radius). The dependence of the scattering cross section on ρ for particles with the refractive index $n = 1.5$ (the refractive index of uranyl fluoride is close to this value) is shown in Fig. 1*a*. As the particle size increases, the angular distribution of the scattered radiation losses its symmetry with respect to the normal to the initial direction of the beam. The scattering phase function for particles of 0.005, 0.1, and 0.5 μm in radius is shown in Fig. 1*b* for the visible wavelength region. From Fig. 1 one can see that as the particle radius changes from 0.05 to 0.5 μm (particles formed at hydrolysis fall just in this size range), the intensity of radiation scattered in the forward and backward directions changes by several orders of magnitude. Consequently, measuring the intensity of radiation scattered in these directions we can estimate the particle size and the rate of particle growth.



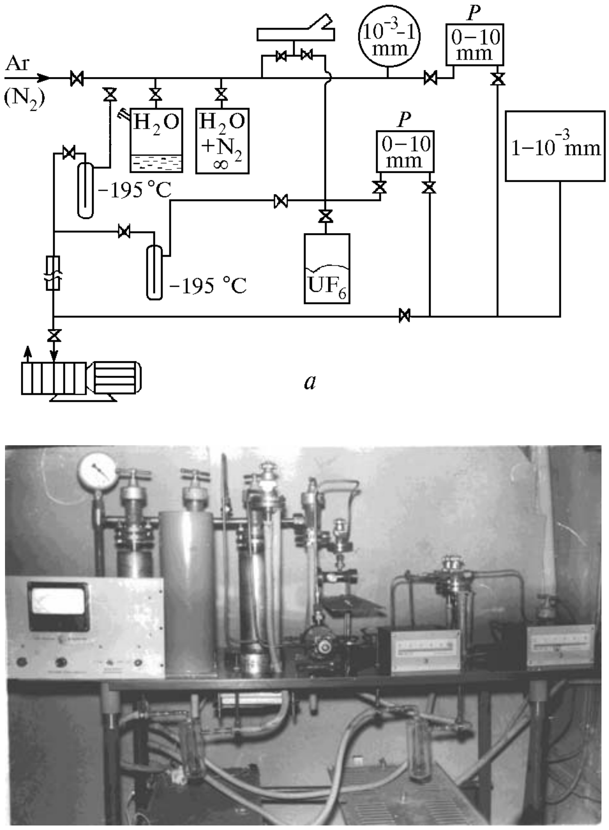
a

b

Fig. 1. Scattering cross section as a function of the Mie parameter (*a*) and scattering phase function in the visible wavelength region for particles of different size (*b*).

Experiment

The block diagram and general view of the experimental setup are shown in Fig. 2. The experimental setup comprised the following principal units: vapor–gas mixture bleed-in system, uranium hexafluoride bleed-in system, vacuum system, pressure measuring system, reactor cell, and measuring system.



a

b

Fig. 2. Block-diagram (*a*) and general view (*b*) of the experimental setup.

The uranium hexafluoride bleed-in system included a sealed off container 1100 cm^3 in volume. It housed solid uranium hexafluoride in equilibrium with its saturated vapor.

The vapor–gas mixture bleed-in system included a container with water being in equilibrium with water vapor. Water vapor was mixed with argon in a 10-liter container. The pipes, vessels, and the cell were pumped out to vacuum with a preevacuation pump. Uranium hexafluoride and water vapor were trapped with a quartz freeze trap. As a reactor we used a cell made from a tube with two transparent windows.

The measuring system comprised a He–Ne laser with the wavelength $\lambda = 0.63$ μm and output power of 50 mW, two photomultiplier tubes to convert the light flux into an electric signal, an active filter with the passband about 10 kHz, and an analog-to-digital converter (ADC). Experimental results were processed with a computer.

To observe the process of uranium hexafluoride hydrolysis at different humidity, we used a beam of the He–Ne-laser (8 mm in diameter) that passed through the center of the cell. Radiation scattered by the products of hydrolysis was recorded at an angle ≈ 4° (scattering in the forward direction) and ≈ 174° (scattering in the backward direction) with two photomultiplier tubes (PMT's). Signals from PMT's came by two different channels to a recorder with a built-in 12-bit fast ADC. The recorder polled the channels at the frequency of 180 kHz. Thus, the quantization frequency for each channel was 90 kHz. The frequency was stabilized with a built-in quartz oscillator. In one measuring event, 4096 points per channel were recorded (this corresponds to 2^{12} for a 12-bit ADC). One measuring event lasted 0.05 s. The process was recorded by cycles. First, we recorded the scattered signal from pure hexafluoride; the level of this signal was taken as a background one. The level of the signal was chosen so that it provided the highest sensitivity of a PMT and, at the same time, enabled to prevent signal cut-off in the case of its maximum intensity. Then, the record of the signal characterizing the process of hydrolysis started simultaneously with water vapor bleeding-in. One cycle lasted 16 s and consisted of four measuring events for every channel with the interval of 4 s. Every experiment as a whole took in most cases 100 to 120 min.

