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A Study of the Thermal Decomposition of $CH_3{}^{131}I$ in a Gas Flow in the Presence of "Fizkhmin"™ Granulated Materials

Alexey A. Bessonov, Sergey A. Kulyukhin, Lubov V. Mizina, Igor A. Rumer

Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia
Email: Bessonov_ipc@mail.ru

Abstract

Thermal decomposition of a volatile organic compound of radioactive iodine, methyl iodide $CH_3{}^{131}I$, in a gas flow in the presence of various modifications of "Fizkhmin"™ granulated materials based on silica gel impregnated with d-elements was studied. Under comparable experimental conditions, 97% - 99% decomposition of $CH_3{}^{131}I$ is achieved at ~770°C without sorbents and at ~540°C and ~465°C in the presence of straight silica gel and of the material based on it, impregnated with compounds of Ni or its mixture with Cu (8 - 10 wt%), respectively.

Keywords

Iodine-131 Trapping, Methyl Iodide, Thermal Decomposition, Sorption

1. Introduction

The localization of volatile radioactive iodine compounds by various sorbents from vapor-gas media is a vital issue for environmental protection during both irradiated nuclear fuel reprocessing and accidents at nuclear power enterprises, including nuclear power plants (NPPs). One of the most difficult-to-localize volatile organic forms of radioactive iodine is methyl iodide (CH_3I). Sorbents based on activated carbon, silica gel, Al_2O_3, etc. are widely used today for its localization [1]-[6]. A study of the $CH_3{}^{131}I$ sorption from the gas phase onto a wide range of sorbents has shown that inorganic sorbents containing 8 - 12 wt% silver ions are the most efficient at emergencies [7]-[9]. However, high cost of silver, one of the main components binding radioactive iodine, makes it topical to develop the cheaper CH_3I localization systems.

Various methods have been suggested for converting CH_3I to readily localizable forms. As noted in [10], under the action of UV radiation CH_3I decomposes to form chemically active atomic iodine. At the same time, we suggested in [11] that decomposition of $CH_3{}^{131}I$ under the action of UV radiation in air yields not only chemically active atomic iodine, but also finely dispersed I_xO_y aerosols. It is also suggested using for CH_3I decomposition a method based on the action of ozone in a field of electric charge [12]. The main product of the action of O_3 on CH_3I is I_2O_5 in the form of aerosols, which were deposited on the walls of the discharge chamber. The major drawback of these procedures is that the CH_3I decomposition yields radioactive aerosols with a wide

range of particle sizes, including nanometric size. Localization of nanoparticles requires the use of special filtration systems. One of alternative pathways of CH_3I conversion without formation of radioactive aerosols is its thermal decomposition. Lorenz *et al.* [13] studied the thermal decomposition of $CH_3{}^{131}I$ and found that 97.9% decomposition of $CH_3{}^{131}I$ was observed only at 800°C. At lower temperatures, the degree of $CH_3{}^{131}I$ decomposition was lower: 13% at 500°C and 83% at 600°C. Published data on materials allowing thermal decomposition of $CH_3{}^{131}I$ to be efficiently performed at lower temperatures are lacking. Therefore, the goal of this work was the development and study of the thermal decomposition of methyl iodide $CH_3{}^{131}I$ in a gas flow in the presence of various modifications of "Fizkhmin"^{TM} granulated materials based on silica gel impregnated with d-elements.

2. Experimental

In our study we used carrier-free ^{131}I supplied in the form of $Na^{131}I$ solution. The radionuclide activity was measured by γ-ray spectrometry using a multichannel analyzer with a semiconductor Ge–Li detector. ^{131}I was used as radioactive tracer for weighable amounts of inactive iodine compounds. Therefore, the designation $CH_3{}^{131}I$ refers to the labeled compound and not to the compound of pure ^{131}I. In the course of experiments, $CH_3{}^{131}I$ was introduced into the system by passing air at a definite rate through the vessel containing $CH_3{}^{131}I$. The required amounts of $CH_3{}^{131}I$ were preliminarily frozen out from the helium flow with liquid nitrogen. $CH_3{}^{131}I$ was obtained by the reaction of dimethyl sulfate with $K^{131}I$ [7].

