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Reactions of ^{125}I Activated by ^{125}Xe(EC)^{125}I Process with Methane

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The reactions of ^{125}I obtained from the ^{125}Xe(EC)^{125}I process with methane have been investigated. It was confirmed that electron scavengers, such as I_2, SF_6, and O_2, play an important role. The main product is only $CH_3{}^{125}I$, the yield decreasing significantly with the concentration of Xe. By adding various additives, the yield of $CH_3{}^{125}I$ in the presence of trace amount of I_2 was assigned as follows: 8.7±6.7% by the hot atom reaction, 35.8±8.0% by $^{125}I^+$ in the $^1D_2$ state, and 31.5±2.0% by $^{125}I^+$ in the ^3P states. The results are discussed in comparison with those reported on similar reactions utilizing different activation processes. Chemical sequences of the formation of $CH_3{}^{125}I$ are proposed.

Many papers have appeared on the reactions of recoil iodine from various nuclear transformations[1–12] with simple alkanes. Iodine ions in excited states always play important roles in the reactions. A number of experiments were carried out dealing with the systematics of the role of excited iodine ions.

Rack and Gordus investigated the reactions of ^{128}I obtained from the $^{127}I(n,\gamma)^{128}I$ reaction with gaseous methane, and they concluded that about 18.4% of the 54.4% organic ^{128}I is formed as a result of hot ^{128}I reactions, 11% as a result of excited iodine ions in $^3P_2$, $^3P_1$, and/or $^3P_0$ states, and 25% as a result of reactions of $I^+(^1D_2)$ ions.[3,4] Nicholas *et al.* reached a similar conclusion in the reactions of ^{130}I activated by the (n,γ) or (IT) process with methanes (CH_4 and CD_4).[5] Due to rather high yield of hot reactions, the recoils, ^{128}I and ^{130}I, however, are not necessarily suitable for a specific study of the role of excited iodine ions.

Loberg and Welch chose ^{123}Xe formed by the $^{122}Te(^3He,2n)^{123}Xe$ reaction as nuclide to give iodine, and studied the ionic reactions of $^{123}I^+$ with CH_4.[10] The nuclide, ^{123}Xe, decays in two modes, electron capture and β^+ decay.[13] In the latter mode, 14% of the ^{123}I recoils are formed initially in the I^- state.[10] This indicates that for a detailed analysis the role of the negative ion should be taken into account. The ^{125}I recoil from ^{125}Xe(EC)^{123}I process is preferable to other recoils for a specific investigation of iodine ions, since the nuclide, ^{125}Xe, decays only by electron capture and the resulting ^{125}I has a maximum kinetic energy of 15.6 eV.[13]

Schroth and Adloff examined the reactions of ^{125}I obtained from ^{125}Xe with methane.[6] Schleiffer and Certout also investigated the same reaction system.[11] However, they reached different conclusions.

We have studied the reactions of ^{125}I obtained from ^{125}Xe with methane in gaseous phases. The reaction yield was carefully investigated by adding various gases to the reaction system. The results are discussed in comparison with those reported from the viewpoint of the role of iodine ions in the excited state.

Experimental

Chemicals. Xenon gas with natural composition (Nippon Sanso Co., purity 99.9%) and methane (Takachiho Chem. Co., purity 99.95%) were used. Other reagents used as additives had the highest purity among those available.

Sample Preparation. Xenon gas with natural composition was introduced in a silica ampoule (18.5 ml) equipped with a breakable seal. The pressure was kept at around 700 Torr. The ampoule was irradiated in the T-pipe of a JRR-4 reactor of JAERI for 30—120 min; the neutron flux at the irradiation port was 4×10^{13} n cm^{-2} s^{-1}. After 4—12 h from the end of irradiation, the radioactive xenon mixture was purified by passing the mixture through a column packed with granular silver in order to remove ^{125}I formed in the ampoule.

Pyrex glass ampoules, with volume either 6.5 or 10.5 ml, were used as the reaction vessels. The irradiated and purified xenon gas, additive gas, when necessary, and methane were introduced into the reaction vessel by means of a vacuum line. The pressure of the reaction system was usually kept constant at 500 Torr, but it was widely varied for investigation of the dependence of the product yields on pressure. The pressure of radioactive xenon was usually kept at 20 Torr [0.04 m.f. (mole fraction)]. For the addition of excess iodine, a small amount of solid iodine was placed in an ampoule. Subsequently, air was pumped off and the radioactive xenon and methane were introduced. The samples were stored in the dark at room temperature for more than 4 days. Some samples were exposed to a 45 kCi ^{60}Co source immediately after their preparation.

