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DEPARTMENT OF CHEMISTRY

MASTER

HALOGEN ATOM REACTIONS ACTIVATED BY RADIATIVE
NEUTRON CAPTURE AND ISOMERIC TRANSITION

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Department of Chemistry

Progress Report No. 6

February, 1971 - February, 1972

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Edward P. Rack, Project Director

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PREFACE

The following is a report of the work completed during the period February 15, 1971 to February 14, 1972. These studies were supported by the U. S. Atomic Energy Commission, Division of Research, Contract No. AT(11-1)-1617, the Department of Chemistry of the University of Nebraska, and the University Research Council. Most of the material for this report has been accepted, submitted, or will be submitted for journal publication. Because of the U. S. Atomic Energy Commission's depository library system and the facilities of the Technical Information Service at Oak Ridge, it is possible to make available through a progress report the extensive original data only summarized in journal publications and results of unsuccessful experiments. It is hoped that this report will be of added value to workers in the field.

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CHAPTER I. FACILITIES

A. Triga Mark II Reactor

All neutron irradiations were made in the Triga Mark II "swimming pool" nuclear reactor at the Veteran's Administration Hospital at Omaha, Nebraska. A flux of 1×10^{17} thermal neutrons $\text{cm}^{-2} \text{sec}^{-1}$ was present at an operating power of 15.5 kilowatts. Various positions in the "lazy susan" sample holder were employed and the assembly was rotated to ensure that all samples received the same neutron flux and radiation dose. For very short irradiations the assembly was not rotated and samples were irradiated in the same position. The radiation dose was approximately 3×10^{17} e.v.g. $^{-1} \text{min}^{-1}$ using Fricke dosimetry.

This past year the reactor operated routinely for at least four eight-hour days a week at 15.5 kilowatts. The radiochemistry group used for the period from August 1, 1970, to July 31, 1971, 330 hours (integrated time in reactor) at 15.5 kilowatts power, making 2,500 irradiations.

B. Radiochemistry Laboratory

All sample preparation and much of the radioassaying were performed in a well-equipped, specially-designed radiochemistry laboratory in the new Hamilton Hall Chemistry building. The two hot laboratories contain four six foot "Oak Ridge-Type" hoods, several radioactive waste sinks, radiation safety equipment, seven separate vacuum lines for preparing gas, liquid and solid state systems, and

the usual laboratory facilities. The counting room is equipped with two radiogas chromatographs, three single-channel analyzers with several 2" x 2" NaI crystals, four GM counting stations, four gas-flow counters, and a Nuclear-Data 128-Channel analyzer with a 3" x 3" NaI crystal specially housed in a concrete, cadmium and lead cave.

If and when we get a neutron generator we have a specially-constructed room for its housing. This room is presently used for equipment storage.

For most of our ^{80}Br , ^{38}Cl and ^{128}I organic yield experiments, we used the radiochemistry facilities and radioassaying equipment of the Omaha VA Hospital. The use of their RIDL 400-channel analyzer with 3" x 3" NaI crystal was most helpful in many of our studies.

CHAPTER II. INFLUENCE OF RARE GAS MODERATORS ON IODINE-130

REACTIONS ACTIVATED BY RADIATIVE NEUTRON CAPTURE AND

ISOMERIC TRANSITION WITH CH_4 AND CD_4

(J. Blair Nicholas)

The reaction of ^{128}I with gaseous methane has been an important illustration of a chemical reaction activated by a nuclear process.^{1,2} The ^{128}I atoms produced by the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ process in gaseous methane are able to displace hydrogen from methane forming methyl iodide, 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. The reactive iodine species in reactions of (n,γ) -activated ^{128}I with methane have been shown to be atoms or ions possessing excess kinetic energy and translationally thermalized but electronically excited $\text{I}^+(^1\text{D}_2)$ ions, or I^+ ions in $^3\text{P}_2$, $^3\text{P}_1$, and/or $^3\text{P}_0$ states.³

One striking feature of iodine reactions is that yields and product distributions of ^{130}I and ^{128}I activated by (IT) and (n,γ) processes, respectively, are similar to yields and analogous product distributions of ^{82}Br activated by (IT) events in cyclohexane and other C_5 - C_9 hydrocarbons. The likeness between ^{130}I , ^{128}I , and ^{82}Br yields and product distributions suggest that activated halogens may trace chemical processes which result from a similarity of environmental activation and/or decomposition.^{4,5}

Both the (n, γ) and (IT) activation processes are capable of imparting kinetic energy to the product atoms, though the mechanism differs in the two events. By (n, γ) activation an atom obtains kinetic energy as it recoils from gamma rays emitted by the excited nucleus produced by neutron capture. Product atoms from isomeric transition acquire kinetic energy from a Coulombic repulsion mechanism as a result of internal conversion and Auger electron emission.

We would not necessarily expect the ^{128}I limiting organic yield to be the same as the ^{130}I limiting organic yield in the gas phase because of the fact that they are born by different nuclear activations. Since iodine reactions are relatively complicated with respect to kinetic energy and excited-state contributions to the organic yield, we would not expect iodine specie to be born in the same ratio between the ^{128}I and ^{130}I isotopes.

In this chapter we report in detail the gas phase reactions of $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}^{\text{m}} + ^{129}\text{I}(\text{n},\gamma)^{130}\text{I}$ and $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ induced reactions with CH_4 and CD_4 in an attempt to gain information concerning isotope effects and mode of activation effects, and relative importance of positive charge, excitation energy, and kinetic energy to the various reactions; and compare the results to the previously-studied ^{128}I system. Specifically we are determining the effects of rare gas moderators on the organic yields in the various organic reaction systems.

Preparation of Reaction Systems

The reactions of $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ activated by neutron capture and the $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ and $^{82}\text{Br}^{\text{m}}(\text{IT})^{82}\text{Br}$ reactions with CH_4 and CD_4 were

studied in reaction mixtures containing I_2 or Br_2 scavenger and rare gas moderators. Vacuum line techniques were used in the preparation of all systems.

Quartz ampoules, varying in size from 7 to 10 ml, were washed with nitric acid, rinsed with ammonium hydroxide, rinsed three times with distilled water, heated to dryness, and then sealed to quartz capillary tubing which could be connected to the vacuum line by means of a ground-glass (12-3) ball-socket joint. After sealing the quartz ampoule to the capillary tubing, the necks of the quartz-ampoules were constricted by heating to facilitate easy sealing of samples after preparation of reaction mixtures. The stem and ampoule were cleaned again in the same manner described above. The rinsing was accomplished by alternately cooling the ampoule in liquid nitrogen while introducing the rinsing liquid and then heating the ampoule to expel the liquid and gaseous waste. The cleaning procedure was effective in removing any soluble contamination from the quartz surface. The sample ampoules were connected to the vacuum line, evacuated, and flamed to a red glow under vacuum to volatilize and remove any absorbed substances inside. After evacuating for several minutes, the ampoules were tested for leaks using a tesla coil.

Quartz, rather than pyrex, was used for several reasons. The neutron-induced activity in quartz was much less than in pyrex or other softer glasses. Sodium-24, which is produced in sodium-containing glasses, could be leached out in chemical extractions, described later, and affect the radioactive assaying. Quartz was also used because of its low coefficient of expansion which allowed it to undergo extreme

and sudden temperature changes without breakage.

Preparation and Irradiation of Gaseous Iodine Samples

Iodine-129 was obtained from Oak Ridge National Laboratory in aqueous NaI^{129} solution. $\text{CH}_3\text{I}^{129}$ was prepared by extracting the NaI^{129} into $\text{CH}_3\text{I}^{127}$ with H_2O_2 catalyzed with a trace of HNO_3 . The solution was washed, dried, degassed four times and sealed under vacuum and allowed to undergo photochemical exchange for five days before using.⁶

Quadruplicate samples were prepared simultaneously on the vacuum line. All compounds used in the preparation of the reaction systems were either sealed directly to the vacuum line or were attached by means of a 10/30 standard ground-glass tapered joint and a system of vacuum stopcocks. All samples contained 0.1 mm I_2 in order to serve as a radical scavenger in the system. The I_2 was metered into the ampoules at its vapor pressure at ambient temperature. After several minutes for equilibrium to be established in the vacuum line and ampoules, the stopcocks leading to the four sample ampoules were closed and the excess iodine vapor was evacuated from the vacuum line. The ampoules were surrounded with aluminum foil during sample preparation to ensure against light induced reactions of I_2 and the gaseous medium. $\text{CH}_3\text{I}^{129}$, as a source molecule, was introduced into the sample ampoule by the use of stopcocks and a container of frozen $\text{CH}_3\text{I}^{129}$ (previously degassed several times) being allowed to thaw slowly. After equilibrium was established at a predetermined pressure in the vacuum line, the stopcocks leading to the four sample ampoules were opened simultaneously just long enough for equilibrium to be re-established. The vapor pressure was noted by reading the manometer

and the excess additive vapor was evacuated from the vacuum line. The rare gas moderator, if used, and the target compound, CH_4 or CD_4 , were introduced to the reaction systems (in that order) from storage containers through metering flasks in just the same manner as described above. The total gas pressure of all systems was approximately one atmosphere. The actual individual compound pressure in the system was equal to the difference between the pressure read on the manometer and the previous pressure existing in the reaction ampoule. The quartz ampoules were frozen in liquid nitrogen after removal of the aluminum foil and sealed off by heating at the thin neck constriction. The ampoules were again wrapped in aluminum foil and stored in the dark and liquid nitrogen until prepared for irradiation. The entire sample preparation was done in a dimmed room with indirect lighting sufficient to allow accurate manometer readings.

With additives having appreciable vapor pressures at liquid nitrogen temperatures, a pressure correction might be considered necessary for the amount of gas between the constricted neck of the ampoule and the stopcock leading to the vacuum system. This correction was minimized to less than experimental error by using large (10 ml) reaction ampoules in comparison to the small volume of the capillary tubing between the constricted neck of the ampoule and the stopcock. Before sealing the ampoule an internal vacuum was accomplished by warming the capillary tubing causing an extreme temperature difference between stem and ampoule which sucked most of the gas in the capillary into the ampoule immediately before sealing. No pressure correction was incorporated in calculating the mole fraction of the reaction systems. The samples were wrapped in

aluminum foil and stored in liquid nitrogen until prepared for neutron irradiation.

For the iodine samples used for the $(n,\gamma)+(IT)$ combined studies, the samples were irradiated at ambient temperature while in the gas phase in the thermal neutron flux for 2 minutes. These samples were then allowed to stand at ambient temperature in the dark for 90 minutes to allow 99.9% of the $^{130}\text{I}^m$ to decay to the ground state before extraction. Samples which were used to determine only the (n,γ) -induced ^{130}I organic yields were irradiated at ambient temperature while in the gas phase for 30 seconds and extracted 1 minute after the beginning of irradiation minimizing the effects of any isomeric transition contribution to the organic yield.

Radiation Induced Reactions

Mixtures containing rare-gas, $\text{CH}_3\text{I}^{129}$, methane, and I_2 tagged with ^{131}I were irradiated for 2 minutes so as to make a direct correlation with the moderator studies and to determine the extent of any radiation-induced reactions in the systems. Under the conditions of preparation and irradiation³ negligible ^{131}I pickup was found in systems which did not contain a rare gas additive. The data from Table I plotted in Figure 1 as percent ^{131}I appearing in organic combination for the various systems vs. mole fraction additive. The best visual straight lines were drawn through the data merging at zero-mole-fraction additive. At unit-mole fraction of rare gas additive (which corresponds to 760 ± 40 mm) the data extrapolated to 9.0%, 5.8% and 1.0% for Xe, Kr, and Ne-Ar, respectively. To determine the correction for radiation induced reactions in the iodine

moderator systems, a quantity equal to the product of the mole fraction of rare gas and the extrapolated maximum extent of ^{131}I pickup was subtracted from the observed ^{130}I organic yields.

No radiation damage correction was found necessary in the bromine moderator systems due to the solid-state irradiations of only 30 sec in duration.

Samples Containing Rare Gas Moderators

In the study of the moderation of ^{130}I and ^{82}Br reactions with CH_4 or CD_4 by rare gases, it is necessary to know whether the rare gases contribute to the measured counting rates. Krypton and xenon have appreciable numbers of radioactive isotopes formed by radiative neutron capture. Generally in the past we found negligible activities in the organic and inorganic phases from krypton containing samples. However, the organic phase of the xenon containing samples has an activity attributed to a 17.0 hr half life, which corresponds to the ^{125}Xe (16.8 hr) activity. Figure 2 shows a gamma ray spectrum of the extracted organic phase resulting from an irradiated xenon sample. The half life activity and photopeak energies correspond to those of ^{125}Xe . Figure 3 shows the gamma ray spectrum of the extracted inorganic phase resulting from the same sample. For comparison Figure 4 gives the combined gamma ray spectra of ^{125}Xe in the extracted organic and inorganic phases showing the relative intensity and contribution to the activities of the two phases.

Organic yields of iodine samples containing xenon moderators were found to be greatly altered by the relative contribution of the ^{125}Xe activity in respect to the ^{130}I activity extracted in the organic and

Table I
 Percent ^{131}I Activity in Organic Combination
 Following Reactor-Radiation Induced Pickup
 of ^{131}I in Methane-Additive Mixtures
 Containing CH_3I and $\text{I}_2\text{-I}^{131}$ (a)

Additive	Mole Fraction Additive (a)	Percent ^{131}I As Organic
Xe	0.3112	2.80
	0.3131	3.33
	0.3706	3.86
	0.5925	4.94
	0.7029	5.25
	0.8244	7.58
Kr	0.3257	1.73
	0.3279	2.52
	0.5467	2.70
	0.8625	4.70
	0.8947	5.40
Ne	0.3095	0.54
	0.4750	0.47
	0.6144	0.39
	0.8337	0.61
Ar	0.3095	0.75
		1.03
	0.4750	0.38
		0.67
	0.6144	0.26
	0.6312	1.02
	0.8337	0.44

- (a) Samples contained $0.1 \pm 0.02\text{mm I}_2\text{-I}^{131}$ and $15.0 \pm 0.3\text{mm CH}_3\text{I}$ at a total pressure approximately one atmosphere. They were irradiated for 2 minutes at ambient temperature.
- (b) Calculated assuming additive pressures. Error ± 0.002 .

Figure 1. Reactor-radiation induced pickup of ^{131}I in methane-additive mixtures containing $\text{CH}_3\text{I}^{129}$ and ^{131}I tagged I_2 . Xenon, $\square$; Krypton, $\blacksquare$; Ne-Ar, $\bullet$.

Figure 2. Gamma ray spectrum of ^{125}Xe extracted into the organic phase measured over a 1-MeV energy range.

Figure 3. Gamma ray spectrum of ^{125}Xe extracted into the inorganic phase measured over a 1-MeV energy range.

Figure 4. Combined gamma ray spectra of ^{125}Xe in the extracted organic and inorganic phases showing the relative intensity and contribution to the activities of the two phases.

Figure 5. Combined gamma ray spectra of ^{125}Xe and ^{130}I extracted into the organic phase measured over a 1-MeV energy range.

Figure 6. Combined gamma ray spectra of ^{125}Xe and ^{130}I extracted into the inorganic phase measured over a 1-MeV energy range.

Figure 7. Combined gamma ray spectra of ^{125}Xe and ^{130}I in the extracted organic and inorganic phases showing the relative intensity and contribution to the activities of the two phases.

inorganic phases. Figure 5 shows the combined gamma ray spectra of ^{125}Xe and ^{130}I extracted into the organic phase; Figure 6 shows the combined gamma ray spectra of ^{125}Xe and ^{130}I extracted into the inorganic phase of the same sample. The comparison of the relative intensity and contribution to the activities of the extracted organic and inorganic phases from ^{125}Xe and ^{130}I is illustrated in Figure 7. It can be easily seen that the low activity from the ^{130}I activation is insignificant in comparison to that activity contributed to the organic phase by the ^{125}Xe activation. Because of the shorter half life in the case of the isotope ^{130}I being studied, waiting for the unwanted isotope, ^{125}Xe , to decay was not feasible. The only way to eliminate the activity from ^{125}Xe was to manually discriminate against the low lying energy gamma rays and monitor only the activity due to the higher energy gamma rays of the ^{130}I isotope.

This problem of conflicting isotope activities, because of the low activation of ^{130}I in the samples, became apparent during our first attempt to establish the effect of rare gas moderation on the ^{130}I reaction with CH_4 initiated by the combined (n, γ) and (IT) processes. The moderation of the $^{130}\text{I} + \text{CH}_4$ reaction by Xe was completely anomalous to what would be expected.³ The data showing the effects of Ne, Ar, Kr, Xe and $\text{CH}_3\text{I}^{129}$ additives on the $^{130}\text{I} + \text{CH}_4$ reaction are given in Table II and are depicted graphically in Figure 8. Xenon, rather than reducing the ^{130}I organic yield by kinetic energy moderation and charge-transfer reactions, as was the case in the $^{128}\text{I} + \text{CH}_4$ system,³ caused the organic yield to increase with an increasing amount of Xe. Reducing the total pressure of the xenon moderated system to 150 mm gave a corresponding decrease in organic yield, since the ratio of xenon to $\text{CH}_3\text{I}^{129}$ in each sample was

Table II

Percent ^{130}I Stabilized in Organic Combination in a Gaseous Mixture of Additive and Methane After Neutron Irradiation at Ambient Temperature and After All Iodine-130m Has Decayed (=90 min) (a)

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)	
Neon	658.0	30.0	0.0436		25.6	24.5
	657.0	32.0	0.0464		25.4	24.0
	650.0	58.5	0.0825	27.0		
				27.8		
				22.3		
				23.4		
					25.6	24.1
	581.5	109.5	0.1600	27.2		
				24.5		
				26.3		
				26.1		
					26.0	24.7
	432.5	243.5	0.3602		23.4	22.1
	439.5	256.0	0.3681	24.4		
				26.4		
					25.4	23.8
	336.0	248.0	0.4246		24.9	23.2
	383.0	318.0	0.4536		21.3	20.0

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
Argon	715.0	17.0	0.0232		23.9
	721.5	37.0	0.0488	27.7 18.9	22.8
					23.3
	661.0	58.5	0.0799	22.9 21.7	22.2
					22.3
	647.5	114.0	0.1497	23.3 20.4	21.1
					21.8
	578.0	191.0	0.2484	20.6	20.5
	499.0	255.0	0.3382	19.5	19.2
	402.5	350.5	0.4655	21.2	18.0
Krypton					19.4
	712.0	10.0	0.0135	27.5 20.5	
					24.0
	735.0	11.0	0.0147	23.8	22.9
	731.0	22.5	0.0298	21.6 25.3	22.7
					23.4
	697.0	57.0	0.0756	16.8 26.4	22.2
					21.6
	603.0	66.0	0.0986	20.9 22.9	20.4
					21.9
					20.6

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n, γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n, γ+IT} (c)
Krypton	637.0	121.5	0.1600	37.0 24.4 11.0 13.1	
					21.4
	564.0	197.0	0.2588	21.4 19.5	19.3
					20.4
	503.5	262.5	0.3427		17.8
	427.5	312.5	0.4223	27.8 14.8	18.3
					21.3
	379.5	391.0	0.5075		17.7
	258.0	506.5	0.6627		18.8
	240.0	540.0	0.6939	15.5 27.1	15.0
					19.4
					21.5
	105.5	589.5	0.8489		16.3
					22.1
Xenon	661.0	17.0	0.0251	25.0 28.2	15.0
					26.6
	645.5	36.0	0.0528		25.5
	653.5	50.5	0.0717		40.3
	571.0	133.5	0.1889	46.5 60.4	38.8
					43.7
					42.0
	529.5	149.0	0.2196		53.4
					60.8
					50.6
					56.7

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
Xenon	491.5	214.0	0.3033	60.2	56.4
	397.0	332.5	0.4555	65.0	60.0
	364.5	332.5	0.4777	62.0 73.8	
				67.9	62.6
	376.0	352.0	0.4827	65.0 69.6 69.4 60.0	
				65.4	59.0
	249.5	468.5	0.6525	66.1 66.6	
				66.4	59.5
	126.0	559.0	0.8161	74.7 75.9	
				75.3	66.9
	118.5	592.5	0.8333	80.3 75.2	
				77.7	69.0
	99.0	32.5	0.2471	40.4 33.2	
				36.8	33.5
Xenon (d)	74.5	74.0	0.4983	42.0	36.4
	53.0	90.0	0.6294	40.7 45.3	
				43.0	36.2

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}		Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
Xenon	30.0	70.5	0.7015	45.2 44.4		
CH ₃ I ¹²⁹					44.8	37.4
	756.0	5.0	0.0065		22.7	21.6
	741.0	10.0	0.0133	20.1 21.7		
					20.9	19.8
	698.0	25.0	0.0346		16.9	15.8
	686.5	41.0	0.0564	14.4 15.2		
					14.8	13.7
	707.5	53.5	0.0703	11.4 12.7		
					12.0	10.9
	695.0	66.5	0.0873	11.3 10.1		
					10.7	9.6
	677.5	90.0	0.1178	6.4 8.0 11.4		
					9.3	8.2
	330.5	87.0	0.2083	5.6 6.0		
					5.8	4.7
	105.5	43.0	0.2896	4.6 2.1		
					3.2	2.1

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
CH ₃ I ¹²⁹	99.0	90.0	0.4762	2.5 2.3	
				2.4	1.3
	170.5	68.0	0.7149	2.0 1.3	
				1.7	0.6

- (a) All rare gas moderated samples contained 0.1 ± 0.3 mm CH₃I¹²⁹. All samples were irradiated for 2 minutes at ambient temperature and left at that temperature until extraction at least 90 minutes after the end of irradiation.
- (b) Calculated assuming additive pressures. Error ± 0.002
- (c) Values were calculated considering 1.1% failure to bond rupture of I¹³⁰ from CH₃I¹³⁰ and reactor-induced radiation reactions (using Figure 2-1) imparted to each system.
- (d) Total pressure equal to 150 mm in comparison to ≈ 1 atmosphere for all other samples.

Figure 8 Effect of rare gas moderation on gas mixtures of CH_3I^{129} , I_2 , and CH_4 after all Iodine-130m has decayed (≈ 90 min). Additives: Xenon, $\square$ (—(total pressure, 1 atm), --- (total pressure 150 mm)); Neon, $+$; Argon, $\bullet$; Krypton, $\blacksquare$; CH_3I^{129} , $\blacktriangle$.

reduced. This anomalous behavior of the xenon moderated system has been attributed to the ^{125}Xe activity contribution to the organic yield which must be corrected for in order to obtain meaningful data. This problem has only been found apparent when large differences in activities are encountered due to differences in activation cross-sections of two isotopes of comparable half life activated in the same sample.

In our previous work on bromine systems, multiple isotope activation was not encountered as a problem. The bromine activity was more than enough to make the xenon activity contribution insignificant. Also by waiting at least 48 hours to count the ^{82}Br activity in the samples the xenon activity in the organic phase had relatively decreased to a level of no consequence and no correction was necessary due to rare gas induced activity.

Determination of Isomeric Transition Induced Organic Yields

Iodine:

When ^{129}I is subjected to a thermal neutron flux, a large percentage of the activated nuclei are born in a metastable nuclear state.⁷ As was shown in Figure 1-6, 67% of the ^{129}I atoms which absorb a thermal neutron will result in $^{130}\text{I}^{\text{m}}$; whereas 33% are born as ground nuclear state ^{130}I . The $^{130}\text{I}^{\text{m}}$ decays to ^{130}I by isomeric transition and to ^{130}Xe by beta decay.