Results and discussion

In the experiments we observed the UF_6 hydrolysis with the initial components taken in different proportions. The UF_6:H_2O ratios corresponded to deficit of humidity for complete hydrolysis (1:1), stoichiometry (1:2), and excess of humidity (1:3, 1:4, 1:6, 1:8, 1:12). The initial concentrations of UF_6 were the following: 1, 1.5, 2, 3, 5, and 6 mm Hg. Figure 3 shows the relative values of the intensity of laser radiation scattered in the backward (*a*) and forward (*b*) directions in the process of hydrolysis of UF_6 with the initial concentration of 1.5 mm Hg. Curves *1*, *2*, and *3* in Fig. 3 correspond to the UF_6:H_2O ratio equal to 1:2, 1:4, and 1:6.

Figure 4 shows the results of similar measurements at the UF_6 concentration of 1.5 mm Hg and water vapor concentration of 18 mm Hg, what is close to the water vapor concentration in the atmosphere under standard conditions.

Figure 4 clearly demonstrates that in the case of a tenfold excess of H_2O, an intense (active) hydrolysis of uranium hexafluoride proceeds[4] in volume with formation of aerosols even at low concentrations of UF_6, and aerosol formation completes in first 20 minutes. Comparing Figs. 3 and 4, we can see that at lower H_2O concentrations the process of intense hydrolysis slows down, and aerosol formation has no certain time limits. It should be emphasized that completion of the intense hydrolysis does not mean termination of the reaction, because the forward and backward scattered signals do not vanish, thus indicating the presence of residual UF_6, which continues to react with H_2O and hydrolysis products.

The scattering signals at the UF_6 concentrations of 3 and 6 mm Hg are shown in Figs. 5 and 6. The time of formation of aerosol particles was estimated as the time during which the scattered radiation achieved the steady state level, and the lifetime of aerosols was estimated as the time during which the intensity drops down to the background level.

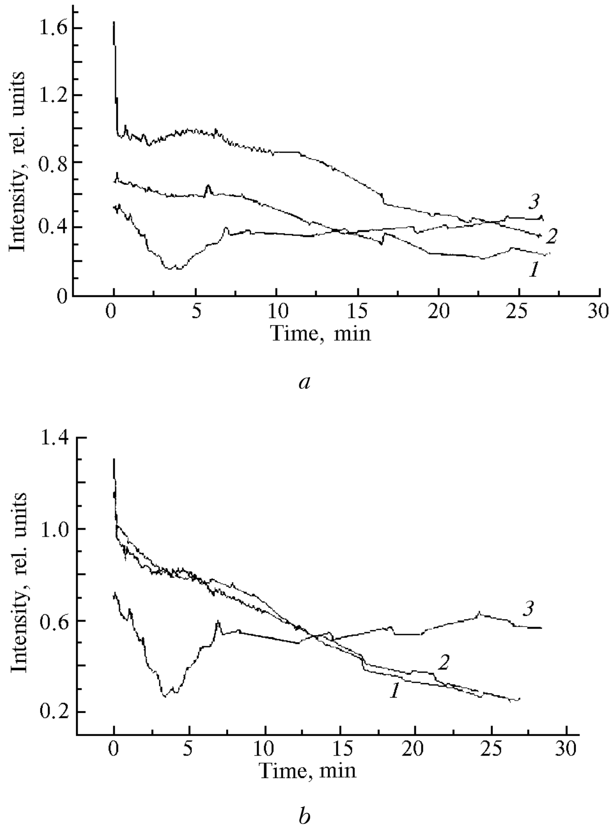


Fig. 3. Dynamics of UF_6 hydrolysis at different stoichiometric ratios.