Sample Processing. The reaction products were separated by means of a radio-gas chromatograph. The sample was directly injected into a radio-gas chromatograph by means of a vacuum line. A potassium hexacyanoferrate(II) 16/20 mesh precolumn of $4\phi\times100$ mm was placed in front of the separation column in order to prevent the introduction of inorganic iodides such as HI and I_2.[14] The separation column was 2.8 m D.O.P. column, Neopak 1A of 60/80 mesh coated with 15% dioctyl phthalate. In the operation, the temperature of the column was raised from room temperature to 115 °C at a rate of 8 °C min^{-1}. The effluent was collected by bubbling through a trap filled with liquid scintillator, after its activities had been continuously measured with a NaI(Tl) counter. The traps were radio-assayed with a liquid scintillation counter.

Total organic yield in the reaction system of Xe(0.04 m.f.) and CH_4 was determined to be 60.7% by the conventional solvent extraction method. This particular reaction system was chosen as a reference in determining the total organic yield in other reaction systems. In the solvent extraction method, toluene with iodine carrier (10^{-3} M) was used as an organic layer and 0.5 M Na_2SO_3 solution as an inorganic layer. The radioactivity of each layer was measured with a NaI scintillation counter and a liquid scintillation counter.

The absolute yields (AY) in other systems were determined according to the equation

$$AY(\%) = 60.7\ (A_{Xe}/A_{CH_3I})_{ref}\cdot(A_P/A_{Xe})_{sam},$$

where 60.7 is the absolute yield in the reference sample.

A_{Xe}, A_P, and A_{CH_3I} denote the activities of xenon, some product of interest and methyl iodide, respectively, in a radiogas chromatogram (A_{CH_3I} and A_P were also measured with a liquid scintillation counter). Subscripts "ref" and "sam" denote the reference system (Xe(0.04 m.f.) and CH_4) and any other reaction systems, respectively.

Results

The vacuum line used in most of the experiments was previously utilized for sampling gases including iodine. The iodine adsorbed on the surface can not be removed completely. Thus, almost all reaction systems will have been contaminated with iodine vapor, unless otherwise stated.

The total organic yield in the reaction system, Xe (20 Torr) and CH_4(480 Torr), was 60.7±4.5%. The results based on the two different measurements, NaI and liquid scintillation counters, agree. The organic yield product in the gaseous phase was only $CH_3{}^{125}I$, unless other additives such as C_2H_6, C_2H_5Cl, and solid-I_2 were present.

When the pressure was changed from 16 to 923 Torr, the Xe/CH_4 ratio being kept at 0.10, the yield of $CH_3{}^{125}I$ remained at 54.8±4.1%. The results obtained at various temperatures are given in Table 1. The yield of $CH_3{}^{125}I$ remained unchanged, showing no temperature-effect. No wall effect was observed. Addition of 0.5 g of quartz wool (1—5 μ) inside a pyrex ampoule of similar size hardly affected the results.

The variation of $CH_3{}^{125}I$-yield with the concentration of Xe is given in Table 2. The yields decreased with an increase in the concentration of Xe, from 74.0 ±5.0% (0.011 m.f. of Xe) to 31.5±2.0% (1.0 m.f. of Xe).

The effects of additives on the reaction system of 0.04 m.f. of Xe and CH_4 containing a trace amount of I_2 are shown in Fig. 1. The yield of $CH_3{}^{125}I$ decreased monotonically with an increase in the concentration of Kr, Ar, and N_2. It was extrapolated to be 52.0±5.0 % at 1.0 m.f. of additives. When O_2 or SF_6 was chosen as an additive, the yield increased at the beginning, but decreased with a further increase in the concentrations. The extrapolated value at 1.0 m.f. of O_2 is also 52.0±5.0%, but 31.5±2.0% for the case of SF_6. With the addition of CH_3Cl, C_2H_5Cl, and C_2H_6, the yield of $CH_3{}^{125}I$ decreased with an increase in the concentrations of additives, the limiting values being 4.9± 0.8%, almost 0%, and 2.4±0.4%, respectively. A small amount of $C_2H_5{}^{125}I$ was detected in the case of C_2H_5Cl and C_2H_6 additives.

