Reactions of Recoil Iodine Formed by the $^{123}Xe \rightarrow {}^{123}I$ System with Simple Hydrocarbons. II. Pressure Studies on the Methane and Ethane Systems[1]

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Abstract: Recoil iodine species produced by the system $^{123}Xe \rightarrow {}^{123}I$ are reacted with methane and ethane, both with and without additives being present, over the density range 10^{-4} to 0.5 g/cc. Qualitatively, major differences are observed between the behavior of methane and ethane. In methane the yield of organic products drops from $\simeq 50$ to $\simeq 10\%$, while in ethane the yield increases over the same density range. The effects observed in the lower density region (10^{-4} to $\simeq 10^{-1}$ g/cc) are interpreted in terms of an ion–molecule mechanism previously developed by us to explain the methane system at 1 atm. The trends observed at the higher densities are explained by the autoradiation hypothesis model.

The reactions of iodine atoms produced by nuclear activation with hydrocarbons have been extensively studied in both the gas[3] and liquid[4] phases. Various researchers have found the gas phase activity to be governed by such factors as charge exchange,[3c,e,f] kinetic energy degradation,[4b,5] and ion–molecule reactions.[3a,6] Although the gas phase reactivity varies with the mode of nuclear activation, it is found that the organic yield for gaseous methane is approximately 35–55%,[3] while that with other saturated hydrocarbons is 1–5%.[3d,h,7] Loberg and Welch[3a] have recently investigated the reactivity of iodine atoms formed by the system $^{123}Xe \rightarrow {}^{123}I$ with simple hydrocarbons. For this system, in which the recoil ^{123}I is produced initially with an average charge of +9 and a recoil kinetic energy of less than 35 eV, they demonstrated that the reactive species in the methane system was a thermal ion in either the $I^+(^3P)$ or $I^+(^1D_2)$ states. They also developed a model involving molecular ion complexes in which the reactive species is a molecular ion of the form AI^+, where A can be CH_4, Xe, Ne, Ar, Kr, or N_2. They proposed that it is this molecular ion which undergoes an ion–molecule reaction to form organic products. This model was found to be in good agreement with the data on the reactivity of three-component systems of the types CH_4–Xe–A.

The reactivity of recoil iodine with liquid hydrocarbons is in marked contrast with that found in the gas phase. The liquid phase reactivity for five-carbon and larger hydrocarbons is characterized by organic yields in the 35–50% range.[4] The liquid phase reactivity of $^{127}I(n,\gamma)^{128}I$ with methane was reported by Hornig, *et al.*,[3b] to vary between 0.25 and 70%, and no value has been reported for the liquid phase reaction of iodine with ethane.

The increased reactivity of halogens in the liquid phase has been attributed to various mechanisms: the autoradiation hypothesis model,[4a] the thermal spike model,[8] the intermediate complex model,[9] and the modified impact model.[10] These mechanisms all involve reactions between the hot atom and the organic radicals it has produced in the medium. Franck and Rabinowitsch[11] were the first to postulate this type of radical recombination reaction within a solvent "cage." The individual models do differ, however, in the source of the radicals. The mechanism that appears to be gaining the greatest acceptance is that of autoradiolysis, which states that the chemical reactivity of a liquid phase system can be attributed to the reactions of the hot atom with the envelope of ions and radicals formed by the Auger electron cascades in the nuclear process. As the density of the reacting media increases, so does its stopping power for Auger and conversion electrons. It is expected that as the density increases this radical and ion envelope will tighten around the hot atom and at some density the chemical energetics of this reaction envelope will be just as important as the chemical nature of the hot atom. Rudolf[12] investigated the nature of the primary radiolysis products following bombardment of methane with 100-eV electrons and demonstrated that 45% of the primary products were positively charged, while 55% were radicals of the type CH_3, CH_2, and H.

Richardson and Wolfgang[13] investigated the large phase dependence in hot halogen organic yields for

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the system $^{18}F + CH_3F \rightarrow CH_3{}^{18}F$ and $CH_2F^{18}F$ by producing the ^{18}F at temperatures above the critical temperature of CH_3F (55°). With a gas phase reaction assured, they were able to change the density of the reaction medium from that characteristic of a dilute gas to approximately 0.6 g/cc. Above this point they cooled the reaction vessel to avoid excessive pressures. They reported a marked increase in the yield of both radioactive products above a density of approximately 0.5 g/cc. They attributed this increase in yield to Franck–Rabinowitsch caging,[11] but were unable to rigorously exclude the possibility that this sharp rise in yield was a temperature rather than a density phenomenon.

Krohn, *et al.*,[14] likewise investigated the reactivity of ^{18}F at pressures up to 40 atm, employing CH_3CF_3 as the substrate. They found that the organic products from primary ^{18}F hot reactions exhibited extensive unimolecular decay and that the rise in yield of stable products at high pressure could be accounted for based on the stabilization of primary reaction products which undergo extensive unimolecular decomposition at lower pressures.

In the present study the system

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

was used to produce iodine atoms. The advantage of this method is that the ^{123}Xe can be prepared prior to addition of the reactant gases. In this manner the decay of ^{123}Xe itself is the only source of radiolytic damage. It also enables one to fabricate metal reaction vessels, since it is no longer necessary to operate under the constraint that the reaction vessel be permeable to charged particles or neutrons. The ^{123}Xe and the reactant gases are placed in the metal vessel and the ^{123}Xe is allowed to decay for 12–18 hr. By maintaining the temperature of the mixture above the critical temperature for the reactant gases, one can ensure a gas phase reaction over a density range characteristic of a dilute gas to those typical of condensed media. Methane and ethane were chosen as the reactant gases because of their low critical temperatures, −82.6 and 32.3°, respectively.

From these high-pressure studies one can gain information about primary iodine reactions. By changing the intermolecular distance and the time between gas phase collisions, one can collisionally stabilize primary reaction products that possess a high degree of excitation. In addition, as the densities in the gas phase approach liquid phase values, one may gain insight into the mechanism responsible for enhanced liquid phase organic yields.

