Oxidative Hydrolysis in Water Vapor–Air Phase of CsI Radioaerosols Produced by CsI Sublimation from Metallic Surface

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Abstract—Behavior of CsI radioaerosols produced by CsI sublimation from a platinum support in argon, air, and water vapor–air mixture was studied. During 10–12 min of the vaporization at 900–1570 K, CsI radioaerosols undergo oxidative hydrolysis with atmospheric oxygen and water vapor to form CsOH aerosols and I_2. The cesium-to-iodine ratio determined in various fractions shows that oxidation of CsI in argon is minimal and is caused by the presence of oxygen and water traces. Oxidative hydrolysis of CsI strongly increases with increasing water vapor content in the vapor–gas flow. The degree of oxidative hydrolysis of CsI in the gas flow depends not only on the content of water vapor and oxygen but also on the initial CsI/O_2 molar ratio.

Accidents at plants of atomic industry make urgent the problem of localization and recovery of volatile radionuclides and radioaerosols. CsI aerosol is one of the most biologically hazardous volatile compounds of fission products of nuclear fuel, penetrating into the environment at accidents at atomic power plants. The behavior of CsI radioaerosols in water vapor–gas phase was extensively studied [1–4]. Previously we found that radioaerosols with a wide particle-size distribution (from hundreds of micrometers to 5–10 nanometers) are formed in the course of CsI vaporization from a platinum surface under argon [5, 6]. Under these conditions, the chemical form of CsI does not change [7].

However, CsI can transform chemically in the presence of oxygen and water vapor in the gas phase. When CsI is sublimed at 630–660°C and 1200–1250°C in dry air, it is partially oxidized with atmospheric oxygen to form I_2 and IO_3^- [3]. The conversion of 100 mg of CsI is 10%. The conversion of CsI in the course of its sublimation at 1000–1200°C from the quartz surface into a small volume (~3.7 cm³) containing ~0.15 cm³ of O_2 is ~3% [8]. It is suggested, however [8], that the conversion should increase with increasing oxygen content in the gas phase.

At high concentrations of water vapors and oxygen in the gas phase and at elevated temperature, oxidative hydrolysis of CsI is possible:

$$4CsI + 2H_2O + O_2 \rightarrow 4CsOH + 2I_2. \qquad (1)$$
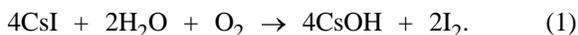
In this case, CsI can be completely oxidized to form large amounts of molecular iodine.

Since the experimental data on CsI behavior in these systems are scarce, the study of the behavior of CsI radioaerosols in the water vapor–air system is an urgent problem. In this work we studied oxidative hydrolysis of CsI radioaerosols formed in the water vapor–gas phase by sublimation of cesium iodide from the metal surface at 900–1570 K.

EXPERIMENTAL

We used carrier-free ^{137}Cs and ^{131}I in the form of a nitric acid solution of ^{137}Cs and an $Na^{131}I$ solution, purchased from the Izotop Joint-Stock Company. The γ-ray radiation of these radionuclides was measured on a γ-ray spectrometer with a Ge–Li detector and a multichannel analyzer (Nokia). Nonradioactive CsI used in weighable amounts was of chemically pure grade. Felt made from Bekipor WB stainless steel, with the fiber thickness of 12 μm and density of about 50 mg cm⁻³, was purchased from Bekaert Fibre Technologies Company (Belgium) [9].

Oxidative hydrolysis of CsI radioaerosols was studied on a unit schematically shown in the figure. The unit consists of a 450 cm³ reaction chamber and a stainless steel column 2.5 cm in diameter and 25.0 cm high. The reaction chamber hermetically connected with the column was placed in a chamber which can be heated to a required temperature. The column was packed with steel felt (20.0 g) to the bed

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[†] Deceased.
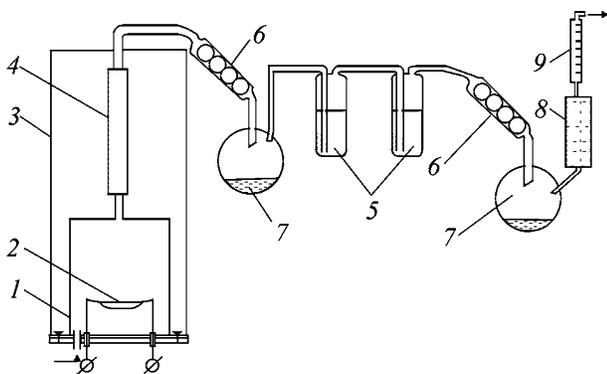
Unit for studying oxidative hydrolysis of CsI radioaerosols: (*1*) reaction chamber, (*2*) platinum heater, (*3*) heated chamber, (*4*) column packed with metal felt, (*5*) bubbler with 0.05 M Na_2SO_3, (*6*) condenser, (*7*) condensate receiver, (*8*) combined filter, and (*9*) rotameter.

height of about 25.0 cm. The top of the column was connected with the system for trapping the aerosols broken through and the products of oxidative hydrolysis. The system consisted of two condensers, two bubblers with 0.05 M Na_2SO_3, and a combined filter (Petryanov's filter and white ribbon paper filter). A rotameter and a roughing pump were arranged at the outlet.