Addition of Br_2 significantly influenced the $CH_3{}^{125}I$ yield; less than 0.5 mol % of Br_2 reduced the yield below 1%. However, the addition of a macroscopic amount of I_2 has no definite effect on the $CH_3{}^{125}I$ yield (Table 1). A concomitant formation of $CH_2{}^{125}II$ scarcely occurred; the yield was less than 1%.

Some experiments with CD_4 were performed. The yield of methyl iodide, $CD_3{}^{125}I$, was 59.9±6.9% at the concentration of Xe, 0.04 m.f. The effects of pressure and Xe-concentration were similar to the case of the

Table 1. Effect of reaction temperature on the yield of $CH_3{}^{125}I$

Temperature (°C)	Iodine	
	Trace	Macroscopic
Room	60.7±4.5%	63.3±7.1%
0	61.2±5.0%	62.3±4.6%
−86	57.9±4.3%	56.7±5.2%

Table 2. Variation of $CH_3{}^{125}I$-yield with the concentration of Xe

Mole fraction of Xe	Yield of $CH_3{}^{125}I$ (%)	Mole fraction of Xe	Yield of $CH_3{}^{125}I$ (%)
0.00	(76.0±6.0)	0.21	46.3±3.4
0.011	74.0±5.5	0.31	39.2±2.8
0.021	71.9±5.3	0.40	35.5±2.6
0.03	67.6±5.0	0.53	31.3±2.3
0.04	60.7±4.5	0.62	31.5±2.3
0.054	59.7±4.4	0.70	31.4±2.3
0.10	54.8±4.1	0.80	31.4±2.2
0.15	51.9±3.8	0.90	31.6±2.3
		1.00	(31.5±2.0)

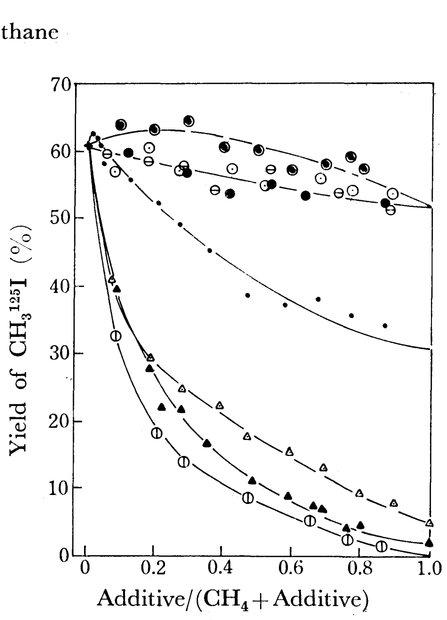

Fig. 1. Variation of the $CH_3{}^{125}I$-yield with the concentrations of various additives.
◉: O_2, ⊙: Ar, ●: Kr, ⊖: N_2, •: SF_6, △: CH_3Cl, ▲: C_2H_6, ⦶: C_2H_5Cl.

Table 3. Yields of $CH_3{}^{125}I$ observed in the reaction system exposed to a ^{60}CO source[a)]

Reaction system	yield of $CH_3{}^{125}I$(%)
CH_4+Xe(0.04 m.f.)	<0.5
CH_4+Xe(0.04 m.f.) +SF_6(0.02 m.f.)[b)]	38.5±1.6

a) Dose rate 2.1×10^6 R/h, exposing time 20 h.
b) Other products: $C_2H_5{}^{125}I$: 12.3±1.2%, i-$C_3H_7{}^{125}I$: 2.1±1.0%, n-$C_3H_7{}^{125}I$: 1.3±0.5%, and n-$C_4H_9{}^{125}I$: 1.2±0.6%.

reaction with CH_4.

Some samples were exposed to a ^{60}Co source of 45 kCi for 20 h within 30 min after preparation in a similar manner to that of other samples. The results are summarized in Table 3 with experimental conditions.