In our attempt to establish the rare gas moderation of the ^{130}I reaction with CH_4 and CD_4 initiated by the isomeric transition process, it was necessary to determine experimentally two values in order to isolate the extent of organic retention in the gaseous environment-due strictly to

isomeric transition. These values were the organic yields for the $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}$ induced reaction and the combined organic yield induced by the $^{129}\text{I}(\text{n},\gamma)^{130}\text{I} + ^{129}\text{I}(\text{n},\gamma)^{130}\text{I}^{\text{m}}$ and $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ reactions. These two values were determined and isolated experimentally according to the irradiation and extraction procedures outlined before. The two values have been conveniently named $\text{O.Y.}_{(\text{n},\gamma)}$ and $\text{O.Y.}_{(\text{n},\gamma)+(\text{IT})}$, respectively. In establishing the values for these variables to be used in the subsequent calculation the necessary corrections for failure to bond rupture and radiation induced reactions were considered.

The extent of organic retention in methane and d-methane due strictly to isomeric transition was calculated using the expression

$$\text{O.Y.}_{(\text{IT})} = \text{O.Y.}_{(\text{n},\gamma)+(\text{IT})} - 0.39(\text{O.Y.}_{(\text{n},\gamma)}) / 0.61.$$

The constants⁷ 0.39 and 0.61 are the fraction of the total activity produced directly by radiative neutron capture and the fraction of the total activity born by (IT)-activated processes decaying in the gaseous state.

Experimental Results

During the irradiation of ^{129}I containing systems, several nuclear phenomena are taking place. By radiative neutron capture ^{130}I and $^{130}\text{I}^{\text{m}}$ are born simultaneously and $^{130}\text{I}^{\text{m}}$ is decaying by isomeric transition to ^{130}I . Because of these conflicting contributions to the formation of ^{130}I during irradiation it is impossible to accurately determine the absolute value for the (n, γ)-activated ^{130}I and $^{130}\text{I}^{\text{m}}$. However, we were successful in our attempt to obtain a value for the (n, γ)-activated process with a minimum contribution of isomeric transition contribution by performing an

immediate post-irradiation extraction after 30 second irradiation as described previously. The most easily obtainable data is the combined (n, γ) plus (IT) contributions to the formation of ^{130}I after the isomeric transition has been allowed to occur in the gas phase.

Various studies were performed to obtain data for comparison between the two isotopes ^{128}I and ^{130}I . These included establishing the limiting organic yield for ^{128}I and ^{130}I in a methane environment using $^{127}\text{I}_2$ and $^{129}\text{I}_2$ as well as $\text{CH}_3\text{I}^{127}$ and $\text{CH}_3\text{I}^{129}$ as source molecules for ^{128}I and ^{130}I . We found samples containing only 0.1 mm of $^{127}\text{I}_2$ or $^{129}\text{I}_2$ with methane gave consistently low yields in the range of 10% or less. These low yields in the gas phase were attributed to micro crystallization of the I_2 on the sides of the reaction ampoule not allowing the iodine to react in the gas phase. This complicating crystallization was an effect of the reactor temperature (9°C) for irradiation times greater than 30 seconds. To alleviate this problem of crystallization, $\text{CH}_3\text{I}^{129}$ was employed as the source molecule of ^{129}I so as to achieve meaningful data.

It was important to have the maximum amount of $\text{CH}_3\text{I}^{129}$ present as a source molecule so as to generate sufficient activity for statistical counting and yet minimize lengthy irradiation and still obtain true representative organic yields. We arbitrarily chose 15 mm $\text{CH}_3\text{I}^{129}$ for all the experimental reaction systems and 2 minute irradiation time for the (n, γ)+(IT)-activated reactions. Table III and Table IV present the observed and corrected organic yield data for the (n, γ)-induced $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ reactions and (n, γ)+(IT)-activated ^{130}I reactions, respectively, in various methane-rare gas or molecular additive reaction systems.

In order to interpret properly the relative effects of the additives,

Table III

Percent ^{130}I Stabilized in Organic Combination in Various Gaseous Mixtures of Additive and Methane Following Neutron Irradiation at Ambient Temperature and Immediate Post-Irradiation Extraction ^(a)

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,y}	Percent I-130 As Organic (corr) O.Y. _{n,y} (c)
Neon	658.0	30.0	0.0436	25.2	24.1
	657.0	32.0	0.0464	24.9	23.5
	650.0	58.5	0.0825	25.3	23.8
	581.5	109.5	0.1600	25.4	24.0
	432.5	243.5	0.3602	24.3	22.8
	439.5	256.0	0.3681	24.1	22.6
	336.0	248.0	0.4246	24.1	22.5
Argon	715.0	17.0	0.0232	24.1	23.0
	721.5	37.0	0.0488	23.5	22.4
	661.0	58.5	0.0799	22.7	21.5
	647.5	114.0	0.1497	22.0	20.7
	578.0	191.0	0.2484	20.4	19.0
	499.0	255.0	0.3382	19.7	18.2
	402.5	350.5	0.4655	20.7	18.9
	371.0	366.0	0.4966	19.5	18.0

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ}	Percent I-130 As Organic (corr) O.Y. _{n,γ} (c)
Krypton	627.5	33.0	0.0499	23.2 23.8	
				23.5	22.2
	603.0	66.0	0.0986	24.5 22.2	
				23.4	21.7
	582.0	155.0	0.2063	21.4	19.1
	569.0	158.5	0.2180	22.4	20.0
	407.0	312.0	0.4320	18.8 19.0	
				18.9	15.5
	364.5	314.5	0.4632	20.8	17.0
	356.0	362.5	0.5050	23.6 14.9	
				19.2	15.1
	223.0	505.0	0.6935	20.4	15.3
	169.0	568.0	0.7707	21.1 21.7	
				21.4	14.7
Xenon	105.5	589.5	0.8489	21.5	14.6
	625.0	73.0	0.1040	22.1	20.2
	483.0	222.5	0.3154	20.5	16.7
	418.5	297.5	0.4155	19.2	14.5

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ}	Percent I-130 As Organic (corr) O.Y. _{n,γ} (c)
Xenon	340.0	364.0	0.5170	18.9	13.3
	268.5	447.0	0.6250	19.6	13.1
CH ₃ I ¹²⁹	649.0	46.5	0.0654	16.6	15.5
	654.0	64.0	0.0891	12.5 11.2	
				11.8	10.7
	330.5	87.0	0.2083	5.6 6.0	
				5.8	4.7
	105.5	43.0	0.2896	4.6 2.1	
				3.4	2.3
	99.0	90.0	0.4762	2.5 2.0	
				2.3	1.2
	68.0	170.5	0.7149	2.1 1.3	
				1.7	0.6

- (a) All rare gas moderated and molecular additive samples contained 0.1 ± 0.02 mm I_2 and 15.0 ± 0.3 mm CH_3I^{129} . All samples were irradiated for 30 seconds at ambient temperature and extracted immediately following irradiation.
- (b) Calculated assuming additive pressures. Error ± 0.002
- (c) Values were calculated considering 1.1% failure to bond rupture of ^{130}I from CH_3I^{130} and reactor-induced radiation reactions (using Figure 2-1) imparted to each system.

Table IV

Percent Total ^{130}I Stabilized in Organic Combination in a Gaseous Mixture of Additive and Methane Following Neutron Irradiation at Ambient Temperature and After All Iodine-130m Has Decayed (=90 min) Correcting for the ^{125}Xe Activity Contribution to the Organic Yield ^(a)

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)	
Neon	658.0	30.0	0.0436		25.6	24.5
	657.0	32.0	0.0464		25.4	24.0
	650.0	58.5	0.0825	27.0		
				27.8		
				22.3		
				23.4		
					25.6	24.1
	581.5	109.5	0.1600	27.2		
				24.5		
				26.3		
				26.1		
					26.0	24.7
	432.5	243.5	0.3602		23.4	22.1
	439.5	256.0	0.3681	24.4		
				26.4		
					25.4	23.8
	336.0	248.0	0.4246		24.9	23.2
	383.0	318.0	0.4536		21.3	20.0

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}		Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
Argon	715.0	17.0	0.0232		23.9	22.8
	721.5	37.0	0.0488	27.7 18.9		
					23.3	22.2
	661.0	58.5	0.0799	22.9 21.7		
					22.3	21.1
	647.5	114.0	0.1497	23.3 20.4		
					21.8	20.5
	578.0	191.0	0.2484	20.6		19.2
	499.0	255.0	0.3382	19.5		18.0
	402.5	350.5	0.4655	21.2		19.4
Krypton	712.0	10.0	0.0135	27.5 20.5		
					24.0	22.9
	735.0	11.0	0.0147		23.8	22.7
	731.0	22.5	0.0298	21.6 25.3		
					23.4	22.2
	697.0	57.0	0.0756	16.8 26.4		
					21.6	20.4
	603.0	66.0	0.0986	20.9 22.9		
					21.9	20.6

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
Krypton	637.0	121.5	0.1600	37.0 24.4 11.0 13.1	
					21.4
	564.0	197.0	0.2588	21.4 19.5	19.3
					20.4
	503.5	262.5	0.3427		17.8
	427.5	312.5	0.4223	27.8 14.8	18.3
					21.3
	379.5	391.0	0.5075		17.7
	258.0	506.5	0.6627		18.8
	240.0	540.0	0.6939	15.5 27.1	15.0
Xenon					21.5
	105.5	589.5	0.8489		22.1
					16.3
	631.0	68.5	0.0985	25.4 20.1	15.0
					22.7
	471.0	219.5	0.3179	21.5 18.1	20.8
					19.8
	472.5	223.0	0.3206	17.9 22.1	16.0
					20.5
					16.6

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. n, γ+IT	Percent I-130 As Organic (corr) O.Y. n, γ+IT (c)
Xenon	412.0	285.5	0.4093	20.5 20.2	
					20.3 15.7
	408.0	301.5	0.4251		18.6 13.9
	359.0	362.5	0.5051	21.9 20.9 20.3 19.9	
					20.3 14.9
	255.5	452.5	0.6391		19.1 13.5
	145.5	557.0	0.7929	21.5 18.6	
					20.0 12.1
CH ₂ F ₂	719.5	30.5	0.0406		22.9 21.8
	664.5	65.0	0.0891		18.6 17.4
	640.5	68.5	0.0966	23.1 13.3	
					18.2 17.0
	653.5	75.5	0.1035		19.5 18.3
	625.0	101.5	0.1403	17.8 15.8	
					16.8 15.6
	551.5	180.0	0.2461		14.2 12.8
	520.0	214.0	0.2915		12.8 11.2
	499.0	243.0	0.3286	10.9 12.0 21.9	
					13.2 11.5

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
CH ₂ F ₂	402.0	348.0	0.4645	10.6 21.1 19.4 17.5 8.8	
					12.9 10.9
	359.5	365.0	0.5038		11.1 9.0
	276.0	479.5	0.6352	12.1 14.1 9.7	
					11.9 9.7
	240.0	511.0	0.6775	12.1 14.5	
					13.3 10.9
	195.5	544.0	0.7356		12.0 9.6
	139.0	573.5	0.8049	11.4 13.7	
					12.0 9.4
CH ₃ I ¹²⁹	756.0	5.0	0.0065		22.7 21.6
	741.0	10.0	0.0133	20.1 21.7	
					20.9 19.8
	698.0	25.0	0.0346		16.9 15.8
	686.5	41.0	0.0564	14.4 15.2	
					14.8 13.7
	690.0	42.0	0.0574		14.2 13.1

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
CH ₃ I ¹²⁹	707.5	53.5	0.0703	11.4 12.7	
					12.0
	695.0	66.5	0.0873	11.3 10.1	10.9
					10.7
	677.5	90.0	0.1178	6.4 8.0 11.4	9.6
					9.3
	330.5	87.0	0.2083	5.6 6.0	8.2
					5.8
	105.5	43.0	0.2896	4.6 2.1	4.7
					3.2
	99.0	90.0	0.4762	2.5 2.3	2.1
					2.4
					1.3

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
CH ₃ I ¹²⁹	170.5	68.0	0.7149	2.0 1.3 1.7	0.6

- (a) All rare gas moderated and molecular additive samples contained 0.1 ± 0.02 mm I₂ and 15.0 ± 0.3 mm CH₃I¹²⁹. All samples were irradiated for 2 minutes at ambient temperature and left at that temperature until extraction at least 90 minutes after the end of irradiation.
- (b) Calculated assuming additive pressures. Error ± 0.002
- (c) Values were calculated considering 1.1% failure to bond rupture of ¹³⁰I from CH₃I¹³⁰ and reactor-induced radiation reactions (using Figure/) imparted to each system.

it was necessary to correct the observed data for (a) the 1.1% failure to bond-rupture of CH_3I , (b) any radiation-induced reactions, and (c) any ^{130}I which reacts with the molecular additive (CH_2F_2) forming organic ^{130}I when applicable. The data of Figure 1 were used to determine the correction for radiation-induced reactions in the rare gas moderator systems studied. In the presence of essentially pure molecular additive, corrected for failure to bond-rupture, ^{130}I was found to react with CH_2F_2 forming organic ^{130}I to the maximum extent of 2.0%.

Presented in Figure 9 are the corrected data of Table IV. The limiting organic yield extrapolation was determined by extrapolating the corrected data in Table IV on a log-log plot of ^{130}I organic yield vs. mole fraction of methane at mole fraction additive less than 0.1. The data are tabulated in Table V and are plotted in Figure 10. All limiting organic yield extrapolations of the corrected and/or normalized data presented in this thesis are determined in the same manner as described above. From Figure 10 we find that at zero-mole-fraction additive the maximum extent of ^{130}I stabilized in organic combination to be 24.5% $\pm$ 2%. The data in Figure 9 appear to extrapolate, at zero-mole-fraction methane, to 0% for the $\text{CH}_3\text{I}^{129}$ additive system, to 14.8% $\pm$ 1% for the Ne, Ar, and Kr additives, and to 9.5% $\pm$ 1% for the Xe and CH_2F_2 additives. All additives behaved as expected from previous moderation studies.³

Since relatively small amounts of $\text{CH}_3\text{I}^{127}$ have been shown to have an inhibiting effect on the ^{128}I organic yields,³ we became concerned with using too great a source pressure of $\text{CH}_3\text{I}^{129}$ in the moderator studies.

Figure 9. Effect of rare gas and additive moderation on the total percent ^{130}I formed as organic activity in CH_4 additive mixtures containing $\text{CH}_3\text{I}^{129}$ and I_2 after all Iodine-130m has decayed (≈ 90 min). Additives: Neon, $\blacklozenge$; Argon, $\bullet$; Krypton, $\blacksquare$; Xenon, $\square$; CH_2F_2 , $\circ$; $\text{CH}_3\text{I}^{129}$, $\blacktriangle$.

Table v

Determination of the Limiting Total Iodine-130 Organic Yield in a Gaseous Mixture of Additive and Methane Following Neutron Irradiation at Ambient Temperature and After All Iodine-130m Has Decayed (≈ 90 min) Correcting for the ^{125}Xe Activity Contribution to the Organic Yield

Additive	Mole Fraction Additive	Mole Fraction Methane	-Log Mole Fraction Methane	Percent I-130 As Organic O.Y. _{n,γ+IT}	Log Percent O.Y. _{n,γ+IT}
Neon	0.0436	0.9564	0.019	24.5	1.389
	0.0464	0.9536	0.021	24.0	1.380
	0.0825	0.9175	0.037	24.1	1.382
	0.1600	0.8400	0.076	24.7	1.373
Argon	0.0232	0.9768	0.010	23.1	1.367
	0.0488	0.9512	0.022	22.2	1.346
	0.0799	0.9201	0.036	21.7	1.337
	0.1497	0.8503	0.071	20.5	1.312
Krypton	0.0135	0.9865	0.006	22.9	1.360
	0.0147	0.9853	0.007	22.7	1.356
	0.0298	0.9702	0.013	22.2	1.346
	0.0756	0.9244	0.034	20.8	1.318
	0.0986	0.9014	0.045	20.3	1.308
Xenon	0.0200	0.9800	0.009	22.3	1.348
	0.0500	0.9500	0.022	21.0	1.322
	0.0985	0.9015	0.045	19.7	1.295

Additive	Mole Fraction Additive	Mole Fraction Methane	-Log Mole Fraction Methane	Percent I-130 As Organic O.Y. _{n,γ+IT}	Log Percent O.Y. _{n,γ+IT}
CH ₂ F ₂	0.0200	0.9800	0.009	21.9	1.340
	0.0406	0.9594	0.023	20.4	1.310
	0.0891	0.9109	0.041	18.0	1.255
	0.0966	0.9034	0.044	17.4	1.241
	0.1035	0.8965	0.047	18.3	1.263
	0.1403	0.8597	0.066	15.6	1.193
CH ₃ I ¹²⁹	0.0065	0.9935	0.003	21.6	1.334
	0.0133	0.9867	0.006	19.8	1.297
	0.0346	0.9654	0.015	15.8	1.199
	0.0564	0.9436	0.025	13.7	1.137
	0.0574	0.9426	0.026	13.1	1.117
	0.0703	0.9297	0.032	10.9	1.037
	0.0873	0.9127	0.040	9.6	0.982

Figure 10. Determination of the limiting total Iodine-130 organic yield in methane as a result of (n, γ +IT) induced reactions in the 15 mm CH₃I¹²⁹ reaction system. The limiting organic yield is 24.0 $\pm$ 0.5%.

For this reason additional experiments were performed. For samples containing rare gases and methane we employed varying conditions ranging from samples containing only 0.1 mm $^{129}\text{I}_2$ to samples containing 0.1 mm $^{127}\text{I}_2$ and 2 mm to 15 mm $\text{CH}_3\text{I}^{129}$. Varying lengths of irradiation time (30 sec to 5 min) were performed on the various component systems. The results showed that the use of 15 mm $\text{CH}_3\text{I}^{129}$ gave iodine organic yields that were too low because of the complicating effect of activated iodine species. The reaction systems showed little or no time dependence for irradiation. We found that the presence of 5 mm $\text{CH}_3\text{I}^{129}$ with 0.1 mm $^{127}\text{I}_2$ gave the best results. Therefore, the original CH_4 data, so far presented, was repeated and extended to the CD_4 system employing only 5 mm or less of $\text{CH}_3\text{I}^{129}$ as the source molecule in the various reaction systems.

A. Organic Yields in the CH_4 System

Table VI presents the observed, corrected, and normalized organic yields for the (n, γ)-induced $^{130}\text{I} + ^{130}\text{I}^m$ reactions in various methane-additive reaction systems. Figure 11 shows the plotted corrected or normalized data from Table VI. The limiting organic yield at zero-mole-fraction additive (as a result of the (n, γ) process) was found to be 42.0% $\pm 2\%$ using the data tabulated in Table VII and plotted in Figure 12. In order to make use of the previously determined (n, γ) data it was found necessary to normalize the data from Table III by using a constant multiplication factor of 1.75. This allowed the existing 15 mm $\text{CH}_3\text{I}^{129}$ data to match that of the current 5 mm $\text{CH}_3\text{I}^{129}$ data. The data in Figure 11 appears to extrapolate, at zero-mole-fraction methane, to 0% for $\text{CH}_3\text{I}^{129}$ additive, 26.0% $\pm 1\%$ for the Ne, Ar, and Kr additives, and to 16.5% $\pm 1\%$

Table VI

Percent ^{130}I Stabilized in Organic Combination in Methane and Various
Gaseous Additive Mixtures Following Neutron Irradiation at Ambient
Temperature for Immediate Post-Irradiation Extraction (a)

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	% I-130 As Organic (obs) O.Y. _{n,γ}	% I-130 As Organic (corr) O.Y. _{n,γ} (c)	% I-130 As Organic (corr) O.Y. _{n,γ} (d)	% I-130 As Organic (norm) O.Y. _{n,γ} (e)
Neon	658.0	30.0	0.0436			24.1	42.2
	657.0	32.0	0.0464			23.5	41.2
	650.0	58.5	0.0825			23.8	41.7
	581.5	107.5	0.1600			24.0	42.0
	432.5	243.5	0.3602			22.8	40.0
	439.5	256.0	0.3681			22.6	39.6
	336.0	248.0	0.4246			22.5	39.2
	383.0	318.0	0.4536			22.4	37.5
Argon	715.0	17.0	0.0232			23.0	40.9
	721.5	37.0	0.0488			22.4	39.2
	661.0	58.5	0.0799			21.5	37.6
	647.5	114.0	0.1497			20.7	36.2
	578.0	191.0	0.2484			19.0	33.3
	499.0	255.0	0.3382			18.2	31.9
	402.5	350.5	0.4655			18.9	33.0
	371.0	366.0	0.4966			18.0	31.5

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	% I-130 As Organic (obs) O.Y. _{n,Y}	% I-130 As Organic (corr) O.Y. _{n,Y} (c)	% I-130 As Organic (corr) O.Y. _{n,Y} (d)	% I-130 As Organic (norm) O.Y. _{n,Y} (e)
Krypton							
	735.0	7.0	0.0094	42.5	41.4		
	678.5	56.5	0.0769	38.7	37.4		
	508.0	210.0	0.2925	33.2	30.5		
	388.0	338.5	0.4659	32.9	29.1		
	170.0	565.0	0.7687	32.3	26.8		
	627.5	33.0	0.0499			22.2	38.9
	603.0	66.0	0.0986			21.7	38.0
	582.0	155.0	0.2063			19.1	33.5
	569.0	158.5	0.2180			20.0	35.0
	407.0	312.0	0.4320			15.5	27.2
	364.5	314.5	0.4632			17.0	29.8
	356.0	362.5	0.5050			15.1	26.4
	223.0	505.0	0.6935			15.3	26.8
	169.0	568.0	0.7707			14.7	25.8
	105.5	589.5	0.8489			14.6	25.6
Xenon							
	698.0	12.0	0.0169	46.0			
				43.9			
				43.5			
				33.8			
					41.8	40.6	
	635.0	69.0	0.0980	37.9			
				38.8			
					38.3	36.3	

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	% I-130 As Organic (obs) O.Y. _{n,γ}	% I-130 As Organic (corr) O.Y. _{n,γ} (c)	% I-130 As Organic (corr) O.Y. _{n,γ} (d)	% I-130 As Organic (norm) O.Y. _{n,γ} (e)
Xenon	422.5	285.5	0.4035	27.8 31.9 29.2 30.4	29.8	25.1	
	156.0	578.5	0.7873	31.8 29.3 22.9 26.2			
					27.5	19.4	
	625.0	73.0	0.1040			20.2	35.4
	483.0	222.5	0.3154			16.7	29.2
	418.5	297.5	0.4155			14.5	25.4
	340.0	364.0	0.5170			13.3	23.3
	268.5	447.0	0.6250			13.1	23.0
	707.0	5.5	0.0077	33.7 45.5	39.6	38.5	
	684.0	32.0	0.0447	21.7 20.9			
CH ₃ I ¹²⁹	649.0	46.5	0.0654		21.4 16.6	20.3 15.5	

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	% I-130 As Organic (obs) O.Y. _{n,γ}	% I-130 As Organic (corr) O.Y. _{n,γ} (c)	% I-130 As Organic (corr) O.Y. _{n,γ} (d)	% I-130 As Organic (norm) O.Y. _{n,γ} (e)
CH ₃ I ¹²⁹	654.0	64.0	0.0891	12.5 11.2			
					11.8	10.7	
	330.5	87.0	0.2083	5.6 6.0			
					5.8	4.7	
	105.5	43.0	0.2896	4.6 2.1			
					3.4	2.3	
	99.0	90.0	0.4762	2.5 2.0			
					2.3	1.2	
	68.0	170.5	0.7149	2.1 1.3			
					1.7	0.6	

(a) All rare gas moderated samples contained 0.1 ± 0.02 mm I₂ and 5.0 ± 0.3 mm CH₃I¹²⁹ where experimentally observed values are reported. All samples were irradiated for 30 sec. at ambient temperature and extracted immediately following irradiation.

