# Radiochemical Diagnostics of Thermal Hydrolysis of Aluminum Trichloride

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**Abstract**—Thermal hydrolysis of aluminum chloride was studied using <sup>36</sup>Cl and <sup>3</sup>H tracers in combination with energy-dispersive and morphological (scanning electron microscopy) analyses. Pure partially hydrated AlCl<sub>3</sub> or mixtures of AlCl<sub>3</sub> and AlCl<sub>3</sub>·6H<sub>2</sub>O were used as initial materials. It was found that Al<sub>7</sub>O<sub>10</sub>Cl·2H<sub>2</sub>O microtubes along with isometric microparticles are formed in the course of thermal hydrolysis due to evaporation and partial hydrolysis of the initial AlCl<sub>3</sub>. In this case, AlCl<sub>3</sub>·6H<sub>2</sub>O acts as a source of water vapor, whereas chlorine atoms contained in this compound do not pass into the microtube material. The tests with water labeled with tritium also showed no incorporation of tritium in microtubes. Thus, thermal hydrolysis of AlCl<sub>3</sub> proceeds predominantly by the recrystallization mechanism.

Hydrolysis of aluminum salts is widely used for preparing materials, in particular, various radionuclide sorbents based on  $Al_2O_3$  [1, 2]. Therefore, detailed study of the process and, especially, of the mechanism of recently discovered [3, 4] self-organization of microparticles of X-ray amorphous aluminum oxide in the course of gas-phase thermal hydrolysis is of particular importance. In the process, tubular particles (microtubes) of the composition  $Al_7O_{10}Cl \cdot 2H_2O$  (I) are formed.

In the course of thermal hydrolysis, recrystallization and topochemical process pathways can be realized simultaneously. In recrystallization, crystals of the initial compound are evaporated and its vapors interact with water vapor with subsequent condensation of the hydrolysis product. In the topochemical process, crystals sorb water vapor, and the hydrolysis product is formed on the surface and in the crystal bulk without evaporation of the initial compound. Both pathways can yield tubular particles due to aggregation and growth of the product nanoparticles formed by condensation (first pathway) or by detachment of fragments from the crystals (second pathway).

The role of each pathway in microtube formation can be evaluated by radiochemical analysis, similar to the isotope dilution procedure. For this purpose, AlCl<sub>3</sub> crystals labeled with <sup>36</sup>Cl are mixed with nonlabeled crystals of AlCl<sub>3</sub>· $6H_2O$ , the mixture is heated in dry air to complete conversion of the mixture into product **I**, and the isotope ratio in the microtubes is determined:

$$\Phi_F = A_F / M_F, \tag{1}$$

where  $A_F$  and  $M_F$  are the amounts of <sup>36</sup>Cl and total amount of chlorine atoms in the microtubes.

The  $A_F$  value at slow isotope exchange between the crystals and gas phase is given as

$$A_F = \Phi_0 M_{01} \alpha_1, \tag{2}$$

and  $M_F$  is described by the following expression:

$$M_F = \alpha_1 M_{01} + \alpha_2 M_{02}, \tag{3}$$

where  $\Phi_0 = A_0/M_{01}$ ,  $A_0$  is the amount of <sup>36</sup>Cl atoms added into the system;  $M_{01}$  and  $M_{02}$  are the amounts of all the chlorine atoms in AlCl<sub>3</sub> and AlCl<sub>3</sub>·6H<sub>2</sub>O microcrystals;  $\alpha_i$  is the probability of transfer of chlorine atoms from AlCl<sub>3</sub> (i = 1) and AlCl<sub>3</sub>·6H<sub>2</sub>O (i = 2) into microtubes.

Chlorine can appear in the microtubes owing to vaporization of AlCl<sub>3</sub> molecules with their subsequent conversion into AlOCl and addition to microtubes (j = 1), vaporization of HCl molecules formed by the topochemical reaction on the surface or in the crystal bulk with subsequent sorption of HCl by microtubes (j = 2), and by detachment of certain fragments of the product of topochemical reaction with composition **I** and their attachment to the microtubes (j = 3).

Thus, the probability  $\alpha_i$  can be given as

$$\alpha_i = \sum_{j=1}^3 \omega_{ij} \beta_{ij}, \tag{4}$$

where  $\omega_{ij}$  and  $\beta_{ij}$  are the probabilities of chlorine escape from the microcrystals and their subsequent

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transfer into the microtubes by one of the above pathways.