To choose the material of the heater for CsI sublimation, we performed special experiments. It was found that stainless steel and nickel strongly corroded under the action of CsI even at 973 K. To exclude the possible effect of the corrosion products on the oxidative hydrolysis, we used a platinum heater.

The oxidative hydrolysis was performed as follows. A solution containing 1 mg of CsI, ~5 μCi of ^{137}Cs, and ~50 μCi of ^{131}I was evaporated to dryness at 50–70°C on a heater made in the form of a 6×36-mm boat from 0.1-mm platinum foil. If necessary, 100 mg of CsI was placed in the boat. Then the heater was fixed in the reaction chamber. The chamber was hermetically sealed and connected with the column and the system for trapping the radioaerosols. Argon or a water vapor–air mixture was passed through the reaction chamber and the column either at room temperature or on heating with a high-performance HABE-2000 thermofan (Atlas Copco Electric Tools, Germany). The water vapor–gas mixture was evacuated from the system with a roughing pump. The system was purged at a required temperature for 15 min with the water vapor–gas mixture being studied. Then CsI was evaporated from the platinum boat by gradual heating to 473 K over a period of 2 min to remove adsorbed moisture and to prevent spraying of the melt and then to 923 K over a period of 2 min to produce homogeneous ^{137}Cs^{131}I melt (melting point of CsI

905 K). Preliminary experiments showed that, under these conditions, the isotope exchange in cesium iodide was complete. Even at 900 K, a CsI vapor is visually observed. Then generation of CsI aerosols was continued at 1470–1570 K (CsI boiling point 1553 K) for 10 min. The process was monitored with a pyrometer through a special quartz window in the wall of the reaction chamber. After sublimation completion, the water vapor–gas mixture was passed for 30 min at the same temperature in the heated chamber. Then the reaction chamber and column were cooled to room temperature and the system was disassembled.

The unit was dismantled and its internal parts were washed with water. The wash waters from the column and the trapping system were combined. The cesium and iodine content in the wash waters from the chamber and in the combined fraction was determined by the activity of ^{137}Cs and ^{131}I, respectively. The Cs/I weight ratio was calculated. The deviation of this ratio from that in CsI (1.04) indicated enrichment of a fraction with cesium or iodine, which, in turn, depended on the degree of oxidative hydrolysis in the system.

RESULTS AND DISCUSSION

To determine the resistance of CsI to water and oxygen, we studied the behavior of CsI radioaerosols in argon, air, and water vapor–air mixture containing up to 93 vol % water. The results of these experiments at the temperature of the reaction chamber (hereinafter, chamber) from 403 to 423 K are presented in Table 1. As seen from Table 1, in the course of vaporization of 1 mg of CsI in argon flow, about 30% of ^{137}Cs and ^{131}I are localized on the heater, walls, and bottom of the chamber. The remaining 70% of the radionuclides are present in the column and the system trapping the oxidative hydrolysis products. The Cs/I weight ratio in the chamber is close to 1.04. These data show that the degree of oxidative hydrolysis in argon is negligible and is due to the presence of traces of water and oxygen. The Cs/I ratio in the combined fraction is below 1, suggesting oxidation of iodide ion to I_2.

The Cs/I ratio in the chamber after sublimation of CsI in air was substantially higher than that in CsI. An increase in the cesium content in the chamber as compared to that in the experiment in argon is due to formation of hydrophilic CsOH aerosols [10]. Thus, in the course of CsI vaporization in air, unlike the experiments in Ar flow, CsOH aerosols and I_2 are formed in large amounts along with CsI aerosols.

The cesium and iodine content in the chamber in the course of CsI vaporization in the water vapor–air

flow containing ~93 vol % water was ~50 and ~39%, respectively. The Cs/I weight ratio was 1.30. Substoichiometric increase of the Cs/I ratio by ~25 % is due to hydrolysis of CsI in water vapor to form CsOH aerosols. Aerosols of cesium hydroxide are readily hydrated and are deposited in the chamber. At the same time, the Cs/I ratio in the combined fraction was lower than the stoichiometric value by ~23%. The ^{137}Cs and ^{131}I content in the combined fraction indicates that the content of molecular iodine formed during CsI sublimation in the water vapor–air mixture containing up to 93 vol % water is larger compared to sublimation in pure air. The Cs/I weight ratio is 0.81. This is due to the fact that the oxygen content in the water vapor–air mixture is lower by an order of magnitude than that in air (~1.5 and 20 vol %, respectively).

