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## Effect of Inert-Gas Moderators on the ( $n, \gamma$ ) Activated Reaction of $I^{128}$ with $CH_4$ †

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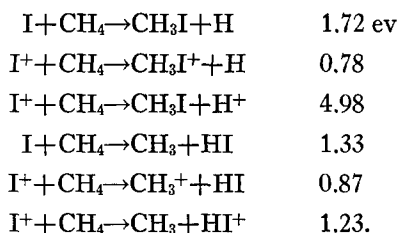
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In the presence of a large excess of gaseous methane,  $54.4 \pm 0.5\%$  of  $I^{128}$  formed by ( $n, \gamma$ ) activation was found to become stabilized in organic combination. The effects of inert-gas additives in moderating the reaction of  $I^{128}$  with  $CH_4$  were determined in an effort to ascertain the mechanism. The data, extrapolated to zero mole-fraction methane, indicate that xenon is capable of reducing the organic  $I^{128}$  to 11% whereas neon, argon, and krypton each reduce it to only about 36%. These data suggest that of the 54.4% organic  $I^{128}$ , about 18.4% forms as a result of hot  $I^{128}$  reactions, 11% as a result of excited iodine atoms or  $I^+$  ions in the  $^3P_2$ ,  $^3P_1$ , and/or  $^3P_0$  states, and 25% as a result of reactions of  $I^+(^1D_2)$  ions.

### INTRODUCTION

HORNIG, Levey, and Willard<sup>1</sup> determined that  $I^{128}$  produced by the  $I^{127}$  ( $n, \gamma$ )  $I^{128}$  process is able to react with gaseous methane to form  $CH_3I^{128}$ . Further investigations by Levey and Willard<sup>2</sup> indicated that molecules with ionization potentials lower than that of an iodine atom are more effective than inert gases in moderating the  $I^{128} + CH_4$  reaction. They interpreted these data as indicating that the positive charge<sup>3</sup> associated with at least 50% of the  $I^{128}$  atoms is an important factor in the reaction.

Single displacement and abstraction reactions of thermal iodine atoms or ions with methane are endothermic:



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

<sup>2</sup> G. Levey and J. E. Willard, *J. Chem. Phys.* **25**, 904 (1956).

<sup>3</sup> S. Wexler and H. Davies, *J. Chem. Phys.* **20**, 1688 (1952).

On considering the relative masses of the two colliding bodies, one can argue further that, to have available as internal energy of the activated complex the energies listed above, the iodine atom or ion must possess a minimum kinetic energy that is  $(128+16)/16=9$  times as great as the endothermicity of the reaction. This energy for reaction is provided to the  $I^{128}$  as a result of the neutron capture-gamma ray recoil. If the neutron binding energy (6.6 Mev)<sup>4</sup> is released as one gamma ray, an  $I^{128}$  atom would acquire 182 ev of recoil kinetic energy. There are available, however, data which indicate that the average number of gamma rays emitted as a result of neutron absorption of  $I^{127}$  is greater than one. The emission of low-energy gamma rays has been demonstrated.<sup>5</sup> In addition, there is indirect<sup>6</sup> and direct<sup>7</sup> experimental evidence that, following neutron absorption, approximately 1% of the  $I^{128}$  fail to dissociate from alkyl iodide molecules. Such failure to bond-rupture could result if there occurs partial cancellation of gamma-ray momenta as a result of multi-gamma emission. Because of the lack of experimental data regarding  $I^{128}$  neutron capture-gamma rays, it is impossible to determine precisely the energy spectrum resulting from the gamma recoil. However, if it is assumed that the energy distribution is similar to

<sup>4</sup> *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), p. 8-135.

<sup>5</sup> M. Reier and M. H. Shamos, *Phys. Rev.* **100**, 1302 (1955).

<sup>6</sup> A. A. Gordus and J. E. Willard, *J. Am. Chem. Soc.* **79**, 4609 (1957).

<sup>7</sup> A. A. Gordus and C. Hsiung, Paper No. 49, IAEA Symposium on the Chemical Effects of Nuclear Transformations, Prague, October, 1960.