Experimental Section

The method used in this work for the production and purification of ^{123}Xe has been described previously.[3a] After purification, the carrier-free ^{123}Xe is Toepler pumped into a series of reaction vessels, followed by the addition of the other components in order of increasing mole fraction. All gases used were purchased from Matheson Gas Co. and were purified by freeze–pump distillation.

Samples between 3 and 500 atm were contained in specially fabricated stainless steel vessels. The maximum allowable pressure for these vessels was calculated to be 1000 atm. A safety factor of at least 2 is therefore maintained throughout the experiments. The body of the vessel was fitted with a Whitey DK forged body stainless steel shut-off valve with 1/8-in. male pipe thread on the inlet and 1/4-in. Swagelok outlet for connection to the vacuum line. The volume of the vessels was determined by filling them with mercury and recording the weight difference. A typical value for the volume was 1.55 cc. Volumes could be measured to within ±0.001 cc.

The method employed for adding the various reactant gases to the ^{123}Xe varied, depending upon the final reaction pressure. Sample vessels at pressures up to 60 atm were filled directly from glass and metal vacuum lines. Sample pressures in excess of 60 atm were achieved by condensing the desired gas from a known volume into the metal vessel, using liquid N_2 to cool the vessel.

The C_2H_6/CF_4 reactant mixture was likewise condensed into the reaction vessels at liquid N_2 temperatures. A stock gas composed of 0.96 mol fraction of CF_4 was prepared in the metal vacuum line and stored in a lecture bottle for future use. The mixture was checked for fractionation both at 22°, when the valve on the lecture bottle was opened, and at −196°, when the mixture was condensed into the reaction vessel. Gas aliquots were taken at each stage of the sample preparation and injected onto a 240-cm SF-96 silicone oil column at 22°. The relative peak areas of the C_2H_6 and CF_4 were invariant throughout the sample preparation. Although the above method is inapplicable to N_2 containing mixtures, it was possible to obtain N_2 pressures in excess of 400 atm by attaching the vessels directly to the two-stage pressure regulator of a nitrogen gas cylinder following addition of ^{123}Xe and the other reactant gases.

With the exception of the solid phase experiments, the reaction temperature (the temperature at which ^{123}Xe decayed) was above the critical temperature of the reactant gases. For all of the gases except ethane 22° was sufficient, but for ethane it was necessary to heat the reaction vessel to 36° to ensure a gas phase reaction at high pressures. For the solid phase experiments the vessels were stored at −196° until the time of analysis. The homogeneity of the mixture was assured by choosing only gas components that did not fractionate at liquid nitrogen temperatures.

In cases in which the total pressure exceeded 5 atm, a gravimetric method[15] was used to determine the exact density of the gas reaction mixture. By recording the weight of the stainless steel vessel before and after filling, and coupling this with the known volume of the vessel, one can obtain the density and convert it to fugacity (P/Z) according to the equation

$$\frac{P}{Z} = \frac{RT}{V}\sum_{i=1}^{n}\frac{g_i}{M_i}$$

where g_i and M_i denote the weight and molecular weight of the ith component of the gas mixture. The data are represented in terms of fugacity to avoid any complications in estimating the gas compressibility factors.

For samples with less than 5 atm the pressure was measured either with a 1.5-mm bore mercury manometer or with compound pressure gauges. These pressure readings were recorded for all samples up to 60 atm and served as a check on the density measurements. The error in filling was less than 1% throughout the entire pressure range.

After allowing the ^{123}Xe to decay for 12 to 18 hr, the metal vessel was opened and the contents expanded into a previously evacuated glass bulb. The volume of the bulb was chosen so as to keep the internal pressure of the bulb just below 1 atm. The bulb was repeatedly extracted with a mixture of hexane containing I_2 and 0.5 M Na_2SO_3 until no additional radioactivity could be removed. The metal vessel was then washed thoroughly with the same mixture. In all cases >95% of the activity was removed from the vessels. The two phases were separated and counted in a NaI(Tl) well scintillation counter or a Ge(Li) solid state detector coupled to a 1024-channel analyzer. The latter procedure was sometimes necessary to correct for the 148-keV γ-ray of undecayed ^{123}Xe. ^{123}Xe was found to have a limited but preferential solubility in the organic phase and the 148-keV γ-ray of ^{123}Xe could not be differentiated from the 159-keV γ-ray of ^{123}I using a scintillation counter.

The chemical form of the ^{123}I in the organic layer was identified by radio gas chromatography using the mixed organic washings. A glass column 240 cm in length and 8 mm i.d., packed with SF-96 silicone oil on 70–80 mesh Anakrom A was used at a tempera-

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[15] K. A. Krohn, N. J. Parks, and J. W. Root, *J. Chem. Phys.*, **55**, 5771 (1971).

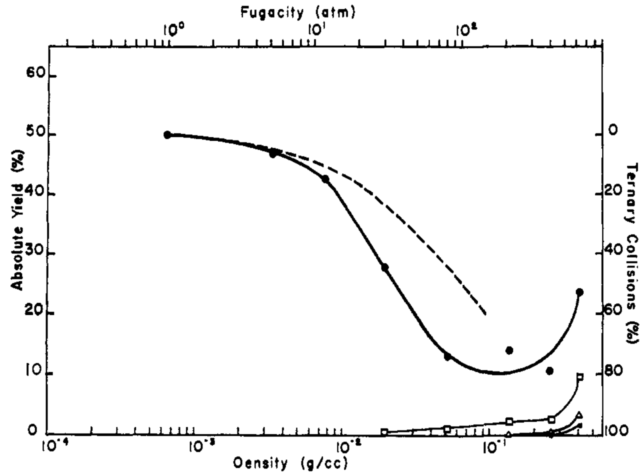

Figure 1. Density dependence of absolute yield data in the CH_4 system. (-----) is the number of ternary collisions expected: (●) CH_3I, (□) C_2H_5I, (△) C_3H_7I, (■) C_4H_9I. The fugacity was determined by $P/Z = (\rho RT)/M_{CH_4}$ where $\rho = g/V$. The ternary collision percentage was calculated using equations for binary and ternary collision frequencies found on pp 47 and 1147, respectively, of ref 24.

