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# Reactions of Methane with Iodine Activated by Radiative Neutron Capture. II

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Further experiments have been conducted to clarify the mechanism of the unique reaction whereby I128 freshly formed by the  $I^{127}(n,\gamma)I^{123}$  process is able to replace hydrogen in methane  $(I^{123}+CH_4\rightarrow CH_3I+H)$ . They show that the yield of CH3I228 is decreased by the presence of the inert gases He, A, and Xe but not to the extent which would be the case if the activation energy for the reaction were supplied solely by kinetic energy of the I<sup>128</sup>. I<sub>2</sub>, CH<sub>3</sub>I, C<sub>2</sub>H<sub>5</sub>I, C<sub>3</sub>H<sub>7</sub>I and NO, which have lower ionization potentials than that of the I atom are all more effective than the inert gases in reducing the yield. The organic yield of I<sup>128</sup> is higher when alkyl iodides are used as the source of iodine than when  $I_2$  is used. The ability of the freshly formed  $I^{128}$  to react with  $C_2H_6$  or  $C_6H_6$  is much less than with  $CH_4$ . Reactions of  $I_2$  with  $CH_4$  sensitized by argon and xenon occur when several hundred mm of the inert gas is present during exposures to 10<sup>5</sup>r or more of gamma radiation.

#### INTRODUCTION

**HE I**<sup>128</sup> atoms produced by the  $I^{127}(n,\gamma)I^{128}$  process in gaseous methane are able to displace hydrogen from methane forming methyl iodide  $(I+CH_4\rightarrow$  $CH_3I+H)^i$  whereas iodine atoms produced photochemically do not react with methane. This unique reaction must be due to either the high kinetic energy of the recoiling iodine atom or the positive charge which it acquires as a result of internal conversion of some of the energy available from the neutron capture process, or both.2

The present research has been designed to further elucidate the mechanism of this type of reaction. Yields have been determined in the presence of pressures of inert gases sufficient to remove the excess kinetic energy of the I<sup>128</sup> atoms before they undergo any collisions with methane, and in the presence of gases with lower ionization potentials than iodine atoms. In other experiments alkyl iodides have been substituted for elemental iodine as the source of recoil atoms, and ethane, benzene and methyl iodide have been tested as the organic reactant in place of methane.

#### **EXPERIMENTAL**

Phillips Petroleum Company "Research Grade" methane and ethane were used. This type of methane has been shown to be free of anything that will react with  $I_2$  even in the presence of intense visible light.<sup>1</sup> Alkyl iodides were purified by the method described earlier.<sup>3</sup> The benzene used was Merck reagent grade. The argon ("99.6%") and helium ("N.S.P. 98.2%") were obtained from the Ohio Chemical and Manufacturing Company.

The gaseous reaction mixtures were irradiated in fused silica flasks ranging in volume from 27 to 370 ml.

These were filled on a vacuum manifold. All irradiations were made in the Argonne National Laboratory CP3' reactor at a flux of  $10^{11}$  neutrons cm<sup>-2</sup> sec<sup>-1</sup> and a gamma ray intensity of about  $3.3 \times 10^4 r/hr^4$  for 30 min., except where otherwise noted below. The metered concentrations of iodine and alkyl iodides were checked by comparison of the amount of I<sup>128</sup> activity induced in the reaction flasks with that in flasks containing  $I_2^{131}$ of known specific activity which were irradiated in the same pile position. Analysis of samples following irradiation was carried out in the manner described previously.1

#### **RESULTS AND DISCUSSION**

#### Effect of $CH_4/I_2$ , and $CH_4/RI$ Ratios

In the previous<sup>1</sup> work on the reaction of newly formed I<sup>128</sup> with CH<sub>4</sub> all the reaction mixtures irradiated contained a mole ratio of  $CH_4/I_2$  of about 2000 (400 mm

TABLE I. Effect of CH<sub>4</sub>/I<sub>2</sub> ratio on fraction of I<sup>128</sup> from the  $I^{127}(n,\gamma)I^{128}$  process which enters organic combination in mixtures of CH<sub>4</sub> and I<sub>2</sub>.