TABLE I. Percent  $I^{128}$  (and  $I^{131}$ ) stabilized in organic combination in various gaseous mixtures.<sup>a</sup>

Additive	Pressure CH <sub>4</sub> -mm	Pressure additive-mm	Mole fraction additive <sup>b</sup>	Percent $I^{128}$ as organic <sup>c</sup>	Percent $I^{131}$ as organic <sup>d</sup>
Neon	594	76	0.113(11)	52.9	
	489	159	0.245(8)	53.1 52.2	
	308	128	0.294(24)	53.3 52.8	2.6 2.2
	362	231	0.390(45)	50.0 54.0	
	205	133	0.394(32)	50.1	
	205	129	0.386(32)	50.1	
Argon	400	189	0.321(27)	54.3 54.5	3.8 3.9
	295	235	0.443(31)	52.2 52.0	3.0 2.0
	109	410	0.765(59)	45.4 47.4	
	50	341	0.872(67)		1.0 1.5
Krypton	595	80	0.119(2)	53.8 53.5	
	483	106	0.180(3)	52.4	5.1
	320	120	0.273(3)	49.5 48.5	
	432	236	0.353(3)	50.5 51.8	6.2 7.3
	194	141	0.421(1)	45.6 45.0	
	143	412	0.742(4)	49.3 49.0	8.8 9.1
	43	456	0.914(3)	48.0	10.8
Xenon	615	40	0.061(2)	50.8 50.5	
	563	61	0.098(4)	48.3 47.3	2.3 3.3
	554	101	0.154(2)	45.2 46.5	
	489	179	0.268(2)	39.6 39.8	
	251	307	0.552(4)	31.6 29.4	7.7 8.0
	179	331	0.649(4)	30.5 29.2	
	72	447	0.865(5)	31.0 30.4	16.0 14.0
	60	454	0.883(5)	29.2 29.3	
	23	515	0.957(5)	24.1 24.5	

<sup>a</sup> All samples contained  $0.1 \pm 0.02$  mm  $I_2$  and  $0.5 \pm 0.3$  mm  $CH_3I$  and were irradiated for 7 sec.

<sup>b</sup> Calculated assuming additive pressures. Uncertainty in last figure or figures (given in parenthesis) is based on estimates of determining individual pressures.

<sup>c</sup> An uncertainty of  $\pm 0.5$  was associated with the positioning of the 25.0 min slope through the decay data.

<sup>d</sup> An uncertainty of  $\pm 1.5$  was associated with the decay data and possible pre-irradiation  $I_2$ - $CH_3I$  exchange.

that resulting in the  $Cl^{135} (n, \gamma) Cl^{136}$  process,<sup>8</sup> then the average recoil energy associated with the  $I^{128}$  would be approximately 100 ev; approximately 96% of the  $I^{128}$  would acquire more than 45 ev and 99+% more than 7.1 ev. Thus, it would be expected that most of the  $I^{128}$  atoms or ions are capable of forming  $CH_3I$  or  $HI$  via a hot reaction with  $CH_4$ .

The formation of  $CH_3I^{128}$  need not, however, be limited to the above reactions. It is also possible that a positively charged  $I^{128}$  react with  $CH_4$  via an ion-molecule mechanism. For example, the following reactions could occur<sup>9</sup>:



The above ion-molecule reaction does not require recoil kinetic energy.

Excited thermal  $I^+$  ions may also react with  $CH_4$ . For example,  $I^+$  in the  $^1D_2$  state possesses an excitation energy of 1.70 ev.

We have been interested in determining qualitatively the mechanism of the reaction of  $I^{128}$  with  $CH_4$ . To do this, we have investigated the manner in which the reaction to produce organic  $I^{128}$  is inhibited by varying amounts of inert-gas additives.

#### EXPERIMENTAL

**Reaction mixtures.** All reaction mixtures were prepared by vacuum-line techniques and sealed in thin quartz bulbets 3–7 ml in size.

Phillips Petroleum Company research-grade  $CH_4$  and Linde Air Products assayed-reagent inert gases were used.  $I_2$  was sublimed from a mixture of Baker reagent  $I_2$  and Merck reagent  $KI$ . Eastman Kodak white-label  $CH_3I$  was purified by concentrated  $H_2SO_4$  treatment followed by washing and distillation.