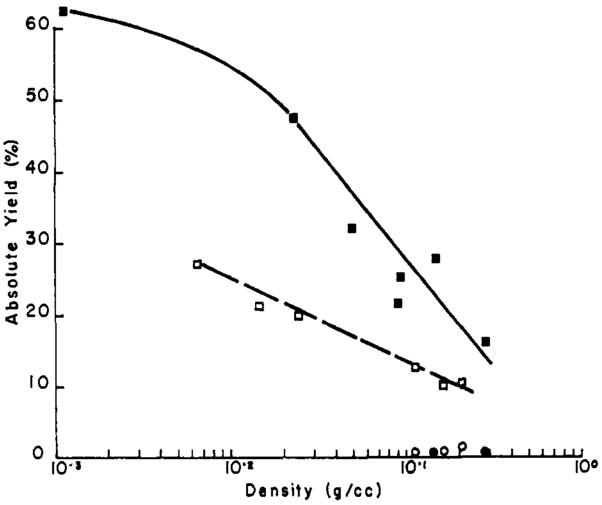

Figure 2. Density dependence of absolute yield in a CH_4/additive system. Mole fraction of Xe (0.95): (□) CH_3I; (O) C_2H_5I. Mole fraction of N_2 (0.95): (■) CH_3I; (●) C_2H_5I.

ture of 80 to 100° to separate alkyl iodides. The chromatograph was used in conjunction with an internal flow proportional counter and the data were recorded on line in a classic LINC computer,[16] where they were corrected for decay, changing background, and flow rate variations. The absolute yield of each product in the reaction mixture was determined by injecting equal aliquots onto the radio gas chromatograph and into a calibrated NaI(Tl) well counter. Combining these data with the per cent organic yield, determined from the organic–aqueous extraction, and using the NaI(Tl) counters to assess the per cent of the organic phase that was eluted from the column, the absolute yield of each volatile reaction product can be determined.

Results and Discussion

The variation in absolute yield of the reaction products with density is shown in Figures 1 to 6; these were all carried out in the absence of molecular iodine scavenger, which has been shown[3a] to have little effect on the organic yield in ethane and methane at 1 atm.

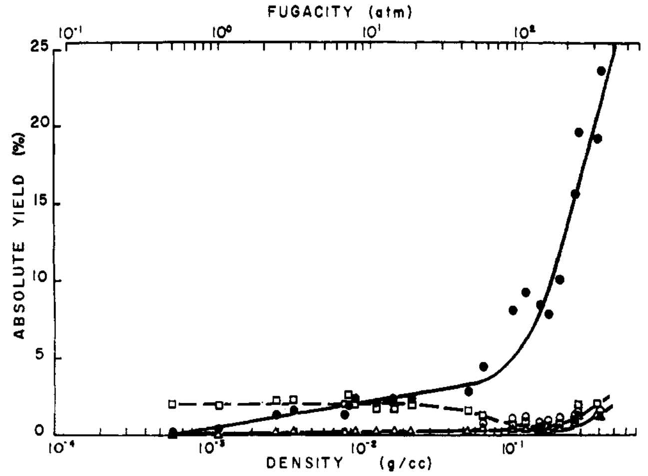

Figure 3. Density dependence of absolute yield in the C_2H_6 system: (□) CH_3I, (△) C_2H_3I, (●) C_2H_5I, (O) C_3H_7I. The fugacity was determined by $P/Z = (\rho RT)/M_{C_2H_6}$.

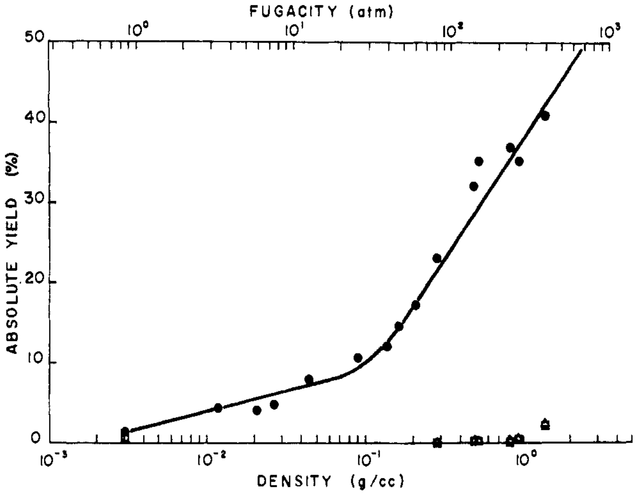

Figure 4. Density dependence of absolute yield in a 0.05 mol fraction of C_2H_6 and a 0.95 mol fraction of CF_4 mixture: (□) CH_3I, (△) C_2H_3I, (●) C_2H_5I. The fugacity was determined by $P/Z = (TR\rho)/(0.96M_{CF_4} + 0.04\,M_{C_2H_6})$.

Absolute organic yield data for the solid phase reactions of ^{123}I with C_2H_6, CH_4, and C_2H_6/CF_4 are given in Table I. Perhaps the most noticeable qualitative feature of these pressure trends is that as the pressure increases the organic yield in methane decreases and that in ethane increases. The difference in reactivity of recoil iodine with methane and the other hydrocarbons has been emphasized by many researchers as one of the most notable effects in iodine hot atom chemistry.[3d,e,6,17] By comparing Figures 1 and 3, it

Table I. Product Distributions in the Solid Phase

	Absolute yield, %				
Substance	CH_3I	C_2H_3I	C_2H_5I	C_3H_7I	C_4H_9I
CH_4	24.3		7.76	1.83	1.60
C_2H_6	1.39	3.09	27.2	3.7	12.3
C_2H_6/CF_4	2.28	2.93	40.8		

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(16) 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.

