Reactions of Recoil Iodine Formed by the ^{123}Xe → ^{123}I System with Simple Hydrocarbons. Effects of Additives on the Reactivity[1]

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Abstract: Iodine atoms formed by the system ^{123}Xe → ^{123}I have been treated with simple hydrocarbons, and the reactivity with methane studied as a function of various additives. Although some additives such as ethane, neopentane, and xenon reduce the organic yield with methane, others such as nitrogen, krypton, argon, and neon have been observed to increase the yield. This effect by additives cannot be explained simply by the direct reaction of two or more excited states of iodine atoms of I^+. A model involving molecular ion complexes has been developed which is consistent with the observed data. In the presence of additives it is postulated that the reactive species is a molecular ion of the form AI^+ where A can be CH_4, Xe, Ne, Ar, Kr, or N_2. It is this species that undergoes an ion-molecular reaction to form organic products.

The reactions of iodine atoms with hydrocarbons have been studied extensively by nuclear activation,[3a] photolysis,[3b] and thermal dissociation.[3c] Willard and coworkers[4] studied the reaction with methane of iodine atoms produced by the $^{127}I(n,\gamma)^{128}I$ nuclear reaction. They observed that 50% of the ^{128}I atoms formed in iodine–methane mixtures react to form methyl iodide and demonstrated that inert moderators such as helium and argon did not lower the methyl iodide yields as much as expected for a kinetically energetic reactant. This led to their conclusion that the reactions were not initiated solely by a kinetically hot iodine species. It was also observed that additives such as CH_3I, C_2H_5I, and NO, all with ionization potentials below that of iodine, reduce the yield of methyl iodide, presumably by charge exchange. Gordus and Willard[5] studied iodine atom reactions with higher alkanes and found lower organic yields varying from 2 to 9%.

By studying the effect of various inert gases, Rack and Gordus[6] postulated that of the 54.4% organic yield obtained from the reaction of ^{128}I with methane, 18.4% resulted from the reaction of a kinetically hot iodine species, 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. They assumed that no electronic state more energetic than the $I^+(^1D_2)$ state could exist in a methane environment, since exothermic charge exchange with methane would quickly reduce these ions to atoms. In addition, additives such as Ar, Kr, Ne, and N_2 were thought to function both as kinetic energy moderators and as species capable of undergoing near resonant exothermic charge exchange with electronically excited I^+ and with multiply charged iodine ions.

However, since the ionization potentials of the above additives are larger than that of methane, it was assumed that they did not play an important role in the removal of electronic energy once the iodine ion had achieved a charge of +1, but rather functioned only as kinetic energy moderators. Rack and Gordus also observed that Xe was capable of lowering the organic yield from the 36% found at unit mole fraction of Ar, Ne, or Kr to 11% at unit mole fraction of xenon. This difference of 25% was attributed to the resonant charge exchange reaction between Xe and the $I^+(^1D_2)$ state.

$$I^+(^1D_2) + Xe \longrightarrow Xe^+ + I_{gs} \quad \Delta H = -0.029 \text{ eV}$$

In the ^{128}I work the results had to be corrected for radiation-induced exchange between methyl iodide and I_2. The magnitude of this effect was monitored by studying the exchange between $^{131}I_2$ and methyl iodide. At high additive concentrations it was found that the amount of radiation-induced pick-up of ^{131}I was similar to the yield of $CH_3{}^{128}I$, so large corrections had to be made.

Schroth and Adloff[7] studied the reaction of iodine atoms with methane using the system

$$^{125}\text{Xe (17-hr half-life)} \xrightarrow{\text{EC}} {}^{125}\text{I (57.9-day half-life)}$$

as a source of iodine atoms. By using this system the problem of radiation-induced exchange was eliminated, but the system was complicated by the presence of carrier xenon, which was used to produce the ^{125}Xe by the $^{124}Xe(n,\gamma)^{125}Xe$ nuclear reaction.

In the present study the system

$$^{122}\text{Te}(^3\text{He},2n)^{123}\text{Xe (2.08 hr half-life)} \xrightarrow{\text{EC}/\beta^+} {}^{123}\text{I (13.3-hr half-life)}$$

was used to produce iodine atoms. In this system carrier-free ^{123}Xe is first prepared and added to the reaction mixtures. By using carrier-free xenon no bulk material is added to the reaction mixture, and as the xenon is prepared separately before being mixed with the reactant, the radiation dose to the system is very low.

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[1] This work was supported in part by U. S. Public Health Service Grant No. HL 13851-10.

[2] National Science Foundation Fellow 1970–1972.

[3] (a) J. E. Willard, "Chemical Effects of Nuclear Transformations," I.A.E.A., Vienna, 1965, p 221; (b) D. Husain and R. J. Donovan, *Advan. Photochem.*, **8**, (1971); (c) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

[4] (a) J. F. Hornig, G. Levey, and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952); (b) G. Levey and J. E. Willard, *ibid.*, **25**, 904 (1955).

[5] A. A. Gordus and J. E. Willard, *J. Amer. Chem. Soc.*, **79**, 4609 (1957).

[6] (a) E. P. Rack and A. A. Gordus, *J. Chem. Phys.*, **34**, 1855 (1961); (b) **36**, 287 (1962).

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

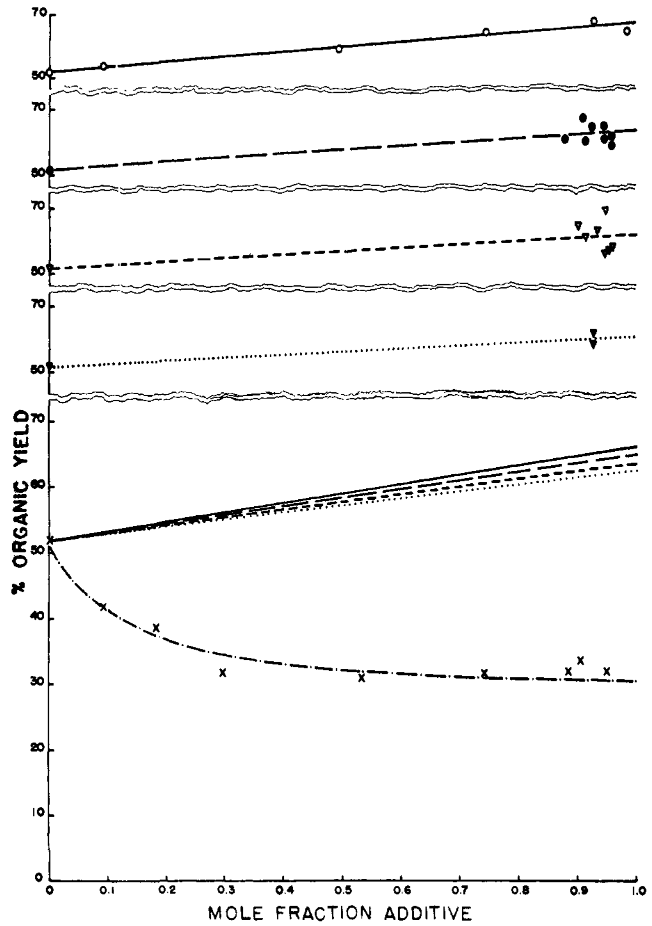

Figure 1. Effects of various additives on the organic yield from the reactions of iodine atoms with methane; the additives are (——○) nitrogen, (– –●) argon, (--▽) neon, (··▼) krypton, and (·–··×) xenon. The curve through the xenon data is a theoretical curve.