All the salts, alkalis, and acids used in the study were of chemically pure grade. We used coarsely porous silica gel in the form of granules of size from 1.0 to 3.0 mm and the "Fizkhmin"^{TM} composite materials based on it:

1) composites based on silica gel, obtained by impregnation of it with a 2 M NH_4OH solution, storage of the wet sorbent for 24 h, and drying in air at a temperature increasing from room temperature to 300°C at a rate of 20 deg/min, followed by conditioning at 300°C for 4 h;

2) composites based on silica gel, obtained by impregnation of it with a 0.13 M NH_4NO_3 solution, followed by storage, drying, and conditioning under the same conditions;

3) composites based on silica gel impregnated with Cu by treatment with Cu(II) nitrate, followed by drying at 110°C, treatment of the dry precursor with ammonia for 24 h, and conditioning in air at 300°C for 4 h. Cu content was 8 wt% (designation KKM-Cu);

4) composites based on silica gel impregnated with Ni and Cu by treatment with a solution of Ni(II) and Cu(II) nitrates, followed by treatment similar to that of KKM-Cu. Total content of Cu and Ni was 10 wt%, Cu : Ni weight ratio 1:1 and 1:4 (designation KKM-CuNi);

5) composites based on silica gel impregnated with Ni by treatment with a solution of Ni(II) nitrate, followed by treatment similar to that of KKM-Cu. Ni content was 8 wt% (designation KKM-Ni).

The localization of $CH_3{}^{131}I$ from a water vapor–air flow was studied on a setup schematically shown in the **Figure 1**. The set-up concluded the following basic parts: rotameters (1); a $CH_3{}^{131}I$ generator (2); scrubber with water (3); the heating furnace of mine type (4); composite materials under study (5); the thermocouple (6); a column with $SiO_2\text{-}Cu^o$ (7); scrubber with 0.05 M Na_2SO_3 solution (8); the heating furnace of tubular type (9); columns with $SiO_2\text{-}AgNO_3$ (10).

In this setup, the column with silica gel containing 10 wt% Cu^0 was intended for trapping $^{131}I_2$ released in thermal decomposition of $CH_3{}^{131}I$. It should be noted that $CH_3{}^{131}I$ is not sorbed on this material. To trap the residual amounts of the unchanged $CH_3{}^{131}I$, we used two columns with silica gel impregnated with $AgNO_3$ (30 mg/g silica gel).

The experiment was performed as follows. The compressor was switched on, and air was passed at a definite rate through the $CH_3{}^{131}I$ generator. The air with $CH_3{}^{131}I$ vapor was fed to the bubbler with water, where it was saturated with water vapor. After that, the water vapor-air flow containing $CH_3{}^{131}I$ was fed to the reaction column with the test materials heated to the required temperature. When passing through these materials, $CH_3{}^{131}I$ decomposed to one or another extent with the formation of violet vapor of molecular iodine. After passing through the reaction column, the gas flow containing the $CH_3{}^{131}I$ decomposition products was fed to a column packed with silica gel containing 10 wt% Cu^0. The major amount of molecular iodine was sorbed on this material. Then, the gas flow was passed through a bubbler with a 0.05 M Na_2SO_3 solution to remove residual traces of molecular iodine and through two columns with silica gel impregnated with $AgNO_3$ (30 mg/g silica gel). After the experiment completion, the compressor was switched off, the columns with various sorbents were cooled,
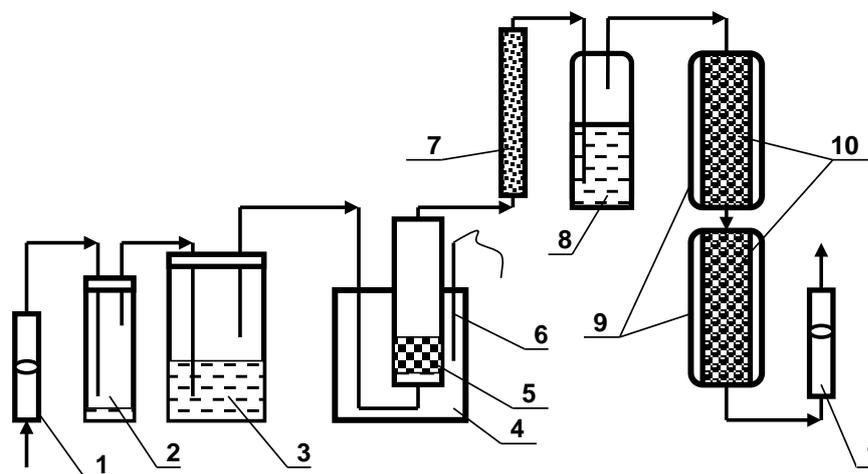
Figure 1. The scheme of the set-up for study of $CH_3{}^{131}I$ thermal decomposition in a gas flow.