(b) Calculated assuming additive pressures. Error ± 0.002

- (c) Values were calculated considering 1.1% failure to bond rupture of ^{130}I from $\text{CH}_3\text{I}^{130}$ and reactor-induced radiation reactions (using Fig. 1) imparted to each system.
- (d) Values were taken from Table III where all rare gas moderated and molecular additive samples contained $0.1 \pm 0.02 \text{ mm I}_2$ and $15.0 \pm 0.3 \text{ mm CH}_3\text{I}^{129}$.
- (e) Values were calculated using a multiplication factor of 1.75 to normalize the existing 15 mm $\text{CH}_3\text{I}^{129}$ data to that of the 5 mm $\text{CH}_3\text{I}^{129}$ data.

Figure 11. Effect of rare gas moderation on the radiative neutron capture reaction in gaseous additive mixtures of CH_3I^{129} , I_2 , and CH_4 . Additives: Neon, + ; Argon, ● ; Krypton, ■ ; Xenon, □ ; CH_3I^{129} , ▲ .

Table VII

Determination of the Limiting Iodine-130 Organic Yield in Methane and Various Gaseous Additive Mixtures Following Neutron Irradiation at Ambient Temperature for Immediate Post-Irradiation Extraction

Additive	Mole Fraction Additive	Mole Fraction Methane	-Log Mole Fraction Methane	Percent I-130 As Organic O.Y. _{n,γ}	Log Percent O.Y. _{n,γ}
Neon	0.0436	0.9564	0.019	42.2	1.625
	0.0464	0.9536	0.021	41.2	1.615
	0.0825	0.9175	0.037	41.7	1.620
	0.1600	0.8400	0.076	42.0	1.623
Argon	0.0232	0.9768	0.010	40.9	1.612
	0.0488	0.9512	0.022	39.5	1.597
	0.0799	0.9201	0.036	37.6	1.575
	0.1497	0.8503	0.070	36.2	1.559
Krypton	0.0094	0.9906	0.004	41.4	1.617
	0.0499	0.9501	0.022	38.9	1.590
	0.0769	0.9231	0.035	37.4	1.573
	0.0986	0.9014	0.045	37.5	1.574
	0.1500	0.8500	0.071	35.2	1.547
Xenon	0.0169	0.9831	0.007	40.6	1.609
	0.0400	0.9600	0.018	39.5	1.597
	0.0700	0.9300	0.032	38.0	1.580
	0.0980	0.9020	0.045	36.3	1.560
	0.1040	0.8960	0.048	35.4	1.549

Additive	Mole Fraction Additive	Mole Fraction Methane	-Log Mole Fraction Methane	Percent I-130 As Organic O.Y. _{n,y}	Log Percent O.Y. _{n,y}
CH ₃ I ¹²⁹	0.0077	0.9923	0.003	38.5	1.586
	0.0447	0.9553	0.020	20.3	1.308
	0.0654	0.9346	0.029	15.5	1.190
	0.0891	0.9109	0.041	10.7	1.029

Figure 12. Determination of the limiting Iodine-130 organic yield in methane as a result of radiative neutron capture reactions. The limiting organic yield is $42.0 \pm 0.5\%$.

Table VII₁

Total Iodine-130 Organic Yields in Methane and Gaseous Additive
Mixtures Following Neutron Irradiation at Ambient Temperature
and After All Iodine-130m Has Decayed (≈ 90 min)^(a)

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	% I-130 As Organic (obs) n, γ +IT	% I-130 As Organic (corr) n, γ +IT ^(c)	% I-130 As Organic (corr) n, γ +IT ^(d)	% I-130 As Organic (norm) n, γ +IT ^(e)
Neon	658.0	30.0	0.0436			24.5	32.5
	657.0	32.0	0.0464			24.0	31.9
	650.0	58.5	0.0825			24.1	32.0
	581.5	109.5	0.1600			24.7	32.8
	432.5	243.5	0.3602			22.1	29.4
	439.5	256.0	0.3681			23.8	31.7
	336.0	248.0	0.4246			23.2	30.9
	383.0	318.0	0.4536			20.0	26.8
Argon	715.0	17.0	0.0232			22.8	30.4
	721.5	37.0	0.0488			22.2	29.5
	661.0	58.5	0.0799			21.1	28.0
	647.5	114.0	0.1497			20.5	27.3
	578.0	191.0	0.2484			19.2	25.6
	499.0	255.0	0.3382			18.0	24.0
	402.5	350.5	0.4655			19.4	25.8

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	% I-130 As Organic (obs) n,γ+IT	% I-130 As Organic (corr) n,γ+IT {c}	% I-130 As Organic (corr) n,γ+IT {d}	% I-130 As Organic (norm) n,γ+IT {e}
Krypton							
	712.0	10.0	0.0135			22.9	30.5
	735.0	11.0	0.0147			22.7	30.2
	731.0	22.5	0.0298			22.2	29.5
	697.0	57.0	0.0756			20.4	27.2
	603.0	66.0	0.0986			20.6	27.4
	637.0	121.5	0.1600			19.3	25.7
	564.0	197.0	0.2588			17.8	23.7
	503.5	262.5	0.3427			18.3	24.3
	427.5	312.5	0.4223			17.7	23.7
	379.5	391.0	0.5075			18.8	25.0
	258.0	506.5	0.6627			15.0	20.0
	240.0	540.0	0.6939			16.3	21.7
	105.5	589.5	0.8489			15.0	20.0
Xenon							
	631.0	68.5	0.0985			20.8	27.7
	471.0	219.5	0.3179			16.0	21.3
	472.5	223.0	0.3206			16.6	22.1
	412.0	285.5	0.4093			15.7	20.9
	408.0	301.5	0.4251			13.9	18.5
	359.0	362.5	0.5051			14.9	19.8
	255.5	452.5	0.6391			13.5	18.0
	145.5	557.0	0.7929			12.1	16.1

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	% I-130 As Organic (obs) n, γ+IT	% I-130 As Organic (corr) n, γ+IT (c)	% I-130 As Organic (corr) n, γ+IT (d)	% I-130 As Organic (norm) n, γ+IT (e)
CH ₂ F ₂	719.5	30.5	0.0406			21.8	29.0
	664.5	65.0	0.0891			17.4	23.2
	640.5	68.5	0.0966			17.0	22.6
	653.5	75.5	0.1035			18.3	24.4
	625.0	101.5	0.1403			15.6	20.8
	551.5	180.0	0.2461			12.8	17.0
	520.0	214.0	0.2915			11.2	14.9
	499.0	243.0	0.3286			11.5	15.3
	402.0	348.0	0.4645			10.9	14.5
	395.5	365.0	0.5038			9.0	12.0
	276.0	479.5	0.6352			9.7	12.9
	240.0	511.0	0.6775			10.9	14.5
	195.5	544.0	0.7356			9.6	12.8
	139.0	573.5	0.8049			9.4	12.5
CH ₃ I ¹²⁹	707.0	5.5	0.0077	28.8 34.4			
					31.6 31.2	30.4 30.1	
	683.5	14.0	0.0201				
	707.0	23.0	0.0315	29.8 26.1			
					27.9	26.8	

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	% I-130 As Organic (obs) n, γ+IT	% I-130 As Organic (corr) n, γ+IT {c}	% I-130 As Organic (corr) n, γ+IT {d}	% I-130 As Organic (norm) n, γ+IT {e}
CH ₃ I ¹²⁹	684.0	32.0	0.0447	26.9 19.9			
					23.5	22.4	
	686.5	41.0	0.0564	15.2 14.4			
					14.8	13.7	
	649.0	46.5	0.0654	16.8 16.1			
					16.4	15.3	
	707.5	53.5	0.0703	11.4 12.7			
					12.0	10.9	
	695.0	66.5	0.0873	11.3 10.1			
					10.7	9.6	
	672.5	89.0	0.1168	6.4 8.0			
					7.2	6.1	
	330.5	87.0	0.2083	5.6 5.9			
					5.8	4.7	
	105.5	43.0	0.2896	4.3 2.1			
					3.2	2.1	

Additive	Pressure Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	% I-130 As Organic (obs) n,γ+IT	% I-130 As Organic (corr) n,γ+IT {c}	% I-130 As Organic (corr) n,γ+IT {d}	% I-130 As Organic (norm) n,γ+IT {e}
CH ₃ I ¹²⁹	99.0	90.0	0.4762	2.7 2.1			
					2.4	1.3	
	68.0	170.5	0.7149	2.2 1.2			
					1.7	0.6	

- (a) All samples contained 0.1 ± 0.02 mm I₂. They were irradiated for 2 minutes at ambient temperature and left at room temperature until extraction at least 90 minutes after the end of irradiation.
- (b) Calculated assuming additive pressures. Error ± 0.002
- (c) Values were calculated considering 1.1% failure to bond rupture of ¹³⁰I from CH₃I¹³⁰ and reactor-induced radiation reactions (using Figure 1) imparted to each system.
- (d) Values were taken from Table IV where all rare gas moderated and molecular additive samples contained 15.0 ± 0.3 mm CH₃I¹²⁹.
- (e) Values were calculated using a multiplication factor of 1.33 to normalize the existing 15mm CH₃I¹²⁹ data to that of the 5mm CH₃I¹²⁹ data.

for the Xe additive.

Table VIII summarizes the total organic yields for the reactions of ^{130}I atoms activated by $(n,\gamma)+(\text{IT})$ processes in methane-additive mixtures after all iodine-130m has decayed. The corrected or normalized data from Table VIII is plotted in Figure 13. Using the data in Table IX and plotted in Figure 14, the limiting total iodine-130 organic yield (as a result of $(n,\gamma)+(\text{IT})$ activation) was found to be $32.0\% \pm 2\%$. The previously measured $(n,\gamma)+(\text{IT})$ data (15 mm $\text{CH}_3\text{I}^{129}$) was used after normalization using a constant multiplication factor of 1.33 which made it consistent with currently measured 5 mm $\text{CH}_3\text{I}^{129}$ reaction data. At zero-mole-fraction methane in Figure 13 the data extrapolate to 0% for $\text{CH}_3\text{I}^{129}$ additive, $19.8\% \pm 1\%$ for Ne, Ar, and Kr additives, and to $12.7\% \pm 1\%$ for Xe and CH_2F_2 additives.

The determinations of the organic yields ^{130}I O.Y. $_{(n,\gamma)}$ (Fig. 4-3) and ^{130}I O.Y. $_{(n,\gamma)+(\text{IT})}$ (Fig. 13) make it possible to calculate the organic yields for the reaction $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$, O.Y. $_{(\text{IT})}$. Since 39% of the ^{130}I resulting from neutron irradiation of ^{129}I is produced by the (n,γ) process and 61% through the decay of the metastable nuclear isomer, it is apparent that the following expression must hold.

$$^{130}\text{I} \text{ O.Y.}_{(n,\gamma)+(\text{IT})} = 0.39 \text{ O.Y.}_{(n,\gamma)} + 0.61 \text{ O.Y.}_{(\text{IT})}$$

Once the values of $\text{O.Y.}_{(n,\gamma)+(\text{IT})}$ and $\text{O.Y.}_{(n,\gamma)}$ are known the value for $\text{O.Y.}_{(\text{IT})}$ can be easily calculated directly from the rearrangement of the above expression.

Table X gives the iodine-130 organic yields in various gaseous mixtures of additive and methane as a result of isomeric transition induced reactions. Figure 15 shows the plotted data. The data in Table XI

Figure 13. Effect of rare gas and additive moderation on the total Iodine-130 organic yields in CH₄ additive mixtures containing CH₃I¹²⁹ and I₂ after all Iodine-130m has decayed (=90 min). Additives: Neon, + ; Argon, ● ; Krypton, ■ ; CH₂F₂, ○ ; Xenon, □ ; CH₃I¹²⁹, ▲ .

Table IX

Determination of the Limiting Total Iodine-130 Organic Yield in Methane
and Gaseous Additive Mixtures Following Neutron Irradiation at Ambient
Temperature and After All Iodine-130m Has Decayed (≈ 90 min)

Additive	Mole Fraction Additive	Mole Fraction Methane	-Log Mole Fraction Methane	Percent I-130 As Organic O.Y. _{n, γ+IT}	Log Percent O.Y. _{n, γ+IT}
Neon	0.0436	0.9564	0.019	32.5	1.512
	0.0464	0.9536	0.021	31.9	1.504
	0.0825	0.9175	0.037	32.0	1.505
	0.1600	0.8400	0.076	32.8	1.516
Argon	0.0232	0.9768	0.010	30.7	1.487
	0.0488	0.9512	0.022	29.9	1.476
	0.0799	0.9201	0.036	29.0	1.462
	0.1000	0.9000	0.046	26.5	1.423
	0.1497	0.8503	0.070	27.3	1.436
Krypton	0.0135	0.9865	0.006	30.5	1.484
	0.0147	0.9853	0.007	30.2	1.480
	0.0298	0.9702	0.013	29.5	1.470
	0.0756	0.9244	0.034	27.2	1.435
	0.0986	0.9014	0.045	27.4	1.438
Xenon	0.0169	0.9831	0.007	31.0	1.491
	0.0985	0.9015	0.045	26.8	1.428
	0.1040	0.8960	0.048	26.6	1.425

Additive	Mole Fraction Additive	Mole Fraction Methane	-Log Mole Fraction Methane	Percent I-130 As Organic O.Y. _{n,γ+IT}	Log Percent O.Y. _{n,γ+IT}
Xenon	0.1500	0.8500	0.071	25.2	1.401
	0.2000	0.8000	0.097	23.8	1.377
CH ₂ F ₂	0.0250	0.9750	0.011	29.0	1.462
	0.0406	0.9594	0.018	27.5	1.439
	0.0891	0.9109	0.041	23.2	1.366
CH ₃ I ¹²⁹	0.0966	0.9034	0.044	22.6	1.354
	0.0077	0.9923	0.003	30.4	1.483
	0.0201	0.9799	0.009	26.0	1.415
	0.0315	0.9685	0.014	22.5	1.352
	0.0447	0.9553	0.020	17.5	1.243
	0.0564	0.9436	0.025	13.7	1.137
	0.0654	0.9346	0.029	13.0	1.114
	0.0703	0.9297	0.032	10.9	1.037
	0.0873	0.9127	0.040	9.6	0.982

Figure 14 Determination of the limiting total Iodine-130 organic yield in methane as a result of $(n,\gamma+IT)$ induced reactions. The limiting organic yield is $32.0 \pm 0.5\%$.

Table X

Iodine-130 Organic Yields in Various Gaseous Mixtures of Additive and Methane As a Result of Isomeric Transition Induced Reactions Following Neutron Irradiation at Ambient Temperature

Additive	Mole Fraction Additive	Percent I-130 As Organic O.Y. _{n,γ} (a)	Percent I-130 As Organic O.Y. _{n,γ+IT} (b)	Percent I-130 As Organic O.Y. _{IT} (c)
Neon	0.0436	42.2	32.5	26.2
	0.0464	41.2	31.9	25.9
	0.0825	41.7	32.0	25.7
	0.1600	42.0	32.8	26.9
	0.2500	41.3	31.7	26.6
	0.3602	40.0	29.4	22.6
	0.3681	39.6	31.7	26.7
	0.4246	39.2	30.9	25.6
	0.5000	37.5	28.6	23.0
	0.6000	35.2	26.8	21.5
	0.7000	32.9	25.1	20.2
	0.8000	30.6	23.3	18.7
	0.9000	28.3	21.5	17.2
Argon	0.0232	40.9	30.4	23.8
	0.0488	39.2	29.5	23.3
	0.0799	37.6	28.0	22.0
	0.1497	36.2	27.3	21.7
	0.2484	33.3	25.6	20.7
	0.3382	31.9	24.0	19.0

Additive	Mole Fraction Additive	Percent I-130 As Organic O.Y. n, γ (a)	Percent I-130 As Organic O.Y. $n, \gamma + IT$ (b)	Percent I-130 Organic O.Y. IT (c)
Argon	0.4655	33.0	25.8	21.2
	0.4966	31.5	23.8	18.9
	0.6000	29.6	22.9	18.7
	0.7000	28.7	22.1	17.9
	0.8000	27.8	21.3	17.2
	0.9000	26.7	20.5	16.6
Krypton	0.0094	41.4	31.2	24.8
	0.0135	41.1	30.5	23.8
	0.0147	41.0	30.2	21.7
	0.0298	39.2	29.5	23.3
	0.0499	38.9	29.2	23.0
	0.0756	38.2	27.2	20.2
	0.0769	37.4	28.1	22.1
	0.0986	38.0	27.4	20.7
	0.1600	34.9	25.7	19.8
	0.2063	33.5	24.7	19.2
	0.2180	35.0	24.6	18.0
	0.2588	31.8	23.7	18.5
	0.2925	30.5	23.9	19.7
	0.3427	29.9	22.9	18.4
	0.4223	28.7	22.2	18.0
	0.4320	27.2	22.2	19.0
	0.4632	29.8	21.9	16.9
	0.4659	29.1	21.8	17.2
	0.5050	28.2	21.7	17.6

Additive	Mole Fraction Additive	Percent I-130 As Organic O.Y. n, γ (a)	Percent I-130 As Organic O.Y. $n, \gamma + IT$ (b)	Percent I-130 As Organic O.Y. IT (c)
Krypton				
	0.6627	25.7	20.0	16.4
	0.6935	27.4	20.8	16.6
	0.7687	26.8	20.6	16.6
	0.7707	25.8	20.5	17.2
	0.8489	25.6	20.0	16.4
Xenon				
	0.0169	40.6	30.7	24.5
	0.0980	36.3	26.7	20.6
	0.1040	35.4	26.7	21.2
	0.2000	31.8	23.8	18.7
	0.3154	29.2	21.6	16.7
	0.3179	27.5	21.3	17.4
	0.3206	27.4	21.7	18.0
	0.4035	25.1	20.3	17.2
	0.4093	25.0	20.2	17.1
	0.4155	25.4	20.2	16.9
	0.4251	24.8	18.5	14.4
	0.5051	23.5	19.0	16.0
	0.5170	23.3	18.8	15.9
	0.6250	23.0	17.5	13.9
	0.6391	21.6	17.3	14.6
	0.7873	19.4	15.4	12.8
	0.7929	19.3	15.3	12.7
	0.9000	17.9	14.0	11.5

Additive	Mole Fraction Additive	Percent I-130 As Organic O.Y. _{n,γ} (a)	Percent I-130 As Organic O.Y. _{n,γ+IT} (b)	Percent I-130 As Organic O.Y. _{IT} (c)
CH ₃ I ¹²⁹	0.0546	17.3	13.7	11.5
	0.0654	15.5	15.3	15.2
	0.0703	14.4	10.9	8.7
	0.0873	11.4	9.6	8.5
	0.1168	8.2	6.1	4.8
	0.2083	4.7	4.7	4.7
	0.2896	2.3	2.1	1.9
	0.4000	1.7	1.6	1.5
	0.4762	1.2	1.3	1.3
	0.6000	1.1	1.1	1.1
	0.7149	0.6	0.6	0.6

(a) Values were taken from Table VI and Figure 11.

(b) Values were taken from Table VIII and Figure 12.

(c) Values were calculated using the expression:

$$\text{O.Y. (IT)} = \{\text{O.Y. (n,γ)} + (\text{IT}) - 0.39(\text{O.Y. (n,γ)})\} / 0.61$$

and plotted in Figure 11 gives a limiting organic yield for the iodine-130 isomeric transition induced reaction in methane of 25.6% $\pm 2\%$. The extrapolated data in Figure 15 at zero-mole-fraction methane gives values of 0% for $\text{CH}_3\text{I}^{129}$ additive, 15.9% $\pm 1\%$ for Ne, Ar, and Kr additives, and 10.3% $\pm 1\%$ for Xe additive.

In addition to the moderator studies several studies were performed as an internal consistency test showing the limiting organic yields of ^{128}I and ^{130}I for the respective radiative neutron capture reactions and as a means of direct comparison between the two isotopes. The results of these studies are summarized in Table XII. It is plainly evident that our systems gave results consistent with those of Rack and Gordus³ and our own limiting organic yield for the (n, γ) process in iodine-130 could be reproduced within experimental error.

B. Organic Yields in the CD_4 System

Table XIII presents the observed and corrected organic yields for the (n, γ)-induced $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ reactions in CD_4 rare gas additive mixtures. Figure 17 shows the plotted corrected data from Table XIII. The limiting organic yield at zero-mole-fraction additive (as a result of the (n, γ) process) was found to be 42.0% $\pm 2\%$ using the data tabulated in Table XIV and plotted in Figure 18. The data in Figure 17 appears to extrapolate, at zero-mole-fraction d-methane, to 0% for $\text{CH}_3\text{I}^{129}$ additive, 26.0% $\pm 1\%$ for Kr additive, and to 16.5% $\pm 1\%$ for the Xe additive.

Table XV summarizes the total iodine-130 organic yields in CD_4 -rare gas additive mixtures for the reactions activated by (n, γ)+(IT) processes after all iodine-130m has decayed. The corrected data from Table XV

Figure 15 Effect of rare gas moderation on the isomeric transition reaction in gas mixtures of $\text{CH}_3\text{I}^{129}$, I_2 , and CH_4 .
Additives: Neon, $\oplus$; Argon, $\odot$; Krypton, $\blacksquare$; Xenon, $\square$; $\text{CH}_3\text{I}^{129}$, $\blacktriangle$.

Table XI

Determination of the Limiting Organic Yield of Iodine-130 in Various
Gaseous Mixtures of Additive and Methane As a Result of Isomeric
Transition Induced Reactions

Additive	Mole Fraction Additive	Mole Fraction Methane	-Log Mole Fraction Methane	Percent I-130 As Organic O.Y. IT	Log Percent O.Y. IT
Neon	0.0436	0.9564	0.019	26.2	1.418
	0.0464	0.9536	0.021	25.9	1.413
	0.0825	0.9175	0.037	25.7	1.410
	0.1600	0.8400	0.076	26.9	1.430
Argon	0.0150	0.9850	0.007	24.8	1.394
	0.0232	0.9768	0.010	24.2	1.384
	0.0488	0.9512	0.022	23.3	1.367
	0.0799	0.9201	0.036	22.4	1.350
	0.1000	0.9000	0.046	22.1	1.344
Krypton	0.0094	0.9906	0.004	24.8	1.394
	0.0135	0.9865	0.006	23.8	1.377
	0.0298	0.9702	0.013	23.3	1.367
	0.0499	0.9501	0.022	23.0	1.362
	0.0756	0.9244	0.034	20.2	1.305
	0.0986	0.9014	0.045	20.7	1.316

Additive	Mole Fraction Additive	Mole Fraction Methane	-Log Mole Fraction Methane	Percent I-130 As Organic O.Y. IT	Log Percent O.Y. IT
Xenon	0.0169	0.9831	0.007	24.5	1.389
	0.0600	0.9400	0.027	22.0	1.342
	0.0980	0.9020	0.045	20.6	1.314
	0.1040	0.8960	0.048	21.2	1.326
	0.1500	0.8500	0.071	19.1	1.281
CH ₃ I ¹²⁹	0.0077	0.9923	0.003	25.2	1.401
	0.0250	0.9750	0.011	20.6	1.314
	0.0564	0.9436	0.025	14.7	1.167
	0.0654	0.9346	0.029	11.7	1.068
	0.0703	0.9297	0.032	8.7	0.940
	0.0873	0.9127	0.040	8.5	0.929

Figure 16 Determination of the limiting Iodine-130 organic yield in methane as a result of isomeric transition induced reactions. The limiting organic yield is $25.6 \pm 0.5\%$.