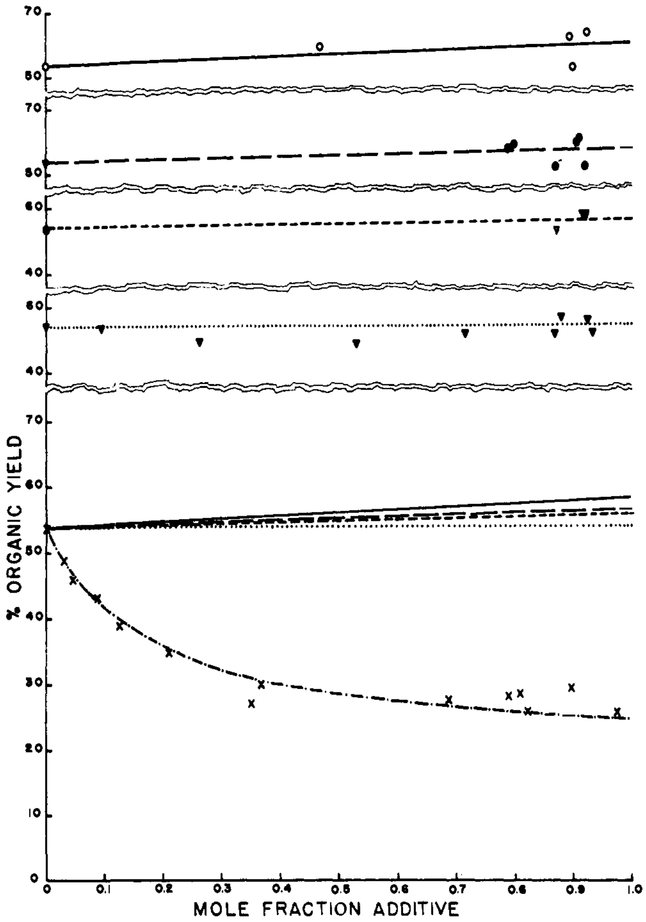

Figure 2. Effect of various additives on the organic yield from the reactions of iodine atoms with methane containing iodine scavenger; the additives are: (——○) nitrogen, (– –●) argon, (--▽) neon, (··▼) krypton, and (–·–·×)xenon. The curve through the xenon data is a theoretical curve.

^{123}Xe decays 22.9% of the time by positron decay and 77.1% of the time by electron capture,[8] and therefore from the data of Snell, *et al.*,[9] it is possible to estimate the charge state of the ^{123}I when it is first formed. It is found that 81% of the ^{123}I atoms are formed initially in a state I^{n+} where $n = 2$ to 16 with the most probable state being I^{9+}. Only 14% of the ^{123}I atoms are formed initially in the I^- state, from which they are unlikely to form organic compounds. The iodine species when formed can also be kinetically excited due to the emission of a neutrino or a positron with a maximum kinetic energy of 34.3 and 20.2 eV in the case of the electron capture and positron decay modes, respectively.[10] The ^{123}I atoms are formed with a complex distribution of various states of kinetic and electronic energy and a wide range of charge states.

Experimental Section

The production of ^{123}Xe by the ^{122}Te(^{3}He,2n)^{123}Xe nuclear reaction has been discussed previously.[11,12] The method used in this work[13] was to irradiate between 5 and 20 mg of ^{122}Te (>90% enrichment obtained from Oak Ridge National Lab.) in an aluminum pouch perpendicular to a beam of 19 MeV ^{3}He particles from the Washington University 52-in. cyclotron. Following a bombardment of between 10 and 20 μA hr of integrated beam current over a duration of 1 to 2 hr, the aluminum pouch is brought back to the laboratory and the ^{123}Xe separated in a flow system. The aluminum is dissolved in 3 *N* hydrochloric acid and the tellurium in 30% hydrogen peroxide, the xenon being swept out by helium through traps containing soda lime, chromous chloride, Drierite, and Dry Ice–acetone, before being collected in a radiator trap maintained at liquid nitrogen temperature. The xenon trap is transferred to a vacuum line, the helium pumped off, and the xenon Töepler pumped into a series of reaction vessels. The other compounds of the reaction mixture are added after the ^{123}Xe. All gases used were purchased from Matheson Gas Co. and were purified by freeze–pump distillation.

After the reaction vessels were filled, they were left in the dark for 12 to 18 hr, during which time most of the ^{123}Xe decayed. A mixture of organic solvent (hexane, toluene, or chloroform) and 0.5 *M* aqueous sodium sulfite was added to the vessel, the two fractions separated, and counted in a well-scintillation counter. The chemical form of the ^{123}I in the organic layer was confirmed by radio-gas chromatography. A glass column 240 cm in length and 8-mm i.d. packed with SF-96 silicone oil on Anakrom A 70–80 mesh was used at a temperature of 80° to separate alkyl iodides. The chromato-

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[8] (a) D. Gfoller, R. Schoneberg, and A. Flammersfeld, *Z. Phys.*, **208**, 299 (1968); (b) C. L. Lederer, J. A. Hollander, and W. Perlman, "Table of Isotopes," 6th ed, Wiley, New York, N. Y., 1967, p 266.

[9] (a) A. Snell, F. Pleasonton, and J. L. Need, *Phys. Rev.*, **116**, 1548 (1959); (b) A. H. Snell and F. Pleasonton, *ibid.*, **100**, 1396 (1955).

[10] The maximum amounts of kinetic energy were calculated using the formulas quoted by A. G. Maddock and R. Wolfgang, "Nuclear Chemistry," Vol. 2, L. Yaffe, Ed., Academic Press, New York, N. Y., 1968, p 186.