As seen from Eqs. (1)-(4),

$$\Phi_F = \Phi_0 (1 + M_{02} Z / M_{01})^{-1}, \qquad (5)$$

where 
$$Z = \left(\sum_{j=1}^{3} \omega_{2j} \beta_{2j}\right) \left(\sum_{j=1}^{3} \omega_{1j} \beta_{1j}\right)^{-1}$$
.

In accordance with Eq. (5), the diagnostics of thermal hydrolysis requires determination of the factor *Z* using the functions  $\Phi_F(M_{01}, M_{02})$  and its dependence  $Z = Z(\eta_i)$  on the process conditions such as temperature *T*, concentration of H<sub>2</sub>O and HCl in the vapor, and parameters characterizing mutual arrangement of AlCl<sub>3</sub> and AlCl<sub>3</sub> · 6H<sub>2</sub>O in the system. The  $Z(\eta_i)$  function allows analysis of the  $\omega_{ij}(\eta_i)$  and  $\beta_{ij}(\eta_i)$  functions characterizing the process mechanism; this problem is considered in our paper.

In the first experimental series, we determined the amount of <sup>36</sup>Cl passing from AlCl<sub>3</sub> crystals containing this radionuclide into the microtubes upon heating of the initial material in tritium-free water vapor. In the second series, a the mixture of  $Al^{36}Cl_3$  and  $AlCl_3 \cdot 6H_2O$  crystals was thermally hydrolyzed, and, finally, unlabeled AlCl<sub>3</sub> was hydrolyzed in the atmosphere of <sup>3</sup>H<sub>2</sub>O vapor.

## EXPERIMENTAL

To prepare AlCl<sub>3</sub> labeled with <sup>36</sup>Cl, ultrapure grade aluminum (99.9999%) was heated in a flow of gaseous HCl obtained from reaction of concentrated sulfuric acid with solid NaCl containing Na<sup>36</sup>Cl (purchased from the Izotop Joint-Stock Company). The resulting crystals were separated and stored in a dry box. The specific activity of these crystals was  $A_{\rm sp} =$  $2.3 \times 10^6$  Bq g<sup>-1</sup>, which corresponded to the isotope ratio  $\Phi_0 = 7.0 \times 10^{-3}$ . In our work we used crystalline AlCl<sub>3</sub> · 6H<sub>2</sub>O and tritium water <sup>3</sup>H<sub>2</sub>O produced by Izotop ( $A_{\rm sp} = 9.0 \times 10^6$  Bq g<sup>-1</sup>,  $\Phi_0 = 7.0 \times 10^{-8}$ ).

In the first series, a porcelain boat with a 4–5-mm bed (bed weight  $m_1 = 1.5$  g) of labeled AlCl<sub>3</sub> crystals was placed in a closed chamber with a water vapor pressure of  $1.5\pm0.5$  kPa. Then, the boat with the crystals was transferred into a tubular reactor heated to T = 473 K, which was purged with air at partial water vapor pressure p = 1.0-1.5 kPa [3]. The gaseous HCl liberated from the reactor was absorbed in a trap packed with solid alkali.

Upon heating, the microtubes growing toward the



Fig. 1. Electron micrograph of a microtube prepared using AlCl<sub>3</sub> layer containing no AlCl<sub>3</sub>  $\cdot$  6H<sub>2</sub>O.

vapor flow were formed on the surface layer (Fig. 1). After cooling in an air flow, the boat was removed from the reactor and the radioactivity  $I_F$  of the resulting microtubes was determined. For this purpose, the microtubes with weight  $m_F$  were placed into a slightly acidified aqueous solution. The solution activity was measured by liquid scintillation counting on a TRI-CARB 2700 TR device (Packard, Australia); the registration efficiency was 40%. We also measured the activity  $I_0$  of the solution obtained after the above treatment of Al<sup>36</sup>Cl<sub>3</sub> crystals ( $m_0$  weight) and calculated the parameter *B* characterizing the stability of the ratio of the number of radionuclide atoms to the total number of atoms of the given element (isotope ratio) in the course of thermal hydrolysis:

$$B = \Phi_F / \Phi_0 = (I_F / I_0) (m_0 / m_F) (C_0 / C_F), \tag{6}$$

where  $I_F/I_0 = A_F/A_0$  and  $C_F$  and  $C_0$  are the numbers of chlorine atoms in 1 g of microtubes and AlCl<sub>3</sub> crystals.