Values of Pl <sub>2</sub>	I <sup>128</sup> in orga combination Individual exps	anic n, % Aver-	I <sup>131</sup> in organic combina- tion, % <sup>a</sup>
coleq, iiiii	caps.		/0
0.2	7, 10	9	
0.016	17	17	0
0.009, 0.2	23, 30, 29		0
,	32, 24	28	
0.018. 0.2	44, 42, 42	44	0
	47		
0.2	39.44	42	
0.018	57.53	55	0
0.010	47	47	
	56	56	5
0.018 0.2	40 45 52	46	ž
0.010, 0.2	56	10	2
0.006	10	19	4
0.000	40	40	+
	Values of P12 tested, mm 0.2 0.016 0.009, 0.2 0.018, 0.2 0.2 0.018 0.018, 0.2 0.018, 0.2 0.006	$\begin{array}{c c} & & & & & & \\ \hline & & & & & & \\ \hline Values of P_{1_2} & & & & \\ \hline & & & & & \\ \hline & & & & & \\ \hline 0.2 & & & & \\ 0.016 & & & & \\ 0.009, 0.2 & & & & \\ 32, 24 & & & \\ 0.018, 0.2 & & & & \\ 0.2 & & & & & \\ 32, 24 & & & \\ 0.018, 0.2 & & & & \\ 0.018 & & & & \\ 57, 53 & & & & \\ 47 & & & & \\ 0.018 & & & & \\ 57, 53 & & & \\ 47 & & & & \\ 0.018 & & & & \\ 56 & & & & \\ 0.018, 0.2 & & & \\ 0.018, 0.2 & & & \\ 0.018, 0.2 & & & \\ 0.006 & & & \\ 48 & & \\ \hline \end{array}$	$\begin{array}{c c} & I^{128} \text{ in organic} \\ \text{combination, \%} \\ \text{Individual} & \text{Aver-exps.} \\ \text{exps.} & \text{age} \\ \hline 0.2 & 7, 10 & 9 \\ 0.016 & 17 & 17 \\ 0.009, 0.2 & 23, 30, 29 \\ & 32, 24 & 28 \\ 0.018, 0.2 & 44, 42, 42 & 44 \\ 0.2 & 39, 44 & 42 \\ 0.018 & 57, 53 & 55 \\ & 47 & 47 \\ & 56 & 56 \\ 0.018, 0.2 & 40, 45, 52 & 46 \\ & 56 \\ 0.006 & 48 & 48 \\ \hline \end{array}$

 $<sup>\</sup>bullet$  In those cases where values are given in this column the I\_2 used was tagged with [Iai (8-day) and the percentage of this in organic combination was determined following the irradiation. It could be distinguished readily from the I128 (25 min).

<sup>4</sup> From data kindly furnished by the Argonne National Laboratory.

<sup>\*</sup> Department of Chemistry, Berea College, Berea, Kentucky. <sup>1</sup> J. F. Hornig, G. Levey, and J. E. Willard, J. Chem. Phys. 20, 1556 (1952).

<sup>&</sup>lt;sup>2</sup> For a review of investigations of chemical effects of nuclear transformations see: J. E. Willard, Ann. Rev. Nucl. Sci. III, 193 (1953); Ann. Rev. Phys. Chem. VI, 141 (1955).
<sup>3</sup> G. Levey and J. E. Willard, J. Am. Chem. Soc. 74, 6161 (1952).

 $CH_4$  and 0.2 mm of  $I_2$ ). They gave yields of organically bound  $I^{128}$  ranging, with one exception, from 43 to 55%with an average of about 50%. The data of Table I, taken from the present work, show that values in this range are also obtained with higher  $CH_4/I_2$  ratios but that the organic yields decrease with decreasing  $CH_4/I_2$ ratios below about 500. The pressures of CH<sub>4</sub> and I<sub>2</sub> may be varied by ten fold or more without affecting the yields if the  $CH_4/I_2$  ratio is maintained constant.