[11] V. J. Sodd, K. L. Scholz, J. W. Blue, and H. N. Wellman, U. S. Department of Health, Education and Welfare Technical Report BRH/DMRE 70-4.

[12] E. Lebowitz, M. W. Greene, and R. Richards, *Int. J. Appl. Radiat. Isotop.*, **22**, 489 (1971).

[13] M. D. Loberg, M. Phelps, and M. J. Welch, *J. Nucl. Med.*, submitted for publication.

graph was used in conjunction with an internal flow proportional counter, and the data were recorded on-line in a classic LINC computer,[14] where it was corrected for decay, changing background, and flow rate variations. A standard integration time of 3 sec was used.

Results

The product yields with simple hydrocarbons were studied both with and without iodine scavenger. In the case of methane, methyl iodide (51.8 ± 2.9% yield) was the only product, and addition of iodine scavenger altered the spectrum only by the production of methylene iodide (2.0 ± 0.3%). With ethane a total yield of 2.5% was found in both scavenged and unscavenged systems (CH_3I = 2.0 ± 0.3%, C_2H_5I = 0.35 ± 0.05%, C_2H_3I = 0.13 ± 0.03%), while in neopentane, methyl iodide (2.78 ± 1%) was formed in the unscavenged system and a mixture of methyl iodide (1.65 ± 0.3%), methylene iodide (3.14 ± 0.2%), and ethyl iodide (0.5 ± 0.2%) in the scavenged system. Figures 1 to 3 show the effects of additives to methane both in the scavenged and unscavenged systems, whereas for ethane and neopentane (Figure 3) only the scavenged system was studied. It was necessary to correct the data reported in Figure 3 for the extent of organic yield attributed directly to reactions of an energetic iodine species with ethane and neopentane. At 1 atm of additive this correction amounted to 2.5 and 5.3% for pure ethane and neopentane, respectively.

The yield in the methane–xenon system was studied as a function of total pressure at constant mole fractions of additive, and over the pressure range 7 to 70 cm the yield was found to be constant.

Tables I through V show the product yield for addition of mixtures of additives to the scavenged and unscavenged systems, where krypton, nitrogen, neon, and argon were added to methane–xenon and methane–neopentane mixtures.

Table I. Organic Yields in the Methane, Xenon, Krypton Systems[a]

Pressure, Torr			Scavenger	Yield, %	
CH_4	Xe	Kr	present	Expected	Obsd
56.4	30.8	90.6	Yes	31.7	33.0
48.8	30.8	50.0	Yes	31.0	34.5
61.2	30.8	480.8	Yes	32.0	44.3
58.8	19.0	248.5	Yes	34.7	43.2
56.7	19.0	289.0	Yes	34.3	44.7
52.2	19.0	358.0	Yes	33.8	40.0
54.8	22.0	88.9	Yes	33.3	37.1
49.5	22.0	144.2	Yes	32.7	41.3
52.0	27.7	452.1	Yes	31.7	43.9
96.7	57.9	67.4	No	33.2	32.6
63.3	57.9	122.1	No	32.2	36.5
140.0	57.9	81.4	No	34.4	35.6
50.0	28.0	510.0	No	33.4	51.9

[a] The expected yield in Tables I–V is that calculated assuming the third additive has no effect on the system.

Table II. Organic Yields in the Iodine, Scavenged Nitrogen, Xenon, Methane System

Pressure, Torr			Yield, %	
CH_4	Xe	N_2	Expected	Obsd
65.6	21.8	39.0	34.4	37.7
57.5	27.8	99.9	32.3	44.0
60.8	21.8	142.1	33.8	49.3
62.0	21.8	289.2	34.1	50.8
60.4	27.8	395.6	32.5	58.8

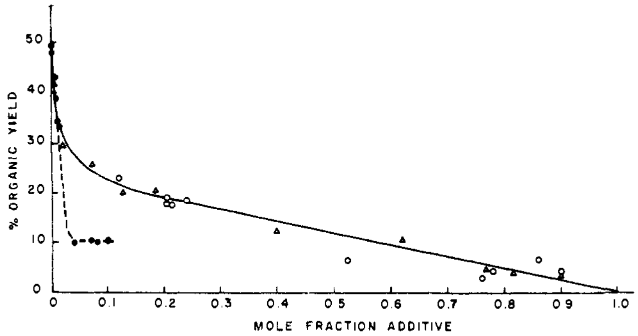

Figure 3. Effect of ethane and neopentane addition on the organic yield from ^{123}I in methane: (△) in pure methane–ethane mixtures, (○) methane–ethane in the presence of 90% xenon, and (●) in pure methane–neopentane mixtures.

Table III. Organic Yields Observed in the Neon, Xenon, Methane System

Pressure, Torr			Scavenger	Yield, %	
CH_4	Xe	Ne	present	Expected	Obsd
55.9	27.9	89.2	Yes	32.1	37.8
57.2	27.9	195.1	Yes	32.3	47.0
58.3	27.9	314.8	Yes	32.4	49.6
54.5	27.9	487.5	Yes	32.5	47.7
54.7	17.4	94.2	Yes	34.7	36.2
54.5	17.4	130.2	Yes	34.7	42.7
52.7	17.4	68.4	Yes	34.5	36.0
57.4	17.4	150.0	Yes	35.0	41.2
58.2	16.0	144.5	Yes	35.8	45.1
56.9	16.0	197.9	Yes	35.6	47.7
51.9	16.0	240.0	Yes	34.9	48.3
52.0	16.0	300.0	Yes	34.9	50.3
56.3	16.0	353.2	Yes	35.5	51.4
49.4	28.3	105.0	No	33.3	37.9
57.4	28.3	76.5	No	33.7	35.1
48.3	28.7	167.5	No	33.2	38.6
48.3	28.7	200.0	No	33.2	48.6
51.8	28.7	248.2	No	33.4	47.4
47.3	28.7	353.5	No	33.2	47.1
44.1	30.7	37.4	No	32.8	30.6
44.1	30.7	23.5	No	32.8	33.2
44.1	30.7	87.7	No	32.8	42.2
206.5	120.3	63.9	No	33.2	31.2
53.9	23.9	539.3	No	34.0	48.5
102.3	53.8	98.7	No	33.5	34.9

Discussion

Figures 1 and 2 demonstrate that additives with ionization potentials[15] above that of the $I^+(^1D_2)$ state (12.156 eV) do not reduce the yield of methyl iodide produced in the methane system. These additives are neon (IP = 21.56 eV), argon (IP = 15.775 eV), krypton (IP = 13.996 eV), and nitrogen (IP = 15.58 eV).