Table XII

Internal Consistency Test Showing the Limiting Organic Yields of ^{128}I and ^{130}I for the Respective Radiative Neutron Capture Reactions in Gaseous Mixtures of CH_3I , I_2 and CH_4 Following Immediate Post-Irradiation Extraction (a)

Composition of Samples	Percent I-128 As Organic O.Y. _{n,y}	Percent I-130 As Organic O.Y. _{n,y}
A. 0.1mm $^{127}\text{I}_2$ + 2.0mm $\text{CH}_3\text{I}^{127}$ + CH_4	54.4 54.5 54.4	
B. 0.1mm $^{129}\text{I}_2$ + 2.0mm $\text{CH}_3\text{I}^{127}$ + CH_4		45.4 42.8 38.9 44.4 42.8
C. 0.1mm $^{129}\text{I}_2$ + 2.0mm $\text{CH}_3\text{I}^{127}$ + CH_4	54.9 53.3 54.4 54.4 54.2	42.6 42.4 42.9 41.6 42.4

(a) All samples contained =1 atmosphere total pressure and were irradiated at ambient temperature for 1 minute.

Table XIII

Percent ^{130}I Stabilized in Organic Combination in CD_4 and Various Gaseous
Additive Mixtures Following Neutron Irradiation at Ambient Temperature
for Immediate Post-Irradiation Extraction (a)

Additive	Pressure d-Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. n, γ	Percent I-130 As Organic (corr) O.Y. n, γ (c)
Krypton	672.5	39.0	0.0548	46.8	
				39.4	
				39.9	
				40.4	
	560.5	131.5	0.1900	41.6	40.2
				36.2	
				35.1	
				35.8	
	475.0	209.5	0.3061	41.0	
				37.1	
				45.0	
				38.3	36.1
	424.0	276.0	0.3936	37.5	
				38.0	
				37.7	34.9
				34.5	
				37.2	
				35.8	32.4

Additive	Pressure d-Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,y}	Percent I-130 As Organic (corr) O.Y. _{n,y} (c)
Krypton	362.5	354.5	0.4940	34.5 34.9	
	271.5	417.5	0.6059	35.3 35.8	34.7 30.7
Xenon	190.0	504.0	0.7262	35.5 34.4	30.9 29.2
	705.0	8.5	0.0119	35.7 35.8 36.8 36.6	
	673.0	39.5	0.0554	29.7 30.5 30.4 28.2	36.3 35.2
	624.0	82.0	0.1163	29.2 26.8 28.1 26.6	30.1 28.6
					27.7 25.7

Additive	Pressure d-Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,y}	Percent I-130 As Organic (corr) O.Y. _{n,y} (c)
Xenon	493.0	203.0	0.2918	23.4 24.0	
				23.7	20.0
	366.5	341.0	0.4821	22.7 22.9	
				22.8	17.4
CH ₃ I ¹²⁹	202.0	509.0	0.7136	22.6 25.8 24.4	
				24.3	16.9
	741.0	4.0	0.0054	42.9 40.9	
				41.9	40.8
	709.5	4.0	0.0056	36.8 37.6	
				37.3	36.2
	725.5	11.0	0.0156	29.4 30.2 30.6 29.8	
				30.0	28.9

Additive	Pressure d-Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ}	Percent I-130 As Organic (corr) O.Y. _{n,γ} (c)
CH ₃ I ¹²⁹	675.5	42.5	0.0591	17.1	
				14.1	
				16.1	
	640.0	70.5	0.0992		15.8
				12.8	
				10.5	
	622.5	99.0	0.1373	10.6	
					11.3
				8.3	
				7.6	
	102.0	115.5	0.5310	8.4	
				7.8	
					8.0
				2.1	
				3.0	
				2.1	
					3.6
					2.5

(a) All rare gas moderated samples contained $0.1 \pm 0.02\text{mm I}_2$ and $5.0 \pm 0.3\text{mm CH}_3\text{I}^{129}$. All samples were irradiated for 30 seconds at ambient temperature and extracted immediately following irradiation.

- (b) Calculated assuming additive pressures. Error ± 0.002
- (c) Values were calculated considering 1.1% failure to bond rupture of ^{130}I from $\text{CH}_3\text{I}^{130}$ and reactor-induced radiation reactions (using Figure 1) imparted to each system.

Figure 17 Effect of rare gas moderation on the radiative neutron capture reaction in gaseous additive mixtures of CH_3I^{129} , I_2 , and CD_4 . Additives: Krypton, ■; Xenon, □; CH_3I^{129} , ▲.

Table XIV

Determination of the Limiting Iodine-130 Organic Yield in CD_4 and Various Gaseous Additive Mixtures Following Neutron Irradiation at Ambient Temperature for Immediate Post-Irradiation Extraction

Additive	Mole Fraction Additive	Mole Fraction d-Methane	-Log Mole Fraction d-Methane	Percent I-130 As Organic O.Y. _{n,γ}	Log Percent O.Y. _{n,γ}
Krypton	0.0100	0.9900	0.004	41.7	1.620
	0.0250	0.9750	0.011	41.2	1.615
	0.0548	0.9452	0.025	40.2	1.604
	0.0750	0.9250	0.034	39.6	1.598
	0.1000	0.8000	0.046	38.6	1.587
	0.1500	0.8500	0.071	37.2	1.571
	0.1900	0.8100	0.092	36.1	1.558
Xenon	0.0100	0.9900	0.004	37.5	1.574
	0.0119	0.9881	0.005	36.5	1.562
	0.0250	0.9750	0.011	33.5	1.525
	0.0554	0.9446	0.025	28.6	1.456
	0.0750	0.9250	0.034	27.0	1.431
$\text{CH}_3\text{I}^{129}$	0.0054	0.9946	0.002	40.8	1.611
	0.0056	0.9944	0.003	36.2	1.559
	0.0156	0.9844	0.007	28.9	1.4611
	0.0591	0.9404	0.026	14.7	1.167
	0.0992	0.9008	0.045	10.2	1.009

Figure 18 Determination of the limiting Iodine-130 organic yield in d-methane as a result of radiative neutron capture reactions. The limiting organic yield is $42.0 \pm 0.5\%$.

Table XV

Total Iodine-130 Organic Yields in CD_4 and Gaseous Additive Mixtures
Following Neutron Irradiation at Ambient Temperature and After All
Iodine-130m Has Decayed (≈ 90 min) (a)

Additive	Pressure d-Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
Krypton	733.5	10.0	0.0154	32.8 34.6	
				33.7	32.5
	658.0	75.0	0.1024	32.5	30.8
	498.5	212.5	0.2989	29.4	25.6
	509.5	225.0	0.3063	29.7 28.9 27.9	
				28.8	25.0
	389.0	338.5	0.4650	29.7 29.2 29.4	
				29.4	24.2
	362.0	378.5	0.5111	28.2 28.8 28.3	
				28.4	22.8

Additive	Pressure d-Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
Krypton	336.0	413.0	0.5515	29.9 26.8	
				28.3	22.3
	238.5	476.5	0.6662	29.7 28.5 25.3	
				27.8	21.3
	141.5	589.5	0.8057	28.7 29.7	
				29.2	20.9
Xenon	704.0	8.5	0.0119		31.8
	699.5	13.0	0.0182		30.7
	698.5	37.0	0.0503		29.5
				28.1 29.5 26.5 27.2	
				27.8	26.3
	661.0	43.5	0.0617	27.1	25.5
	650.5	57.5	0.0815	28.2 27.6 22.4	
				25.0	23.2

Additive	Pressure d-Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
Xenon	508.5	212.0	0.2923	22.3 17.8 21.7 18.9	
	360.5	354.0	0.4953	23.7 20.1 16.5	20.2 16.4
	206.0	507.0	0.7108	22.5 20.6 19.6	20.1 14.5
CH ₃ I ¹²⁹	696.5	11.0	0.0155	27.3 28.4 26.8 34.1	20.8 13.4
	697.5	39.5	0.0536	17.7 13.1 11.9 12.2	29.1 28.0
					13.7 12.6

Additive	Pressure d-Methane (mm)	Pressure Additive (mm)	Mole Fraction Additive (b)	Percent I-130 As Organic (obs) O.Y. _{n,γ+IT}	Percent I-130 As Organic (corr) O.Y. _{n,γ+IT} (c)
CH ₃ I ¹²⁹	610.0	67.0	0.0990	8.1	
				12.8	
				8.9	
				13.4	
	625.0	98.5	0.1361	10.8	9.7
				7.3	6.2
	73.0	123.0	0.6287	3.9	
				3.3	
	32.5	142.5	0.8142	3.6	2.5
				2.8	
				1.8	
				2.3	1.2

(a) All rare gas moderated samples contained 0.1 ± 0.02 mm I₂ and 5.0 ± 0.3 mm CH₃I¹²⁹. All samples were irradiated for 2 minutes at ambient temperature and left at room temperature until extraction at least 90 minutes after the end of irradiation.

(b) Calculated assuming additive pressures. Error ± 0.002

(c) Values were calculated considering 1.1% failure to bond rupture of ¹³⁰I from CH₃I¹³⁰ and reactor-induced radiation reactions (using Figure) imparted to each system.

Figure 19 Effect of rare gas moderation on the total Iodine-130 organic yields in CD₄ additive mixtures containing CH₃I¹²⁹ and I₂ after all Iodine-130m has decayed (≈ 90 min). Additives: Krypton, ■ ; Xenon, □ ; CH₃I¹²⁹, ▲ .

Table XVI

Determination of the Limiting Total Iodine-130 Organic Yield in CD_4 and Gaseous Additive Mixtures Following Neutron Irradiation at Ambient Temperature and After All Iodine-130m Has Decayed (≈ 90 min)

Additive	Mole Fraction Additive	Mole Fraction d-Methane	-Log Mole Fraction d-Methane	Percent I-130 As Organic O.Y. $n, \gamma + \text{IT}$	Log Percent O.Y. $n, \gamma + \text{IT}$
Krypton	0.0134	0.9866	0.006	32.5	1.512
	0.0500	0.9500	0.022	31.0	1.491
	0.0750	0.9250	0.034	30.4	1.483
	0.1024	0.8976	0.047	30.8	1.489
	0.1500	0.8500	0.071	28.7	1.458
	0.2000	0.8000	0.097	27.5	1.439
Xenon	0.0119	0.9881	0.005	30.7	1.487
	0.0182	0.9812	0.008	29.5	1.470
	0.0503	0.9497	0.023	26.3	1.420
	0.0617	0.9383	0.028	25.5	1.407
	0.0815	0.9185	0.037	23.2	1.366
$\text{CH}_3\text{I}^{129}$	0.0155	0.9845	0.007	28.0	1.447
	0.0250	0.9750	0.011	22.0	1.342
	0.0536	0.9464	0.024	12.6	1.100
	0.0750	0.9250	0.034	9.7	0.987

Figure 20 Determination of the limiting total Iodine-130 organic yield in d-methane as a result of $(n,\gamma+IT)$ induced reactions. The limiting organic yield is $32.0 \pm 0.5\%$.

Table XVII

Iodine-130 Organic Yields in Various Gaseous Mixtures of Additive and
 CD_4 As a Result of Isomeric Transition Induced Reactions Following
 Neutron Irradiation at Ambient Temperature

Additive	Mole Fraction Additive	Percent I-130 As Organic O.Y. _{n,γ} (a)	Percent I-130 As Organic O.Y. _{n,γ+IT} (b)	Percent I-130 As Organic O.Y. _{IT} (c)
Krypton	0.0134	41.7	32.5	25.6
	0.0548	40.2	30.9	25.0
	0.1024	38.5	29.7	24.1
	0.1900	36.1	27.7	22.3
	0.2989	34.2	25.6	20.2
	0.3061	34.9	25.3	19.2
	0.3063	34.0	25.0	18.8
	0.3936	32.4	23.7	18.2
	0.4650	31.8	24.2	19.8
	0.4940	30.7	22.4	17.1
	0.5111	31.3	22.8	17.4
	0.5515	30.9	22.3	16.9
	0.6059	30.9	21.7	15.9
	0.6662	29.7	21.3	15.9
	0.7262	29.2	21.1	15.9
	0.8057	28.1	20.9	16.0
Xenon	0.0119	35.2	30.7	26.0
	0.0182	35.0	29.5	26.1

Additive	Mole Fraction Additive	Percent I-130 As Organic O.Y. _{n,γ} (a)	Percent I-130 As Organic O.Y. _{n,γ+IT} (b)	Percent I-130 As Organic O.Y. _{IT} (c)
Xenon	0.0503	33.7	26.3	21.6
	0.0554	28.6	25.8	23.9
	0.0617	31.5	25.5	21.7
	0.0815	26.5	23.2	21.2
	0.1163	25.7	21.6	16.4
	0.2000	21.4	18.5	16.7
	0.2918	20.0	16.6	14.4
	0.2923	19.5	16.4	14.3
	0.4000	18.1	15.3	13.4
	0.4821	17.4	14.8	13.1
	0.4953	17.5	14.5	12.6
	0.6000	17.2	14.0	11.9
	0.7108	17.0	13.4	11.1
	0.7136	16.9	13.2	10.8
CH ₃ I ¹²⁹	0.0054	40.8	30.0	23.1
	0.0056	36.2	29.8	25.8
	0.0155	28.9	28.0	25.0
	0.0591	14.7	11.4	9.3
	0.0992	10.2	9.7	9.5
	0.1361	7.0	6.2	5.7
	0.1373	6.9	6.1	5.6
	0.2000	5.0	4.8	4.7
	0.3000	3.6	4.1	4.4
	0.4000	3.0	3.4	3.6

Additive	Mole Fraction Additive	Percent I-130 As Organic O.Y. _{n,γ} (a)	Percent I-130 As Organic O.Y. _{n,γ+IT} (b)	Percent I-130 As Organic O.Y. _{IT} (c)
CH ₃ I ¹²⁹	0.5310	2.5	2.7	2.8
	0.6287	1.8	2.5	2.9
	0.8142	0.9	1.2	1.5

(a) Values were taken from Table XIII and Figure 17.

(b) Values were taken from Table XII and Figure 19.

(c) Values were calculated using the expression: $O.Y._{IT} = (O.Y._{n,\gamma+IT} - 0.39(O.Y._{n,\gamma})) / 0.61$

Figure 21 Effect of rare gas moderation on the isomeric transition reaction in gas mixtures of CH_3I^{129} , I_2 , and CD_4 . Additives: Krypton, $\blacksquare$; Xenon, $\square$; CH_3I^{129} , $\blacktriangle$.

Table XVIII

Determination of the Limiting Organic Yield of Iodine-130 in Various
Gaseous Mixtures of Additive and CD₄ As a Result of Isomeric
Transition Induced Reactions

Additive	Mole Fraction Additive	Mole Fraction d-Methane	-Log Mole Fraction d-Methane	Percent I-130 As Organic O.Y. _{IT}	Log Percent O.Y. _{IT}
Krypton	0.0134	0.9866	0.006	25.6	1.408
	0.0250	0.9750	0.011	25.5	1.407
	0.0548	0.9452	0.025	25.0	1.398
	0.0750	0.9250	0.034	24.5	1.389
	0.1024	0.8976	0.047	24.1	1.382
	0.1500	0.8500	0.071	22.8	1.358
	0.1900	0.8100	0.092	22.3	1.348
Xenon	0.0119	0.9881	0.005	25.2	1.401
	0.0182	0.9818	0.008	24.6	1.391
	0.0503	0.9497	0.022	21.6	1.334
	0.0617	0.9383	0.028	21.7	1.337
	0.0815	0.9185	0.037	20.2	1.305
	0.1163	0.8837	0.054	18.1	1.258
CH ₃ I ¹²⁹	0.0054	0.9946	0.002	23.1	1.364
	0.0056	0.9944	0.003	25.0	1.398
	0.0155	0.9845	0.007	23.5	1.371
	0.0250	0.9750	0.011	20.8	1.318

Additive	Mole Fraction Additive	Mole Fraction d-Methane	-Log Mole Fraction d-Methane	Percent I-130 As Organic O.Y. _{IT}	Log Percent O.Y. _{IT}
CH ₃ I ¹²⁹	0.0591	0.9409	0.026	13.5	1.130
	0.0750	0.9250	0.034	10.0	1.000
	0.0992	0.9008	0.045	9.5	0.977

Figure 22 Determination of the limiting Iodine-130 organic yield in d-methane as a result of isomeric transition induced reactions. The limiting organic yield is $25.6 \pm 0.5\%$.

is plotted in Figure 19. Using the data in Table XVI and plotted in Figure 20, the limiting total iodine-130 organic yield (as a result of $(n,\gamma)+(IT)$ activation) was found to be $32.5\% \pm 2\%$. At zero-mole-fraction d-methane in Figure 19 the data extrapolate to 0% for CH_3I^{129} additive, $19.8\% \pm 1\%$ for Kr additive, and to $11.0\% \pm 1\%$ for Xe additive.

By employing the relationship described above we calculated the isomeric transition induced organic yields for ^{130}I in CD_4 . Table XVII gives these calculated yields for various gaseous mixtures of additive and d-methane. Figure 21 shows the plotted data. The data in Table XVIII and plotted in Figure 22 gives a limiting organic yield for the iodine-130 isomeric transition induced reaction in d-methane of $26.4\% \pm 2\%$. The extrapolated data in Figure 21 at zero-mole-fraction d-methane gives values of 0% for CH_3I^{129} additive, $15.9\% \pm 1\%$ for Kr additive, and $10.3\% \pm 1\%$ for Xe additive.

Summary of Iodine Experimental Results

Table XIX summarizes the maximum extent of iodine-130 stabilized in organic combination with methane and d-methane as a result of activation by neutron capture and isomeric transition. These results are obtained from samples containing 0.1 mm I_2 , 5 mm CH_3I^{129} , moderator, and target molecule at a total pressure of approximately one atmosphere and determined from extrapolated data on a log-log plot as described above. The values were experimentally determined except the value for the O.Y. (IT) which is calculated from O.Y. $(n,\gamma)+(IT)$ and O.Y. (n,γ) .

Table XIX

Limiting Organic Yields for Iodine Atoms Activated
by Nuclear Processes in the Presence of Gaseous
Methane or d-Methane

Activating Event	System	Designation	Limiting Organic Yield
$^{127}\text{I}(n,\gamma)^{128}\text{I}$	(CH ₄)	$^{128}\text{I}(n,\gamma)$	54.4% ±2%
$^{129}\text{I}(n,\gamma)^{130}\text{I}$	(CH ₄)	$^{130}\text{I}(n,\gamma)$	42.0% ±2%
$^{129}\text{I}(n,\gamma) + (\text{IT})^{130}\text{I}$	(CH ₄)	$^{130}\text{I}(n,\gamma) + (\text{IT})$	32.0% ±2%
$^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$	(CH ₄)	$^{130}\text{I}(\text{IT})$	25.6% ±2%
$^{129}\text{I}(n,\gamma)^{130}\text{I}$	(CD ₄)	$^{130}\text{I}(n,\gamma)$	42.0% ±2%
$^{129}\text{I}(n,\gamma) + (\text{IT})^{130}\text{I}$	(CD ₄)	$^{130}\text{I}(n,\gamma) + (\text{IT})$	32.5% ±2%
$^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$	(CD ₄)	$^{130}\text{I}(\text{IT})$	26.4% ±2%

Discussion of Experimental Results

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

Considering the relative masses of CH_4 and I atoms, in order to have available as internal energy of the activated complex the necessary energies listed above for reaction, the iodine atom or ion must possess a minimum kinetic energy that is $(128 + 16)/16 = 9$ times as great as the endothermicity of the reaction. Thus, to be able to undergo reactions for which the activation energy is provided by their kinetic energy, iodine atoms must possess at least $1.72 \times 9 = 15.5$ eV, and I^+ ions must have $0.78 \times 9 = 7.1$ eV. From average recoil energies associated with iodine atoms, it would be expected that most of the I^* atoms or ions are capable of forming CH_3I^* or HI^* via a hot reaction with methane.

The formation of CH_3I^* need not, however, be limited to the above reactions. It is possible that a positively charged iodine atom react with methane via an ion-molecule mechanism. For example, the following reactions could occur:⁸

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

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

The product atoms from an isomeric transition process such as $^{130}I^m(IT)^{130}I$ can also acquire kinetic energy. In this case, the atoms obtain the energy by a Coulombic repulsion mechanism. As a result of internal conversion and Auger electron emission occurring as an alternative to gamma ray emission in the decay of the metastable state, the atoms are produced with a positive charge. The build-up of charge is followed by a charge-transfer process as the atom attains partial neutralization by attracting electrons from other atoms in the molecule. As a consequence, some or all of the atoms in the molecule are positively charged, and they repel each other with considerable force. The distribution of energies resulting from such a "Coulombic explosion" depends upon the charge distribution of the ions produced by the vacancy cascade, the distances separating the atoms in the molecule, and the relative masses of the atoms. Carlson and White⁹ observed that, when the iodine atom was originally bound as CH_3I , iodine ions were produced with initial charges as high as +10 and with recoil energies as high as 49 eV (See Table XX). The most probable product is I^{5+} with a recoil kinetic energy of about 9 eV. An atom undergoing isomeric transition in CH_3I must be charged to I^{4+} or higher for the atoms to obtain the 7.1 eV kinetic energy required to displace H from CH_4 .

The kinetic energy obtained by I atoms following isomeric transition in a CH_3I molecule can be calculated, provided the charges of two repelling atoms at the time of the "Coulombic explosion" can be estimated.

Table XX
 Relative Abundances and Recoil Energies of the
 Fragment Ions from the Decomposition of CH_3I
 Following an Innershell Vacancy in Iodine

Ion	Relative Abundance (Relative to $\text{I}^{5+} = 1.00$)	Recoil Energy ^(a) (eV)
I^{1+}	0.27 ± 0.02	----
I^{2+}	0.44 ± 0.02	2.2 ± 0.4
I^{3+}	0.61 ± 0.02	5.3 ± 0.8
I^{4+}	0.77 ± 0.02	7.1 ± 1.0
I^{5+}	1.00	8.9 ± 1.0
I^{6+}	0.63 ± 0.02	12.8 ± 2.0
I^{7+}	0.49 ± 0.02	15 ± 2
I^{8+}	0.23 ± 0.01	20 ± 4
I^{9+}	0.10 ± 0.01	41 ± 8
I^{10+}	0.03 ± 0.01	----

(a) Recoil energies relative to $\text{I}^{5+} = 8.9$ eV.