Discussion

Formation of $CH_3{}^{125}I$ via *Energetic Process.* Schroth and Adloff[6] and Schleiffer and Certout[11] studied similar reaction systems to those in the present experiments, although no reference was made to the hot atom reaction. The latter gave the extrapolated value of 55±3% at 1.0 m.f. of additives of He, Ne, Ar, and Kr.[11] This is in good agreement with our results, 52.0±5.0%. Schleiffer and Certout maintained the concentration of Xe at 0.025 m.f. throughout their experiments.

Loberg and Welch investigated the reaction of ^{123}I from ^{123}Xe with methane and mentioned the following for the hot atom reactions: "this lack of reactivity due to kinetically hot species indicates that by the time the iodine ion has attained a charge of +1 it has come to thermal equilibrium with its surroundings."[10] However, they observed the hot atom reactions with ethane and neopentane as reactants. The ^{123}I atom from ^{123}Xe has the maximum kinetic energy of 34.4 eV as a result of the electron capture decay.[13] The excess kinetic energy corresponds to the median kinetic energies of ^{80}Br and ^{82}Br from the isomeric transition processes.[15] In the reactions of these recoil bromines with alkanes, it has been confirmed that the reactivity of methane was higher than that of other alkanes.[16,17] From the chemical similarity between bromine and iodine, the trend may be maintained also in the energetic reaction of recoil iodine. Thus, the failure of detection of energetic yield in the reaction of ^{123}I with methane[10] would not necessarily indicate the absence of the hot atom reactions.

The nuclide of ^{125}I decays only by electron capture, and the Q value of the decay is reported as 1.9 MeV.[13] From this value, the maximum recoil energy possessed by the ^{125}I atom is calculated to be 15.6 eV. The limiting yield of $CH_3{}^{125}I$ at 1.0 m.f. of additives is 52.0±5.0% for Kr, Ar, N_2, and O_2 (Fig. 1). The difference between the yield at 0.04 m.f. of Xe, 60.7±4.5%, and this limiting value, 52.0±5.0%, should be considered to result from hot atom reactions. Although the presence of 0.04 m.f. of Xe may influence the yield dependence on kinetic energy, its extent is considered to be unimportant, being less than 1% as referred to the results of bromine hot atom reaction.[18] Thus, the yield of hot atom reaction is assigned to be 8.7±6.7%.

Main Mechanisms of $CH_3{}^{125}I$-formation via *Ionic Process.* The absence of the wall effect of vessel indicates that the reactions mainly occur in gaseous phase and the reactions are not catalyzed by the wall.

The yield of $CH_3{}^{125}I$ decreased with an increase in the concentration of Xe (Table 2). The value extrapolated to zero m.f. of Xe is 76.0±6.0% and the limiting value at 1.0 m.f. of Xe is 31.5±2.0%. This reduction of the yield is due to the near resonant charge exchange between xenon and I^+ in the $^1D_2$ state, and the limiting yield, 31.5±2.0%, should be ascribed to reactions of I^+ in the ^3P states.[3,4,10,11]

TABLE 4. EFFECTS OF ELECTRON SCAVENGERS ON THE YIELD OF $CH_3{}^{125}I$

Additive[1]	Yield of $CH_3{}^{125}I$(%) By new line	Yield of $CH_3{}^{125}I$(%) By old line
no	47.8±4.8	60.7±4.5
SF_6(0.07 m.f.)	57.3±4.8	60.1±5.9
O_2 (0.30 m.f.)	59.3±4.3	64.0±6.0

[1] All reaction systems contain 0.04 m.f. of Xe.

The yield of $CH_3{}^{125}I$ increases first with an increase in the concentration of O_2 and SF_6(Fig. 1). This suggests that an electron scavenger plays an important role in the mechanism of $CH_3{}^{125}I$-formation. Since I_2 is also an excellent electron scavenger, experiments were carried out with a new vacuum line in order to investigate of the effect of trace amout of I_2 in the reaction. The results are shown in Table 4. The yield obtained by the new line was significantly lower than that by the old line contaminated with iodine vapor, the yield increasing by about 10%, on addition of SF_6 or O_2 to the system.

This trend was not observed with use of the old line. We see that the presence of electron scavengers raises the yield of $CH_3{}^{125}I$. The following finding also supports the result.