In the second series, thermal hydrolysis was performed by the same procedure, but the mixture of anhydrous AlCl<sub>3</sub> and AlCl<sub>3</sub>. 6H<sub>2</sub>O was heated without preliminarily exposure to the humid atmosphere. In several tests, a bed of AlCl<sub>3</sub>. 6H<sub>2</sub>O was placed over a bed of Al<sup>36</sup>Cl<sub>3</sub>, and in the other tests, these compounds were thoroughly mixed. The weight of AlCl<sub>3</sub>. 6H<sub>2</sub>O in the bed was  $m_2 = 1.0-1.5$  g.

In the third series, an aliquot of tritium water was placed in a Petri dish over which (in a closed volume) a boat with  $AlCl_3$  containing no  ${}^{36}Cl$  was kept for 4 h. Then,  $AlCl_3$  was thermally hydrolyzed by the above procedure; the content of  ${}^{3}H$  in the microtubes

Bed composition	Radionuclide	$M_{02}/M_{01}$	$(I_F/I_0) \times 10^3$	В
AlCl <sub>3</sub> AlCl <sub>3</sub> Homogeneous mixture of AlCl <sub>3</sub> and AlCl <sub>3</sub> $\cdot$ 6H <sub>2</sub> O Two-layer mixture of AlCl <sub>3</sub> and AlCl <sub>3</sub> $\cdot$ 6H <sub>2</sub> O	<sup>36</sup> Cl <sup>3</sup> H <sup>36</sup> Cl <sup>36</sup> Cl	0 0 0.83 0.83	1.38 <0.02 1.45 1.37	$ \begin{array}{r} 1.0\pm0.04 \\ <0.04 \\ 1.00\pm0.04 \\ 1.00\pm0.03 \end{array} $

Content of radionuclides in the microtubes at  $m_0/M_F = 75.8$ 

was determined immediately after completion of the experiment. The atomic composition of the microtubes was studied by energy-dispersive analysis and  $\Phi_{ac} = E_F/C_F$  was evaluated, where  $E_F$  is the number of aluminum atoms in 1 g of microtubes of composition **I** and  $E_F = 1.0 \times 10^{22} \text{ g}^{-1}$ .

## **RESULTS AND DISCUSSION**

Our experimental data showed that, when exposed to humid atmosphere for 1 h, the bed of AlCl<sub>3</sub> crystals sorbs water in amounts of 4 mol per mole of AlCl<sub>3</sub>. Upon heating, this bed liberates gaseous HCl and AlCl<sub>3</sub> and H<sub>2</sub>O vapors. The microtubes formed have the diameter from 20 to 500  $\mu$ m (5–50  $\mu$ m wall thickness). The length of each tube increases at a rate of 0.25 mm s<sup>-1</sup> until the moment when the front of the growing tube reaches the reactor wall or the initial material is fully consumed.

In the first series, in which  $M_{01} = 0$  and  $\Phi_F \equiv \Phi_0$  (see table), i.e., the isotopic composition of each system section is similar and constant,  $I_F$  determines the number of all the chlorine atoms in the microtubes of weight  $m_F$ :

$$M_F = (I_F/I_0)(A_0/\Phi_0),$$

which corresponds to the following values:

$$\Phi_{\rm ac} = E_F m_F / M_F = 0.15 \pm 0.01, \ C_F / C_0 = 0.106 \pm 0.007.$$

These values are similar to the results obtained using the energy-dispersive method ( $C_F = 1.37 \times 10^{21} \text{ g}^{-1}$  and thus  $C_F/C_0 = 0.101 \pm 0.006$  and  $\Phi_{ac} = 0.14 \pm 0.01$ ).