The most probable result of an isomeric transition occurring in an iodine atom bound in CH_3I is the loss of 10-11 electrons. Then the I atom would be charged to I^{5+} following the charge-transfer process. Coulombic repulsion of C^{2+} and I^{5+} atoms separated by a distance of $2.14 \text{ \AA}$, corresponding to the C-I bond length¹⁰ in CH_3I , could result in a maximum kinetic energy of 211 eV, or about 150 eV for the recoiling I atom⁹. Calculations of the type described by Willard² indicate that the average number of collisions needed to reduce the 150 eV kinetic energy of the ^{130}I ions below the 7.1 eV required for reaction with CH_4 without encountering a CH_4 molecule is 11.1 for collisions with Ne, 6.1 for Ar, 3.6 for Kr, and 3.0 for Xe. Iodine atoms which have undergone the average number of collisions required to reduce the energy from 150 eV to 7 eV will, of course, have a spectrum of energies ranging above and below these specified values.

A. Comparison of the (n, γ) organic yields for ^{128}I and ^{130}I in CH_4

Some of the most interesting information obtained in this work concerns the organic yields in the $^{130}\text{I}-\text{CH}_4$ system given in Table XIX. The fact that the $^{128}\text{I}_{(n,\gamma)}$ and $^{130}\text{I}_{(n,\gamma)}$ organic yields are different by about 12% is important that it demonstrates that activation of the iodine atoms by the $^{127}\text{I}_{(n,\gamma)}$ ^{128}I and $^{129}\text{I}_{(n,\gamma)}$ ^{130}I reactions are somewhat different. This is in contrast with the results of Wilkey¹¹ who found the organic yields to be the same within experimental error. In comparison with evidence from previous work³ that the ^{128}I atoms produced by the (n, γ) process react partly as a result of their kinetic energy and partly as a result of charge, our results suggest that the

fractions of the $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}$ produced atoms capable of reacting with methane as a result of kinetic energy and charge are similar to those of ^{128}I atoms but different in relative proportions. This would indicate that the ^{128}I and ^{130}I isotopes have different populations in the various states such as the $\text{I}^+(\text{D}_2)$, etc.

The difference between Wilkey's result¹¹ (52.0%) and our result (42.0%) for the $^{130}\text{I}(\text{n},\gamma)$ organic yield in methane may be explained by the possibility that the chemical origin of the recoiling atom could have an effect on its reactions if the energy required for the atom to break its chemical bonds are large enough to significantly change the fraction of the atoms which have sufficient kinetic energy to react with CH_4 following bond rupture. This could result from either differences in the bond energies of I in $^{129}\text{I}_2$ used by Wilkey and $\text{CH}_3\text{I}^{129}$ used in this research as source molecules, or inertial effects caused by differences in the masses of the recoil partners. The $\text{CH}_3\text{-I}$ bond energy is 2.2 eV as compared to 1.6 eV for the I-I bond energy. Nearly all ^{130}I atoms formed by the $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}$ reaction are produced with energy well in excess of these values, and it is unlikely that the small difference in the CH_3I and I_2 bond energies could have an important effect on the distribution of energies. However, even if the bond energies were the same, rupture of the $\text{CH}_3\text{-I}$ bond requires higher energy than is needed for the I-I bond because the fraction of the recoil energy which is available for bond rupture is $M_{\text{CH}_3}/(M_{\text{CH}_3} + M_{\text{I}}) = 0.105$ for CH_3I and $M_{\text{I}}/(M_{\text{I}} + M_{\text{I}}) = 0.5$ for I_2 . This suggests that in comparison a significant fraction of the ^{130}I atoms from $\text{CH}_3\text{I}^{129}$ would fail to escape their parent as a result of recoil. This would explain,

perhaps the 10% difference in the two reported results.

B. Comparison of organic yields for $^{130}\text{I}_{(n,\gamma)}$ and $^{130}\text{I}_{(n,\gamma)} + (\text{IT})$

The $^{130}\text{I}_{(n,\gamma)}$ and $^{130}\text{I}_{(n,\gamma)} + (\text{IT})$ organic yields are different by 10%. All isomeric transition daughter atoms are initially charge regardless of their chemical combination, but the kinetic energy depends upon the relative masses and number of electrons of the atoms in the parent molecule. The production of molecular ions CH_3I^+ by the $^{130}\text{I}^m(\text{IT})^{130}\text{I}$ process occurring in the source molecule CH_3I could conceivably cause the difference in the yields in the $^{130}\text{I}_{(n,\gamma)}$ and $^{130}\text{I}_{(n,\gamma)} + (\text{IT})$ systems. Isomeric transition events which are not accompanied by Auger emission produce only singly charged $^{130}\text{I}^+$ ions which cannot cause bond rupture by Coulombic repulsion. However, the most probable result of an isomeric transition occurring in an iodine atom incorporated in a complex molecule, such as CH_3I , which increases the extent of ionization, is a vacancy cascade most probably resulting in the loss of 10-11 electrons to form I^{5+} following charge-transfer.⁹

Again our results for the $^{130}\text{I}_{(n,\gamma)} + (\text{IT})$ yield (32.0%) differ slightly from that reported by Wilkey¹¹ (37.2%) for the same activation event. It is possible that the $^{130}\text{I}^+$ ions are in different excited electronic states following neutralization of a thermal $^{130}\text{I}^{x+}$ from CH_3I than following neutralization from $^{130}\text{I}^{y+}$ born from I_2 . It has been shown by Rack and Gordus³ that reactions of atoms or ions in excited electronic states are important in determining the fate of ^{128}I formed by the $^{128}\text{I}_{(n,\gamma)}$ -activation in methane, and therefore it is reasonable to expect that they would be important following (IT)-activation as well.

It is possible for the difference between the ^{130}I (n, γ)-activated process and the ^{130}I (n, β)+(IT)-activated process organic yields to be due to differences in excitation probabilities. This conclusion is due, at least in part, to a lower probability of forming the excited state of I^+ capable of reacting with CH_4 when the charging process occurs in an atom bound as CH_3I than in the recoil I atom from the (n, γ) reaction.

C. Isomeric transition organic yields for ^{130}I in methane

The 25.6% $^{130}\text{I}_{(\text{IT})}$ (Table XIX) compares well with the value 26.2% $^{130}\text{I}_{(\text{IT})}$ determined by Wilkey.¹¹ These yields show that the ability of the product atoms to react with CH_4 is less following activation by isomeric transition than when the atoms are formed by the (n, γ) reaction. The low isomeric transition yield relative to that for (n, γ) activation may indicate that a significant fraction of the isomeric transition product atoms do not have sufficient kinetic energy to react. This is predictable from studies by Carlson and White⁹ on vacancy cascades in iodine which show that an appreciable fraction of the I ions formed after ejection of a K electron do not have high enough charge to give the Coulombic repulsion necessary to yield sufficient kinetic energy to displace hydrogen from methane. However, insufficient kinetic energy imparted to the activated I atoms may not be the only reason for lower isomeric transition organic yields than (n, γ) organic yields. The results of Rack and Gordus³ indicate that, even if none of the isomeric transition daughter atoms are capable of reacting as a result of their kinetic energy, the $^{130}\text{I}_{(\text{IT})}$ organic yield should be about 36%. However, as

mentioned in the preceding section, the lower-than-36% organic yield observed for isomeric transition may in part be due to lower probability of forming the excited states of I^+ capable of reacting with CH_4 when the charging process occurs in an atom bound as CH_3I than in the recoil I atom from the (n,δ) reaction.

D. Effect of moderators on the $^{130}I-CH_4$ system

Hot reactions are sensitive to moderators (e.g., rare gases) which, though chemically inert, will efficiently remove energy from the hot species. If kinetic energy is a requirement for reaction, increasing concentrations of rare gas additive can decrease the organic yield by reducing the kinetic energy of the hot atom below that required for reaction. If positive ions are involved in the chemical reaction they can be removed from organic combination by charge-transfer reactions with the moderator if the energy defect approaches zero.

The effects of Ne, Ar, Kr, Xe, and CH_3I^{129} additives on the reaction of CH_4 and ^{130}I activated by (n,γ) , $(n,\gamma)+(IT)$, and (IT) processes are shown in Figures 11, 13, and 15, respectively. The Xe extrapolated value (Fig. 13) at zero-mole-fraction CH_4 was verified using CH_2F_2 as a molecular additive which gives the same extrapolation as xenon in the $^{128}I-CH_4$ system.¹² The extrapolated data show that the rare gases only partially suppress the reaction indicating that only a fraction of the CH_3I^{130} is formed as a result of hot processes which occur due to kinetic energy of the ^{130}I atoms or ions. It is noted that Xe reduces the CH_3I^{130} yield to a greater extent than the other rare gas additives. This suggests that of the 42.0% $^{130}I_{(n,\gamma)}$ organic yield, about 16%

forms as a result of hot ^{130}I reactions, 16.5% as a result of excited iodine atoms or I^+ ions in the $^3\text{P}_2$, $^3\text{P}_1$, and/or $^3\text{P}_0$ states, 9.5% as a result of reactions of $\text{I}^+(\text{D}_2)$ ions; and of the 25.6% $^{130}\text{I}_{(\text{IT})}$ organic yield 9.7% forms as a result of hot ^{130}I reactions, 10.3% as a result of excited iodine atoms or I^+ ions, and 5.6% as a result of $\text{I}^+(\text{D}_2)$ ions.

If the 16% $^{130}\text{I}_{(\text{n},\gamma)}$ and 9.7% $^{130}\text{I}_{(\text{IT})}$ organic yield which is sensitive to Ne, Ar, and Kr moderation results from an excess kinetic energy (hot atom) process, the relative effectiveness of the moderators would depend on the relative size of the rare gas atoms and on the fractional energy transfer per ^{130}I rare gas collision. Figures 11, 13, and 15 are in accord with increasing moderation efficiencies for kinetic energy moderation by showing more effective moderation in the order: Ne, Ar, Kr.

The fact that xenon reduces the extent of formation of $\text{CH}_3\text{I}^{130}$ by an additional 9.5% in the $^{130}\text{I}_{(\text{n},\gamma)}$ system and 5.6% in the $^{130}\text{I}_{(\text{IT})}$ system must be due to a unique ability of xenon to neutralize or quench excited ^{130}I ions or atoms. However, rare gases are not considered effective quenching agents. Therefore, this additional inhibition to the organic yield by xenon must be due to a charge-transfer process. For xenon alone to reduce the extent of reaction by charge-transfer requires that the energy defect of the reaction approach zero more closely than that for charge-transfer with the other rare gases.

The first four excited states of I^+ (ionization potential, 10.454 eV) and their excitation energies are as follows: ($^3\text{P}_0$) 0.800, ($^3\text{P}_1$) 0.879, ($^1\text{D}_2$) 1.702, and ($^1\text{S}_0$) 4.044 eV. The ionization potential of CH_4 is 12.71 eV. It is unlikely that excited states of I^+ higher than $^1\text{D}_2$ will

exist in the methane environment since charge-transfer between CH_4 and I^+ in the $^1\text{S}_0$ or higher states is exothermic.

The ionization potential of xenon is 12.127 eV. Thus, the charge-transfer process $\text{I}^+(^1\text{D}_2) + \text{Xe} \rightarrow \text{I} + \text{Xe}^+$ is exothermic by 0.029 eV. The smallest energy defect for the possible charge-transfer processes involving the other rare gases is 1.84 eV endothermic for the $\text{I}^+(^1\text{D}_2) + \text{Kr}$ reaction. Hence, these processes involving Kr, Ar, or Ne charge-transfer with I^+ ions in energy states of $^1\text{D}_2$ or less have an extremely small probability of occurrence.

Referring to Figure 13 CH_2F_2 would not be expected to quench $\text{I}^+(^1\text{D}_2)$ and itself. Charge-transfer cannot occur easily between CH_2F_2 and $\text{I}^+(^1\text{D}_2)$ since the ionization potential of CH_2F_2 is 12.55 eV. Therefore, the 7.1% additional inhibition of the $^{130}\text{I}_{(\text{n},\gamma)+(\text{IT})}$ organic yield by CH_2F_2 must be to a thermal ion-molecule reaction of $\text{I}^+(^1\text{D}_2) + \text{CH}_2\text{F}_2$. Reactions leading to organic ^{130}I are endothermic. However, one-step reactions leading to HI are exothermic for the products: $\text{CHF}_2^+ + \text{HI}$, $H = -1.0$ eV; for $\text{CH}_2\text{F}_2 + \text{HI}^+$, $H = -0.4$ eV. Thus, it would appear that the 7.1% inhibition by CH_2F_2 could be due to either of the two reactions yielding HI.

Interesting observations to mention in comparing the moderation results of ^{128}I and ^{130}I are that relative to the maximum extent of organic combination (a) the kinetic energy contribution in the $^{130}\text{I}_{(\text{n},\gamma)}$ system is about the same as that for the $^{128}\text{I}_{(\text{n},\gamma)}$ system, (b) the $\text{I}^+(^1\text{D}_2)$ contribution for $^{130}\text{I}_{(\text{n},\gamma)}$ is about one-half that of $^{128}\text{I}_{(\text{n},\gamma)}$, and (c) the excited state contributions for $^{130}\text{I}_{(\text{n},\gamma)}$ is about twice that of $^{128}\text{I}_{(\text{n},\gamma)}$. These observations can probably be best explained by the facts mentioned

above that there is an extremely good possibility that the $^{130}\text{I}^+$ ions are born in different proportions than the $^{128}\text{I}^+$ ions as a consequence of different low lying gamma ray emission spectra of ^{128}I and ^{130}I .

CHAPTER III. KINETIC ENERGY ISOTOPE EFFECTS OF BROMINE REACTIONS ACTIVATED
BY RADIATIVE NEUTRON CAPTURE IN GASEOUS CH_3F AND CD_3F

(R. W. Helton)

Although there have been many studies¹³⁻¹⁵ relating to isotope effects (differences in organic yields) of (n, γ)-activated bromine reactions in condensed state hydrocarbons, aromatics, and alkyl halides, no study reports, for a single gaseous system, organic yields for (n, γ)-activated ^{80}Br , $^{80}\text{Br}^m$, and $^{82}\text{Br}^m + ^{82}\text{Br}$ reactions. For condensed state systems employing high purity reagents and correcting for $^{82}\text{Br}^m(\text{I.T})$ ^{82}Br reactions,^{16,17} no bromine isotope effects were generally found.

Unlike the reactions of (n, γ)-activated ^{128}I with CH_4 ,³ reactions of (n, γ)-activated ^{80}Br with CH_4 ¹⁸ occur principally as a result of the recoil kinetic energy acquired by the ^{80}Br in the (n, γ)-activation process. While other activation processes such as the (γ ,n) and (n,p) processes impart to the atom a very high kinetic energy (10^5ev), the (n, γ) activation process results in a distribution of energies ranging from some very low value (near zero) to a maximum of 10^2ev . Bromine-80 hot atoms can have a maximum of about 357 ev. kinetic energy. If the three activation processes, $^{79}\text{Br}(\text{n},\gamma)^{80}\text{Br}$, $^{79}\text{Br}(\text{n},\gamma)^{80}\text{Br}^m$, and $^{80}\text{Br}(\text{n},\gamma)^{82}\text{Br}^m + ^{82}\text{Br}$ impart to the respective atoms different kinetic energy spectra, and if the population of atoms with kinetic energies comparable to the reactive region $E_2 - E_1$ is great enough, then we would expect bromine isotope effects for systems involving endothermic reactions. Since the complete neutron capture γ -ray cascade spectrum is not known for bromine isotopes, it is not possible to calculate the distribution of bromine

recoil energies. Because of partial cancellation of γ -recoil momenta in cascade γ -emission, bromine atoms will be formed with a distribution of energies. Wolfgang¹⁹ originally suggested that the initial energy of atoms produced by (n,γ) processes may not meet the requirements of Assumption Ia of the kinetic theory, which states that the initial energy E_0 of the hot atom is sufficiently high so that the atom has made a large number of collisions above energy E_2 .

In this chapter we report the existence of an isotope effect between (n,γ) -activated ^{80}Br , $^{80}\text{Br}^m$, and $^{82}\text{Br}^m + ^{82}\text{Br}$ in gaseous CH_3F and CD_3F . A general description of our sample making techniques, irradiation procedures and extraction techniques can be found elsewhere.^{14, 15, 18, 20, 21} Ten ml quartz bulblets filled with 10 mm of Br_2 , CH_3F and CD_3F , and rare gas additive with a total gas pressure of 500 Torr were irradiated for 30 seconds. Pressure study samples contained only CH_3F and Br_2 with system pressures ranging from 50 to 800 Torr. Samples for (n,γ) studies were extracted immediately after irradiation (1.5 minutes from start of irradiation). This prevented the possibility of thermal reactions between labeled inorganic bromine with impurities, resulting in an "impurity" isotope effect. The data for ^{80}Br , $^{80}\text{Br}^m$, and $^{82}\text{Br}^m + ^{82}\text{Br}$ organic yields were acquired from the same sample. Samples for $^{82}\text{Br}^m$ isomeric transition (I.T.) studies were allowed to stand before extraction. See reference 13 for details.

Results and Discussion

Two different kinds of experiments were performed: (a) those systems containing only CH_3F or CD_3F with varying concentrations of Br_2 at

various system pressures, (b) those systems containing CH_3F , Br_2 source, and rare gas additives. From experiment (a) we determined possible pressure effects and limiting bromine isotope organic yields at zero mole fraction Br_2 . The results of experiment (b) suggested the role of kinetic energy on bromine reactions with CH_3F and the importance, if any, of thermal reactions to the organic yield.

Presented in Tables XXI through XXIX are some of our experimental results. The most interesting result, the isotope effect among the three bromine isotopes, is depicted in Figure 23. It should be noted that the extrapolation of the points in Figure 23 to zero mole fraction moderator is for a system containing 10 mm Br_2 . These extrapolated results are, of course, lower than the organic yields reported for extrapolation to zero-mole fraction Br_2 . Our experimental results can be briefly summarized as follows:

1. A pressure effect between 50 and 200 Torr total system pressure for all bromine-isotope organic yields was found. The organic yields increased with total system pressure from 50 to 200 Torr, remaining constant from 200 Torr to 800 Torr, the highest pressure studied. Apparently above 200 Torr, energetically excited molecules are collisionally stabilized.

2. The limiting (n,y) organic yields at zero mole fraction Br_2 in CH_3F at 800 Torr system pressure are ^{80}Br : $8.50 \pm 0.3\%$; $^{80}\text{Br}^m$: $10.0 \pm 0.3\%$; $^{82}\text{Br}^m$ + ^{82}Br : $5.0 \pm 0.3\%$.

3. The limiting (n,y) organic yields at zero mole fraction Br_2 in CD_3F at 800 Torr system pressure are ^{80}Br : $5.8 \pm 0.3\%$; $^{80}\text{Br}^m$: $7.5 \pm 0.3\%$; $^{82}\text{Br}^m$ + ^{82}Br : $5.0 \pm 0.3\%$.

4. From Fig. 23, it can be seen that the limiting bromine organic

yield at zero mole fraction CH_3F for both He and Ar additives is zero, indicating that the reactions occur entirely as a result of the recoil kinetic energy acquired by the bromine in its activation process. The efficiency of He, Ar and Br_2 moderation of the Br endothermic reaction with CH_3F is as we would expect of a kinetic energy moderator. Similar results were found in CD_3F systems.

5. The bromine isotope effect appeared regardless of additive, concentration of additive, or total system pressure. From the several hundred samples irradiated, the average organic yields of fifty samples picked at random from the CH_3F systems studied were ^{80}Br :5.27; $^{80}\text{Br}^m$:7.66; $^{82}\text{Br}^m + ^{82}\text{Br}$:4.42, showing that the effect is a general one, and not specific for a particular condition.

6. The limiting (I.T.) induced ^{82}Br organic yields at zero mole fraction Br_2 in CH_3F and CD_3F at 800 Torr system pressure were $7.5 \pm 0.5\%$ and $4.5 \pm 0.5\%$, respectively. From moderation plots similar to Fig. 1, the data appeared to extrapolate at zero mole fraction CH_3F or CD_3F to 1%. This indicates for $^{82}\text{Br} + \text{CH}_3\text{F}$ systems 7.5% minus 1% is formed via kinetic energy processes and that 1% is formed via thermal ionic processes.

A bromine isotope effect can be due to either a difference in the population of positively charged bromine species produced by the three (n,γ) activation processes or due to different kinetic energy spectra of the (n,γ) activated bromine atoms. Since it has been previously shown⁸ that reactions of bromine activated by (n,γ) occur independently of any positive charge, we suggest that the observed bromine isotope effect is due to differences in the kinetic energy spectra of the activated atoms. The organic yields increase in the order $^{82}\text{Br}^m + ^{82}\text{r}$, ^{80}Br , and $^{80}\text{Br}^m$.

TABLE XXI

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic Combination With
 CH_3F After Neutron Irradiation at Ambient Temperature

Pressure CH_3F (mm)	Pressure Bromine (mm)	Mole Fraction Bromine (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^m$ As Organic (b)	Percent ^{82}Br As Organic (b)
780.0	20.0	0.025	7.61	9.24	6.46
762.0	40.0	0.050	7.26	8.87	6.00
755.0	59.0	0.072	6.64	7.77	5.56
102.0	4.0	0.038	6.00	6.58	5.21
90.0	10.0	0.100	5.07	7.03	4.54
72.0	30.0	0.294	3.22	4.21	2.75
51.0	49.0	0.490	1.97	2.33	1.77
25.0	77.0	0.755	0.75	0.55	0.68

(a) Error ± 0.002

(b) These values represent the averages of at least three samples. The reproducibility was with $\pm 0.5\%$.

TABLE XXII

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic Combination With
 CH_3F After Irradiation at Ambient Temperature

Pressure CH_3F (mm)	Pressure Bromine (mm)	Mole Fraction Bromine (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^m$ As Organic (b)	Percent ^{82}Br As Organic (b)
31.5	3.5	0.10	4.58	3.95	5.47
70.0	7.5	0.10	5.08	7.69	4.60
135.0	15.0	0.10	5.39	6.00	4.49
180.0	20.0	0.10	5.43	6.70	4.72
320.0	35.0	0.10	5.70	8.04	4.77
450.0	50.0	0.10	5.86	6.96	5.16
632.0	71.0	0.10	5.88	7.34	4.96

(a) Error ± 0.01 .

(b) These values represent the averages of at least three samples. The reproducibility was within $\pm 0.5\%$.

TABLE XXIII

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic CombinationWith CH_3F After Irradiation at Ambient Temperature

Pressure CH_3F (mm)	Pressure Helium (mm)	Pressure Bromine (mm)	Mole Fraction Helium (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^m$ As Organic (b)	Percent ^{82}Br As Organic (b)
450.0	33.5	20.0	0.067	6.88	11.45	5.80
410.0	70.0	20.0	0.140	6.86	9.15	5.67
350.0	130.0	20.0	0.260	6.16	7.78	5.32
210.0	270.0	20.0	0.460	6.02	7.30	5.02
75.0	410.0	20.0	0.812	2.55	3.11	2.17

(a) Error ± 0.002 .(b) These values represent the average of at least three samples. The reproducibility was within $\pm 0.5\%$.

TABLE XXIV

Percent ^{82}Br Stabilized in Organic Combination in CH_3F After Neutron
Irradiation at Ambient Temperature

Pressure CH_3F (mm)	Pressure Bromine (mm)	Mole Fraction Bromine (a)	Percent 82 O.Y. obs	As Organic O.Y. IT (b)
780.0	5.5	0.007	7.29	7.35
784.0	16.0	0.020	4.75	4.57
789.0	20.0	0.025	6.76	6.79
775.0	32.0	0.040	9.35	9.65
741.0	39.0	0.050	6.98	7.07
734.0	60.0	0.076	5.82	5.85
736.0	64.0	0.080	4.99	4.95
96.0	4.0	0.040	8.51	8.82
93.0	8.0	0.079	8.71	9.10
90.0	10.0	0.100	4.41	4.40
70.0	30.0	0.300	3.71	3.83
62.0	35.5	0.364	3.70	3.85
50.0	50.0	0.500	2.25	2.32
25.0	78.0	0.757	0.96	0.99

(a) Error ± 0.005 .