The absence of kinetic energy moderation by the noble gases is consistent with the fact that the iodine species is created initially with an average charge of +9 and a maximum kinetic energy of 35 eV. This

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[14] M. D. Loberg, C. Coble, N. Mullani, M. Straatmann, and M. J. Welch, presented at the 6th International Hot Atom Chemistry Symposium, Brookhaven, N. Y., 1971.

[15] All ionization potentials are taken from V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Mednedevev, and Y. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," English translation, Edward Arnold, London, 1966.

Table IV. Organic Yields in the Argon, Xenon, Methane System

Pressure, Torr			Scavenger present	Yield, %	
CH_4	Xe	Ar		Expected	Obsd
52.2	36.7	101.8	Yes	30.5	35.5
58.1	36.7	512.4	Yes	31.0	46.3
76.8	84.5	165.8	Yes	28.8	36.8
76.8	110.5	208.9	Yes	28.0	35.1
52.7	15.6	148.0	Yes	35.4	38.9
52.9	15.6	198.0	Yes	35.4	45.5
55.6	15.6	247.9	Yes	35.6	46.7
56.7	23.1	96.9	No	34.4	45.3
56.7	23.1	196.4	No	34.4	46.3
56.7	23.1	345.5	No	34.4	52.0
56.7	23.1	494.3	No	34.4	52.4
50.0	28.0	536.0	No	33.3	51.3
21.3	38.2	561.5	No	31.3	45.6
48.5	28.8	15.7	No	33.2	31.8
48.5	28.8	22.9	No	33.2	35.7
48.5	28.8	37.3	No	33.2	38.0
206.9	197.9	190.3	No	32.1	36.9
201.1	133.0	106.6	No	32.9	35.9
18.4	42.7	548.2	No	31.0	46.5
18.4	42.7	145.7	No	31.0	41.2
206.5	120.3	55.6	No	33.2	31.4
258.8	97.3	105.0	No	34.7	36.7
243.1	97.3	196.0	No	34.4	39.6

Table V. Effect of Third Bodies on the Yields in the Methane, Neopentane System

Pressure, Torr			Additive pressure,	Yield, %	
CH_4	C_5H_{12}	Additive	Torr	Expected	Obsd
9.85	0.75				13.50
9.85	0.75	Ar	50.18	13.50	32.60
9.85	0.74	N_2	51.02	13.50	31.90
10.00	0.92				7.86
10.09	0.91	N_2	7.49	7.86	14.80
10.01	0.91	N_2	14.25	7.86	14.60
10.10	0.91	N_2	29.39	7.86	22.30
12.18	0.91	N_2	43.14	14.00	33.60

lack of reactivity due to a 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. This is a simplification over the $^{127}I(n,\gamma)^{128}I$ system investigated by Rack and Gordus, in which the larger recoil energy of the ^{128}I resulted in a portion of the reactivity being attributed to a kinetically hot attacking species.

Xenon addition at high mole fractions of additive reduces the methyl iodide yield in the methane system from 53.8 to 25.4% and from 51.8 to 30.6% in the scavenged and unscavenged cases, respectively. This decrease in yield upon increasing the mole fraction of xenon is consistent with the near resonant charge exchange between xenon and the $I^+(^1D_2)$ state observed by Rack and Gordus.

Neopentane (Figure 3), when present to the extent of only a few per cent in a methane environment, rapidly reduces the organic yield to less than 10%. This can be interpreted as being due to resonant charge exchange between neopentane (IP = 10.29 eV) and I^+ in the ground state (IP = 10.454 eV) or any excited state. The reaction

$$C_5H_{12} + I^+(^3P_2) \longrightarrow (C_5H_{12}^*)^+ + I_{gs}$$

has a large cross section compared to ion-molecular reactions with neopentane to form compounds containing ^{123}I, since the exothermicity of the charge exchange reaction can be distributed within the vibrational modes of freedom of neopentane.[16]

Figure 3 also shows a graph of organic yield as a function of mole fractions of ethane in a methane environment both with and without xenon present. After observing, upon the addition of ethane, that there were two different deactivating rates, 90% xenon was added to determine if the initial rapid deactivation was due to the exothermic charge exchange between ethane and the $I^+(^1D_2)$ state. If ethane were rapidly deactivating a state other than the $I^+(^1D_2)$ state, then the addition of 90% xenon should decrease the methyl iodide yield to approximately zero. Since this deactivation did not occur, it is proposed that the following reaction occurs

$$I^+(^1D_2) + C_2H_6 \longrightarrow C_2H_6^+ + I_{gs} \quad \Delta H = -0.51 \text{ eV}$$

with the exothermicity of the reaction being distributed between the vibrational modes of freedom of the ethane ion. Charge exchange is not expected to occur between ethane (IP = 11.65 eV) and $I^+(^3P_0)$ (IP = 11.25 eV) or $I^+(^3P_1)$ (IP = 11.333 eV) since these reactions would be endoergic.

The less efficient deactivation can be explained, therefore, by the formation of HI either directly by a reaction of the type

$$I^+(^3P_2) + C_2H_6 \longrightarrow (C_2H_6I^*)^+ \longrightarrow HI$$

via formation of an excited $C_2H_6I^+$ or an excited C_2H_5I intermediate which then undergoes unimolecular decay.[17]

Rack and Gordus developed a theory for two component systems which related the extent of organic yield that is deactivated by the additive, R, to the mole fraction of additive, N, through the equation

$$R = \frac{R_0(1 - N)}{1 + N(C - 1)} \qquad \text{(I)}$$

where R_0 is the maximum organic yield that is deactivated by the particular additive and C is defined as the relative cross sections for the two types of reactions.

$$C = \frac{\sigma\{I^+(R) + \text{Add} \rightarrow I^+(NR)\}}{\sigma\{I^+(R) + CH_4 \rightarrow CH_3I\}}$$

Using eq 1 and letting R_0 = 53.8%, the deactivation caused by neopentane in a methane environment can be expressed. It is found that C = 42 gives the best fit for the data obtained in this work.

For the ethane–methane system where there appears to be two different modes by which ethane can reduce the yield of methyl iodide, it was necessary to modify eq I from that originally derived by Rack and Gordus. Equation I adequately described the neopentane–methane system, since both the $I^+(^1D_2)$ and the $I^+(^3P)$ states were deactivated by charge exchange and thus one cross section applied for both states. For ethane where the $I^+(^1D_2)$ state is deactivated by charge exchange (by an amount R_{ce}) and the $I^+(^3P)$ states *via* an ion–molecule reaction leading to HI (by an amount

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(16) (a) E. F. Gurnee and J. L. McGee, *J. Chem. Phys.*, **26**, 1237 (1957); (b) L. Tomcho and M. J. Haugh, *ibid.*, **56**, 6089 (1972).