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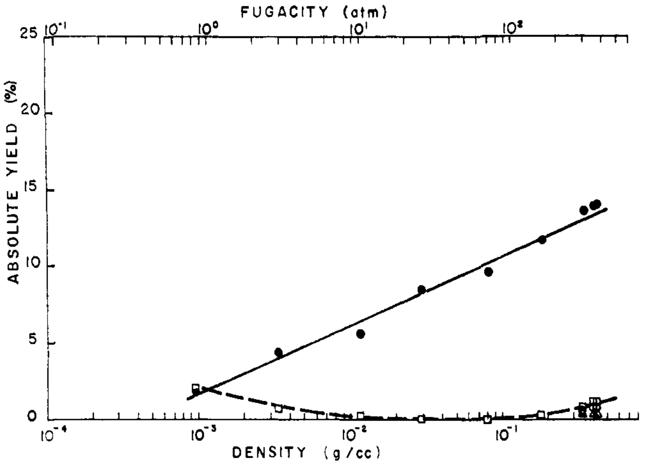


Figure 5. Density dependence of absolute yield in a 0.05 mol fraction of C_2H_6 and a 0.95 mol fraction of N_2 mixture: (□) CH_3I, (△) C_2H_3I, (●) C_2H_5I. The fugacity was determined by $P/Z = (TR\rho)/0.95M_{N_2} + 0.05M_{C_2H_6}$.

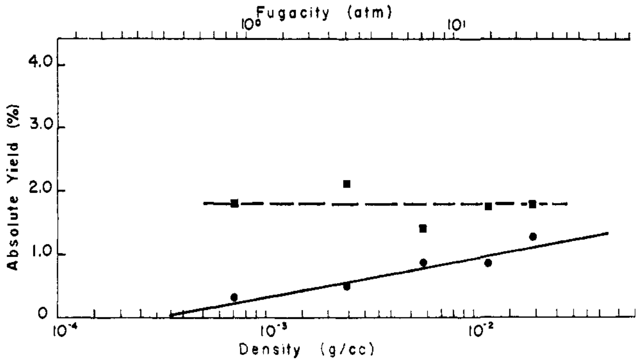


Figure 6. Density dependence of absolute yield in a 0.05 mol fraction of C_2H_6 and a 0.95 mol fraction of Ne mixture: (■) CH_3I, (●) C_2H_5I. The fugacity was determined by $P/Z = (TR\rho)/(0.95 \cdot M_{Ne} + 0.05\ M_{C_2H_6})$.

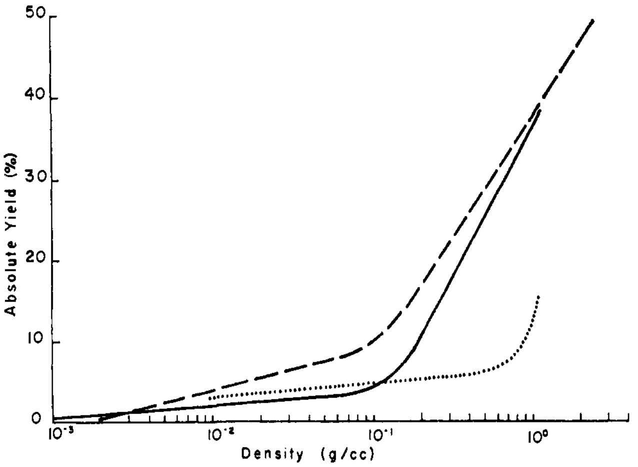


Figure 7. Comparison of the density dependence of the absolute yields of C_2H_5I in the C_2H_6 and C_2H_6/CF_4 systems with the absolute yield of $CH_3{}^{18}F$ in reactions of ^{18}F with CH_3F: (——) $C_2H_5{}^{123}I$ in C_2H_6, (- - - - - -) $C_2H_5{}^{123}I$ in C_2H_6/CF_4, (. . . . . .) $CH_3{}^{18}F$ in CH_3F (ref 13).

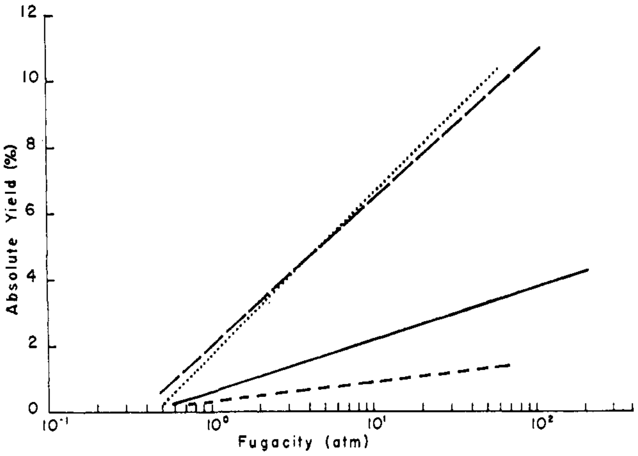


Figure 8. Comparison of the fugacity dependence of the absolute yield of $C_2H_5{}^{123}I$ in the low-pressure region: (. . . . . . .) C_2H_6/CF_4, (- - -) C_2H_6/N_2, (——) C_2H_6, (- - - - - -) C_2H_6/Ne.

is seen that the difference in reactivity with ethane and methane is drastic at 1 atm where the ratio of

$$\frac{\text{organic yield in methane}}{\text{organic yield in ethane}}$$

equals 25. However, at 100 atm the ratio is only 1.25, and in the liquid phase the ratio is 0.85. So qualitatively at these high pressures the reactivity of the iodine species with ethane and methane is approximately equal. When comparing the reactivity of iodine with methane and another hydrocarbon, it appears essential to compare the reactivity over a wide pressure range.

Figure 7 is a composite of Richardson and Wolfgang's data on the reaction of ^{18}F with CH_3F as a function of the logarithm of the density, as well as the data from the study on the ethyl iodide yields in the C_2H_6 and C_2H_6/CF_4 systems. As can be seen, the general characteristics of the curves are identical. This similarity helps substantiate Richardson and Wolfgang's hypothesis that the hot atom reaction of ^{18}F with CH_3F is insensitive to large temperature changes, as the data in our work were obtained entirely in the gas phase at a constant temperature.