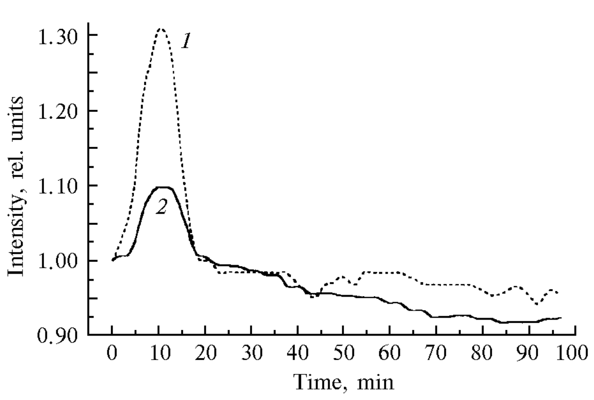
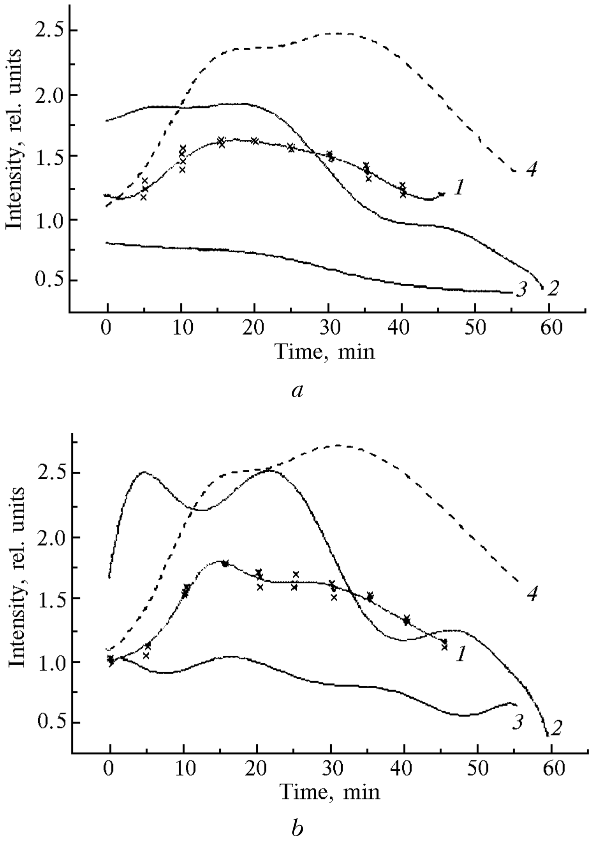


Fig. 4. Dynamics of UF_6 hydrolysis in the case of water vapor excess: scattering in the backward (*1*) and forward (*2*) directions.

From the results obtained it is clear that the time of aerosol formation mainly depends on the time of hydrolysis, while the aerosol lifetime depends on the diffusion and convective processes, as well as on the coagulation processes. At low concentrations of the initial substances, coagulation insufficiently influences the process of aerosol formation because of the low probability of particle collisions. In this case the time of aerosol formation and aerosol lifetime change only slightly at varying the stoichiometric ratios (see Fig. 3). The particle size estimated from the forward-to-backward intensity ratio appeared to be 0.05 to 0.08 μm. At any stoichiometric ratio the concentrations were $N_{HF} = 2.4 \cdot 10^{20}$ m^{-3} and $N_{UO_2F_2} = 0.7 \cdot 10^{20}$ m^{-3}.