and the setup was disassembled. All parts of the setup were treated with a 0.1 M $Na_2S_2O_3$ solution to avoid the loss of radioactive iodine and then were washed two times with water. The content of ^{131}I in various parts of the setup was determined by γ-ray spectrometry. After determining the ^{131}I content in various parts of the setup, we calculated the degree of decomposition of $CH_3{}^{131}I$.

3. Results and Discussion

Data on thermal decomposition of 10 mg of $CH_3{}^{131}I$ in an air flow without composite materials are given in **Table 1**. As can be seen, the degree of decomposition of $CH_3{}^{131}I$ increases with temperature and reaches a maximum at ~760°C. For example, with an increase in temperature from ~540°C to ~760°C the degree of decomposition of $CH_3{}^{131}I$ increases from ~9.5% to ~98.0%. In all the cases, ^{131}I was virtually fully localized on the column packed with silica gel containing 10 wt% Cu^0. This fact suggests that the major decomposition product of $CH_3{}^{131}I$ is atomic iodine which instantaneously transforms into molecular iodine. Our data on thermal decomposition of $CH_3{}^{131}I$ are well consistent with the data of Lorenz *et al.* [13], who showed that the degree of thermal decomposition of $CH_3{}^{131}I$ at ~800°C was 97.9%.

As follows from **Table 1**, an increase in the linear velocity of the gas flow by a factor of approximately 2 does not affect strongly the degree of decomposition of $CH_3{}^{131}I$. For example, with an increase in the linear velocity of the gas flow from ~4.5 to 8.9 cm/s the degree of decomposition of $CH_3{}^{131}I$ decreases by only ~2.0%.

To stabilize the flow in the heating zone, we placed glass cylinders ~2 mm in diameter and ~4 mm high into the reaction column. As seen from **Table 1**, introduction of the glass cylinders into the heating zone leads to an increase in the degree of decomposition of $CH_3{}^{131}I$ at ~550°C and exerts virtually no effect at ~660°C. The observed effect is probably associated with the residence time of the gas flow containing $CH_3{}^{131}I$ in the heating zone. At ~550°C, introduction of glass cylinders led not only to stabilization of the flow in the heating zone, but also to a relative increase in the residence time of $CH_3{}^{131}I$ in the heating zone, which increases the degree of decomposition of $CH_3{}^{131}I$. At ~660°C, the glass cylinders underwent sintering owing to fusion of their surface. The monolithic mass formed in the processes decreased the effective cross section of the reaction column and the free volume in the heating zone. Therefore, simultaneously with stabilization of the gas flow in the heating zone, its linear velocity increased and hence the residence time of $CH_3{}^{131}I$ in the heating zone decreased. Owing to simultaneous occurrence in the heating zone of two processes exerting opposite effects on the thermal decomposition of $CH_3{}^{131}I$, the degree of decomposition of $CH_3{}^{131}I$ at ~660°C remained unchanged.

Because of fusion of glass cylinders at ~660°C, it was interesting to study the thermal decomposition of $CH_3{}^{131}I$ using other materials as gas flow stabilizers. The best of them is coarsely porous silica gel.

Data on thermal decomposition of $CH_3{}^{131}I$ in the presence of silica gel and of certain "Fizkhmin"^{TM} composite materials based on it are given in **Table 2**.

As can be seen, in the presence of silica gel the degree of decomposition of $CH_3{}^{131}I$ is ~96.8% even at ~540°C. Therefore, it was interesting to study the thermal decomposition of $CH_3{}^{131}I$ at still lower temperatures. **Table 2**

Table 1. Thermal decomposition of $CH_3{}^{131}I$ (10 mg) in air flow. (temperature of steam-air flow ~23˚C, linear rate of gas flow ~4.0 - 5.0 cm/s, steam content in steam-air mixture ~3 - 4 vol.%, volume rate of gas flow (17˚C - 20˚C)~0.8 dm^3/min, time of the air flow presence in the heating zone with length 5.2 cm-1.1 - 1.3 s, S_{column}~3.5 cm^2, experiment time-4 h).