The data of both groups indicate that there are two distinct mechanisms that operate at these high fugacities. At densities up to approximately 0.1 g/cc there is a linear increase in the ethyl iodide yield. As the density continues to increase beyond this point, there is a rapid rise in the total organic retention. Gas phase values obtained at high pressures extrapolate to the identical values found in the solid state at 77°K. The second phase is also characterized by the appearance of iodine compounds containing three- and four-carbon atoms, and in the pure ethane experiments there was an initial drop in the CH_3I yield. Ethane and 0.05 mol fraction of ethane in a CF_4 environment both extrapolate to the same yield at maximum density, 48%. The C_2H_6/CF_4 and C_2H_6/N_2 mixtures differed from the pure C_2H_6 in that there was no evidence for either propyl or butyl iodides in the former.

The variation of product yield *vs.* the log of the density for the CH_4 system also has two components. The second phase is still characterized by an increase in organic yield around 0.1 g/cc, but the initial phase shows a decrease in the methyl iodide yield from 50% at 5 atm to 12% at 100 atm.

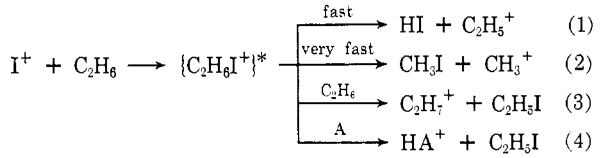
Low-Density Region. C_2H_6 System. Figure 8 is a plot of absolute yield *vs.* fugacity for the low-density regions of the various ethane systems. This linear portion is similar to that found in unimolecular decay data, when a vibrationally excited product is stabilized with increasing pressure. This sort of competition between unimolecular decay and collisional stabilization is not possible in our system, since the direct production of either $C_2H_5I^+$ or C_2H_5I by a displacement reaction with I^+ is thermodynamically disallowed for I^+ with less than 18.3 kcal/mol energy above ground state $I^+(^3P_2)$ (Table II). The excited triplet states, $^3P_0$ and $^3P_1$, possess 18.4 and 20.7 kcal/mol, respectively, and have sufficient energy to form $C_2H_5I^+$. However, as exothermic charge exchange cannot occur, the C_2H_5I molecule would decompose following charge neutralization due to the >200 kcal/mol exothermicity of this reaction.[3a] The possible role of high-pressure stabilization of excited C_2H_3I will be discussed later. The $I^+(^1D_2)$ state will, as previously shown,[3a] undergo exothermic charge exchange with C_2H_6. Further evidence that this increase in the $C_2H_5{}^{123}I$ yield is not due to unimolecular decay of an excited intermediate will be given at the end of this section.

Table II. Thermodynamic Data for the Reaction of $I^+(^3P_2)$ with C_2H_6

Reaction	ΔH^a
$I^+ + C_2H_6 \rightarrow C_2H_5I^+ + H$	18.3
$I^+ + C_2H_6 \rightarrow C_2H_5I + H^+$	117.4
$I^+ + C_2H_6 \rightarrow HI + C_2H_5{}^+$	−21.5
$I^+ + C_2H_6 \rightarrow CH_3I + CH_3{}^+$	9.4
$I^+ + 2C_2H_6 \rightarrow C_2H_5I + C_2H_7{}^{+b}$	−7.4
$I^+ + C_2H_6 + CF_4 \rightarrow C_2H_5I + CF_4H^+$	−9.6
$I^+ + C_2H_6 + N_2 \rightarrow C_2H_5I + N_2H^+$	1.4
$I^+ + C_2H_6 + Ne \rightarrow C_2H_5I + NeH^+$	69.4

[a] All thermochemical data in kcal/mol at 298°K. Data taken from "Electron Impact Phenomena," revised ed, Field and Franklin, Ed., Academic Press, New York, N. Y., 1970, and from J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971). [b] $C_2H_7{}^+$ can also dissociate to form $C_2H_5{}^+$ and a hydrogen molecule.

Another type of competition which would give a linear increase in $C_2H_5{}^{123}I$ yield with pressure is shown in the following reaction scheme (eq 1–4) where $\{C_2H_6I^+\}^*$ is internally excited and can either eliminate HI or transfer a proton to ethane. If this model is correct, one would expect that additives such as N_2 and CF_4 would be capable of accepting a proton, while substances with lower gas phase basicities such as Ne would be incapable of accepting a proton. Figure 8 demonstrates that the yield of ethyl iodide is much greater in the CF_4/C_2H_6 and N_2/C_2H_6 systems than in the Ne/C_2H_6 system, with the thermodynamic data for ground state I^+ summarized in Table II. Persistent complexes such as $C_2H_6I^+$ have been seen in high-pressure mass spectrometry. Field and Beggs[18] observed that the "unreactive" $CH_5{}^+$ ion will form a complex with methane at temperatures in the range 77–370°K and at pressures of 0.1–1 Torr. In addition, it was seen that the $CH_4 \cdot CH_5{}^+$ species was capable of undergoing the reaction



$$CH_4 \cdot CH_5{}^+ + CH_4 \rightleftarrows (CH_4)_2 \cdot CH_5{}^+$$

In all cases the lifetimes of these complexes increased as the temperature was lowered. Bennett, *et al.*,[19] observed the same type of persistent complex in the ethane system and demonstrated a variety of decomposition pathways as well as collisional stabilization of these intermediates at pressures of only 0.1 Torr. Ausloss, *et al.*,[20] demonstrated the importance of a proton acceptor in stabilization of these intermediates. In particular, they studied the radiolysis of ethane at 100 Torr and observed the reaction

$$C_2H_5{}^+ + C_2H_6 \longrightarrow C_4H_{11}{}^+ \xrightarrow{A} C_4H_{10} + AH^+$$

where A is a proton acceptor.

Loberg and Welch[3a] invoked intermediates of the same type to account for the reactions of recoil iodine with CH_4, giving evidence for the formation of a persistent complex followed by proton transfer to stabilize the intermediate.