Samples prepared in a similar way using the old line were exposed to a ^{60}Co source. The yield of $CH_3{}^{125}I$ in the system of CH_4±0.04 m.f. of Xe was reduced to less than 0.5% (Table 3). However, in the system containing SF_6, the yield was 38.5±1.6% under the same conditions. The trace amount of I_2 originally contained in the system would have been consumed by the reactions with radiolysis-products of CH_4 and stabilized to either HI or organic iodides. As a result, the system would be cleaned from I_2 in the early stage of the reactions. Thus, we see that $CH_3{}^{125}I$ can not be produced in the system with carrier free ^{125}I unless some other electron scavenger is present, and that the samples prepared by the new line are still contaminated by a trace amount of I_2, although the extent is much less than with the old line. (Pumps and reagents were used in common in both experiments.)

Schleiffer and Certout proposed the following reaction sequences:

$$CH_4 + {}^{125}I^+ \rightarrow CH_3{}^{125}I^+ + H \quad (1)$$

$$CH_3{}^{125}I^+ + I_2 \rightarrow CH_3{}^{125}I + I_2{}^+ \quad (2)$$

$$CH_3{}^{125}I + e^- \rightarrow CH_3 + {}^{125}I^- \quad (3)$$

The mechanism involves a neutralization process of $CH_3{}^{125}I^+$ with additives and is consistent with the results. If the neutralization of $CH_3{}^{125}I^+$ is the working process, the role of SF_6 observed in the systems exposed to ^{60}Co-source can be ascribed to the following scheme in analogy with Reaction 2:

$$CH_3{}^{125}I^+ + SF_6 \rightarrow CH_3{}^{125}I + SF_6{}^+ \quad (4)$$

However, a similarity in the effects of Xe and SF_6 on the $CH_3{}^{125}I$ yield (Fig. 1 and Table 2) predicts that the ionization potential of SF_6 is in the same range of

TABLE 5. COMPARISON OF THE PRESENT RESULTS WITH THOSE REPORTED

Reaction system	Iodine carrier	Yield of CH_3I(%)				Reference
		Total	Hot	$^1D_2$	^3P	
$^{127}I(n,\gamma)^{128}I+CH_4$	yes	54.4±2.0	18.4±2.0	25.0±2.0	11.0±2.0	3
$^{129}I(n,\gamma)^{130,130m}I+CH_4$	yes	42.5±2.0	16.5±2.0	9.5±2.0	16.3±2.0	5
$^{130m}I(IT)^{130}I+CH_4$	yes	25.6±2.0	9.7±2.0	5.6±2.0	10.3±2.0	5
$^{129}I(n,\gamma)^{130,130m}I+CD_4$	yes	41.3±2.0	15.3±2.0	9.5±2.0	16.5±2.0	5
$^{130m}I(IT)^{130}I+CD_4$	yes	26.4±2.0	10.5±2.0	5.6±2.0	10.3±2.0	5
$^{123}Xe(EC, \beta^+)^{123}I+CH_4$	no	51.8±2.9	0	21.2	30.6	10
$^{123}Xe(EC, \beta^+)^{123}I+CH_4$	yes	53.8	0	27.0	25.4	10
$^{125}Xe(EC)^{125}I+CH_4$	—	58±6	0	40±7	18±2[a)]	6
$^{125}Xe(EC)^{125}I+CH_4$	yes	75	0	55	20	11
$^{125}Xe(EC)^{125}I+CH_4$	yes	76.0±6.0	8.7±6.7	35.8±8.0	31.5±2.0	present work

a) Assigned as the yield resulting from the reaction of I^+ in the $^1S_0$ state.

Xe, both being higher than that of CH_3I. This implies that Reaction 4 is unimportant. Loberg and Welch reported that the reaction to form $CH_3{}^{125}I^+$ is exothermic only with $I^+(^1D_2)$.

Reaction 3 would not be important under the low electron density as in the present case. When samples which had been stored for more than 4 days after their preparation were exposed to a ^{60}Co-source up to the total dose 6.6×10^5 R, more than 10% of $CH_3{}^{125}I$ still survived, even in the absence of an electron scavenger.