**Neutron irradiations.** The samples were irradiated for 7 sec in a pneumatic tube of the University of Michigan megawatt pool reactor at a thermal neutron flux of about  $1.4 \times 10^{12}$  n/cm<sup>2</sup>-sec and a background radiation dosage of about 8000 r/min. As discussed below, corrections for radiation-induced reactions were made.

**Extraction procedure.** In all experiments, the irradiated bulbet was broken in a separatory funnel containing a two-phase mixture of  $CHCl_3 + I_2$  and approximately 0.5M aqueous  $Na_2SO_3$ . The organic fraction was separated from the inorganic and each fraction was counted using an Amperex Geiger tube. The data were then corrected for coincidence loss, decay, and relative counting efficiencies.

#### RESULTS

**Summary of data.** Summarized in Table I are the observed extents of production of organically bound

<sup>8</sup> C. Hsiung, H. Hsiung, and A. A. Gordus, *J. Chem. Phys.* **34**, 535 (1961).

<sup>9</sup> A. Henglein and G. A. Muccini, *Z. Naturforsch.* **15a**, 584 (1960).

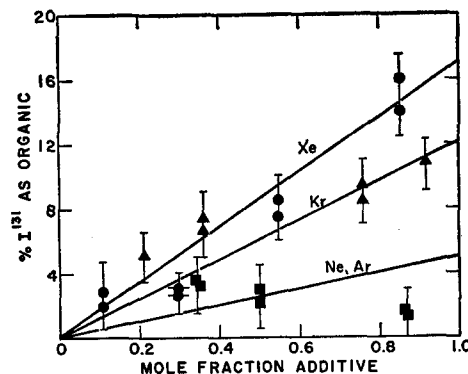


FIG. 1. Reactor-radiation induced pickup of  $I^{131}$  in  $CH_4$ -inert gas mixtures containing  $CH_3I$  and  $I_2$ - $^{131}$ . Xenon, ●; krypton, ▲; argon, ■; neon, -●-.

$I^{128}$  for various methane-inert gas reaction systems. These mixtures contained four substances: methane, inert gas, 0.5 mm  $CH_3I$ , and 0.1 mm  $I_2$  scavenger.

In order to interpret properly the relative effects of the additives, it is necessary to correct these data of Table I for (a) the 1.1% failure to bond-rupture of  $CH_3I^+$  and (b) any radiation-induced reactions.

**Radiation induced reactions.** Mixtures containing  $I_2$  tagged with  $I^{131}$  were also irradiated; the percent  $I^{131}$  appearing in organic combination is listed in Table I. These data are also depicted in Fig. 1. Negligible  $I^{131}$  pickup was found in  $I_2$ - $CH_4$  systems which did not contain an inert-gas additive.

In order to avoid any possible thermal or photochemical exchange reaction between the  $I_2$ - $^{131}$  and  $CH_3I$ , all samples were prepared in a minimum of light and, if neutron irradiation was not immediately feasible, stored at 4°C in the dark. This technique resulted in a pre-irradiation  $I^{131}$  organic pickup of only 0–1.5%.

Comparable total pressures ( $540 \pm 60$  mm) existed for each sample of Table I. In addition, all samples were (1) irradiated in the same position in the reactor and thus were subjected to the same dose rate; (2) irradiated for the same period of time and thus were subjected to the same total dose; and (3) contained comparable amounts of  $I_2$ .

The average energy of the gamma rays in a nuclear reactor is of the order of 2 Mev; therefore, the interaction of such gamma rays with matter proceeds mainly via Compton scattering. To a first approximation the primary interaction probability is related directly to the first power of the atomic number of the material. Levey and Willard<sup>2</sup> found that the amount of organic iodide formed in the  $I_2$ - $CH_4$  system by radiation-induced reactions increased with the pressure of the inert gas and with the number of electrons per atom of inert gas. It would be expected that the data of Fig. 1 should also indicate a similar dependence. The best visual straight lines were drawn through these data and at unit mole-fraction of inert gas (which corresponds to  $540 \pm 60$  mm) extrapolate to about 17%, 12%, and 5%