A mechanism of the same type can also be used to explain the results of the reactivity of recoil iodine with ethane. Here it is shown that, although there is less than 0.5% ethyl iodide produced at 1 atm by the reaction of recoil ^{123}I with ethane, there is a linear increase in the yield of ethyl iodide with the log of the pressure and that this rate of increase is proportional to the gas phase basicity of the bath gas. Since ethyl iodide is the predominant product at densities of approximately 0.1 g/cc, and since formation of C_2H_5I is thermodynamically disallowed in a direct process, we take this correlation between the gas phase yield of ethyl iodide and the reactive gas phase basicity as good evidence for a competition of the type illustrated by reactions 1 and 4.

Pure C_2H_6 has an intermediate C_2H_5I yield indicative of its ability to form $C_2H_7{}^+$, but the pressure-dependent increase is much less than in a CF_4 or N_2 bath. This reduced slope can be attributed to a more energetic $C_2H_6I^+$ coming from a direct associative complex of C_2H_6 and I^+, rather than an I^+ transfer between an excited intermediate and C_2H_6. A larger amount of internal energy for the complex is consistent with a shorter lifetime for HI elimination. Further evidence for increased excitation of the complex can be found in the fact that considerably more CH_3I is produced in pure C_2H_6 than in C_2H_6 mixtures with either N_2 or CF_4. The production of CH_3I from a reaction of I^+ and C_2H_6 is a considerably more energetic process than the reaction pathway leading to C_2H_3I or HI and requires I^+ to be in an excited electronic state to initiate the reaction. Thus at 1 atm of pressure the predominant reaction pathway leading to stabilization of the C–I bond is the reaction of an electronically excited I^+ species with pure ethane (reaction 2). As the density increases to 0.1 g/cc, proton transfer from the excited intermediate (reaction 3) competes on a time scale comparable with HI elimination (reaction 1).

The constant yield of CH_3I throughout this density

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region is to be expected. One might expect the relative rates for HX elimination and radical dissociation to be similar for the decay of both excited radicals and ions. Radical dissociation pathways for neutral molecules have preexponential factors for unimolecular decay two or more orders of magnitude faster than competing 1,2-HX elimination pathways.[21,22] Thus the rate constant (k_e) for radical dissociation of neutral molecules is a much steeper function of energy than is k_e for elimination. Consequently, at energies only 20% above the critical energy for that decomposition pathway, radical dissociation of ethane has been predicted to predominate over elimination.[22]

Low-Density Region. CH_4 System. As seen from Figures 1 and 2, the organic yield in the methane system decreases up to pressures of 100 atm in pure methane and in the methane/nitrogen and methane/xenon systems. The yield in methane/xenon is always less than in pure methane, which is less than that in methane/nitrogen. This selectivity, which we have reported previously at 1 atm, continues throughout the pressure range studied. That the chemical selectivity of the reaction appears to be preserved leads us to believe that the decrease in organic yield with pressure involves all the reactive states (^3P, $^1D_2$, and ^1S) that we have invoked to explain the difference in reactivity at 1 atm.

The pressure dependence in the methane system contrasts drastically with that in the ethane system, as in this system we are observing a decrease in organic yield. Whereas in the ethane system collisional stabilization leads to organic products, in the methane it yields inorganic products.

In the methane system we propose that the reaction to form methyl iodide is

$$I^+ + CH_4 \longrightarrow \{CH_4I^+\}^*$$

$$\{CH_4I^+\}^* + CH_4 \longrightarrow CH_3I + CH_5^+$$

$$\Delta H_0(\text{total}) = -3.1 \text{ kcal/mol for } I^+(^3P_2)$$

whereas in the ethane system the sequence will be

$$I^+ + C_2H_6 \longrightarrow \{C_2H_6I^+\}^*$$

$$\{C_2H_6I^+\}^* + C_2H_6 \longrightarrow C_2H_5I + C_2H_7^+$$

$$\Delta H_0(\text{total}) = -7.4 \text{ kcal/mol for } I^+(^3P_2)$$

In these mechanisms we assume that the intermediate XI^+ is a persistent collision complex rather than a molecular ion. Assuming that this is the case, we can estimate ΔH_0 for the reaction

$$I^+ + X \longrightarrow XI^+$$

which will be the potential energy due to the attraction of the species at a collision distance (r).

In the Langevin treatment[23] of a collision between a singly charged ion and a nonpolar molecule the potential, V_p, between the pair is

$$V_p(r) = -{}^1/_2(\alpha e^2/r^4)$$

where α is the electronic polarizability of the neutral molecule, e is the charge on the electron, and r is the ion–molecule separation distance. Using values for α of 2.699×10^{-24} and 4.326×10^{-24} cc/mol[24] for CH_4 and C_2H_6, respectively, setting r equal to 3.18 and 3.46 Å[25] for CH_4I^+ and $C_2H_6I^+$, respectively, and equating $-V_p(r)$ to the vibrational energy of the intermediate, one finds that the persistent complexes CH_4I^+ and $C_2H_6I^+$ have vibrational energies of 4.36 ± 0.3 and 4.99 ± 0.3 kcal/mol, respectively. In these intermediates the carbon will exist as pentavalent carbon, so presumably the C–H bonds are weakened, leading to a weak bonding of the iodine.

From these calculations we see that

$$CH_4I^+(gs) + CH_4 \longrightarrow CH_3I + CH_5^+$$

$$\Delta H_0 = +1.4 \text{ kcal/mol}$$

$$C_2H_6I^+(gs) + C_2H_6 \longrightarrow C_2H_5I + C_2H_7^+$$

$$\Delta H_0 = -2.4 \text{ kcal/mol}$$

Therefore, for the reaction to methyl iodide the intermediate must be vibrationally excited. Normally this is likely to be the case, as even the ground state $I(^3P_2)$ will leave the intermediate with over 4 kcal/mol, and the excited I^+ states will leave the intermediate with more energy. However, if the initial collision of I^+ is a three-body collision, the intermediate could be formed in the ground state and so the reaction to methyl iodide would not proceed. The number of three-body collisions predicted in the iodine/methane system is shown in Figure 1. It is seen that this curve has a similar shape to that of the organic yield in methane. In fact, a competitive reaction treatment of the data predicts the experimentally obtained curve if the ratio

$$\frac{\text{probability of deactivation upon 3-body collision}}{\text{probability of reaction upon 2-body collision}} = 2.3$$

We do know from our previous work with additives[26] that the overall reaction of

$$I^+ + CH_4 \longrightarrow CH_3I$$

occurs at the most on one out of every 60 collisions, so this model predicts that one out of 26 of the three-body collisions affects the intermediate formed.