(17) We are currently investigating this mode of reaction by studying the pressure dependence of the iodine reaction with ethane.

Table VI. ΔH Values for Various Reactions of the I^+ Species with Methane

Substrate	Products	Reactants (ΔH^{298}, eV) $I(^2P_{3/2})$	$I^+(^3P_2)$	$I^+(^3P_0)$	$I^+(^3P_1)$	$I^+(^1D_2)$
CH_4	$CH_3I + H$	2.11				
CH_4	$CH_3I^+ + H$		1.16	0.36	0.28	−0.54
CH_4	$CH_3I + H+$		5.26	4.46	4.38	3.56
CH_4	$CH_3 + HI$	1.34				
CH_4	$CH_3 + HI^+$		1.29	0.49	0.41	−0.41
CH_4	$CH_3^+ + HI$		0.75	−0.05	−0.13	−0.95

R_{im}), it was necessary to modify eq I

$$R = \frac{R_{ce}(1 - N)}{1 + N(C_{ce} - 1)} + \frac{R_{im}(1 - N)}{1 + N(C_{im} - 1)} \tag{II}$$

where R_{ce} and R_{im} are the maximum yields attributed to the $I^+(^1D_2)$ reactant and the $I^+(^3P)$ reactants, respectively. Letting R_{ce} and R_{im} be set equal to 28.4 and 25.4%, respectively, one obtains the solid line shown in Figure 3 when $C_{ce} = 70$ and $C_{im} = 1$. The slow component of the deactivator extrapolates to 24% at zero mole fraction of ethane, in good agreement with the extent of the reaction attributed to the $I^+(^3P)$ states. All of the effects discussed to date are consistent with the observations of Rack and Gordus.

Qualitatively, there are three features to the data that are contrary to the behavior of iodine atoms as observed by Rack and Gordus. Firstly, some "inert" moderators increase the amount of reaction with methane and the magnitude of this effect increases from krypton to neon to argon to nitrogen.

Secondly, although the additive curves with and without iodine scavenger are qualitatively similar, there are differences. The organic yield in pure methane with iodine present is slightly higher than that measured in the absence of scavenger. This would be expected due to the ability of iodine to scavenge $CH_2{}^{123}I$ and form $CH_2{}^{123}II$. The organic yields obtained upon rare gas addition are always higher in the unscavenged case, although the yields in both cases are in the sequence $N_2 > Ar > Ne > Kr > Xe$.

The third feature of the data is the effect of adding N_2, Ar, Ne, or Kr to a methane–xenon mixture. In the mechanism of Rack and Gordus, xenon deactivates the $I^+(^1D_2)$ state by resonance charge exchange, with the other moderators having no effect on the system because the analogous reactions are endoergic. As we have shown that varying the pressure from 71.5 to 640.6 Torr has a minor effect on the organic yield in the methane–xenon system, the third component should have no effect on the yield. It should be governed only by the mole fraction of xenon in the gas mixture.

It is apparent from the data in Tables I to IV that the third body increases the yield considerably from that predicted by this simple relationship.

One possible explanation of this "third body phenomenon" is that the third body is simply deactivating the $I^+(^1D_2)$ state to a lower energy reactive state,[18] *i.e.*, $I^+(^1D_2) + A \rightarrow I^+(^3P) + A^*$. This lower energy state is still reactive, but cannot be deactivated by xenon as resonance charge exchange is not possible. Although xenon reduces only part of the organic yield, neopentane (see Figure 3) reduces the yield rapidly to <10%. Table V shows that addition of a third body to methane–neopentane mixtures also increases the yield. As under the simple mechanism the reaction

$$C_5H_{12} + I^+ \longrightarrow (C_5H_{12}{}^*)^+ + I$$

occurs for both the $I^+(^1D_2)$ and $I^+(^3P)$ states, the result in the neopentane system cannot be explained by the third body converting $I^+(^1D_2)$ to $I^+(^3P)$. This is to be expected as inert gases are inefficient at transferring electronic energy into translational energy.[19]

The Rack and Gordus mechanism also necessitates that a reactive species of lower energy than $I^+(^1D_2)$ should be able to react with methane to form CH_3I^+. Table VI, generated from the data of Vedeneyev, *et al.*,[15] shows that the reaction to form CH_3I^+ or CH_3I is only exothermic with $I^+(^1D_2)$. It seems unlikely that a long-lived excited neutral atom would form CH_3I, as these species produced by nonnuclear techniques are known to rapidly abstract hydrogen[20] from simple hydrocarbons.

It appears, therefore, that the mechanism involving direct attack by $I^+(^1D_2)$ plus a second I^+ species is probably oversimplified.

Our results appear consistent with a mechanism involving the following series of reactions

$$Xe + {}^{123}I^+(R) \longrightarrow Xe^+ + {}^{123}I(NR)^{21} \tag{1}$$

$$CH_4 + {}^{123}I^+(R) \rightleftarrows CH_4{}^{123}I^+ \tag{2}$$

$$CH_4{}^{123}I^+ + CH_4 \longrightarrow CH_3{}^{123}I + CH_5{}^+ \tag{3}$$

$$Xe + {}^{123}I^+(R) \rightleftarrows Xe^{123}I^+ \tag{4}$$

$$Xe^{123}I^+ + CH_4 \longrightarrow CH_3{}^{123}I + XeH^+ \text{ (net reaction)} \tag{5}$$

$$A + {}^{123}I^+(R) \rightleftarrows A^{123}I^+ \tag{6}$$

$$A^{123}I^+ + CH_4 \longrightarrow CH_3{}^{123}I + AH^+ \text{ (net reaction)} \tag{7}$$

$$A^{123}I^+ \; (Xe^{123}I^+) + I_2 \longrightarrow AI^+ \; (XeI^+) + I^{123}I \tag{8}$$

where A represents some additive.

In this scheme, xenon can undergo resonance charge exchange with I^+ presumably in the $I^+(^1D_2)$ state (reaction 1), or can react with I^+ to form the molecular ion XeI^+ (reaction 4), which then reacts with methane to form methyl iodide, either directly or perhaps through the CH_4I^+ intermediate. The reactions postulated

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(18) Deactivation of this type has been shown to occur once every 40 collisions for $C(^1D_2) + N_2 \rightarrow C(^3P) + N_2$: W. Braun, A. M. Bass, D. D. Davis, and J. D. Simmons, *Proc. Roy. Soc., Ser. A*, **312**, 417 (1969).