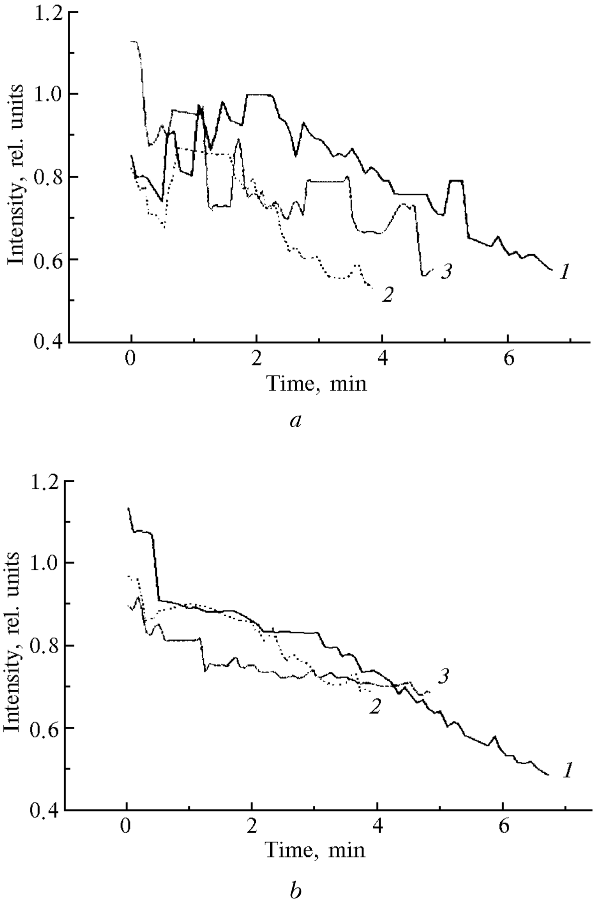


a

b

Fig. 5. Dynamics of the normalized intensity of the scattered signal for hydrolysis of uranium hexafluoride with the partial pressure of 3 mm Hg. UF_6:H_2O ratio: 1:1 (curve *1*), 1:2 (*2*), 1:3 (*3*), and 1:4 (*4*); points marked with × are sampled experimental data, scattering in the backward (*a*) and forward (*b*) directions.

As the initial concentration of UF_6 increases, the process speeds up, and the aerosol formation time becomes shorter: fractions of minute (see Fig. 6) rather than tens of minutes (see Figs. 3–5). At the same time, the particle lifetime decreases because of the increasing effect of sedimentation, convection, coagulation, and diffusion. In this case the degree of particle inhomogeneity cannot be estimated from scattering, because the particle size is comparable with the wavelength of laser radiation. The dynamics of the scattered radiation is indicative of the duration of diffusion and convective processes and coagulation, which lead to particle size redistribution and change the particle concentration. In the case of the increased initial concentration of the components and excess of H_2O, we observed the appearance of the second stage in the process of aerosol formation within 20 to 40 min, on the average, after the beginning of hydrolysis (see Figs. 4–5). The intensity of the scattered signal at the second stage is always lower than that at the first stage. This phenomenon can be caused by interaction of water vapor with hydrolysis products, in particular, HF molecules and molecular complexes, as well as with residual uranium hexafluoride. The second stage is most pronounced at low concentrations of UF_6. Figure 7 shows the experimental results averaged over five measurements at the UF_6 initial concentration of 1 mm Hg and H_2O concentration of 12 mm Hg. One can see from the figures that hydrolysis in volume proceeds with formation of aerosol even at low concentrations of the uranium hexafluoride.



a

b

Fig. 6. Dynamics of the normalized intensity of the scattered signal at hydrolysis of UF_6 with the partial pressure of 6 mm Hg. UF_6:H_2O ratio: 2:1 (curve *1*), 1:1 (*2*), 1:2 (*3*), and 1:4 (*4*).

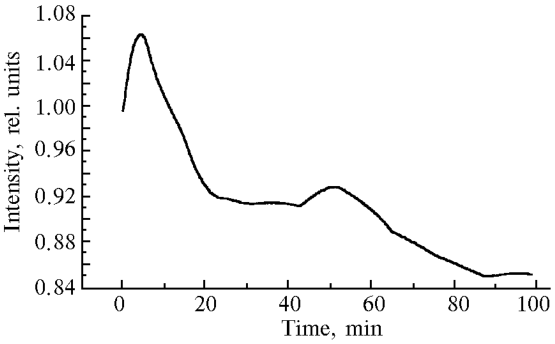


Fig. 7. Intensity of backscattered radiation at hydrolysis of UF_6 with the concentration corresponding to the pressure of 1 mm Hg at the water vapor partial pressure of 12 mm Hg.

Conclusions

At uranium hexafluoride concentrations about 1 mm Hg and higher, the process of active hydrolysis with formation of uranyl fluoride aerosol particles completes in the first 20–25 min; the size of the particles formed is much less than the wavelength of He–Ne-laser radiation, and the particles have no time to grow during the gravitational sedimentation. As the UF_6 concentration increases, the process of active hydrolysis proceeds faster, and the time of particle formation becomes equal to fractions of a minute, rather than tens of minutes.

At a high excess of H_2O, the second stage was observed in the process of aerosol formation (on the average, within 20 to 40 min after the beginning of hydrolysis). The intensity of the scattered signal at the second stage is always lower than that at the first stage. This effect most likely results from continuing interaction of residual UF_6 and the products formed at the active stage of hydrolysis, in particular, HF molecules and molecular complexes, with H_2O with formation of aerosol particles. This allows the optical methods to be used for estimating the fraction of residual uranium hexafluoride.

In our further investigations we plan to continue the study of the dynamics of hydrolysis of UF_6 of low concentrations corresponding to the partial pressure from 1 to 10^{-6} mm Hg.

Acknowledgments

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