In the ethane system the second reaction will proceed even if the intermediate is in the ground state and so the opposite trend is observed, and our mechanism is a possible explanation of the observed trends.

High-Density Region. C_2H_6 and CH_4 Systems. The reaction component which occurs at high density was attributed by Richardson and Wolfgang[13] to caging. This region appears at densities corresponding to 0.1 and 0.5 g/cc for iodine and fluorine, respectively, and continues on to densities characteristic of the particular solid. Helton, *et al.*,[27] have recently studied the reactions of recoil ^{80}Br with CH_3F and likewise report a large increase in the high-density region. Their work was done entirely in the liquid phase, with the density being changed by varying the reaction temperature, and reveals that the high-pressure reactivity region for bromine begins around or below 0.3 g/cc.

An examination of the three systems studied to date

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[22] H. W. Chang, N. L. Craig, and D. W. Setser, *J. Phys. Chem.*, 76, 954 (1972).

[23] E. W. McDaniel, "Collisional Phenomenon in Ionized Gases," Wiley, New York, N. Y., 1964, p 67 and Appendix II.

[24] E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1961, p 383.

[25] A. P. Kudchadker, G. H. Alani, and B. J. Zwolinski, *Chem. Rev.*, 68, 659 (1968). Value for I^+ estimated to be 1.28 Å.

[26] We have shown that neopentane deactivates I^+ at least 60 times as efficiently as the reactivity with methane.

[27] R. W. Helton, S. M. Grover, and E. P. Rack, *Radiochim. Acta*, in press.

indicates that as the van der Waals diameter of the reacting atom is decreased, the density necessary to bring about the enhanced organic yields increases. This is, of course, consistent with the autoradiolysis hypothesis as the smaller the diameter of the halogen species the denser the radical and ion cage necessary to contain it. The fact that the recoil iodine reacts with this radical and ion cage to form organic products attests to the greater diffusion coefficients of inorganic radicals compared with organic radicals.

The exact nature of the primary reactions occurring in the high-density environment is difficult to elucidate, as both ion–molecule and radical recombination mechanisms have been shown to be important. Richardson and Wolfgang[13] attributed the radiolytic reactions to secondary recombinations

$$CH_3 + {}^{18}F \longrightarrow CH_3{}^{18}F$$

$$CH_2F + {}^{18}F \longrightarrow CH_2F{}^{18}F$$

The high-density region in the methane and ethane systems is characterized by a rapid increase in the yields of methyl and ethyl iodide, respectively. This density region is also marked by the appearance of polymerization products. These three and four carbon containing iodine compounds show a steady increase throughout the high-density region. Their appearance could be attributed to both ion–molecule reactions and radical recombinations. Tiernan and Hughes[28] examined ion–molecule reactions in C_2H_5Cl at a pressure of 1 Torr. Although they found that the major stable ion in their system was $C_4H_{10}Cl^+$, when they compared these results with the results for radiolysis of the same system, they concluded that the major radiolytic mechanism was excited neutral molecule decomposition rather than ion formation. The production of radical products from the radiolysis of CH_4 and C_2H_6 followed by radical recombination with incorporation of iodine into the organic product appears quite consistent with the data, but definitive evidence for either ionic or free-radical mechanisms cannot be deduced from the appearance of polymerization products. Some additional information about the radiolytic mechanism can be found by examining the C_2H_6/CF_4 and the C_2H_6/N_2 systems, Figures 4 and 5. In these mixed systems the reactant, ethane, is present to the extent of only 0.05 mol fraction. The bath gases, CF_4, and N_2, have been shown to be inert in low-pressure regions by us and others.[3f] These gases were also examined in the high-pressure regions and found to negligibly enhance organic yields. The difference between the two systems, C_2H_6/CF_4 and C_2H_6/N_2, can be found in the fact that the former mixture displays a marked change in the slope of the C_2H_5I yield at a density of 0.1 g/cc, while the latter system does not show any such change up to a density of 0.4 g/cc. This observation can be explained in terms of the manner in which the radical radiolytic products of the two bath gases vary in their behavior toward $I\cdot$. Examination of the radiolytic behavior of CF_4[29] has shown that when CF_4 is bombarded by electrons and γ-rays at high fluxes for 4 weeks, 98–99% of the CF_4 is recovered as CF_4. This fact attests to the very high recombination rates of the two initial radical products, CF_3 and F, as compared with dimerization to form C_2F_6. This high recombination rate for the radical debris to re-form the parent, CF_4, is consistent with the fact that this radiolytic debris from CF_4 does not deactivate the high-density mechanism.

The three and four carbon ^{123}I containing compounds that are characteristic of the high-density region are absent in the C_2H_6/CF_4 system, but the total organic retention is approximately the same for the C_2H_6 and the C_2H_6/CF_4 systems extrapolated to the solid state. The decrease in the yield of the C_3 and C_4 compounds in the C_2H_6 system is compensated for by the increase in maximum C_2H_5I yield from 27.2 to 40.8% in the C_2H_6 and C_2H_6/CF_4 systems, respectively. All of these facts indicate initial radiolysis of both the C_2H_6 and the CF_4 followed by fast recombination of the CF_3 and F to reproduce the parent CF_4, resulting in the radiolysis products of C_2H_6 being dispersed in a bath gas of CF_4. The iodine species is apparently capable of migrating to these hydrocarbon species before the radiolysis debris can diffuse away. The lack of dimerization products in the C_2H_6/CF_4 system is indicative of the fact that the C_2H_6 radiolysis products are being diluted by an inert bath gas of CF_4. The inertness of CF_4 as a bath gas was confirmed by reacting ^{123}I with pure CF_4 at densities greater than 0.4 g/cc. The total organic yield was 1.5% CF_3I identified by radio gas chromatography. The small yield of this stable compound is further evidence of the rapidity of the CF_3–F recombination.