We studied the behavior of CsI aerosols as influenced by the temperature in the reaction chamber. First, we sublimed CsI in air without heating of the chamber. It should be noted that the temperature in the chamber in the course of CsI sublimation from the heated platinum boat was lower than 373 K. The temperature of the column bottom being in the direct contact with the reaction chamber did not exceed 313 K. As seen from Table 2, under these conditions, the cesium and iodine content in the chamber increased by ~10 and ~3%, respectively, as compared to the experiment at 423 K. The Cs/I ratio in the chamber increased by 20%. This confirms our assumption on formation of CsOH aerosols in the course of CsI sublimation in air at 900–1570 K. Since the temperature in the chamber is low, CsOH particles are rapidly agglomerated and are deposited on the internal parts of the chamber. At the same time, radioactive I_2 passes through the column and is localized in the trapping system. The Cs/I weight ratio in the combined fraction decreases to 0.85.

We also studied the behavior of CsI aerosols with the initial amount of CsI increased from 1 to 100 mg. The distribution of ^{137}Cs and ^{131}I after CsI sublimation in air and argon at different water vapor content in the gas phase is presented in Table 3. As seen from Table 3, the oxidative hydrolysis in argon is negligible even at a 52 vol % concentration of water vapor. In this case and in an air flow containing 3–4 vol % water, the Cs/I ratio in the chamber is constant [±(3–7)% of the theoretical value]. When the content of water vapor increases to 33–50 vol %, large amounts of radioactive iodine, probably in the form of HI and HIO_3 (CsI < 1), are deposited in the chamber. The cesium content in the combined fraction noticeably increases (Cs/I > 1), which can be due to forma-

Table 1. Content of ^{137}Cs and ^{131}I in various fractions* formed in the course of oxidative hydrolysis of CsI (1 mg) evaporated from a platinum heater (initial temperature in the chamber 403–423 K) at different compositions of the gas phase

Frac-tion no.	Content, %		Cs/I weight ratio
	^{137}Cs	^{131}I	
Argon			
1	30.71	30.15	1.02
2	69.29	69.85	0.99
Air (3–4 vol % H$_2$O)			
1	32.76	29.65	1.10
2	67.24	70.35	0.95
Water vapor–air mixture (93 vol % H$_2$O)			
1	50.56	38.97	1.30
2	49.44	61.03	0.81

* Fraction 1 is wash waters of the reaction chamber; fraction 2 is combined wash waters from the column, receivers, bubblers, and filter; the same for Tables 2–4.

Table 2. Content of ^{137}Cs and ^{131}I in various fractions formed in the course of oxidative hydrolysis of CsI (1 mg) evaporated from a platinum heater in air at different temperatures of the reaction chamber

Frac-tion no.	Content, %		Cs/I weight ratio
	^{137}Cs	^{131}I	
Initial temperature of the chamber 292 K			
1	42.98	32.91	1.31
2	57.02	67.09	0.85
Initial temperature of the chamber 403–423 K			
1	32.76	29.65	1.10
2	67.24	70.35	0.95

tion of CsOH·CsI aerosols, more volatile than those of CsOH and CsI taken separately [11].

The behavior of the oxidative hydrolysis products formed at different initial molar ratios of CsI and oxygen in the gas flow is shown in Table 4. In these experiments, CsI was evaporated from the platinum boat without heating of the chamber. After sublimation of 1 mg of CsI (CsI : O$_2$ molar ratio 1 : 1100), the Cs/I ratio in the chamber and in the combined fraction considerably differes from the theory. When

Table 3. Content C of ^{137}Cs and ^{131}I in various fractions formed in the course of oxidative hydrolysis of CsI (100 mg) evaporated from a platinum heater (initial temperature in the chamber 393–403 K) at different water vapor concentrations in the gas flow

Atmosphere	C, vol %	Fraction no.	Content, %		Cs/I weight ratio
			^{137}Cs	^{131}I	
Air	3–4	1	47.89	44.62	1.07
		2	52.11	55.38	0.94
"	32.7	1	46.03	47.27	0.97
		2	53.97	52.73	1.02
"	50.5	1	40.55	42.68	0.95
		2	59.45	57.32	1.04
Argon	52.3	1	35.44	32.55	1.09
		2	64.56	67.45	0.96

100 mg of CsI is sublimed (CsI : O_2 molar ratio 1 : 11), the ratios in these fractions are similar and are close to that in CsI.

Thus, CsI aerosols formed in the course of CsI evaporation from the platinum heater at 900–1570 K in water vapor–air phase undergo oxidative hydrolysis with water vapor and atmospheric oxygen to form CsOH and I_2 within 10–12 min. This process depends not only on the content of water vapor and oxygen in the gas phase but also on the initial molar ratio of CsI and oxygen in the reaction chamber.

Table 4. Content of ^{137}Cs and ^{131}I in various fractions formed in the course of oxidative hydrolysis of CsI evaporated from a platinum heater (initial temperature in the chamber 293 K) at different molar ratios of CsI and oxygen in the air flow

Frac-tion no.	Content, %		Cs/I weight ratio
	^{137}Cs	^{131}I	
CsI : O_2 = 1 : 1100 (1 mg of CsI)			
1	42.98	32.91	1.31
2	57.02	67.09	0.85
CsI : O_2 = 1 : 11 (100 mg of CsI)			
1	48.62	48.33	1.01
2	51.38	51.67	0.99

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