It would not be expected that the form of chemical combination of the  $I^{127}$  would influence the fate of  $I^{128}$ produced from it by the  $I^{127}(n,\gamma)I^{128}$  process since the I<sup>128</sup> should easily break its parent bond in every case (except possibly HI). This expectation is borne out qualitatively by the data of Table II which show that mixtures of CH4 with CH3I, C2H5I or C3H7I irradiated with neutrons give organic yields similar to those for  $I_2$  in CH<sub>4</sub>. As in the case of the latter, the yields increase as the ratio of CH<sub>4</sub> to iodine-containing molecule increases, reaching a limiting value at a ratio between 100 and 800. This limiting value is about 65% as compared to the 50% when  $I_2$  is the source of iodine. This difference may result from one or more of the following causes: (1)  $I_2$  molecules may be more strongly adsorbed on the walls than RI molecules and hence a greater fraction of the recoil I atoms may lose their energy to the walls; (2) The charge<sup>5</sup> resulting from internal conversion may spread over I2 and RI molecules to a different extent before bond rupture is complete so that the reactive I atoms carry different charges; (3) an I atom which recoils directly toward its parent partner loses all of its energy if the partner is an I atom but not if it is an alkyl radical; (4) in the absence of macro amounts of molecular  $I_2$  a detectable fraction of the tracer amounts of inorganic radioiodine formed as a result the  $(n,\gamma)$  process may be returned to organic combination by reaction with organic radicals produced by radiation.

Dilute  $C_2H_5I$  in liquid hydrocarbons, like the gaseous samples of Table II, shows a higher organic yield than  $I_2$  at the same concentration.<sup>6</sup>

## Effect of Added He, A, and Xe

If the reaction of freshly formed  $I^{128}$  with  $CH_4$  were due to the kinetic energy of the I128, one would expect that the percentage of organically bound I128 formed when  $CH_4 - I_2$  or  $CH_4 - RI$  mixtures are irradiated with neutrons would decrease with increasing pressures of added inert gas because the latter would moderate the recoil atoms and thus decrease the number of high energy collisions with CH4. We have carried out experiments with He, A and Xe using both  $I_2$  and  $C_2H_5I$ as sources of I<sup>128</sup>. Some of the results are given in Table III. The last two columns show the probability that an

TABLE II. Effect of CH<sub>4</sub>/RI ratio on fraction of I<sup>128</sup> from the  $\mathrm{I}^{127}(n,\gamma)\mathrm{I}^{128}$  process which enters organic combination in mixtures of CH4 and alkyl iodides.

	I <sup>128</sup> in organic combina	${ m I}^{128}$ in organic combination, $\%$				
$P_{\rm CH_4}/P_{\rm RI}$	Individual exps. <sup>a</sup>	Average				
1	$12_{100}^{m}$	12				
7	$20_{50}^{m}, 20_{60}^{m}$	20				
20	$21_{35}^{m}$ , $27_{35}^{m}$ , $26_{30}^{e}$	24				
100	$42_{0,13}^{m}$ , $43_{0,11}^{m}$ , $51_{5,1}^{e}$					
	$50_{54^e}$ , $51_{73^e}$ , $50_{43^e}$	48				
800	$64_{0.21}^{m}$ , $63_{0.15}^{m}$ , $60_{0.68}^{m}$	62				
1500	$68_{0.21}^{m}$ , $73_{0.16}^{m}$ , $66_{0.6}^{p}$					
	$68_{0.6}^{p}, 63_{0.4}^{e}$	68				
2000	630.05°, 720.05°	67				
3000ь	$60_{0}  {}_{03}^{e},  62_{0}  {}_{03}^{e}$	61				
5000	$65_{0,14}^{m}, 65_{0,17}^{e}$	65				
7500	$64_{0.09}^{m}$ , $64_{0.09}^{e}$ , $65_{0.11}^{e}$	64				
11 000	$69_{0.032}^{m}, 68_{0.032}^{m}, 65_{0.07}^{m}$	-				
	$67_{0} \text{ or}^{p}, 70_{0} \text{ or}^{p}$	68				

\* The superscripts m, e, and p indicate the alkyl iodide used, i.e., methyl, ethyl and *n*-propyl, respectively; the numerical subscripts give the pressure of the alkyl iodide in mm of Hg. b Both of the tests at this ratio were made with 0.5 mm of air added to the reaction mixture.