The parameters *B* evaluated in the second experimental series are given in the table. As seen, for <sup>36</sup>Cl,  $B = 1.00 \pm 0.05$  irrespective of the presence of AlCl<sub>3</sub>. 6H<sub>2</sub>O and distribution of AlCl<sub>3</sub> and AlCl<sub>3</sub>. 6H<sub>2</sub>O crystals in the mixture. This fact indicates that, under the experimental conditions, the following ratios

were fulfilled:

$$\Phi_F = \Phi_0, \ Z \ll 1, \tag{7}$$

i.e.,

$$\sum_{i=1}^{3} \omega_{1j} \beta_{1j} \gg \sum_{j=1}^{3} \omega_{2j} \beta_{2j}.$$
 (8)

Expression (8) shows that transition of AlCl<sub>3</sub> molecules into the gas phase on heating of AlCl<sub>3</sub>.  $6H_2O$ crystals is negligible ( $\omega_{21} \rightarrow 0$ ). This suggests that AlCl<sub>3</sub>.  $6H_2O$  is hydrolyzed by the topochemical mechanism. In this case, crystals of aluminum chloride hexahydrate liberate HCl molecules, i.e.,  $\omega_{22} \gg 0$ . However, HCl molecules do not penetrate into the microtubes ( $\beta_{22} \rightarrow 0$ ) irrespective of distribution of AlCl<sub>3</sub> and AlCl<sub>3</sub>.  $6H_2O$  crystals (homogeneous or two-layer system).

Low  $\beta_{22}$  values indicate that sorption of HCl in the microtubes is insignificant. If the sorption were strong, then, in the presence of AlCl<sub>3</sub> hexahydrate whose hydrolysis increases concentration of hydrogen chloride in the gas phase near the microtubes,  $\Phi_F$  would decrease owing to an increase in the content of nonradioactive chlorine, required by the  $\beta_{22}(\eta_i)$  function related to the isotherm of HCl sorption in the microtubes. However, the probability  $\beta_{22}$  is too low to provide strong decrease in  $\Phi_F$ . The probability of detachment of hexahydrate crystal fragments with their attachment to microtubes is also relatively small  $\omega_{23}\beta_{23} \rightarrow 0$ ). Under the experimental conditions studied, AlCl<sub>3</sub>.6H<sub>2</sub>O acts only as a water source. Taking into account that  $\omega_{23}\beta_{23} \rightarrow 0$ , we assume that  $\omega_{13}\beta_{13}$  is also very low, because the probability of attachment of crystal fragments hardly depends on the mechanism of their formation. Since the microtubes do not sorb HCl, then

$$\omega_{11}\beta_{11} \gg \omega_{12}\beta_{12}, \ \omega_{13}\beta_{13}.$$
 (9)

Expression (9) indicates that the microtubes grow

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Fig. 2. Electron micrograph of a microtube end. Particle aggregates are seen to cover the microtube surface.

owing to the sublimation and hydrolysis of  $AlCl_3$  vapor, i.e., thermal hydrolysis of aluminum chloride proceeds by the recrystallization mechanism.

The third series data (table) confirm that sorption of HCl in the microtubes is rather small. Otherwise,  $I_F$  for tritium in this experimental series would be very high. Small  $I_F$  values also confirm the absence of HCl sorption in the microtubes.

If microtubes acquire composition I directly while growing, then *B* for tritium determined immediately after their formation is close to zero. In the further process, however, tritium atoms escape from the microtubes as a result of the isotope exchange with water vapor on cooling of the reactor and dissolution of the microtubes for radioactivity measurements. As a result, by the moment of measurements B = 0. However, our experimental data do not allow us to rule out incorporation of water molecules in the microtubes by sorption after the nanotube formation, rather than during the nanotube growth.

Our conclusions on the processes occurring in the porous bed of  $AlCl_3$  and  $AlCl_3.6H_2O$  on heating are as follows. When heated,  $AlCl_3.6H_2O$  crystals decompose with liberation of  $H_2O$  and HCl molecules and formation of amorphous  $Al_2O_3$  areas on the surface of each crystal and their further growth into the crystal bulk. Simultaneously,  $AlCl_3$  crystals sublime and sorb water vapor generated by aluminum chloride

hexahydrate. The vapors of AlCl<sub>3</sub> are mixed with water vapor to form product particles in two morphological forms: microtubes and isometric particles, whose certain fraction is precipitated on the microtube surface as aggregates of various shapes (Fig. 2). The recrystallization pathway of AlCl<sub>3</sub> thermal hydrolysis is morphologically branched. At the same time, the results of radiometric and energy-dispersive analyses show that the composition of the microtubular form is constant. This can be explained by the fact that the microtubes are composed by cyclic clusters of composition I; under given experimental conditions, the probability of their formation is significantly higher than that of the clusters of the other compositions. In these clusters, the mobility of chlorine atoms is small and they do not participate in the isotope exchange with the gas phase, which is confirmed by expression (7).

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