(19) A. B. Callear and J. D. Lambert, "Comprehensive Chemical Kinetics," C. H. Bamford and C. F. H. Tipper, Ed., Vol. 3, Elsevier, Amsterdam, 1969, p 253.

(20) (a) T. W. Broadbend and A. B. Callear, *Trans. Faraday Soc.*, **67**, 3030 (1971); (b) A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 5478 (1967).

(21) Since the exact nature of this species is in question, the symbol I(NR) will be used to indicate an iodine species that lacks sufficient energy to react with methane, while I(R) signifies the species that do react with methane.

with methane (2 and 3) are also those to form a molecular ion which then undergoes an ion–molecule reaction. Reaction 2 has previously been suggested as a possible reaction in this system.[6a]

The general reaction scheme for formation of CH_3I is a two-step process (reactions 2 and 3). The enthalpy of these two reactions taken together is 0.0435 ± 0.22 eV for ground-state I^+.[15,22] The individual enthalpies of reactions 2 and 3 are difficult to evaluate since the heat of formation of CH_4I^+ is not accurately known. The exothermicity of reaction 2 will be partitioned between the vibrational modes of the product ion, CH_4I^+, and the internal energy of the CH_4I^+ intermediate would be available to allow reaction 3.[23] It should be pointed out that reaction 3 can be endothermic by as much as 0.65 eV and still have the reaction proceed essentially to completion since the ratios of reactants and products are governed by the relationship

$$\Delta H = -RT \ln \frac{\{CH_3I\}\{CH_5^+\}}{\{CH_4I^+\}\{CH_4\}}$$

where ΔS is assumed to be approximately equal to zero. Since our system contains carrier-free, radioactive iodine atoms, $\sim 10^{10}$, in a bath of CH_4 atoms, $\sim 10^{21}$, an equilibrium constant for reaction 2 equal to 10^{-11} will drive the reaction essentially to completion.

This pair of reactions does answer another question posed by the Rack and Gordus mechanism, that being the manner in which a CH_3I^+ intermediate is neutralized. In a pure methane system it is impossible for electron capture to occur since the reaction

$$CH_3I^+ + e^- \longrightarrow CH_3I$$

is exothermic by 9.54 eV.[24] This recombination energy would leave a highly excited CH_3I which one would expect to undergo unimolecular decay.

In this reaction scheme we postulate that the other rare gases and nitrogen will form a complex with I^+. ArI^+ and KrI^+ have been observed mass spectrometrically, and have lifetimes greater than 10^{-6} sec.[25] The gas-phase acidities of XH^+ increase from neon to argon to krypton,[26] so one would expect the complex to be more stable with the heavier inert gases. With regard to the formation of N_2I^+, the isoelectronic N_2H^+ has been prepared by several reactions, and has been shown to be very stable.[27]

Persistent complexes of this type were observed following the radiolysis of Xe–C_2H_2 mixtures.[28] The formation of $\{XeC_2H_2\}^+$ from Xe^+ was observed in a mass spectrometer at 0.1 Torr of pressure. It was postulated that the other inert gases formed such persistent complexes but that the lifetimes of these complexes were shorter than the $\sim 10^{-6}$ sec needed to detect them.

In addition, ArI^+, KrI^+, and XeI^+ are isoelectronic with ICl, IBr, and I_2, respectively. The ability of the latter species to iodinate various compounds is well documented.[29] It is not surprising then that species such as ArI^+ would not only be relatively stable, but would also be capable of producing a nucleogenic iodinating species that could undergo reaction 7.

Reaction 8, exchange of the labeled AI^+ with unlabeled iodine, would explain qualitatively the higher yields at high mole fraction of additive in the unscavenged systems compared to those which are iodine scavenged. The difference between scavenged and unscavenged xenon additive will also be due to a reaction of this type.

Another consideration in the mechanism is the rather large exothermicity of reactions 2, 4, and 6, especially when the attacking species is $I^+(^1D_2)$. It is certain that a larger percentage of these inert gas complexes will undergo unimolecular decay back to the original reactants. This process can be repeated until collisional stabilization occurs and is consistent with the general inefficiency of the reaction,[19] and points out why addition of a few per cent of a species with a lower ionization potential than iodine can deactivate the reaction *via* charge exchange.

Since the attacking species at high moderation, AI^+, differs from that without any moderator present, CH_4I^+, it is to be expected that the yield of methyl iodide should differ with addition of moderator. The $I^+(^1S_2)$ state (14.496 eV) is above the ionization potential of methane, and so one would expect it to be deactivated by methane. At high moderation the $I^+(^1S_2)$ state which normally undergoes charge exchange with methane can become a reactive state that yields CH_3I through reactions 6 and 7. Therefore at high mole fractions of additive the $I^+(^1S_2)$ species may react to form CH_3I before it can undergo charge exchange with methane.

Considering Figures 1 and 2, it is seen that the yield elevation is less for krypton than for neon and argon, even though the gas-phase acidity of krypton is the highest. For krypton we have the competing reaction

$$Kr + I^+(^1S_2) \longrightarrow Kr^+ + I\cdot \ (\Delta H = -0.5 \text{ eV})$$

The charge exchange reaction is not a resonance reaction, and so will not have a high cross section,[16] and unlike the deactivation of $I^+(^1S_2)$ by methane, the excess energy cannot be transferred to a vibrational mode of the deactivating species.

Using the model described in reactions 1 to 8, we can explain the data observed in this work. By making several assumptions, it is possible to derive an expression for the behavior of the three component systems. In the general reaction scheme, reactions 2 through 7 can be considered as three pairs of reactions of the general form

$$A + I^+(R) \longrightarrow AI^+ \qquad (n)$$

$$AI^+ + CH_4 \longrightarrow CH_3I + AH^+ \qquad (n + 1)$$

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(22) The heat of formation of CH_5^+ was taken as 9.95 eV from J. L. Beauchamp and E. Butrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

(23) Preliminary results using ion cyclotron resonance spectroscopy (J. Henis, M. D. Loberg, and M. J. Welch, unpublished) have shown that reaction 3 does occur, but that the reaction is endothermic for CH_4I^+ in its lowest vibrational level. We estimate that 8.8 eV < ΔH-$\{CH_4I^+\}$ < 10.6 eV in which case the reaction is endothermic by between 0.26 and 2.0 eV.