(b) $\text{O.Y. (IT)} = \frac{\text{O.Y. obs} - 0.09 (\text{O.Y. n.})}{0.91}$

These values represent the averages of at least three samples.

The reproducibility was within $\pm 0.5\%$.

TABLE XXV

Percent ^{82}Br Stabilized in Organic Combination in CD_3F After Neutron
Irradiation at Ambient Temperature

Pressure CD_3F (mm)	Pressure Bromine (mm)	Mole Fraction Bromine (a)	Percent ^{82}Br O.Y. (obs)	As Organic O.Y. (IT) (b)
397.0	5.0	0.013	5.13	5.21
390.0	10.0	0.025	3.63	3.56
376.0	27.0	0.067	3.73	3.71
354.0	47.0	0.117	2.93	2.88
330.0	69.0	0.173	2.71	2.67

(a) Error ± 0.005 .

(b) $\text{O.Y. (IT)} = \frac{\text{O.Y. obs} - 0.09 (\text{O.Y. n.})}{0.91}$

These values represent the average of at least three samples.

The reproducibility was within $\pm 0.5\%$.

TABLE XXVI

Percent Br Stabilized in Organic Combination in CH_3F After Neutron
Irradiation at Ambient Temperature

Pressure CH_3F (mm)	Pressure Argon (mm)	Pressure Bromine (mm)	Mole Fraction Argon (a)	Percent ^{82}Br O.Y. obs	As Organic O.Y. IT (b)
455.0	25.0	20.0	0.050	4.93	4.87
450.0	38.0	20.0	0.075	5.74	5.78
400.0	70.0	20.0	0.143	4.60	4.56
360.0	150.0	20.0	0.283	4.94	5.02
230.0	200.0	20.0	0.444	3.09	3.09
250.0	250.0	20.0	0.481	3.04	3.06
145.0	335.0	20.0	0.670	2.67	2.74
50.0	430.0	20.0	0.860	1.51	1.56

(a) Error ± 0.005 .

(b) $\text{O.Y. (IT)} = \frac{\text{O.Y. obs} - 0.09 (\text{O.Y. n.})}{0.91}$

These values represent the averages of at least three samples.

The reproducibility was within $\pm 0.5\%$.

TABLE XXVII

Percent ^{82}Br Stabilized in Organic Combination in CH_3F After Neutron
Irradiation at Ambient Temperature

Pressure CH_3F (mm)	Pressure Helium (mm)	Pressure Bromine (mm)	Mole Fraction Helium (a)	Percent ^{82}Br O.Y. obs	As Organic O.Y. IT (b)
450.0	30.0	20.0	0.060	4.55	4.44
400.0	70.0	20.0	0.143	4.52	4.42
385.0	105.0	20.0	0.206	5.10	5.06
300.0	185.0	20.0	0.367	4.75	4.70
160.0	300.0	20.0	0.625	3.85	3.87
145.0	335.0	20.0	0.670	4.71	4.85
80.0	400.0	20.0	0.800	4.92	5.16
65.0	416.0	20.0	0.830	1.91	1.89

(a) Error ± 0.005 .

(b) O.Y. (IT) = $\frac{\text{O.Y. (obs)} - 0.09 (\text{O.Y. n.})}{0.91}$

These values represent the averages of at least three samples.

The reproducibility was within $\pm 0.5\%$.

TABLE XXVIII

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic Combination
 With CH_3F After Neutron Irradiation at Ambient Temperature

Pressure CH_3F (mm)	Pressure Argon (mm)	Pressure Bromine (mm)	Mole Fraction Argon (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^m$ As Organic (b)	Percent ^{82}Br As Organic (b)
440.0	40.0	20.0	0.080	6.28	9.30	5.27
415.0	75.0	20.0	0.147	5.79	8.18	5.00
350.0	130.0	20.0	0.260	5.20	7.54	4.49
250.0	220.0	20.0	0.450	3.70	7.02	3.04
90.0	390.0	20.0	0.780	1.90	4.34	1.52

(a) Error ± 0.005 .

(b) These values represent the averages of at least three samples. The reproducibility was within $\pm 0.5\%$.

TABLE XXIX

Percent ^{80}Br , $^{80}\text{Br}^{\text{m}}$, and ^{82}Br Stabilized in Organic Combination with
 CD_3F After Neutron Irradiation at Ambient Temperature

Pressure CD_3F (mm)	Pressure Bromine (mm)	Mole Fraction Bromine (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^{\text{m}}$ As Organic (b)	Percent ^{82}Br As Organic (b)
390.0	10.0	0.025	4.99	6.33	4.21
404.0	29.0	0.067	4.40	6.26	3.79
360.0	46.5	0.114	3.84	4.10	3.44
330.0	70.0	0.175	3.36	4.12	3.08

(a) Error ± 0.002 .

(b) These values represent the averages of at least four samples. The reproducibility was within $\pm 0.5\%$.

This would mean that the initial kinetic energies imparted to the bromine atoms are not sufficiently high that the atoms have made a number of collisions before reaching the upper limit of the reaction zone E_2 .¹⁹ If the conditions of Wolfgang's assumption 1(a)¹⁹ are met, no isotope effect would be expected. Therefore, we conclude that the kinetic energy spectra are such that more $^{80}\text{Br}^m$ than ^{80}Br , than $^{82}\text{Br}^m + ^{82}\text{Br}$ are born with energies greater than the reaction zone E_2-E_1 .

A simple test to determine if the isotope effect is really due to a difference in kinetic energy spectra of the bromine atoms is to plot the ratio of individual isotope organic yields in CH_3F to CD_3F as a function of bromine concentration. As mentioned previously, the organic yields are consistently lower in CD_3F than in CH_3F . Although we really do not know what molecular parameters - moderation effects, difference in reactivity integrals, or differences in bond strength - are responsible for the target molecule isotope effect, all are related directly to the bromine kinetic energy, if a sufficient population of atoms have energies near the reaction zone E_2-E_1 . If more $^{80}\text{Br}^m$ atoms are born with higher kinetic energies than are ^{80}Br , than are $^{82}\text{Br}^m + ^{82}\text{Br}$ then we would expect the ratio in organic yields to decrease in the order $^{82}\text{Br}^m + ^{82}\text{Br}$ ^{80}Br $^{80}\text{Br}^m$. This is what we find. In a plot of organic yield ratio in CH_3F to CD_3F as a function of bromine concentration from zero to 0.1 mole fraction bromine, the ratios for the three isotopes are parallel to the mole fraction axis extrapolating for $^{82}\text{Br}^m + ^{82}\text{Br}$, ^{80}Br , and $^{80}\text{Br}^m$ to 1.625, 1.550, and 1.388 respectively.

CHAPTER IV. EFFECT OF PHASE CHANGE ON BROMINE REACTIONS WITH CH_3Br

(R. W. Helton)

One of the most significant questions we ask for condensed state systems where halogens react in organic media is what are the relative roles of displacement and radical formation mechanisms for those combination events which are not sensitive to low concentrations of scavenger and the specific mechanisms by which the radicals are formed. If radical reactions are involved, what are the relative roles of

- (a) impact of neutral atoms on molecules of the medium,
- (b) ion-molecule reactions,
- (c) neutralization of a solvent envelope which has been changed by charge transfer to the recoil atom following a vacancy cascade,
- (d) radiolytic effects of conversion and Auger electrons,
- (e) billiard-ball mechanisms.

Considering the various activation processes - especially involving the heavy halogens - interpretation of hot atom data from radiative neutron captors and isomeric transition can be quite difficult. In addition to a relatively high kinetic energy, the activated atom can acquire a positive charge and electronic excitation energy and have associated with it effects due to internal conversion and Auger electrons. The kinetic energy the hot atom does acquire is only in the order of a maximum of several hundred electrons-volts as compared to much higher energies from such processes as the (n,p) and $(n,2n)$ processes.

It is our point of view that at the present time there is no good

understanding of radiative neutron captured and isomeric transition activation processes in the condensed state, and therefore no definite view of the relative importance of caging and molecular reactions.

For the last several years we favored the Auger Electron Reaction Hypothesis introduced by Geissler and Willard²² to explain at least part of our (n, γ)-and (I.T.) produced reactions in hydrocarbons and halomethanes. The basis for our support rested mainly on the qualitative similarity between the product yields by (n, γ) and (I.T.) activations, even though for the liquid hydrocarbons and carbontetrachloride (I.T.) activated yields were generally higher than (n, γ) yields.

Recently Shaw et.al. questioned the Auger model for (n, γ), (n, 2n) activated $^{80}\text{Br}^m$ and (I.T.) activated ^{80}Br reactions in ethyl bromide and bromine mixtures. His group found that the distributions of products, from these nuclear activations formed at low or at high bromine concentrations differed markedly from those obtained from radiolysis. Even the yields obtained from $^{80}\text{Br}^m + ^{80}\text{Br}$ (I.T.) which definitely results from Auger electron emission differed considerably from radiolysis yields.

In our recent study of radiative neutron capture reactions of ^{128}I with various pentene olefins,²⁴ where we compared the ^{131}I radiolytically induced product distribution with the corresponding (n, γ)-activated ^{128}I products, we found two major differences between the relative quantities of the various products produced by these dissimilar processes.

(1) A significant increase in the relative yields of the individual fragmentation products, in most instances 50% produced by the (n, γ) activation process in comparison to the radiolytically procured fragmentation products, and (2) the C_5 iodides produced by the radiolysis process exhibit

less sensitivity to the isomeric composition of the C_5 hydrocarbon, whereas the yields of the C_5 iodides obtained from the (n,γ) activation show a definite preference for addition of the activated iodine at the position of the double bond.

These differences between the product distributions of the organic iodides resulting in the two processes, clearly suggest that the "autoradiation hypothesis" does not adequately explain the total product distributions observed for the (n,γ) activation of iodine in these systems. Therefore, other mechanisms must account, either in-part or completely, for the formation of the observed products in these systems.

In our estimation the most potentially significant experiment for the condensed state in recent years is the gas to condensed phase transition experiment of ^{18}F in CH_3F by Richardson and Wolfgang.²⁵ For one thing it ties in work done in low pressure, high pressure, and condensed state systems in terms of a density parameter. These authors found that the two labelled products, methyl fluoride and methylene fluoride show sharp rises in their product yields from the lower densities leveling off at 0.2 g/cm^3 .

This is characteristic of improving collisional de-excitation of primary products formed with such high internal energy that they would otherwise undergo secondary decomposition.

A second rise in yields is observed at higher densities. The authors feel that it is implausible to ascribe this phenomenon to collisional stabilization of excited molecules. The most natural explanation of the final rise in yields is that it is due to caging effects.

Hot fluorine atoms can break bonds forming radicals such as CH_2F and CH_3 .

The ^{18}F after losing its excess energy can undergo recombination as shown below:

While Franck--Rabinovitch caging has long been postulated in condensed phase hot atom chemistry, there has never been any direct evidence for it.

It is of great importance for condensed state studies to perform similar experiments for ^{38}Cl , $^{80}\text{Br}^{\text{m}}$, ^{80}Br , ^{82}Br and for ^{128}I and ^{130}I atoms activated by radiative neutron capture and isomeric transition. We have conducted a program where we are studying the product yields of Bromine activated by radiative neutron capture and isomeric transition, as well as individual organic yields of $^{80}\text{Br}^{\text{m}}$, ^{80}Br , $^{82}\text{Br}^{\text{m}} + ^{82}\text{Br}$, and ^{82}Br (by I.T.) - to observe the effect of density and phase change on the bromine isotope effect - as a function of system density. The three systems we are studying are:

- (1) $^{38}\text{Cl} + \text{CH}_3\text{Cl}$ (n, γ)
- (2) (a) $^{80}\text{Br}^{\text{m}} + \text{CH}_3\text{Br}$ (n, γ)
- (b) $^{80}\text{Br} + \text{CH}_3\text{Br}$ (n, γ)
- (c) $^{82}\text{Br}^{\text{m}} + \text{CH}_3\text{Br}$ (n, γ)
- (d) $^{82}\text{Br} + \text{CH}_3\text{Br}$ (I.T.)
- (3) (a) $^{80}\text{Br}^{\text{m}} + \text{CH}_3\text{F}$ (n, γ)
- (b) $^{80}\text{Br} + \text{CH}_3\text{F}$ (n, γ)
- (c) $^{82}\text{Br}^{\text{m}} + \text{CH}_3\text{F}$ (n, γ)
- (d) $^{82}\text{Br} + \text{CH}_3\text{F}$ (I.T.)

At this time all we wish to report are tables of some of our experimental results in the bromine + CH_3Br systems. No attempts will be made to analyze these data at this time. A preliminary observation we would like to report, however, is that the bromine organic yields as a function of density are similar to those reported by Richardson and Wolfgang.²⁵

TABLE XXX

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic Combination With
After Irradiation at Ambient Temperature

Pressure CH_3Cl (mm)	Pressure Bromine (mm)	Mole Fraction Bromine (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^m$ As Organic (b)	Percent ^{82}Br As Organic (b)
98.0	2.0	0.020	5.10	6.43	3.75
95.0	6.0	0.059	4.30	5.18	3.32
92.0	10.0	0.098	3.74	5.39	2.80
70.0	30.0	0.300	2.80	3.85	1.62
50.0	50.0	0.500	1.17	1.29	1.04
30.0	70.0	0.700	0.62	0.91	0.50
694.0	20.0	0.028	5.77	5.62	3.21
660.0	39.5	0.057	5.36	6.65	3.23
640.5	59.5	0.085	4.28	4.81	3.43

(a) Error ± 0.002 .

(b) These values represent the averages of at least three samples. The reproducibility was within $\pm 0.5\%$.

TABLE XXXI

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic Combination With
After Irradiation at Ambient Temperature

Pressure CH_3Br (mm)	Pressure Bromine (mm)	Mole Fraction Bromine (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^m$ As Organic (b)	Percent ^{82}Br As Organic (b)
95.0	5.0	0.050	3.39	3.03	2.54
475.0	25.0	0.050	3.61	3.96	2.97
760.0	40.0	0.050	3.55	3.39	2.92
1255.0	65.0	0.049	3.86	--	3.27
1473.0	77.0	0.049	3.27	--	3.40
1568.0	82.5	0.050	4.86	--	5.57
1795.0	95.0	0.050	3.59	--	4.40
194.0	6.0	0.030	2.90	3.78	2.66
390.0	12.0	0.049	3.02	3.47	2.96
365.0	20.0	0.052	3.45	3.92	3.07
775.0	24.0	0.050	3.16	4.13	2.92

(a) Error ± 0.002 .

(b) These values represent the average of at least three samples. The reproducibility was within $\pm 0.5\%$.

TABLE XXXII

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic Combination
 With CH_3Br After Irradiation at Ambient Temperature

Pressure CH_3Br (mm)	Pressure Helium (mm)	Pressure Bromine (mm)	Mole Fraction Helium (a)	Percent ^{80}Br As Organic	Percent $^{80}\text{Br}^m$ As Organic	Percent ^{82}Br As Organic
46.0	19.0	10.0	0.250	1.77	1.52	1.60
39.0	26.5	10.0	0.350	2.03	2.59	1.75
26.0	39.0	10.0	0.520	1.78	2.71	1.90
19.0	47.0	10.0	0.630	1.49	1.40	1.91
355.0	40.0	5.0	0.100	2.92	3.93	2.80
286.0	119.0	5.0	0.290	2.96	3.87	2.86
155.0	240.0	5.0	0.600	2.26	3.80	2.14
95.0	305.0	5.0	0.753	2.60	4.11	2.57
11.0	384.0	5.0	0.960	1.36	1.27	1.99

(a) Error ± 0.005 .

(b) These values represent the averages of at least three samples. The reproducibility was within $\pm 0.5\%$.

TABLE XXXIII

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic Combination With
 CH_3Br After Neutron Irradiation at Ambient Temperature

Pressure CH_3Br (mm)	Pressure Bromine (mm)	Mole Fraction Bromine (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^m$ As Organic (b)	Percent ^{82}Br As Organic (b)
710.0	3	0.004	2.94	5.24	2.80
692.0	13.5	0.019	3.15	3.89	2.73
975.0	29.0	0.041	2.87	4.06	2.67
664.0	50.0	0.071	2.93	3.55	2.99
600.0	100.0	0.143	3.38	3.83	3.29

(a) Error ± 0.002 .

(b) These values represent the average of at least three samples. The reproducibility was within $\pm 0.5\%$.

TABLE XXXIV

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic Combination With
 CH_3Br After Neutron Irradiation at Ambient Temperature

Pressure CH_3Br (mm)	Pressure Argon (mm)	Pressure Bromine (mm)	Mole Fraction Argon (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^m$ As Organic (b)	Percent ^{82}Br As Organic (b)
355	45	5	0.111	2.44	2.98	2.39
295	105	5	0.259	2.69	3.03	2.46
210	180	5	0.444	2.20	4.20	2.16
120	275	5	0.679	2.12	3.32	1.56
25	370	5	0.925	1.40	--	0.81

(a) Error ± 0.005 .

(b) These values represent the averages of at least three samples. The reproducibility was within $\pm 0.5\%$.

TABLE XXXV

Percent ^{80}Br , $^{80}\text{Br}^{\text{m}}$, and ^{82}Br Stabilized in Organic Combination With CH_3Br After Neutron Irradiation in Liquid State at Ambient Temperature

Mole Fraction Bromine (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^{\text{m}}$ As Organic (b)	Percent ^{82}Br As Organic (b)
0.05	27.7	32.1	21.2
0.11	23.1	24.4	18.8
0.20	17.4	20.2	16.4
0.27	17.4	15.2	13.7
0.33	16.2	14.8	13.5
0.38	11.0	12.6	10.7
0.56	10.0	--	8.30
0.59	6.60	7.55	5.80
0.67	4.78	6.00	4.70
0.73	5.66	5.62	4.04

(a) Error ± 0.01 .

(b) These values represent the averages of at least three samples. The reproducibility was within $\pm 1.0\%$.

TABLE XXXVI

Percent ^{82}Br Stabilized in Organic Combination in CH_3Br After Neutron
Irradiation in Liquid State at Ambient Temperature

Mole Fraction Bromine (a)	Percent ^{82}Br O.Y. obs	As Organic O.Y. IT (b)
0.114	20.88	21.10
0.200	24.56	25.30
0.375	18.07	18.76
0.500	11.83	12.22
0.560	8.98	9.18

(a) Error ± 0.002 .

(b) $\text{O.Y. IT} = \frac{\text{O.Y. obs} - 0.09 \text{ O.Y. n.}}{0.91}$

These values represent the averages of at least three samples. The reproducibility was within $\pm 1.0\%$.

TABLE XXXVII

Percent ^{80}Br , $^{80}\text{Br}^m$, and ^{82}Br Stabilized in Organic Combination With
 CH_3Br After Neutron Irradiation at 77°K

Mole Fraction Bromine (a)	Percent ^{80}Br As Organic (b)	Percent $^{80}\text{Br}^m$ As Organic (b)	Percent ^{82}Br As Organic (b)
0.05	54.2	58.	49.2
0.10	48.3	52.8	46.4
0.20	40.4	43.6	41.0
0.27	32.5	34.1	27.3
0.33	26.5	28.4	22.7
0.67	9.65	14.3	7.90

(a) Error ± 0.01 .

(b) These values represent the averages of at least five samples.

The reproducibility was within $\pm 1.5\%$.

CHAPTER V. GAS PHASE REACTIONS OF ^{128}I ACTIVATED BY RADIATIVE NEUTRON
CAPTURE IN ETHYLENE AND PROPYLENE

(R. R. Pettijohn)

A program has been initiated in the gas phase to study the reactions of ^{128}I activated by radiative neutron capture with ethylene and propylene. The present study has been carried out in order to better understand the relative contributions of the various physical processes such as charge, electronic excitation, recoil, and electromagnetic radiation accompanying the (n,γ) activation process in heavy halogens. In addition we hope to complete a definitive study of the systematics of iodine reactions with alkenes.

A recent condensed phase study²⁴ showed that a definite preference was found for addition of the activated iodine at the position of the double bond in pentenes for (n,γ) activated iodine species over that by radiolysis produced ^{131}I organic products.

The inherent complexity of the condensed phase is due to the little-understood solvent "cage" effect. Even though reaction mechanisms can be hypothesized, the lack of suitable liquid phase scavengers and moderators have made these systems unapproachable from that means of study. However, if one starts by obtaining a firm understanding of the corresponding gaseous phase reactions (with their lack of the complicating cage effects) it may be possible to extrapolate the data and knowledge gained back to the condensed phase²⁵. It is for these reasons that we have begun this study of the (n,γ) produced ^{128}I species with ethylene and propylene.

Previous researchers investigated the reactions of (n,γ) activated ^{128}I

with saturated hydrocarbons. An interesting phenomena found in going from single carbon methane to multi carbon molecules was that the organic yield drastically decreased. See Table XXXVIII(a).

This effect has been explained by consideration of the ionization potentials of the first excited states of I^+ :

$I(^2P_{3/2}) \longrightarrow I^+(^3P_2)$	10.454 (Ground state)
$I^+(^3P_0)$	11.254
$I^+(^3P_1)$	11.333
$I^+(^1D_2)$	12.156

The following exothermic ion molecule reactions can take place for C_2H_6 or C_3H_8 but not for CH_4 due to its relatively high ionization potential:

Neutralization of I^+ was thought to make it less reactive in these low ionization potential systems since ion-molecule reaction modes would no longer be available.

However, in our current study of ethylene and propylene systems organic yields of 18% and 24% were obtained. A consideration of the ionization potentials for ethylene (10.52 eV) and propylene (9.73 eV) showed that the charge transfer process should also be present in these systems.

It was therefore concluded that:

- (1) A new reaction pathway for organic stabilization may be present in alkenes.
- (2) This pathway would most likely be due to iodine ions or radicals attacking the electron-rich double bond.
- (3) If it is due to an iodine ion then the reaction rate for the

TABLE XXXVIII(a)

Species Studied	Organic Yield With No Additive	Components	Ionization Potential
CH ₄	54% (3)	CH ₃ I 18% from hot I ¹²⁸ 25% from I ⁺ (¹ D ₂) 11% from excited iodine atoms or ions in the ³ P ₂ , ³ P ₁ , ³ P ₀ states.	12.99 eV
C ₂ H ₆	3% (27)	Not given	11.65 eV
C ₃ H ₈	4% (27)	Not given	11.08 eV

organic product must be faster than that for the charge transfer de-activation mechanism described.

EXPERIMENTAL

Reaction Mixtures

Approximately 350 samples in quartz ampoules were filled on a greaseless vacuum line and irradiated at a thermal neutron flux of 1.1×10^{17} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ in the Omaha, Nebraska, V.A. Hospital TRIGA reactor. The accompanying γ -radiation flux was $3 \times 10^{17} \text{ev. g}^{-1} \text{min}^{-1}$.

All samples were filled in a dark room, wrapped in foil and stored at liquid nitrogen temperature until just prior to irradiation.

Each sample contained

1. 0.10 ± 0.02 mm Hg of I_2 to serve as a thermal scavenger. The iodine was sublimed from a mixture of Mallinckrodt reagent grade I_2 and Baker reagent grade KI and CaO.