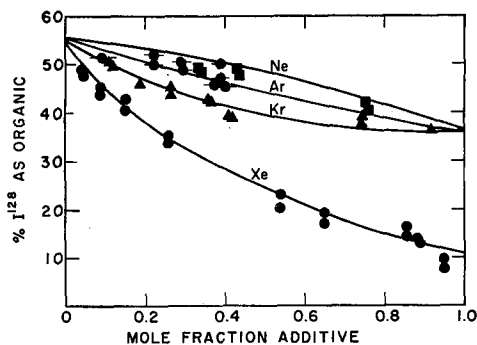


FIG. 2. Percent  $I^{128}$  formed as organic activity in  $CH_4$ -inert gas mixtures containing  $CH_3I$  and  $I_2$ . Moderator symbols are listed in caption for Fig. 1. The solid curves are calculated.

for Xe, Kr, and Ar-Ne, respectively. These values are in approximately the same ratio as the number of electrons per atom of inert gas.

If a sample contained  $I^{131}$ , the observed percent organic  $I^{131}$  was subtracted from the organic  $I^{128}$  yield. Since the remaining samples were similar in terms of total pressure and irradiation conditions, we used the data of Fig. 1 to determine the correction for radiation-induced reactions in these systems. To do this, we subtracted a quantity equal to the product of the mole-fraction of the inert gas and the extrapolated maximum extent of  $I^{131}$  pickup as determined in Fig. 1.

These  $I^{128}$  data of Table I, corrected for failure to bond-rupture and radiation-induced reactions, are depicted in Fig. 2.

*Maximum extent of reaction.* Extrapolations of the various data<sup>10</sup> to zero mole fraction of additive indicate that  $54.4 \pm 0.5\%$  of the  $I^{128}$  reacts with methane to become stabilized in organic combination.

On the basis of previous gas chromatographic analyses,<sup>6</sup> it is known that  $CH_3I^{128}$  is the major organic product. The only other observable organic product was  $CH_2I^{128}$ , present to the extent of only about 1%.

#### DISCUSSION

If the  $CH_3I^{128}$  is formed only as a result of processes requiring excess kinetic energy, then a large excess of an inert gas should be capable of suppressing completely the formation of  $CH_3I^{128}$ . As seen in Fig. 2, the extrapolated data indicate that the inert gases only partially suppress the reaction. Apparently, then, only a fraction of the  $CH_3I^{128}$  is formed via hot processes which occur as the result of kinetic energy of the  $I^{128}$  atoms or ions. It should be noted that xenon reduces the  $CH_3I^{128}$  yield to  $11 \pm 2\%$  whereas the other inert gases reduce this yield to only about  $36 \pm 2\%$ . The assumption that the reduction to 36% is a result mainly of excess kinetic-energy reactions is justified by the mathematical analysis given in the next section.

<sup>10</sup> These data include those presented in this paper as well as additional unpublished data concerned with the moderation of the  $I^{128} + CH_4$  reaction by molecular additives.

The fact that xenon reduces the extent of formation of  $CH_3I^{128}$  by an additional  $25 \pm 3\%$  must be due to a unique ability of xenon to neutralize or quench excited  $I^{128}$  ions or atoms. Inert gases, however, are not effective quenching agents.<sup>11</sup> Therefore, this additional inhibition by xenon must be due to a charge-transfer process. For xenon alone to reduce the extent of reaction by charge transfer requires that the energy defect of the reaction approach zero more closely than that for charge transfer with the other inert gases.

The first four excited states of  $I^+$  (ionization potential, 10.454 ev) and their excitation energies are as follows<sup>12</sup>: ( $^3P_0$ ) 0.800, ( $^3P_1$ ) 0.879, ( $^1D_2$ ) 1.702, ( $^1S_2$ ) 4.044 ev. The ionization potential of  $CH_4$  is 12.99 ev.<sup>13</sup> It is unlikely that excited states higher than the  $^1D_2$  will exist in the methane environment since charge transfer between  $CH_4$  and  $I^+$  in the  $^1S_2$  or higher states is exothermic. Such processes are very probable since the excess energy (energy defect) is assimilated by the various internal degrees of freedom of the methane ion. However, for charge transfer to take place between methane and  $I^+$  ions in ( $^1D_2$ ) or lower energy states requires much greater relative energies of the reacting species than that supplied by the ( $n, \gamma$ ) activation.<sup>14</sup>