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(27) (a) F. C. Fehsenfeld, A. L. Schmeltekopt, P. D. Goldon, H. I. Schiff, and E. E. Ferguson, *J. Chem. Phys.*, **44**, 4087 (1966); (b) F. C. Fehsenfeld, A. L. Schmeltekopt, G. I. Gilman, L. G. Puls, and E. E. Ferguson, *Bull. Amer. Phys. Soc.*, (2) 11, 505 (1966); (c) F. C. Fehsenfeld, A. L. Schmeltekopt, and E. E. Ferguson, *J. Chem. Phys.*, **46**, 2802 (1967); (d) J. Henis, personal communication, 1972.

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(29) (a) R. S. Yalow and S. A. Benson, *J. Clin. Invest.*, **39**, 1157 (1960); (b) E. Samols and H. S. Williams, *Nature* (*London*), **190**, 1211 (1961); (c) A. S. MacFarlane, *ibid.*, **182**, 53 (1958).

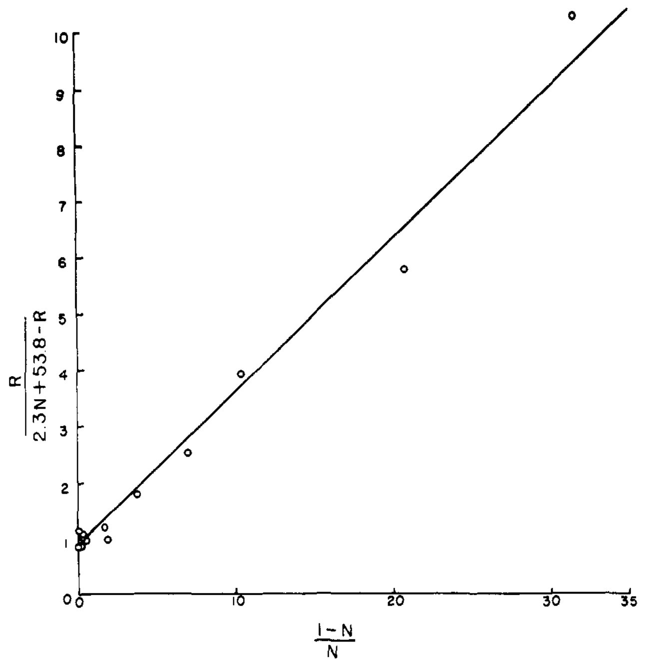

Figure 4. Plot of $R/(mN + R_0 - R)$ against $(1 - N)/N$ for the scavenged methane–xenon system.

When A equals CH_4, Xe, or additive, then $n = 2$, 4, or 6, respectively. In this manner reactions 2 through 7 are considered as three pairs of reactions, and we assume that each of these pairs has a unique cross section to form CH_3I which will be designated σ_n. In this assumption we disregard the decomposition of AI^+ by all but the reaction path to form CH_3I and so σ is a measure of reactive cross section to form CH_3I. In the scavenged system, we ignore reaction 8, which is a reaction of AI^+ that does not lead to the desired product.

If we designate partial pressures of methane, xenon, and additives as $\{CH_4\}$, $\{Xe\}$, and $\{A\}$, respectively, the measured organic yield ($CH_3I + CH_2I_2$) can be written as a simple sum.

$$R_{CH_3I} = \{CH_4\}\sigma_2 + \{Xe\}\sigma_4 + \{A\}\sigma_6$$

Reactivity to form I(NR) by reaction I is

$$R_{I(NR)} = \{Xe\}\sigma_1$$

Then

$$\frac{R_{CH_3I}}{R_{I(NR)}} = \frac{\{CH_4\}}{\{Xe\}}\frac{\sigma_2}{\sigma_1} + \frac{\sigma_4}{\sigma_1} + \frac{\{A\}}{\{Xe\}}\frac{\sigma_6}{\sigma_1}$$

Let $Y = \sigma_2/\sigma_1$, $D = \sigma_4/\sigma_1$, and $F = \sigma_6/\sigma_1$.

$$\frac{R_{CH_3I}}{R_{I(NR)}} = \frac{\{CH_4\}}{\{Xe\}}Y + D + \frac{\{A\}}{\{Xe\}}F \qquad \text{(III)}$$

Here, Y, D, and F are the cross sections for the pair of reactions relative to the cross section for deactivation by xenon. Now $R_{CH_3I} + R_{I(NR)}$ is equal to the total reactivity with no xenon deactivation. With no additive present this is simply equal to the yield with pure methane (R_0), but it is necessary to estimate the amount of increase in xenon reactivity one would expect if there were no $I^+(^1D_2)$ deactivation.

It seems reasonable to assume that the amount of ($^1S_2$) reaction with xenon addition would also increase,

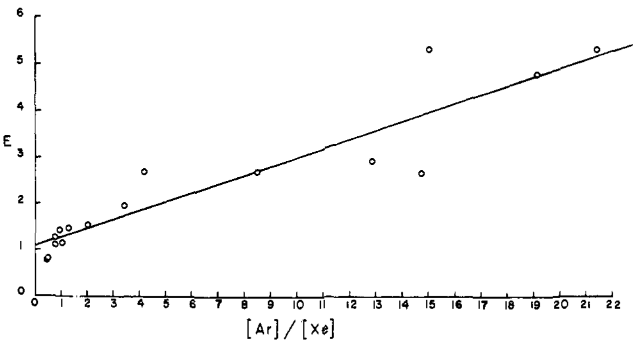

Figure 5. Plot of E against $\{A_1\}/\{Xe\}$ for the iodine scavenged system methane, xenon, and argon.

as is observed with all the other "inert" additives. In order to develop the theory it is necessary to estimate this increase.

The reaction $I^+(^1S_2) + Xe \rightarrow Xe^+ + I\cdot$ is exothermic by 2.267 eV and so is not a near-resonant charge-exchange reaction. We have assumed that the increase in total reaction with xenon addition is the average of the increases observed with argon and krypton, *i.e.*, $R_{CH_3I} + R_{I(NR)} = mN + R_0$, where N is the mole fraction of xenon and m is the mean of the slopes of the krypton and argon data (Figures 1 and 2). For the CH_4–Xe system without additive, eq III simplifies to

$$\frac{R_{CH_3I}}{mN + R_0 - R_{CH_3I}} = \frac{1 - N}{N}Y + D \qquad \text{(IV)}$$

A plot of $(R_{CH_3I}/mN + R_0 - R_{CH_3I})$ *vs.* $(1 - N)/N)$ should be a straight line with slope Y and intercept D. Figure 4 contains this plot for the scavenged system. It is found that with scavenger $Y = 0.285$ and $D = 0.80$, and without scavenger $Y = 0.289$ and $D = 1.08$. It should be noted that the curves drawn to the xenon data in Figures 1 and 2 are theoretical curves generated by rearranging eq 3 and calculating the yield variation *vs.* mole fraction of xenon.