I<sup>128</sup> atom did not strike a CH<sub>4</sub> molecule in undergoing the average number of collisions required to reduce the energy to 20 ev or 2 ev, assuming that all recoil atoms started with 268 ev (the recoil energy from an 8 Mev ray). The value of 20 ev is the approximate energy the atoms must have in a head-on collision with CH<sub>4</sub> if 2 ev or *ca* 50 kcal/mole is to be available for internal energy, i.e. for chemical reaction.1 Fifty kcal/mole is the approximate endothermicity of the reaction  $I+CH_4 \rightarrow$  $CH_{3}I+H$ . The fraction of the kinetic energy available for internal energy is  $M_{\rm CH_4}/(M_{\rm I}+M_{\rm CH_4})$ . The average decrease per collision in the logarithm of the I atom energy is given by

$$\xi = \ln E/E_0 = 1 + [r/(1-r)] \ln r$$

where  $r = [(M_1 - M_2)/(M_1 + M_2)]^2$  and  $M_1$  and  $M_2$  are the masses of the colliding partners.7 The average number of collisions, n, needed to reduce the energy of the I<sup>128</sup> atoms from 268 ev to 2 ev is,  $n = \lceil \ln(268/2) \rceil / \xi$ . For collisions with He, n=80; with A, 9.6; with Xe, 4.9. The fraction of iodine atoms which undergo the specified number of collisions with inert gas atoms without encountering a CH<sub>4</sub> molecule is  $p^n$ , where p is the probability that a given single collision will be with the inert gas, considering that all of the molecules involved have equal collision cross sections.

It may be seen from Table III that the probabilities of the I128 atoms being reduced below 20 ev, or even 2 ev before encountering a CH<sub>4</sub> molecule are in general greater than the fractional reductions in the organic yields below the average upper limits of about 50% for  $I_2$  and 65% for alkyl iodides, suggesting that there is a mechanism for the reaction which is not subject to the 20 ev energy limitation. It should be noted that the values in the last two columns of Table III are mini-

<sup>7</sup> J. Kaplan, Nuclear Physics (Addison-Wesley Publishing Company, 1955), pp. 450-456.

<sup>&</sup>lt;sup>5</sup> S. Wexler and H. Davies, J. Chem. Phys. **20**, 1688 (1952). <sup>6</sup> (a) S. Goldhaber and J. E. Willard, J. Am. Chem. Soc. **74**, 318 (1952); (b) S. Aditya and J. E. Willard (unpublished).

Added gas	Added gas, mm	Ratio of additive to CH4	Source of I, mm, ×10 <sup>3</sup>	I <sup>131</sup> in organic combination, %	I <sup>128</sup> in organic combination, %	Cooling Pr 20 ev	robabilityª 2 ev
He	700	100	I <sub>2</sub> , 0.95	5	24	0.65	0.45
	700	100	0.99	2	33	0.65	0.45
	600	100	$C_2H_5$ , 1.7		55	0.65	0.45
	600	100	1.5		54	0.65	0.45
	500	500	0.35		50	0.92	0.85
	500	500	0.22		47	0.92	0.85
Α	700	16	$I_2, 8.3$	1	48	0.73	0.56
	700	16	7.8	0	38	0.73	0.56
	93	19	$C_2H_5I$ , 0.43		32	0.77	0.61
	93	19	0.37		30	0.77	0.61
	425	85	0.29		8 <sup>b</sup>	0.94	0.89
	425	85	0.40		4ь	0.94	0.89
Xe	200	10	$I_2, 6.5$	4	29	0.78	0.63
	200	10	8.7	13	26	0.78	0.63
	200	2	31	8	35	0.35	0.14
	200	2	18	6	31	0.35	0.14
	40	0.4	53	3	39	0.04	0
	40	0.4	67	0	36	0.04	0
	100	10	$C_{2}H_{5}I, 4.8$		58	0.78	0.63
	100	10	3.1		33	0.78	0.63
NO	110	1.1	$C_{2}H_{5}I, 31$		35	0	0
	110	1.1	40		30	0	0
	6	0.01	30		58	0	0
	6	0.01	35		59	0	0

TABLE III. Effect of inert gases and NO on the organic yield of I128 in methane.