The ionization potential of xenon is 12.127 ev.<sup>12</sup> Thus, the process  $I^+(^1D_2) + Xe \rightarrow I + Xe^+$  is exothermic by 0.029 ev. For this near-resonance charge-transfer process, the cross-section will be maximum for relative energies of about 2 ev and will slowly decrease for energies greater than 2 ev.<sup>14</sup> The smallest energy defect for the possible charge-transfer processes involving the other inert gases is 1.840 ev endothermic for the  $I^+(^1D_2) + Kr$  reaction. Hence, these processes involving Kr, Ar, or Ne charge-transfer with  $I^+$  ions in energy states of  $^1D_2$  or less have an extremely small probability of occurrence.

It is reasonable to expect the excited iodine ions to react with methane prior to becoming deactivated by fluorescence. The iodine ions would have undergone of the order of 1000 collisions in the  $10^{-8}$ – $10^{-7}$  sec associated with fluorescent deactivation. Only in systems containing a large excess of inert gas would there be a possibility of fluorescent deactivation. This could be the reason that the last xenon data of Fig. 2 are low.

#### KINETIC-ENERGY MODERATION

*Qualitative.* If billiard-ball collisions are assumed to occur, then the average kinetic-energy transfer per collision would depend on the atomic weight of the moderator. The most effective inert gas would be xenon and the efficiency would decrease in the order: Kr, Ar, Ne. To interpret Fig. 2, where the data are

<sup>11</sup> K. J. Laidler, *The Chemical Kinetics of Excited States* (Oxford University Press, New York, 1955), p. 103.

<sup>12</sup> C. E. Moore, Natl. Bur. Standards Circ. No. 467, 108 (1958).

<sup>13</sup> K. Watanabe, J. Chem. Phys. 26, 542 (1957).

<sup>14</sup> E. F. Gurnee and J. L. Magee, J. Chem. Phys. 26, 1237 (1957).

presented as a function of the mole fraction of the inert gas, it is also necessary to consider the gas-kinetic cross sections. Again, the order would be as stated above. Thus, qualitatively, the observed inert-gas moderation takes place in a manner characteristic of kinetic-energy removal.

**Kinetic theory.** Estrup and Wolfgang<sup>15</sup> have developed a kinetic theory of hot-atom reactions and have applied it successfully to the inert-gas moderation of the reaction of gaseous  $CH_4$  with tritium produced by  $He^3(n, p)H^3$  activation. Their theory involves three assumptions: (1) the collisions are elastic, (2) the minimum energy required for reaction is large compared with thermal energies; and (3) the energies of the hot atoms form a statistical distribution.

We can assume that the collisions between the inert gases and the  $I^{128}$  ions or atoms are elastic. Regarding the second assumption, we have stated earlier that for ground-state  $I^{128}$  ions or atoms to react with  $CH_4$  requires that the  $I^{128}$  possess at least 7.1 eV of kinetic energy. We must also assume that the  $I^{128}$  atoms or ions are formed with energies which are distributed statistically.

Since the neutron capture-gamma ray cascade spectrum for the  $I^{127}(n, \gamma)I^{128}$  process is not known, it is not possible to calculate the recoil-energy distribution. However, as discussed above, a distribution of energies does occur. This distribution is probably similar to that resulting in the  $Br^{79}(n, \gamma)Br^{80}$  activation.<sup>16</sup> It has been shown<sup>17</sup> that moderation of the reaction of  $Br^{80}+CH_4$  can be described in terms of the Estrup-Wolfgang theory. Thus, it may be assumed that there results an approximate statistical distribution of  $I^{128}$  energies.