For the three-component systems

$$R_{CH_3I} + R_{I(NR)} = R_0 + \frac{n\{A\}}{\{CH_4\} + \{A\} + \{Xe\}} + \frac{m\{Xe\}}{\{CH_4\} + \{A\} + \{Xe\}} \qquad \text{(V)}$$

when n is the slope of the curve for additive addition to methane.

If MF_A is the mole fraction of additive and MF_{Xe} is the mole fraction of xenon

$$\frac{R_{CH_3I}}{R_0 + n(MF_A) + m(MF_{Xe}) - R_{CH_3I}} = \frac{\{CH_4\}Y}{\{Xe\}} + D + \frac{\{A\}}{\{Xe\}}F \qquad \text{(VI)}$$

Here a plot of

$$E = \frac{R_{CH_3I}}{R_0 + n(MF_A) + m(MF_{Xe}) - R_{CH_3I}} - \frac{\{CH_4\}}{\{Xe\}}Y \ vs.\ \frac{\{A\}}{\{Xe\}}$$

should have a slope of F and an intercept of D. A typical plot is shown in Figure 5 for the scavenged

CH_4–Xe–Ar system, which we derived from the data in Table IV. The values obtained from the systems in Tables I through IV are summarized in Table VII.

Table VII. Summary of Parameters Calculated from the Theory

Sub-stance	Value with I_2 F	Value with I_2 D	Value without I_2 F	Value without I_2 D
Xe		0.80 ± 0.09		1.08 ± 0.09
Kr	0.21 ± 0.05	0.94 ± 0.59	0.32 ± 0.01	0.71 ± 0.06
Ar	0.19 ± 0.02	1.07 ± 0.21	0.19 ± 0.02	1.09 ± 0.20
Ne	0.39 ± 0.06	0.42 ± 0.75	0.15 ± 0.04	0.15 ± 0.35
N_2	0.57 ± 0.06	0.47 ± 0.51		

Conclusion

The lines drawn to determine *F* values for the additives are plotted with a regression analysis where the intercept (which should equal *D*) is not fixed. The errors given are the rms errors for the slope and intercept. It is seen that the intercept values for the series without I_2 scavenger are much closer to the value of *D* determined from the xenon data than are those with I_2. It appears that the extra assumption necessary for the experiments with I_2, that the reaction 8

$$A^{123}I^+ + I_2 \longrightarrow AI^+ + I^{123}I$$

can be ignored probably decreases the validity of the parameters. The *F* values for the rare gases in the experiments without I_2 present, increase with the gas-phase acidities of the rare gases.[30] Iodine ions would form stronger complexes with species with higher gas-phase acidities. Once formed the complex would undergo exchange of the iodine with methane as methane has an even higher gas-phase acidity. The *F* value obtained with nitrogen is the highest obtained with any additive, and this is consistent with the high (116 kcal/mol)[31] proton affinity of nitrogen. The values of *F* obtained in the study do appear to show some correlation with gas-phase acidity, and so the trends observed are very reasonable. It should also be noted that addition of iodine has little effect on the data, and this can be explained simply by adding reaction 8, the exchange reaction. For the products that are observed in this work I_2 does not act as a scavenger, and indeed need not be added to the system when one is considering only the organic products.[32]

In the general reaction scheme we have developed, the I^+ ions can all be in the $I^+(^1D_2)$ state, and the parameter *D* would then be simply a measure of the ability of xenon to form the complex $AI^+\{I^+ = (^1D_2)\}$ relative to its ability to deactivate the state. It is, however, also possible that as in the Rack and Gordus mechanism, there are two reactive species, one of which $\{I^+(^1D_2)\}$ is deactivated and the other, $\{I^+(^3P)\}$, forms XeI^+.

Such a reactive intermediate would explain the large amount of radiation induced labeling in $^{131}I_2$–CH_4 inert gas mixtures observed by Rack and Gordus.[6] They found at a reactor dose of 933 rads the mixtures gave yields of CH_3I of 17, 12, and 5% for high mole fractions of Xe, Kr, and Ar/Ne, respectively. Therefore ions could be formed by the reactions observed by Henglein and Muccini[25] for xenon and krypton.

$$Xe^* + I_2 \longrightarrow XeI^+ + I + e^-$$

Such metastable excited electronic species as Xe* have been shown to be one of the major species produced from the high doses found in reactor cores, and the subsequent Penning ionization has been shown to play a part in building up the electron density in the core.[33]

We have shown that the ethane data can be explained by the simple Rack and Gordus model, and also that after the initial fast deactivation from ≃52% organic yield to ≃28% yield, the yield obtained is the same with and without 90% xenon being present. The amount of deactivation by xenon and ethane appears to be very similar; as it is unlikely that the ratio of deactivation to complex formation would be identical for ethane and xenon, the most rational mechanism is that there are two states and that in ethane we are observing the following reactions

$$I^+(^1D_2) + C_2H_6 \longrightarrow C_2H_6^+ + I$$

$$I^+(^3P) \text{ or } XeI^+(^3P) + C_2H_6 \longrightarrow C_2H_6I^+ \longrightarrow \text{HI (final product at 1 atm pressure)}$$

$$I^+(^3P) \text{ or } XeI^+(^3P) + CH_4 \longrightarrow CH_4I^+ \longrightarrow CH_3I \text{ (final product)}$$

where $I^+(^3P)$ and the xenon complex have similar relative reactivities with methane and ethane.

In conclusion, this work has shown that the reactions of iodine with methane can be explained only by the intermediate formation of species of the form AI^+. Secondly, it has been shown that when considering organic products, I_2 scavenger only affects the product by an exchange reaction with AI^+. Thirdly, the data with ethane leads us to confirm that there are two iodine species that are reactive.

Acknowledgments. The authors thank Mr. John Hood and the staff of the Washington University 52 in. cyclotron for their help with the irradiation. They also thank Professor P. P. Gaspar and Drs. K. A. Krohn and J. Henis for many helpful discussions and Mr. D. Maddox for his assistance.

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(30) J. L. Beauchamp (ref 26) gives proton affinities (in kcal/mol) of Ne as 48; Ar, 82; Kr, 104; Xe, 123; and CH_4, 127.

(31) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, **92**, 7484 (1970).

(32) It is, however, possible that the species that does not react to form an organic product could be scavenged by I_2 as opposed to abstracting hydrogen to form HI. Owing to the fact that I_2–HI exchange is very fast it is impossible to distinguish abstraction product from the scavenged product.

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