Probability that an I<sup>128</sup> atom starting with 268 ev of kinetic energy did not strike a CH<sub>4</sub> molecule in undergoing the average number of collisions required to reduce the energy to that indicated. b\_These values are much lower than those for the He system with similar probability of cooling but as far as is known, they are valid.

mum probabilities because each I<sup>128</sup> atom has been assumed to have recoil energy from the emission of a single 8 Mev/ray rather than several weaker gamma rays. Iodine atoms which have undergone the average number of collisions required to reduce the energy from 268 to 20 ev or 2 ev will, of course, have a spectrum of energies ranging above and below this specified value. In view of our lack of knowledge of the initial energy of the I<sup>128</sup> atoms, and our ignorance of the average number of collisions of I<sup>128</sup>+CH<sub>4</sub> required for reaction, as well as of favored energy ranges for reaction, it seems of no significance to calculate this distribution.

## **Reactions Sensitized by Inert Gases**

Experiments with still higher ratios of Xe to CH4 gave erratic and usually unexpectedly high values of the organic yield of I128. This must have been the result of reactions of CH<sub>4</sub> with I<sub>2</sub> sensitized by the inert gas as a result of the energy which it absorbed from the gamma radiation accompanying the neutron exposure. The percentage of iodine entering organic combination by such processes in the  $CH_4-I_2$  mixtures would be expected to increase with the pressure of the inert gas and with the number of electrons per molecule of the inert gas. Iodine tagged with I<sup>131</sup> was used to show that such reaction was negligible relative to the  $(n,\gamma)$ activated reaction in the  $CH_4-I_2$  experiments of Table III. When higher pressures of Xe were used, the fraction of the I<sup>131</sup> which entered organic combination was often as high as the I128, thus making the results valueless for the present purpose. To test the effect of gamma radiation alone on mixtures of CH4, I2 and inert gases, samples of such mixtures containing  $I_2^{131}$ were irradiated with a 40 curie Co<sup>60</sup> source. Table IV shows the observed conversions of inorganic iodine to organic iodide. These results are consistent with the low or negligible organic pickup of I<sup>131</sup> shown in Table III for exposures of about  $1.6 \times 10^4 r$ .

## Consideration of Influence of Charge and Kinetic Energy

From Tables I, II, and III it appears that  $I_2$ ,  $CH_3I$ ,  $C_2H_5I$ ,  $C_3H_7I$  and NO (ionization potentials 9.41, 9.67, 9.47, 9.41, and 9.23 respectively)<sup>8a,b</sup> at ratios to  $CH_4$ 

TABLE IV. Production of organically bound iodine by gamma irradiation of A and Xe containing  $CH_4$  and  $I_2^{131}$ .

CH4, mm	Inert gas	Pinert gas/ PCH4	Dose, roentgen ×10 <sup>-5</sup>	${}^{ m Moles}_{ m I_2}_{ m  imes 10^{-5}}$	Organic 1 <sup>131</sup> , %	Relative number of electrons in system
50	None	0	3.70	1.0	3.4	1
50		0	2.45	1.0	2.6	
40 40 40	A	17 17 17	$6.05 \\ 3.49 \\ 2.45$	0.82 0.82 0.82	41 28 25	26
24 24 24	Xe	8.7 8.7 8.7	3.70 2.61 0.90	0.49 0.49 0.49	46 38 18	23

 $^{\rm a}$  Irradiation was done with a 40 ml flask placed adjacent to a 40-curie Com source. The source was calibrated by ferrous sulfate dosimetry,

<sup>8</sup> (a) J. D. Morrison and A. J. C. Nicolson, J. Chem. Phys. 20, 1021 (1952). (b) E. C. Y. Inn, Phys. Rev. 91, 1194 (1953). (c) *Atomic Energy Levels* (National Bureau of Standards, 1949), Vol. 1, Circular 467.

of 1/1 or less are effective in reducing the organic yields in  $CH_4-I_2$  and  $CH_4-RI$  mixtures to less than half their limiting upper values whereas much higher ratios of He, A, and Xe (ionization potentials 24.58, 15.76, and 12.13 respectively),<sup>8c</sup> are necessary to cause the same reduction. Members of the first group of gases all have lower ionization potentials than I atoms (10.44 ev) while members of the latter have higher. At least 50%of the I<sup>128</sup> atoms produced by the  $(n,\gamma)$  process are born with a positive charge.<sup>6</sup> From Tables I and II it may also be seen that the limiting upper values of the organic yields which are reached with progressively more dilute  $I_2$  or RI in CH<sub>4</sub> are both achieved at about the same dilution. This is in the range where the probability becomes nearly 100% that an I<sup>128</sup> will be cooled to less than 2 ev by CH<sub>4</sub> collisions before undergoing a collision with  $I_2$  or RI.