The reaction sequences proposed by Schleiffer and Certout do not seem to be able to explain our results. Let us introduce the following reaction mechanisms:

$$^{125}I^+ + CH_4 \rightarrow (CH_4{}^{125}I)^+ \qquad (5)$$

$$(CH_4{}^{125}I)^+ + CH_4 \rightarrow CH_3{}^{125}I + CH_5{}^+ \qquad (6)$$

$$(CH_4{}^{125}I)^+ + e^- \rightarrow CH_4 + {}^{125}I \qquad (7)$$

$$SF_6,\ I_2,\ \text{or}\ O_2 + e^- \rightarrow SF_6{}^-,\ I + I^-,\ \text{or}\ O_2{}^- \qquad (8)$$

According to the reaction sequences, $CH_3{}^{125}I$ is formed by Reactions 5 and 6. However, the formation will be interferred by Reaction 7. In the presence of SF_6, O_2, or I_2, Reaction 8 occurs in competition with Reaction 7. As a result the yield of $CH_3{}^{125}I$ would increase.

As is shown in Table 1, no temperature effect was observed within experimental error. $CH_3{}^{125}I$ will be predominantly produced by Reactions 5 and 6, and hot atom reactions. These reactions usually occur adiabatically in a very short period. The energy required for the reactions is supplied by the excitation energy of I^+ ions or the kinetic energy of recoils. This explains the fact that the yield is independent of temperature.

In the reactions of ^{123}I obtained from the decay of ^{123}Xe, Loberg and Welch stressed the importance of a molecular ion complex, AI^+, where A can be any molecule involved in the system, for the formation of CH_3-^{123}I, based on the observation that the yield increased with some additives such as Kr, Ar, and Ne.[10)] However, we have observed no such characteristic behavior of the yield. This suggests that the role of AI^+ is much less important in the reactions of ^{125}I as compared with those of ^{123}I.

Effects of Reactive Additives. When the additives CH_3Cl, C_2H_5Cl, and C_2H_6 were added to the reaction system, the yield of $CH_3{}^{125}I$ decreased with an increase in the concentration of additives and continuously approached the values found in the absence of CH_4, *i.e.*, 480 Torr of additive gas and 20 Torr of Xe (4.9±0.8 % for CH_3Cl, almost zero % for C_2H_5Cl, and 2.4±0.4% for C_2H_6).

The results indicate that the $CH_3{}^{125}I$-yield resulting from the reaction with CH_4 can be suppressed by any of the additives. The ionization potentials (IP) of the reagents are 11.28±0.01 eV for CH_3Cl, 10.97±0.02 eV for C_2H_5Cl, and 11.65±0.03 eV for C_2H_6.[20)] Thus, the IP alone as a determining factor of the yield can not explain the efficient reduction of the yield by C_2H_6, since the I.P. of C_2H_6 is higher than that of I^+ state, 11.34 eV. Thus, an alternative reaction pathway for the reaction of $^{125}I^+$ will be present, such as the one suggested by Loberg and Welch.[10)]

$$^{125}I^+(^3P_2) + C_2H_6 \rightarrow (C_2H_6{}^{125}I)^+ \rightarrow H^{125}I + C_2H_5{}^+ \qquad (9)$$

Similarly in the presence of CH_3Cl, Reaction 10 would be important.

$$^{125}I^+(^3P_2) + CH_3Cl \rightarrow (CH_3Cl^{125}I)^+ \rightarrow {}^{125}ICl + CH_3{}^+ \qquad (10)$$

The addition of Br_2 remarkably reduced the yield. However, when Br_2 was added to the reaction system after the completion of the reactions (after more than 4 days from the preparation of the sample), the yield was also reduced to less than 1%. This is due to the fact that Br_2 undergoes exchange with ^{125}I in $CH_3{}^{125}I$ as follows:

$$Br_2 + CH_3{}^{125}I \rightarrow CH_3Br + {}^{125}IBr \qquad (11)$$

Comparison of the Results. The present results as well as previous ones are summarized in Table 5. A general trend exists in the reactivities of excited iodine. Hot yields show a remarkable dependence on the initial kinetic energies possessed by the recoil iodines, decreasing in the order $(n,\gamma) > (IT) \geq (EC)$. The maximum kinetic energies imparted to the recoils are 194 eV for ^{128}I and 177 eV for ^{139}I from the (n,γ) process[21)] and 15.6 eV for ^{125}I from the (EC) process.[13)] From these values and experimental findings, the kinetic energy for ^{130}I from the (IT) process is assumed to be *ca.* 20 eV when $CH_3{}^{130m}I$ is used as an iodine source.