It is important to emphasize that attempts to fit the data of Fig. 2 directly to this kinetic theory were unsuccessful. If, however, we assume that the maximum

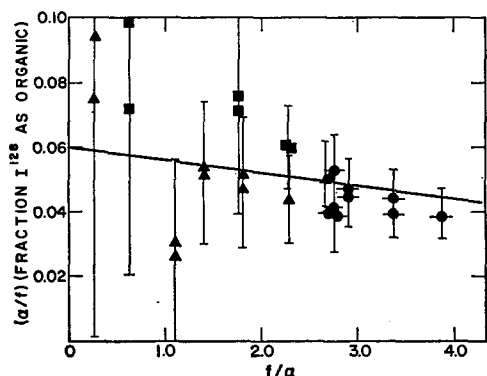


FIG. 3. Plot corresponding to Eq. (15) of reference 15. Moderator symbols are listed in caption for Fig. 1.

<sup>15</sup> P. J. Estrup and R. Wolfgang, *J. Am. Chem. Soc.* **82**, 2665 (1960).

<sup>16</sup> A. A. Gordus (unpublished data).

<sup>17</sup> E. P. Rack and A. A. Gordus, *J. Phys. Chem.* (to be published).

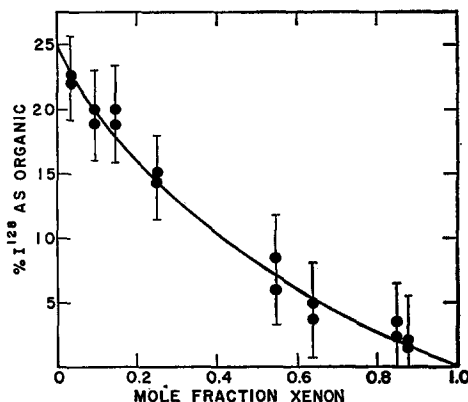


FIG. 4. Effect of xenon in moderating the reaction  $I^+(^1D_2) + CH_4 \rightarrow CH_3I^+ + H$ . The solid curve is calculated.

inert-gas kinetic-energy moderation is  $54.4 - 36 = 18.4\%$  we then find that the theory serves to describe the observed effects.

Using the notation of Estrup and Wolfgang, we have calculated  $\alpha$  values (which are concerned with the average energy loss per collision) and  $f$  values (which are related to the probability of collision between an iodine and an inert gas and thus include the mole-fraction as well as the relative diameters<sup>18</sup> of the colliding species).

**Neon, argon, krypton.** Thirty-six percent was subtracted from the individual values for the Ne, Ar, and Kr samples. For essentially pure methane,  $f/\alpha = 4.29$ ; thus,  $(\alpha/f) \cdot (\text{fraction of } I^{128} \text{ as organic}) = 0.0428$ . Figure 3 is a plot of the experimental data corresponding to Eq. 15 of reference 15:  $(\alpha/f) \cdot (\text{fraction of the activity in a given form}) = I - (f/\alpha)K$ . A straight line representation indicates agreement with theory. Equally important, all points, regardless of moderator, should fall on the same straight line. The best visual straight line drawn through the data and ending at the point (4.29, 0.0428) has a slope  $-K = -0.004 \pm 0.003$  and an intercept  $I = 0.06 \pm 0.01$ . It is interesting to note that, within the limits of uncertainty, these values correspond to those found for the  $Br^{80}+CH_4$  reaction.<sup>17</sup> The solid curves of Fig. 2 for Ne, Ar, and Kr were calculated using these values of  $K$  and  $I$ .

**Xenon.** As stated earlier, the xenon data are not described by the kinetic theory. A lack of agreement still exists even after subtracting 11% from each experimental result. It was suggested in the previous section that xenon could be a more effective moderator since it could easily undergo charge transfer with  $I^+(^1D_2)$ . To determine the inhibition via the charge-transfer process, we subtracted from the original data: (1) the 1.1%  $CH_3I$  failure to bond rupture; (2) the

<sup>18</sup> The diameters used<sup>19</sup> were: I-4.8, Xe-4.9, Kr-4.3, Ar-3.6, Ne-2.6, and  $CH_4$ -4.2 Å.

<sup>19</sup> S. Chapman and T. J. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, New York, 1953), p. 229.

radiation-induced production of  $\text{CH}_3\text{I}^{128}$ ; (3) the 11% organic  $\text{I}^{128}$  which is not effected by xenon; and (4) the expected kinetic-energy moderation by xenon. This last factor varied from zero to 18.4% and was calculated in terms of Eq. 15 of reference 15 using the slope and intercept determined from Fig. 3 above. Depicted in Fig. 4 is the percent organic  $\text{I}^{128}$  remaining after correcting for these four effects.