The C_2H_6/N_2 system does not exhibit the rapid increase in C_2H_5I yield at a density of 0.1 g/cc, but rather continues the product distributions characteristic of the low-density region up to the maximum obtainable density, 0.4 g/cc. This absence of the effects due to radiolysis may be attributed to the reactions of the resultant iodine species with the radiolysis products of N_2.

The Possible Role of Unimolecular Decomposition of C_2H_5I. The pressure dependence of product yields can be used to estimate the internal energy of molecules activated through energetic atomic substitution reactions. In the past such calculations have been applied to recoil tritium[30] and fluorine[14] reactions in a straightforward extension of the chemical activation technique of unimolecular kinetics. We have considered the possible role of unimolecular decay of $C_2H_5{}^{123}I$ to the observed products $CH_3{}^{123}I$ and $C_2H_3{}^{123}I$ as an alternative to the ion–molecule arguments.

$${}^{123}I + C_2H_6 \longrightarrow (C_2H_5{}^{123}I)^* + H$$

$$(C_2H_5{}^{123}I)^* \xrightarrow{S} C_2H_5{}^{123}I$$

$$\xrightarrow{D1} C_2H_4 + H^{123}I$$

$$\xrightarrow{D2} C_2H_3{}^{123}I + H_2$$

$$\xrightarrow{D3} C_2H_5\cdot + {}^{123}I$$

$$\xrightarrow{D4} CH_3 + CH_2{}^{123}I$$

$$CH_2{}^{123}I + C_2H_6 \longrightarrow CH_3{}^{123}I + C_2H_5\cdot$$

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[28] T. O. Tiernan and B. M. Hughes, ref 12, p 412.

[29] (a) W. C. Askew and T. M. Reed, *Nucl. Sci. Eng.*, **29**, 143 (1967); (b) T. M. Reed, J. C. Mairen, and W. C. Askew, AEC Report No. TID 22421.

[30] (a) E. K. C. Lee and F. S. Rowland, *J. Amer. Chem. Soc.*, **85**, 897 (1963); (b) Y. N. Tang and F. S. Rowland, *J. Phys. Chem.*, **72**, 707 (1968); (c) C. F. McKnight, N. J. Parks, and J. W. Root, *ibid.*, **74**, 217 (1970).

The thermochemical minimum energy for process D1 is 50 ± 2 kcal/mol[31] and the value for D3 is 51 kcal/mol.[32] The minimum energy for H_2 elimination (process D2) would be even higher. We estimate the energy required for process D4 to be 83 ± 3 kcal/mol.[33] In the limit of very low pressure, any primary reaction product formed with sufficient internal energy to decompose will do so. Because no $C_2H_5{}^{123}I$ stabilized product is observed at low pressure, one is forced by a unimolecular decay model to conclude that the primary product $(C_2H_5{}^{123}I)^*$ is always formed with greater than 50 ± 2 kcal/mol of internal excitation. The mean energy determined from the half-pressure for stabilization would be even higher. Some molecules always decompose by C–C bond rupture (D4) so that they are formed with more than 83 kcal/mol of internal excitation.

All of the available studies in iodine hot atom chemistry point to low-energy reaction pathways. In contrast to recoil tritium or ^{18}F systems, the attacking ^{123}I atom does not have translational excitation sufficient to impart this degree of internal excitation to the primary reaction product. The enthalpy of the ion–molecule reactions summarized in Table II shows that they also cannot be a source of 50 kcal or more of internal excitation. Any unimolecular energetics arguments therefore lead to conclusions which are completely inconsistent with the observed behavior and known energetics of recoil ^{123}I systems, and we feel they lend support to the argument that excited neutral ethyl iodide molecules are not important as intermediates in the $^{123}I/C_2H_6$ reaction systematics. The high-pressure yields are also not accounted for by collisional stabilization of $(C_2H_5{}^{123}I)^*$. Unimolecular decomposition rate constants favor stabilization of the highest energy decomposition pathway at very high pressure because a smaller amount of energy must be transferred by the primary product to reduce its internal energy below the minimum for decomposition. The highest energy decomposition pathway (D4) leads to an experimentally measurable product $(CH_3{}^{123}I)$ which should therefore exhibit a decrease in yield complementary to the sharp increase in $C_2H_5{}^{123}I$ yield above 100 atm. Such a relationship is not observed. The increase in $C_2H_5{}^{123}I$ yield at high pressures is therefore not due to stabilization of a primary substitution product that is extensively decomposed below 100 atm, but rather to a new species characteristic of the high-density radical and ion environment as discussed in the previous section.

Conclusion

In these experiments the density has been varied continuously throughout the range characteristic of a dilute gas to that typical of condensed media. In this range we have found that there are two distinct mechanisms, one governed by the chemical energetics of the hot ^{123}I species reacting with its thermoequilibrated solvent, the other governed by the chemical energetics of the radiolytic envelope surrounding the hot ^{123}I atom. In addition, we have shown that the second system, $^{123}Xe \rightarrow {}^{123}I$, allows one to study the reactions of thermal $^{123}I^+$ ions up to a density of 0.1 g/cc without any reactor or cyclotron produced radiolysis of the system. The mechanism at the lower pressure involves molecular ions and is an extension of that developed by us to explain the reactions of iodine atoms with methane moderated systems. The previous mechanism has to be modified to include the formation of CH_4I^+ in all systems. In pure CH_4 the mechanism of formation is direct associative combination, whereas in highly moderated systems it involves I^+ transfer from the excited intermediate to CH_4.

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(33) We do not have a measured bond dissociation energy for CH_3-CH_2I but estimate our value based upon those for C_2H_6 and C_2H_5Br given in ref 32.