Material	T, ˚C	Degree of ^{131}I sorption, %			The total degree of ^{131}I sorption, %	
		Column with material	Column with SiO_2-Cu^0	Scrubber with 0.05 M Na_2SO_3	Without accounting of thermal decomposition	With accounting of thermal decomposition
-*	540	-	~7.49	~0.004	~0	~7.50
	550	-	~9.45	~0.004	~0	~9.50
-	640	-	~74.97	~0.004	~0	~75.00
	760	-	~97.95	~0.004	~0	~98.00
Glass cylinders	550	~0.004	~19.51	~0.003	~0	~19.51
	660	~0.03	~73.94	~0.015	~0	~73.99

*-linear rate of gas flow~8.9 cm/s, time of the air flow presence in the heating zone with length 5.2 cm - 0.6 s.

Table 2. Thermal decomposition of $CH_3{}^{131}I$ (10 mg) on silica gel in air flow. (temperature of steam-air flow ~23˚C, linear rate of gas flow~4.8 - 5.2 cm/s, steam content in steam-air mixture ~3 - 4 vol.%, volume rate of gas flow (17-20ºC) ~ 0.8 dm^3/min, time of the contact between material under study and steam-air mixture - 1.0-1.1 s, weight of material under study-10 g, size of granules of material under study-3.0 mm, height of layer of material under study-5.2 cm, S_{column} ~3.5 cm^2, experiment time-4 h).

Material under study	T, ˚C	Degree of ^{131}I sorption, %			The total degree of ^{131}I sorption, %	
		Column with material under study	Column with SiO_2-Cu^0	Scrubber with 0.05 M Na_2SO_3	Without accounting of thermal decomposition	With accounting of thermal decomposition
Silica gel	240	~2.12	~0.03	~0.006	~2.12	~2.16
	350	~1.15	~8.99	~0.007	~1.15	~10.15
	460	~0.54	~76.20	~0.009	~0.54	~76.74
	540	~0.31	~96.75	~0.012	~0.31	~97.07
Silica gel-NH_4OH	340	~0.45	~7.99	~0.002	~0.45	~8.44
Silica gel-NH_4NO_3	340	~0.23	~3.09	~0.002	~0.23	~3.32

shows that the degree of decomposition drastically decreases with a decrease in temperature. For example, as the temperature is decreased from ~540˚C to ~240˚C, the degree of $CH_3{}^{131}I$ decomposition decreases from ~96.8 to ~0.03%. It should be noted that, under the experimental conditions studied, silica gel absorbs ^{131}I weakly (0.3% - 2.1%), with the degree of absorption decreasing with an increase in temperature. Thus, the use of silica gel allows the temperature required for the $CH_3{}^{131}I$ decomposition to be decreased by more than 200˚C. The observed effect is probably associated both with high porosity of silica gel and with the presence of microimpurities of various elements in silica gel, catalyzing the decomposition of $CH_3{}^{131}I$ at high temperatures.

It is known that the heat treatment of silica gel with an ammonia solution leads to significant changes in the silica gel structure, associated with its porosity [14]. In this connection, it was interesting to study the thermal decomposition of $CH_3{}^{131}I$ in the presence of composite materials based on silica gel and containing products of thermal reaction of ammonia with silica gel. As seen from **Table 2**, the degree of decomposition of $CH_3{}^{131}I$ in the presence of these composite materials not only did not increase but even decreased by a factor of ~3 in the case of silica gel with NH_4NO_3. Because the drying of the material was performed on heating from room temperature to 300˚C and the melting and decomposition points of NH_4NO_3 are 170 and 239˚C, respectively [15], in the course of conditioning the ammonium salt, probably, initially melted, impregnated the whole silica gel structure, and only then decomposed. Apparently, during the conditioning time the ammonium salt decomposed

incompletely; therefore, a part of the volume and especially silica gel micropores were filled with NH_4NO_3, which prevented the access of $CH_3{}^{131}I$ to active sites on the silica gel surface. As a result, the degree of decomposition of $CH_3{}^{131}I$ in the presence of the silica gel with NH_4NO_3 composite material decreased relative to straight silica gel.