Let us assume that we may consider the effects separately and that this remaining extent of reaction of  $\text{I}^{128}$  with methane to produce organically bound  $\text{I}^{128}$ ,  $R$ , depends on the probability  $P$  that the  $\text{I}^{128}$  "collides" with  $\text{CH}_4$ . Thus,  $R=25P$ . The probability will depend on (1) the mole fraction of methane,  $(1-N)$ , where  $N$  is the mole fraction of additive; and (2) the relative cross sections  $C$  for the two types of interactions;  $C=\sigma[\text{I}^+(^1D_2)+\text{Xe charge exchange}]/\sigma[\text{I}^+(^1D_2)+\text{CH}_4 \text{ to yield } \text{CH}_3\text{I}^{128}]$ . Using these definitions,  $C=[(25-R)(1-N)]/RN$ .

The value of  $C$  calculated from the data of Fig. 4 is  $2.2\pm 0.6$ . Considering the various subtractions and uncertainties, it is somewhat fortuitous that the calculated  $C$  curves are in reasonable agreement. The solid curve of Fig. 4 was calculated using this value of  $C$ .

#### REACTION PROCESSES

On the basis of the previous discussions, we conclude that of the  $54.4\pm 0.5\%$   $\text{I}^{128}$  found as organic:

$18.4\pm 2\%$  is formed via a hot reaction requiring kinetic energy. The experimental evidence, however, is insufficient to conclude whether the hot  $\text{I}^{128}$  species is an ion or an atom.

$25\pm 3\%$  is formed as a result of the  $\text{I}^+(^1D_2)+\text{CH}_4$  reaction. Considering the energy requirements, if the reaction is a simple hydrogen displacement, then the reaction must be  $\text{I}^+(^1D_2)+\text{CH}_4\rightarrow\text{CH}_3\text{I}^++\text{H}$ .

$11\pm 2\%$  is formed as a result of the reaction of  $\text{I}^{128}$  ions (or highly excited atoms). Either  $^3P_2$ ,  $^3P_1$ , or  $^3P_0$   $\text{I}^+$  ions are involved since, as stated above, ions in energy states greater than the  $^1D_2$  would not exist in the methane environment. If the ionic reaction taking place involves hydrogen displacement, then, considering the energy available, the reaction must also be  $\text{I}^++\text{CH}_4\rightarrow\text{CH}_3\text{I}^++\text{H}$ .

The manner in which the  $\text{CH}_3\text{I}^+$  gains an electron is not known. It is difficult to accept electron capture as the process. The 9.54-ev exothermicity<sup>13</sup> would most probably be dissipated partially in the form of the internal energy of the molecule and thus probably result in C—I bond rupture.<sup>20</sup> If, instead, C—H bond rupture occurred, then, because of the presence of  $\text{I}_2$  in the reaction system,  $\text{CH}_2\text{I}_2$  should be a major product. Gas chromatographic analysis<sup>9</sup> indicated that only a small amount of  $\text{CH}_2\text{I}_2$  was formed. However, because of the presence of  $\text{CH}_3\text{I}$  and  $\text{I}_2$  in the reaction mixture, neutralization of the  $\text{CH}_3\text{I}^+$  probably takes place via charge transfer.

#### FURTHER STUDIES

We are also investigating the effects of molecular additives on the moderation of the  $\text{I}^{128}+\text{CH}_4$  reaction. Preliminary evidence indicates that, in addition to kinetic-energy moderation and charge neutralization, the molecular additives may also deactivate the  $\text{I}^{128}$  via what are probably ion-molecule reactions.

#### ACKNOWLEDGMENT

The authors appreciate the assistance of the staff of the Michigan Phoenix Reactor and wish to thank Professor Reed A. Howald for helpful discussions.

<sup>20</sup> (a) Reference 11, p. 57; (b) J. L. Magee and M. Burton, J. Am. Chem. Soc. **72**, 1965 (1950).