2. 4.0 ± 0.5 mm Hg of CH_3I (total organic yields). 50.0 ± 0.5 mm Hg of CH_3I (chromatographic product distributions).
to serve as major source of I. Matheson Coleman and Bell reagent grade. Vacuum distilled twice and stored under vacuum with copper turnings.

3. Either ethylene or propylene. Both were Phillips research grade. Ethylene 99.98% mole percent purity. Propylene 99.98% mole percent purity.

4. Various mole fractions of the following gas additives:

He	Matheson Research Grade 99.9995% Min. purity
Ar	Airco Research Grade 99.9995% Min. purity
Kr	Airco Research Grade 99.9995% Min. purity
Xe	Airco Research Grade 99.995% Min. purity

- O₂ Airco Research Grade 99.995% Min. purity
H₂S Matheson C.P. Grade 99.6% Min. purity
CH₃I Matheson, Coleman and Bell Reagent Grade
5. A total pressure of 760±10 mm Hg.

Total Absolute Organic Yields

All samples were thawed to room temperature immediately prior to irradiation and, unless otherwise specified, were irradiated for 1.0 minute. The irradiated bulblet was broken within 30 seconds in a separatory funnel containing a two phase mixture of CCl₄ + I₂ and 0.5M aqueous Na₂SO₃. The organic fraction was separated from the inorganic and each fraction was counted using a 3 inch NaI well crystal with Ortec electronics. The data was corrected for:

1. Time lapse between which the organic and aqueous fraction were counted.
2. 1.1% failure to bond rupture²⁶.

In most cases two or more identical samples were analyzed. After a complete set (varying over a wide range of mole fraction additive) of data had been taken for a particular additive, a least squares fit curve to the data was drawn by a Cal Comp plotter and the equation of the line calculated by an IBM 360. From this equation a listing of mole fraction additive vs. the total organic yield were calculated. See Figures 28-39.

Radiation Damage Corrections

Radiation damage studies for both krypton and xenon additives in the ethylene system were made. This was accomplished by irradiating identical

samples varying lengths of time (0.5 to 15 minutes). The change in organic yield appeared to be linear in time for both krypton and xenon. See Figures 24 and 26. The difference between the extrapolated organic yield at time = 0.0 and time = 1.0 minutes (all other samples except 2.0 minutes for Xenon) was then taken to be the radiation damage at the particular mole fraction additive studied. It was then assumed that the damage was linear with respect to mole fraction additive (4) and extrapolated to mole fraction additive = 1.0 to determine the maximum radiation damage (R_{max}). See Figures 25 and 27. The entire organic yield plot was then corrected in the following way:

0. Yield (corrected for radiation damage) = 0. Yield (not corrected) $\times$ X (mole fraction) $\times R_{max}$. See Tables 28 and 29, and Figures

All Xenon samples were irradiated for 2.0 minutes (instead of the usual 1.0 minute) then let decay for 30 minutes after extraction to allow for Xe - 137 (3.9 minute half life) to decay. These samples were also counted with the single channel's lower window set at 0.4 Mev in order to discriminate the lower energy emitting Xe isotopes.

Absolute Product Yields

The radiogas chromatograph used in this research is that previously described in detail.^{35,36} Two modifications to that instrument have been made.

1. Gas samples are now injected into the helium carrier gas stream by use of the apparatus described in appendix A.
2. Radioactive peaks are now integrated by use of a Peak Analyzer. The circuit used is a refined version of that described previously³⁴.

Modifications were made by L. L. Lucas.

Sample analysis is handled in the following steps:

1. Peak identification is made .
2. Background subtracted.
3. Decay correction applied to calculate the number of counts in the peak at the time of injection.
4. Correction for failure to bond rupture²⁶.
5. The absolute yield for a particular product is computed by using total absolute yield data from the extraction procedure (this is not corrected for radiation damage).
6. A plot of the data with that of other identical samples of varying irradiation times (5.0 to 15.0 minutes) is made and the best straight line is drawn and extrapolated to irradiation time = 0.0. The organic yield at time 0.0 is then the corrected relative yield.
7. The corrected relative yields must then be normalized back to the total absolute yield thus giving the absolute product yields.

The column used was a 3m. SS column containing di(2-ethylhexyl-sebacate on 50/60 mesh firebrick at 50°C. Linear temperature programming to 100°C was used for the propylene study.

By using radiogas chromatography for product distribution analysis in conjunction with the total organic yields from extraction experiments the following absolute product yields were obtained:

TABLE XXXVIII(b)

<u>C₂H₄</u>		<u>C₃H₆</u>	
CH ₃ I	10%	CH ₃ I	19%
C ₂ H ₃ I	4%	CH ₃ CI=CH ₂	4%
C ₂ H ₅ I	4%	Total of all other products	1%
	<hr/>		<hr/>
Total	18%		24%

Mechanisms for Recoil ^{128}I Atom Reactions With Ethylene $\text{C}_2\text{H}_3\text{I}$ (4% organic yield)

The first product to be considered is that of $\text{C}_2\text{H}_3\text{I}$. It is seen in Figs. 30 and 31 that this product decreases as the amount of moderator (helium or krypton) is increased. The fact that the yield extrapolates to zero at an additive mole fraction of 1.00 has led to the interpretation that all 4% are due to hot iodine reactions of the direct ^{128}I for H substitution illustrated below:

This reaction is endothermic by 2 eV however in order to have available as internal energy of the activated complex the iodine atom must possess a minimum kinetic energy that is $(128+32)/32=5$ times as great as the endothermicity of the reaction. Thus it must have at least 10 eV of kinetic energy to undergo this reaction. Such substitution reactions are well established in the literature^{3,27,28}. It is interesting to note that if this were the only reaction path available to ethylene, then it too would fit into the pattern shown in Table XXXVIII. The non-zero extrapolation with xenon moderation, Fig. 33, is not understood at this time.

 $\text{C}_2\text{H}_5\text{I}$ (4% organic yield)

From Figures 30, 31 and 33 it is again evident that this product occurs entirely by a hot reaction path. Also, evidence is shown in

Figure 34 that the intermediate must be a radical since the addition of a small amount of oxygen substantially quenches the formation of C_2H_5I . Various authors²⁹⁻³¹ have discussed the formation of activated chloroethyl radicals and Kistiakowsky et al.³² have found photochemically produced bromoethyl radicals. It is therefore hypothesized that the intermediate in this case is an activated iodoethyl radical formed as a result of attack of the double bond:

This intermediate can either decompose to give products or can react as a radical with its environment. The absence of the product di-iodoethane from the scavenging reaction

is most likely due to the instability of this product with respect to decomposition to the olefin and I_2 ³¹. This has been given as the reason for lack of evidence of photochemical addition of iodine to olefins as is found for chlorine and bromine³¹. It is therefore believed that the iodoalkyl radicals formed in the initial addition step must be very much less stable than the corresponding bromo and chloroalkyl radicals. Once the radical is formed its abstraction of a hydrogen atom from C_2H_4 should be extremely favorable from an energy standpoint.

CH₃I (10% organic yield)

Each analyzed sample contained 0.1 mm (saturated vapor pressure at 25°C) of I₂ to serve as thermal scavenger and 4.0 mm CH₃I (50.0 mm for chromatography samples) as a source of iodine atoms.

In focusing attention to the large amount of CH₃¹²⁸I found in these experiments it is necessary to consider the possible contributions to the CH₃¹²⁸I yields from reaction pathways not including C₂H₄. The following three mechanisms are of this type.

The contribution from case (c) has been previously studied. It was found that 1.1% of all of the recoil ¹²⁸I produced from CH₃I remains as labeled CH₃¹²⁸I. Both organic yields and product distributions have been corrected by subtracting off this contribution of CH₃¹²⁸I.

In order to investigate the next two cases a series of samples were filled and analyzed. See Table XXXIX.

These organic yields are negligible when compared to the absolute yield of 10% at zero mole fraction additive. If these organic yields are due to case (E) then the values in Table XXXIX are the upper limit of contribution from that pathway since the incorporation of C₂H₄ into the system

would provide competitive reactions for the recoil iodine. The conclusion is that the methyl iodide must be formed by reaction with the ethylene.

In comparing and contrasting the CH_3I curves of the helium moderation Fig. 30 with that of krypton moderation Fig. 31, we find that they both extrapolate to 5% within experimental error. However, the shapes of the curves are such that for a given mole fraction, the helium additive is reducing the amount of CH_3I more than that of krypton. With xenon moderation Fig. 33, the CH_3I yield is not only higher at mole fraction additive = 1.00, but it is higher for all mole fractions. Clearly, this is not the effect that we would expect for moderation of hot iodine species. In fact it is entirely the opposite effect one would expect for kinetic energy moderation of hot iodine.

To summarize, the CH_3I organic yield appears to be stabilized by inert gas additives in the sequence $\text{Xe} > \text{Kr} > \text{He}$. Physical properties that follow this trend are:

1. Decrease in ionization potential
2. Decrease in mass.

A decrease in ionization potential would account for the observed trend if the CH_3I intermediate could be stabilized by the ability to gain an electron from the rare gas additive. If the intermediate failed to gain this electron within a few collisions it may decompose to give labeled inorganic products.

The decrease in mass may also account for the observed trend. If the intermediate is born with excess energy successive collisions with a more massive molecule would collisionally stabilize the intermediate faster

TABLE XXXIX

Percent I-128 Stabilized in Organic Combination at Mole Fraction = 1.000

Additive	Percent I-128 As Organic (corr)*	Average
Helium	1.00	1.1
	0.86	
	1.32	
Krypton	1.30	1.7
	2.14	
Xenon	1.55	1.9
	1.36	
	2.95	

*These samples contained 0.1 mm I₂, 50.0 mm CH₃I and 755.0 mm additive.

and thereby prevent decomposition.

The following further experiments are presently being undertaken to identify the mechanism for $\text{CH}_3^{128}\text{I}$ formation in this system:

1. Studies involving $^{127}\text{I}^+$ in the ground state and excited states reacting with C_2H_4 by the means of ion cyclotron resonance mass spectrometry should be extremely helpful in determining if the reactions leading to the formation of CH_3I is of ion-molecule origin. We hope to verify or negate the existence of CH_2I^+ and/or $\text{C}_2\text{H}_4\text{I}^+$ as relatively stable species.

The existence of such intermediates would certainly enforce the ionization potential theory (#1 above).

2. A series of samples at constant mole fraction additive (≈ 0.5) but of varying total pressure will be filled and analyzed. If the CH_3I yield increases at higher pressures it would appear that the explanation would lie in the ability of the system to dissipate the excess energy of an excited intermediate quickly. This effect would lend support to the decrease in mass theory (#2 above).

TABLE XL

Least Squares Values for Mole Fraction Additive = 0.000

Additive	Percent I-128 as Organic (Least Squares Fit)
Helium	17.99
Argon	17.88
Krypton	18.35
Xenon	17.39
Average	17.9

TABLE XLI

Percent I-128 Stabilized in Organic Combination with Ethylene

Additive	Mole Fraction Additive	Percent I-128 As Organic (corr.)	Least Squares Organic Yield
He	0.190	12.7	10.8
	0.190	7.0	
	0.299	12.5	8.3
	0.299	6.1	
	0.372	6.5	7.1
	0.372	7.3	
	0.850	4.8	4.7
	0.902	7.1	4.7
	0.902	2.5	
	0.902	3.5	
	0.955	3.0	4.5
	0.955	3.1	
	0.955	8.2	

TABLE XLII

Percent I-128 Stabilized in Organic Combination with Ethylene

Additive	Mole Fraction Additive	Percent I-128 As Organic (corr.)	Least Squares Organic Yield
Krypton	0.132	19.5	19.5
	0.345	14.5	18.5
	0.345	22.9	
	0.466	21.2	17.0
	0.511	14.8	16.4
	0.652	12.2	13.9
	0.652	16.1	
	0.823	7.7	10.0
	0.851	5.7	9.2
	0.851	7.7	
	0.904	7.9	7.7
	0.904	6.3	
	0.904	5.4	
	0.952	8.0	6.2
	0.952	8.9	
	0.952	9.2

Fig. 24. Determination of the radiation damage contribution to the percent ^{128}I formed as organic activity. Ethylene study with krypton additive.

Fig. 25. Krypton radiation damage correction extrapolation assuming a linear dependence on mole fraction krypton additive. Determination of $R_{\max}$ at mole fraction = 1.00.

TABLE XLIII

Percent I-128 Stabilized in Organic Combination with Ethylene

Additive	Mole Fraction Additive	Percent I-128 As Organic (corr.)*	Least Squares Organic Yield
Krypton	0.132	19.4	19.4
	0.345	14.2	18.1
	0.345	22.6	
	0.466	20.8	16.6
	0.511	14.3	16.0
	0.652	11.6	13.4
	0.652	15.6	
	0.823	6.9	9.2
	0.851	5.0	8.4
	0.851	7.0	
	0.904	7.1	6.9
	0.904	5.5	
	0.904	4.6	
	0.952	7.2	5.4
	0.952	8.0	
	0.952	8.3	

*This data has been corrected both for failure to bond rupture and radiation-induced I-128 organic pickup (0.9% at unit mole fraction additive).

TABLE XLIV

Percent I-128 Stabilized in Organic Combination with Ethylene

Additive	Mole Fraction Additive	Percent I-128 As Organic (corr.)	Least Squares Organic Yield
Argon	0.085	17.8	16.9
	0.136	12.2	16.3
	0.290	17.5	14.9
	0.484	15.2	13.9
	0.582	14.4	13.6
	0.582	10.9	
	0.827	13.0	14.1
	0.827	12.4	
	0.827	16.8	
	0.912	15.3	14.6
	0.912	14.0	

TABLE XLV

Percent I-128 Stabilized in Organic Combination with Ethylene

Additive	Mole Fraction Additive	Percent I-128 As Organic (corr.)*	Least Squares Organic Yield
Xenon	0.089	17.8	18.6
	0.089	14.1	
	0.162	18.6	18.9
	0.288	12.0	19.4
	0.288	24.8	
	0.479	27.4	20.3
	0.479	17.1	
	0.713	20.5	21.5
	0.846	23.7	22.4
	0.931	21.2	22.9
	0.931	21.7	
	0.931	24.4

Fig. 26. Determination of the radiation damage contribution to the percent ^{128}I formed as organic activity. Ethylene study with xenon additive.

Fig. 27. Xenon radiation damage correction extrapolation assuming a linear dependence on mole fraction xenon additive. Determination of $R_{\max}$ at mole fraction = 1.00.

Fig. 28. Effect of krypton additive on the total percent ^{128}I formed as organic activity due to ^{128}I reactions with C_2H_4 .

□ Uncorrected for radiation damage (upper curve).

◇ Corrected for radiation damage (lower curve).

TABLE XLVI

Percent I-128 Stabilized in Organic Combination with Ethylene

Additive	Mole Fraction Additive	Percent I-128 As Organic (corr.)*	Least Squares Organic Yield
Xenon	0.089	17.2	18.0
	0.089	13.5	
	0.162	17.5	17.8
	0.288	22.9	17.4
	0.288	10.1	
	0.479	24.1	17.0
	0.479	13.8	
	0.713	15.7	16.7
	0.846	18.0	16.6
	0.931	14.9	16.5
	0.931	15.3	
	0.931	18.1	

*This data has been corrected both for failure to bond rupture and radiation-induced I-128 organic pickup (6.8% at unit mole fraction additive).

Fig. 29. Effect of xenon additive on the total percent ^{128}I formed as organic activity due to ^{128}I reactions with C_2H_4 .

□ Uncorrected for radiation damage (upper curve).

◇ Corrected for radiation damage (lower curve).

TABLE XLVII

Percent I-128 Stabilized in Organic Combustion with Ethylene

Additive	Mole Fraction Additive	Percent I-128 As Organic (corr.)
Oxygen	0.079	7.3
	0.079	6.4
	0.205	4.8
	0.205	7.3
	0.334	5.2
	0.345	6.2
	0.345	4.7

TABLE XLVIII

Percent I-128 Stabilized in Organic Combination with Ethylene

Additive	Mole Fraction Additive	Percent I-128 As Organic (corr.)
Methyl Iodide	0.0053	12.3
	0.0053	20.6
	0.1187	8.2
	0.1187	11.8
	0.2981	5.6
	0.2981	4.7
	0.4090	2.1
	0.4090	4.1

TABLE XLIX

Percent I-128 Stabilized in Organic Combination with Ethylene

Additive	Mole Fraction Additive	Percent I-128 As Organic (corr.)
Hydrogen Sulfide	0.079	3.9
	0.079	5.1
	0.460	2.4
	0.460	2.4
	0.595	2.1
	0.595	2.0
	0.716	3.0
	0.716	1.3

TABLE XLX
Relative Yields* of Organic ^{128}I Products Formed by the $^{127}\text{I}(\text{n}, \gamma)^{128}\text{I}$
Activation of Iodine in Mixtures of Ethylene and Gas Additives

Additive	Mole Fraction Additive	Irradiation Time In Minutes	CH_3I	$\text{C}_2\text{H}_3\text{I}$	$\text{C}_2\text{H}_5\text{I}$
None	0.0000	5.0	10.88	2.99	4.03
None	0.0000	10.0	11.65	2.29	3.96
Helium	0.2132	10.0	6.41	1.14	2.74
	0.4632	5.0	3.66	1.50	0.90
	0.4632	10.0	3.88	1.30	0.89
	0.4632	15.0	4.68	0.37	0.87
	0.7105	10.0	3.72	0.58	0.65
	0.7105	15.0	3.90	0.72	0.32
Krypton	0.4937	5.0	10.51	2.02	1.46
	0.7162	10.0	7.80	0.68	1.52
	0.7162	15.0	7.29	0.49	2.23
Xenon	0.4827	5.0	10.96	1.71	4.54
	0.4827	10.0	11.49	1.22	4.49
	0.4827	15.0	11.51	1.12	4.57
	0.7520	5.0	11.22	2.58	2.99
	0.7520	10.0	12.97	1.06	2.77
	0.7520	15.0	13.25	1.06	2.33

*Relative yields are corrected for failure to bond rupture but not corrected for radiation induced contributions.

TABLE XLXI
Relative Yields* of Organic ^{128}I Products Formed by the $^{127}\text{I}(\text{n}, \gamma)^{128}\text{I}$
Activation of Iodine in Mixtures of Ethylene and Gas Additives Continued

Additive	Mole Fraction Additive	Irradiation Time In Minutes	CH_3I	$\text{C}_2\text{H}_3\text{I}$	$\text{C}_2\text{H}_5\text{I}$
Methyl Iodide	0.0947	5.0	6.75	2.89	1.56
	0.0947	10.0	6.90	2.13	2.17
	0.2553	10.0	4.82	0.65	0.93
	0.2553	15.0	5.11	0.52	0.77
	0.4053	10.0	3.15	0.07	0.28
	0.4053	15.0	3.14	0.07	0.29
Oxygen	0.2079	10.0	3.25	2.27	0.18
	0.2079	15.0	3.64	1.85	0.20
	0.4710	5.0	2.25	2.65	0.08
	0.4710	10.0	2.50	2.39	0.09
	0.4710	15.0	2.76	1.94	0.32
	0.7526	5.0	1.67	2.79	0.04
	0.7526	10.0	2.76	1.64	0.09
	0.7526	15.0	2.40	2.04	0.09
Hydrogen Sulfide	0.0767	10.0	4.14	1.23	0.13
	0.0767	15.0	4.17	0.99	0.34
	0.2302	5.0	1.75	0.97	0.76
	0.2302	10.0	1.98	0.76	0.06
	0.7249	5.0	1.56	0.40	0.04

*Relative yields are corrected for failure to bond rupture but not corrected for radiation induced contributions.

TABLE XLXII
Absolute Yield Product Distributions
Corrected for Failure to Bond Rupture and Radiation Damage*

Additive	Mole Fraction Additive	Relative Yields(%) Extrapolated to An Irradiation Time of Zero Minutes			Relative Yields Normalized to the Total Absolute Yield(%)			Total Absolute Yield(%) ^a
		CH ₃ I	C ₂ H ₃ I	C ₂ H ₅ I	CH ₃ I	C ₂ H ₃ I	C ₂ H ₅ I	
None	0.0000	10.1	3.7	4.1	10.1	3.7	4.1	17.9
Helium	0.2132	6.4	1.1	2.7	6.4	1.1	2.7	10.3
	0.4632	3.4	1.9	0.9	3.3	1.9	0.9	6.1
	0.7105	3.3	0.3	0.6	3.8	0.4	0.7	4.9
Krypton	0.4937	10.5	2.0	1.5	10.5	2.0	1.5	14.0
	0.7162	8.6	1.0	0.0	8.9	1.1	0.0	10.0
Xenon	0.4827	10.9	1.9	4.5	10.9	1.9	4.5	17.3
	0.7520	10.6	1.1	3.3	11.9	1.2	3.7	16.8
Methyl Iodide	0.0947	6.6	3.6	1.0	6.6	3.6	1.0	11.2
	0.2553	4.2	1.9	1.1	3.7	1.7	1.0	6.4
	0.4053	3.1	0.1	0.3	3.1	0.1	0.3	3.5
Oxygen	0.2079	2.4	3.0	0.1	2.5	3.1	0.1	5.7
	0.4710	2.0	3.0	0.1	2.0	3.0	0.1	5.1
	0.7526	1.6	3.3	0.0	1.5	3.0	0.0	1.5
Hydrogen Sulfide	0.0767	4.1	1.7	0.0	3.9	1.6	0.0	5.5
	0.2302	1.5	1.1	0.1	1.5	1.1	0.1	2.7
	0.7249	1.5	0.4	0.0	1.6	0.4	0.0	2.0

^aFrom least squares fit of organic yield data using extraction technique.

Fig. 30. Effect of helium additive on the percent ^{128}I formed as organic activity due to ^{128}I reactions with C_2H_4 .

Total organic yield, $\square$; Absolute yields: CH_3I , $\circ$; $\text{C}_2\text{H}_5\text{I}$, $\triangle$; $\text{C}_2\text{H}_3\text{I}$, $\diamond$.

Fig. 31. Effect of krypton additive on the percent ^{128}I formed as organic activity due to ^{128}I reactions with C_2H_4 .

Total organic yield, □; Absolute yields: CH_3I , ○; $\text{C}_2\text{H}_3\text{I}$, ◊; $\text{C}_2\text{H}_5\text{I}$, △.

Fig. 32. Effect of argon additive on the percent ^{128}I formed as organic activity due to ^{128}I reactions with C_2H_4 .

Fig. 33. Effect of xenon additive on the percent ^{128}I formed as organic activity due to ^{128}I reactions with C_2H_4 .

Total organic yield, $\square$; Absolute yields: CH_3I , $\circ$; $\text{C}_2\text{H}_3\text{I}$, $\triangle$; $\text{C}_2\text{H}_5\text{I}$, $\diamond$.

Fig. 34. Effect of oxygen additive on the percent ^{128}I formed as organic activity due to ^{128}I reactions with C_2H_4 .

Total organic yield, $\square$; Absolute yields: CH_3I , $\circ$; $\text{C}_2\text{H}_3\text{I}$, $\diamond$; $\text{C}_2\text{H}_5\text{I}$, $\triangle$.

Fig. 35. Effect of methyl iodide on the percent ^{128}I formed as organic activity due to ^{128}I reactions with C_2H_4 .

Total organic yield, $\square$; Absolute yields: CH_3I , $\circ$; $\text{C}_2\text{H}_3\text{I}$, $\diamond$; $\text{C}_2\text{H}_5\text{I}$, $\triangle$.