As noted above, another possible factor decreasing the $CH_3{}^{131}I$ decomposition temperature in the presence of silica gel is the presence of impurities of various metals. In this connection, it was interesting to study the thermal decomposition of $CH_3{}^{131}I$ in the presence of "Fizkhmin"^{TM} composite materials based on silica gel impregnated with Cu and Ni compounds. These d-elements are widely used as base components of catalysts in various chemical processes [16].

Data on thermal decomposition of $CH_3{}^{131}I$ in an air flow in the presence of "Fizkhmin"^{TM} composite materials based on silica gel impregnated with Cu and Ni compounds are given in **Table 3**. As seen from **Table 3**, the use of "Fizkhmin"^{TM} composite materials containing d-elements allowed the decomposition temperature of $CH_3{}^{131}I$ to be decreased from ~540˚C to ~450˚C, *i.e.*, by almost 100˚C more. For example, with KKM-8Ni the degree of decomposition of $CH_3{}^{131}I$ increased from ~39% to ~92% with an increase in temperature from ~340˚C to ~450˚C.

Similar effect was observed with the other composite materials containing Cu and Ni compounds. It should be noted that the composite materials under consideration sorb from ~7.0% to ~49% of ^{131}I at relatively low temperatures (~240˚C - 350˚C). As a result, the total degree of ^{131}I localization in the systems with KKM-8Ni and KKM-2Cu8Ni at ~350˚C is close to 90%. The observed effect is probably associated with simultaneous occurrence of several processes in the system: (1) catalytic decomposition of $CH_3{}^{131}I$ with the formation of atomic iodine; (2) reaction of iodine atoms with each other to form molecular iodine and with d-elements to form iodides; (3) thermal decomposition of d-element iodides with the formation of finely dispersed particles of their oxides or metals. It should be noted that the prevalence of one or another process depends on temperature. Therefore, increased ^{131}I uptake will be observed either in the column with the composite material or in the column with silica gel containing 10 wt% Cu^0.

Table 3. Thermal decomposition of $CH_3{}^{131}I$ (10 mg) on composite material "Fizkhimin"^{TM} in air flow. (temperature of steam-air flow ~23˚C, linear rate of gas flow ~6.0 - 7.0 cm/s, steam content in steam-air mixture ~ 3 - 4 vol.%, volume rate of gas flow (17˚C - 20˚C) ~ 0.8 dm^3/min, time of the contact between composite "Fizkhimin"^{TM} and steam-air mixture - 0.7 - 0.9 s, weight of composite "Fizkhimin"^{TM}-10 g, size of composite granules-1.0 mm, height of composite "Fizkhimin"^{TM} layer-4.8 cm, S_{column} ~3.0 cm^2, experiment time-4 h).

Composite "Fizkhimin"^{TM}	T, ˚C	Degree of ^{131}I sorption, %			The total degree of ^{131}I sorption, %	
		Column with composite Fizkhimin"^{TM}	Column with SiO_2-Cu^0	Scrubber with 0.05 M Na_2SO_3	Without accounting of thermal decomposition	With accounting of thermal decomposition
KKM-8Cu	240	~9.31	~4.40	~0.002	~9.31	~13.72
	340	~3.96	~58.14	~0.002	~3.96	~62.10
	450	~1.33	~91.80	~0.013	~1.33	~93.15
KKM-5Cu5Ni	235	~6.93	~1.60	~0.002	~6.93	~8.52
	345	~15.97	~51.19	~0.003	~15.97	~67.15
	445	~2.89	~94.96	~0.009	~2.89	~97.85
KKM-2Cu8Ni	250	~12.48	~7.15	~0.006	~12.48	~19.64
	350	~37.59	~51.62	~0.026	~37.59	~89.24
	480	~2.26	~96.45	~0.039	~2.26	~98.75
KKM-8Ni	260	~15.86	~12.68	~0.016	~15.86	~28.56
	340	~48.75	~38.88	~0.016	~48.75	~87.79
	450	~7.63	~91.82	~0.026	~7.63	~99.48

Thus, the use of "Fizkhmin"^{TM} composite materials based on silica gel impregnated with d-elements allows the $CH_3^{131}I$ decomposition temperature to be decreased by more than 300˚C. The revealed features of thermal decomposition of $CH_3^{131}I$ in the presence of the composite materials studied can be taken into account in the development of new and improvement of existing systems for environment protection at enterprises of nuclear industry.

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