These data suggest strongly that the positive charge carried by some or all of the I128 atoms is an important factor in the reaction with CH<sub>4</sub>. It is apparent from Table III that the inert gases have some effect in reducing the organic yields although less than would be expected if the reaction were  $I+CH_4\rightarrow CH_3I+H$  with an endothermicity of about 2 ev and hence about 20 ev of kinetic energy required to supply the necessary internal energy of the activated complex. By the same reasoning the still more endothermic process,  $I^++CH_4 \rightarrow$  $CH_{3}I+H^{+}$ , involving  $I^{+}$  ions in their ground state, is ruled out. The reaction  $I^++CH_4\rightarrow CH_3I^++H$  would require I<sup>+</sup> ions with a minimum of about 7 ev of kinetic energy.

Quite certainly the majority of the I<sup>128+</sup> ions formed in the system are born with a multiple charge. Possibly the I<sup>1+</sup> ions formed by partial neutralization may be produced in metastable states with sufficient electronic excitation to lead to the  $ICH_4^+ \rightarrow ICH_3^+ H^+$  step after they have associated with methane. Mechanisms involving neutralization of a CH4I\*+ cluster could also be postulated. A complete evaluation of the possible events which may occur to the I<sup>128</sup> from the time of its birth to the time it enters stable chemical combination would require a knowledge of:

(1) the recoil energy spectrum and charge distribution spectrum of the I<sup>128</sup> at birth;

(2) the charge transfer cross sections as a function of

TABLE '	<b>V.</b> 1	Reactio	on of	C <sub>2</sub> F	I6 and	$C_6H_6$	with	$I^{128}$	activate	ed
		by	the	I127 (	$(n,\gamma)$ I <sup>1</sup>	28 proc	ess.			

Hydrocarbon gas, mm	Source of I, mm	Hydrocargon to I2 ratio	Organic yield, %
C <sub>2</sub> H <sub>6</sub> , 410	$I_2, 0.14$	3000	4
410	0.16	3000	4
115	0.14	1000	3
115	0.11	1000	3
C <sub>6</sub> H <sub>6</sub> , 90	$C_2H_5I, 0.034$	3000	5
90	0.034	3000	9

kinetic energy9 for its encounters with each of the gases in the systems tested;

(3) the possible metastable states formed by charge neutralization, and the collisional deactivation cross sections for these states;

(4) the extents of ion cluster formation in the systems observed and the characteristics of the energy transfer process involved in the neutralization of such clusters.

## **Analogous Reactions**

No explanation is yet apparent for the high selectivity of the I<sup>128</sup> which leads it to give yields of only a few percent with  $C_2H_5I^2$ ,  $C_2H_6$  and  $C_6H_6$  (Table V) as compared to 50% or more with CH<sub>4</sub>. Evidence is now available that Br<sup>80 10</sup> and Cl<sup>38 11</sup> activated by the  $(n,\gamma)$ process, and Br<sup>80 10</sup> activated by isomeric transition can undergo inversion type hydrogen replacement reactions similar to those of I<sup>128</sup>, although with lower yields. The Br<sup>80</sup> (18 min) atoms from the isomeric transition are born with an average charge of  $+10^{12}$  and may also acquire kinetic energy as a result of the coulombic repulsion of different parts of the molecule over which the charge spreads.

### ACKNOWLEDGMENTS

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(1953)

<sup>12</sup> S. Wexler and T. H. Davies, Phys. Rev. 88, 1203 (1952).

<sup>&</sup>lt;sup>9</sup> (a) H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London 1954); (b) J. B. Hasted, Proc. Roy. Soc. (London) A212, 235 (1952).
 <sup>10</sup> A. Gordus and J. E. Willard (unpublished).
 <sup>11</sup> J. C. W. Chien and J. E. Willard, J. Am. Chem. Soc. 75, 6160