In contrast, the thermal ionic yield was the highest for ^{125}I obtained from the (EC) process. It can be concluded that the population of the iodine ion in each excited state depends on the decay mode of precursors. We found that the population of $^{125}I^+(^1D_2)$ is slightly higher than that of $^{125}I^+$ in the ^3P states. This is in line with the results by Schleiffer and Certout[12] and by Loberg and Welch[10] in the presence of a macroscopic amount of I_2. However, Schroth and Adloff[6] and Schleiffer and Certout[12] reported lower yields for ^3P states than ours. This discrepancy may be due to the amount of I_2 in the reaction system. In the former cases, they examined the system with saturated vapor pressure of I_2. We see from the results by Loberg and Welch[10] that the presence of a macroscopic amount of I_2 would protect I^+ in the $^1D_2$ state.

As regards the reactant-isotope-effect between CH_4 and CD_4, the present results, together with those reported by Nicholas *et al.*[5] provide no positive evidence, indicating that the effect, if it exists at all, should be very small. In the reactions of ^{80}Br obtained from $^{79}Br(n,\gamma)^{80}Br$ process with methane the large reactivity-isotope-effect was observed in the hot yields.[18,22] However, it has been confirmed that the isotope effect is not present in the yield due to ionic processes.[23,24] In the present system, over 80% of $CH_3{}^{125}I$ is formed by the reaction of I^+ in the excited states. Thus, the expected isotope effect in hot reactions might have been overlooked because of large fluctuations in experimental conditions.

References

1) J. F. Hornig, G. Levey, and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).

2) G. Levey and J. H. Willard, *J. Chem. Phys.*, **25**, 904 (1956).

3) E. P. Rack and A. A. Gordus, *J. Chem. Phys.*, **34**, 1855 (1961).

4) E. P. Rack and A. A. Gordus, *J. Chem. Phys.*, **36**, 287 (1962).

5) J. B. Nicholas, M. Yoog, and E. P. Rack, *Radiochim. Acta*, **19**, 124 (1973).

6) F. Schroth and J. P. Adloff, *J. Chim. Phys.*, **61**, 1373 (1964).

7) V. M. Zaitsez, I. S. Kirin, V. A. Serova, and V. I. Tikhonov, *Soviet Radiochem.*, **14**, 900 (1972).

8) V. M. Zaitsev, V. A. Serova, and V. I. Tikhonov, *Soviet Radiochem.*, **15**, 768 (1973).

9) V. M. Zaitsev, V. A. Serova, and V. I. Tikhonov, *Radiochem. Radioanal. Lett.*, **16**, 231 (1974).

10) M. D. Loberg and M. J. Welch, *J. Am. Chem. Soc.*, **95**, 1073 (1973).

11) J. J. Schleiffer and G. Certout, *Radiochim. Acta.*, **20**, 59 (1973).

12) J. J. Schleiffer and G. Certout, *Radiochim. Acta.*, **20**, 66 (1973).

13) C. M. Lederer, J. M. Hollander, and I. Perlman, "Table of Isotopes," 6th ed., John Willy and Sons, Inc., New York.

14) W. E. Harris, "Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Vienna (1961), p. 229.

15) A. R. Kazanjian and W. F. Libby, *J. Chem. Phys.*, **42**, 2778 (1965).

16) L. D. Spicer and A. A. Gordus, "Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Vienna (1965), p. 185.

17) M. Saeki and E. Tachikawa, *Radiochim. Acta*, **20**, 27 (1973).

18) M. Saeki, K. Numakura, and E. Tachikawa, *Bull. Chem. Soc. Jpn.*, **45**, 1715 (1972).

19) M. Saeki and E. Tachikawa, *J. Nucl. Sci. Technol.*, in press.

20) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

21) J. H. E. Mattauch, W. Thiele, and A. H. Wapstra, *Nucl. Phys.*, **67**, 32 (1965).

22) E. Tachikawa and T. Kahara, *Bull. Chem. Soc. Jpn.*, **43**, 1293 (1970).

23) E. Tachikawa and K. Yanai, *Radiochim. Acta*, **17**, 138 (1972).

24) M. Saeki and E. Tachikawa, *Bull. Chem. Soc. Jpn.*, **46**, 839 (1973).