Fig. 36. Effect of hydrogen sulfide on the percent ^{128}I formed as the organic activity due to ^{128}I reactions with C_2H_4 .

Total organic yield, $\square$; Absolute yields: CH_3I , $\circ$; $\text{C}_2\text{H}_3\text{I}$, $\diamond$; $\text{C}_2\text{H}_5\text{I}$, $\triangle$.

Mechanisms for Recoil ^{128}I Atom Reactions with Propylene

The following products are detected at 0.0 mole fraction additive:

Methyl Iodide	18.7%
2-iodo propene	4.0%
Vinyl Iodide	0.3%
Ethyl Iodide	0.1%
3-iodo-propene	0.5%
propyl iodide	
2-iodo propane	<u>0.5%</u>
Total organic yield	23.1%

Because of the small yields of the last five products, there will be no attempt made at discussing the origin of these species.

Inert gas studies to date have been with krypton, Fig. 37, Argon, Fig. 38, and Methyl Iodide, Fig. 39.

From the krypton moderation study Fig. 37 it appears that $\text{CH}_3\text{CI} = \text{CH}_2$ is formed from a hot I for H substitution reaction. This would explain why at higher mole fractions of krypton the yield goes to zero.

Most likely the very large CH_3I contribution in the propylene system is primarily due to the same mechanism as that present in the ethylene system (see ethylene discussion on CH_3I). Further studies with helium and xenon should confirm this.

TABLE XLXIII

Percent I-128 Stabilized in Organic Combination with Propylene

Additive	Mole Fraction Additive	Percent ¹²⁸ I As Organic (corr.)	Least Squares Organic Yield
None	0.0000	25.54	--
None	0.0000	25.60	Average --
None	0.0000	21.07	23.4 --
None	0.0000	21.44	--
Argon	0.1386	14.13	19.6
	0.3520	16.15	16.0
	0.5411	17.63	14.5
	0.7440	13.88	14.2
	0.7705	13.42	14.2
	0.8801	15.46	14.2
	0.8801	12.56	14.2
Krypton	0.1387	26.06	20.9
	0.3351	21.13	16.6
	0.4738	11.88	14.2
	0.5053	10.02	13.7
	0.6390	10.12	11.7
	0.9011	7.17	9.0
	0.9011	12.24	9.0
Methyl Iodide	0.0053	19.30	21.6
	0.1447	20.17	18.2
	0.1447	16.21	18.2
	0.2500	15.64	15.6
	0.4105	9.45	11.0
Hydrogen Sulfide	0.2079	6.48	
	0.2079	8.82	
	0.4026	7.07	
	0.5921	4.69	
	0.7289	5.19	
	0.7289	5.59

Fig. 37. Effect of krypton on the percent ^{128}I formed as organic activity due to ^{128}I reactions with C_3H_6 .

Total organic yield, □ ; Absolute yields: CH_3I , ○ ; $\text{CH}_3\text{Cl}=\text{CH}_2$, △ ; all other products, ◇ .

Fig. 38. Effect of argon on the percent ^{128}I formed as organic activity due to ^{128}I reactions with C_3H_6 .

Fig. 39. Effect of methyl iodide on the percent ^{128}I formed as organic activity due to ^{128}I reactions with C_3H_6 .

CHAPTER VI: KINETIC ENERGY SPECTRA OF HOT ATOMS ACTIVATED BY RADIATIVE NEUTRON CAPTURE

(M. Yoong)

Introduction

Information regarding the absorption of a slow neutron by an iodine or a bromine nucleus which results in the prompt emission of a γ -cascade is somewhat sparse. However, observations and measurements of high and low-energy γ -rays for ^{128}I activated by radiative neutron capture have been made by Archer et al.³⁷, and those of $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$ by Denis et al.³⁸ We have attempted using these data to obtain a kinetic energy spectrum for hot iodine atoms and will attempt to do the same for bromine atoms activated by radiative neutron capture. Our purpose in evaluating the kinetic energy spectra is to obtain data regarding the distribution of recoil energies imparted to an iodine or a bromine atom as a result of cascade gamma emission in (n,γ) activation processes. Calculations implementing the idea of a nuclear cascade have been carried out previously by Goldberger³⁹, Bernardine et al.⁴⁰, McManus et al.⁴¹, Meadows et al.⁴², Metropolis et al.⁴³, and other authors. Their calculations have all been performed by a Monte Carlo technique for various nuclear activations but none for the (n,γ) processes. However, Hsuing and Gordus⁴⁴ have studied the recoil energy spectra for $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ by using 3-dimensional random walk equations.⁴⁴

Method

In spite of the simplification of the random-walk model, it was felt

desirable to use it for our calculations using an IBM-360 Model 651H computer. The object was to improve the statistics that can be obtained by extending our calculations to all possible allowed combinations of γ -energies that are randomly selected and not limiting our calculations to only a few possible combinations as Hsuing and Gordus had done. Our method utilizes the closed general solutions of the probability distribution function for the three-dimensional random-walk process.⁴⁴ The conditions governing the use of these equations and the equations are tabulated in Appendix B. The general course of the calculations was also very similar to previous computations of this type and will not be discussed except in details where it differs from them. Although we have written three separate programs for each of the 2, 3, and 4-steps processes, it would just have been as easy to compliment all three into a single program. It is important to note that these random-walk equations require the use of momentum vectors. In our particular case of gamma-ray emission, the energy of a gamma-ray differs from the momentum by only a multiplicative constant (the velocity of light).⁴⁴ Thus the gamma-ray energies were used in our calculations. To apply the foregoing considerations to the iodine recoil problem, the intensities (per 100 captures) of the measured γ -ray energies were taken into account by weighting each γ -ray energy by a degenerate factor equal to its intensity. Also, an estimate must be made of the neutron binding energy for iodine. The neutron binding energy associated with the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ process was taken to be 6.826 Mev. Computations were carried out for cases where 2, 3, and 4 γ -rays of unequal energies may be emitted.

Discussion

If in the radiative capture of a neutron by an iodine atom, all the binding energy is carried away by a single γ -ray, a recoil possessing energy in an amount of about 196 eV (see Appendix B) is easily sufficient to break the C-I bond in CH_3I . However, Hsuing and Gordus²⁶ have shown that a overall fraction of the order of 1% of the ^{128}I fails to rupture from the parent molecule. At the present time, no level scheme is available for the γ -cascade resulting from a $^{127}\text{I}(n,\gamma)^{128}\text{I}$ reaction. Draper⁴⁵ has reported that the absorption of a neutron by a nucleus results promptly in a cascade of 4 gamma-rays, and Archer et al.³⁷ have used two-steps cascades in their estimation of the separation energy for ^{128}I . The question is: If 2, 3, or 4 γ -rays are emitted following neutron capture, what is the probable resultant recoil energy imparted to an ^{128}I atom?

Our results in figures 40, 41, and 43 show the probability distributions of gamma-ray energies (in units of Mev^{-1}) plotted against the fraction of the maximum resultant gamma-ray energy for the 2, 3, and 4 unequal-length random steps. The resultant gamma-ray energy tends to decrease as the number of γ -rays increases. Thus the stochastic analysis gives result that when the number of γ -rays is very large, a self cancellation of their recoils becomes quite probable. The sum probability distribution of the 2, 3, and 4-steps processes is shown in figure 43. The maximum probability distribution occurs at $R/R_{\text{max}} = 0.89$ where $R_{\text{max}} = 6.826$ Mev, and R/R_{max} is the fraction of the resultant gamma-ray energy. When $R/R_{\text{max}} = 0.89$, the corresponding initial recoil energy, E_v , for an ^{128}I atom activated by radiative neutron capture is 154.94 eV. This initial recoil energy of (n,γ) -activated ^{128}I is low compared with E_0 (in the order

of 10^{-5} ev) for tritium activated by (n,p) reactions; therefore, we do not have a statistically well-defined distribution of energies for (n, γ)-activated ^{128}I atoms, violating assumption Ia of the Estrup-Wolfgang kinetic theory.

Table XLXIV shows a significant difference between the organic yield of (n, γ) activated ^{130}I with CH_4 and (I.T.) activated ^{130}I with CH_4 . The iodine recoil atoms initiated by different nuclear process have different energies and consequently, the initial distribution of atoms or ions after an (n, γ) and (I.T.) processes are different. I.T. processes usually do not impart appreciable recoil energy to the atom.⁴⁶ Filatov⁴⁷ has suggested that the recoil atom spectra for atoms activated by (n, γ) and (IT) processes may be the same in the range of chemical interaction E_2-E_1 .⁴⁶ Our experimental data for (n, γ) ^{130}I and (I.T.) ^{130}I with methane suggest that their recoil atom spectra are probably different.

The foregoing considerations lend to the important role played by kinetic energy in the hot reactions activated by radiative neutron capture. The kinetic isotope effect is dependent on the relative population of hot atoms or ions in the chemically reactive zone E_2-E_1 ,⁴⁶ where the probability of reaction with a hot specie, $P(E)$, is greater than zero. Two important criteria arise in this study of (n, γ) activated reactions.

- a) The kinetic energy spectra of the recoil atoms.
- b) The efficiency of the internal moderator.

At the present time, there is insufficient data in the literature to allow any calculation of a kinetic energy spectra for (n, γ) activated ^{130}I atoms. However, the experimental data tabulated in Table XLXIV suggest that the kinetic energy spectra of ^{129}I (n, γ) ^{130}I may be quite similar to that of

$^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ since there is little or no difference in their organic yields. Figure 44 shows the organic yields of $^{82}\text{Br}^{\text{m}} + ^{82}\text{Br}$, ^{80}Br , and $^{80}\text{Br}^{\text{m}}$ as a function of mole fraction additive.⁴⁹ The O.Y. increases in the order $^{82}\text{Br}^{\text{m}} + ^{82}\text{Br}$, ^{80}Br , $^{80}\text{Br}^{\text{m}}$. This would mean that the initial kinetic energy imparted to the bromine atom are not sufficiently high that the atoms have made a number of collisions before reaching the upper limit of the reactive zone E_2 .⁴⁶ Again, if the conditions of Wolfgang's assumption 1(a)⁴⁶ are met, no isotope effects would be expected. Therefore, we conclude that the kinetic energy spectra are such that more $^{80}\text{Br}^{\text{m}}$ than ^{80}Br , than $^{82}\text{Br}^{\text{m}} + ^{82}\text{Br}$ are born with energies greater than the reactive zone E_2-E_1 .⁴⁶

Table XLXV shows the progressive decrease in organic yields for the reaction of (n, γ)-activated ^{128}I with a series of halomethanes, CH_3F , CH_3Cl , CH_3Br , and CH_3I . The data suggest that the predominant reason for low hot yields in halomethanes as compared with CH_4 is the more efficient moderation of the ^{128}I atoms by the halomethane molecules to energies below the reactive zone E_2-E_1 .⁴⁶ A similar trend is also observed for the ^{80}Br , $^{80}\text{Br}^{\text{m}}$, and $^{82}\text{Br}^{\text{m}} + ^{82}\text{Br}$ isotopes with the halomethanes. Thus an energy degradation effect for (n, γ)-activated reactions and not for (γ ,n) and (n,p) reactions is consistent with a kinetic isotope effect for (n, γ) activated bromine reaction in CH_3F .⁴⁹ An appreciable fraction is born near or in the reactive zone E_2-E_1 . With increasing degradation factors of halomethane system, the collisional efficiency in reducing the initial kinetic energy of ^{128}I atoms below the reactive zone E_2-E_1 ⁴⁶ increases, hence a decrease in the observed hot organic yields.

Figure 40. Probability distribution of gamma ray energy (in units of Mev vs the fraction of the maximum resultant gamma ray energy for 2 random gamma rays.

Figure 41. Probability distribution of gamma ray energy (in units of Mev) vs the fraction of the maximum resultant gamma ray energy for 3 random gamma rays.

Figure 42. Probability distribution of gamma ray energy (in units of MeV^{-1}) vs the fraction of the maximum resultant gamma ray energy for 4 random gamma rays.

Figure 43. Sum probability distribution of gamma-ray energies (in units of Mev^{-1}) vs the fraction of the maximum resultant gamma ray energy for all possible 2, 3, and 4 random gamma rays.

Figure 44. Effect of additives on the reaction of gaseous CH_3F with $^{80}\text{Br}^m$, ^{80}Br , ^{82}Br + $^{82}\text{Br}^m$ activated by radiative neutron capture: $^{80}\text{Br}^m$ with helium, ^{80}Br with helium, ^{82}Br + $^{82}\text{Br}^m$ with helium, $^{80}\text{Br}^m$ with argon, ^{80}Br with argon, ^{82}Br + $^{82}\text{Br}^m$ with argon.

COMPARISON OF ACTIVATION PROCESSES OF HOT $I^{130} + CH_4/CD_4$ SYSTEMS

	isotope	CH_4	CD_4
$P(n,\gamma)$	I^{130}	.170	.148
	I^{130}	.102	.104
ΔP		.068	.044

ACTIVATION EFFECTS OF HOT $I + CH_4/CD_4$

	isotope	CH_4	CD_4
$P(n,\gamma)$	I^{128}	.185	.170
$P(n,\gamma)$	I^{130}	.170	.148
ΔP		.015	.022

Table XLXV

	CH ₄	CH ₃ F	CH ₃ Cl	CH ₃ Br	CH ₃ I
observed organic yields with (n,γ) activated ¹²⁸ I	18.40	10.10	4.12	0.07	0.20
energy ⁵⁰ degradation	0.40	0.66	0.81	0.98	0.99
observed organic yields with (n,γ) activated ⁸⁰ Br	13.52	6.50	5.50	3.30	----
⁸⁰ Br ^m	15~16	7.95	6.50	4.50	----
⁸² Br ^m	9.00	5.35	4.00	3.00	----

APPENDIX A

(R. Pettijohn)

Gas Sample Injection System

Figure 40 shows in schematic form the gas sample injection system used in this research. This apparatus is used in conjunction with the radio-gas chromatograph described in Progress Report No. 5, February 15, 1971. This injection design is practical only for products readily condensable at liquid nitrogen temperature. For substituted alkyl iodides it has worked extremely well.

With valve A in position I the system is bypassed and the helium carrier gas is free to travel directly to the gas chromatograph. In this position the valve shorts the ends of loop (B). The vacuum tight glass bulb to metal seal is made by fitting 5/8 inch vinyl tubing over the machined stainless fitting (H) and the 17 mm O.D. sample bulb. With the bulb in place (F) the entire system up to valve A may be pumped to a vacuum by opening valves (C) and (D). The gas sample is then frozen into loop (B) by: 1. closing valve D; 2. immersing the loop in a dewar of liquid nitrogen; 3. breaking the sample bulblet's tip off. The sample may be kept frozen in readiness for injection for an indefinite length of time. Injection of the sample is accomplished by: 1. closing valve (C); 2. replacing the liquid nitrogen dewar with one containing hot tap water (G) thus vaporizing the sample; 3. turning valve A from position I to II, then back to I after 20 seconds (for 100 cc/min carrier gas flow). This injection period was experimentally determined by optimizing both peak shape as well as obtaining an injection of 99.9% of the volatile organic

products. This procedure can then be repeated for the next sample with essentially continuous carrier gas flow.

POSITION I. — BYPASS
 POSITION II. — INJECT

- A. CIRCLE SEAL 4 WAY VALVE (2 POSITIONS)
- B. FREEZE-VAPORIZE LOOP
- C. VALVE 1.
- D. VALVE 2.
- E. VINYL TUBING
- F. SAMPLE BULBLET
- G. DEWAR CONTAINING EITHER LIQUID NITROGEN OR HOT WATER
- H. MACHINED FITTING

Fig. . Condensable gas sample injection system.

APPENDIX B

(M. Yoong)

$$*Recoil = 537 Er^2/Mn$$

Er = energy in Mev of the gamma quantum.

Mn = mass of the hot atom specie in amu.

E recoil = recoil energy in ev of the activated specie.

*(see reference 44).

PROBABILITY DISTRIBUTION FUNCTIONS FOR 2-UNEQUAL-LENGTH RANDOM STEPS*

R range	$w_2(R)$
0 (A-B)	0
(A-B) (A + B)	$\frac{1}{8 RAB}$

A>B

PROBABILITY DISTRIBUTION FUNCTIONS FOR 3-UNEQUAL-LENGTH RANDOM STEPS*

R range	Condition		$w_3(R)$
	1	2	
0 (A-B-C)	X		0
0 (-A+B+C)		X	$\frac{1}{8 ABC}$
(A-B-C) (A-B+C)	X		$\frac{R-A+B+C}{16 RABC}$
(-A+B+C) (A-B+C)		X	
(A-B+C) (A+B-C)	X	X	$\frac{1}{8 RAB}$
(A+B-C) (A+B+C)	X	X	$\frac{-R+A+B+C}{16 RABC}$

A>B

*(see reference 44)

```

IX=12345
DO 9 I=1,20000
CALL AMCD
SUM=AC+BC
IF ((SUM-6.826).GT.0.008,OR,(6.826-SUM).GT.0.008) GO TO 9
A=AC/SUM
B=BC/SUM
WRITE (10,100) A,B
100 FORMAT (2X,F10.3,2X,F10.3,16X,'*',15X,'*PROB-DIST*')
S1=A-B
S2=A+B
DO 101 N=1,1000
E=N
R=E/100.0
IF (R,LT,S1) GO TO 102
IF (R,GT,S1) GO TO 103
102 PD=0.000
GO TO 104
103 PD=R/(2.000*S1)
104 WRITE (10,105) R,PD
105 FORMAT (34X,F10.3,12X,F10.3)
101 CONTINUE
9 CONTINUE
STOP
END
    
```

SUBROUTINE AMCD

DIMENSION AS(2),EH1(2535),EH2(1766),EL1(4100),EL2(13260),

IEH(21661)

EQUIVALENCE (EL1(1),EH(1)),(EL2(1),EH(4101)),(EH1(1),EH(1736)),

1(EH2(1),EH(19896))

COMMON AC,BC,IX,IY

DATA EH1/26*6.740,193*6.694,47*6.681,23*6.663,55*6.645,13*6.597,

A 17*6.570,11*6.547,12*6.532,22*6.478,47*6.454,45*6.445,

B 17*6.430,71*6.392,179*6.302,44*6.294,63*6.273,29*6.216,

C 180*6.160,15*6.148,44*6.994,41*6.985,23*6.945,35*6.887,

D 47*6.793,34*6.752,14*6.728,22*6.633,17*6.462,254*6.562,

E 51*6.527,105*6.486,133*6.462,47*6.450,19*6.412,96*6.340,

F 27*6.365,26*6.335,129*6.300,90*6.291,36*6.277

DATA EH2/34*6.296,25*6.115,152*6.095,25*6.090,34*6.062,50*6.045,

G 50*6.033,116*6.018,82*6.001,49*6.983,195*6.954,34*6.894,

H 25*6.871,11*6.852,163*6.802,12*6.789,40*6.759,24*6.743,

I 24*6.711,24*6.590,31*6.565,16*6.645,27*6.621,23*6.590,

J 23*6.567,63*6.546,45*6.518,22*6.502,11*6.465,33*6.398,

K 33*6.367,21*6.312,23*6.264,35*6.156,31*6.100,27*6.075,

L 13*6.957,27*6.979,60*6.810,26*6.659,39*6.595,26*6.486/

DATA EL1/10*1.005,110*1.660,110*1.541,160*1.614,110*1.593,

A 18*1.587,110*1.563,120*1.533,90*1.519,60*1.511,

B 110*1.497,160*1.477,110*1.465,160*1.433,110*1.427,

C 50*1.400,10*1.375,30*1.355,150*1.297,150*1.293,70*1.269,

D 40*1.241,100*1.225,40*1.215,40*1.170,50*1.150,50*1.142,

E 50*1.127,50*1.117,80*1.099,50*1.066,70*1.053,100*1.039,

F 20*1.032,200*1.017,60*1.002,70*0.976,70*0.965,30*0.951,

G 50*0.911,90*0.885,200*0.855,90*0.842,70*0.835,60*0.822,

H 70*0.814,50*0.792,120*0.760,50*0.768,150*0.740,50*0.722,

I 60*0.710,200*0.701/

DATA EL2/112*6.039,10*6.500,70*6.700,60*6.699,110*6.637,110*6.636,


```

C CASE STUDY OF CLOSED GENERAL SOLUTIONS OF THE PROBABILITY DISTRI-
C BUTION FOR (3-STEPS) THREE DIMENSIONAL RANDOM-WALK PROCESSES . 200
C COORD. AC,BC,CC,IX,IY
C IX=12345
C DO 9 I=1,20000
C CALL APCD
C SUM=AC+BC+CC
C IF ((SUM-6.826).GT.0.008 .OR. (6.826-SUM).GT.0.008) GO TO 9
C A=AC/SUM
C B=BC/SUM
C C=CC/SUM
C WRITE (6,200) A,B,C
200 FORMAT (7X,F10.3,2X,F10.3,2X,F10.3)
C S1=A+B+C
C S2=B+C
C S3=A-B-C
C S4=B-A+C
C S5=A-B+C
C S6=A+B-C
C TEST FOR THE APPLICABILITY OF CONDITION 1 AND 2
C IF (A.GT.S2) GO TO 101
C IF (A.LE.S2) GO TO 102
C APPLICABILITY OF CONDITION1
101 WRITE (6,103)
103 FORMAT (' CONDITION1',30X,'R',15X,'PROB-DIST')
C DO 104 M=1,100,3
C E=M
C R=E/100.0
C IF (R.LT.S3) GO TO 105
C IF (R.GE.S3.AND.R.LT.S5) GO TO 106
C IF (R.GE.S5.AND.P.LT.S6) GO TO 107
C IF (R.GE.S6.AND.R.LT.S1) GO TO 108
C IF (R.GE.S1) GO TO 104
105 PD=0.0
C GO TO 110
106 PD=(R*(R-S3))/(4.0*A*B*C)
C GO TO 110
107 PD=R/(2.0*A*B)
C GO TO 110
108 PD=(P*(S1-R))/(4.0*A*B*C)
110 WRITE (6,111) R,PD
111 FORMAT (30X,F10.3,12X,F10.3)
104 CONTINUE
C GO TO 9
C APPLICATION OF CONDITION2
102 WRITE (6,109)
109 FORMAT (' CONDITION2',30X,'R',15X,'PROB-DIST')
C DO 112 M=1,100,3
C E=M
C R=E/100.0
C IF (R.LT.S4) GO TO 113
C IF (R.GE.S4.AND.R.LT.S5) GO TO 114
C IF (R.GE.S5.AND.P.LT.S6) GO TO 115
C IF (R.GE.S6.AND.P.LT.S1) GO TO 116
C IF (R.GE.S1) GO TO 112
113 PD=(R*(R-S4))/(2.0*A*B*C)
C GO TO 117
114 PD=(P*(P-S3))/(4.0*A*B*C)

```


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```
GO TO 117
115 PD=R/(2.0*A*B)
GO TO 117
116 PD=(R*(S1-R))/(4.0*A*B*C)
117 WRITE (6,118) R,PD
118 FORMAT (34X,F10.3,12X,F10.3)
112 CONTINUE
--- 9 CONTINUE
STOP
END
```

SUBROUTINE ABCD

DIMENSION AS(3);EH1(2535),EH2(1766),EL1(4100),EL2(13260),

IEH(21661)

EQUIVALENCE (EL1(1),EH(1)),(EL2(1),EH(4101)),(EH1(1),EH(17361)),

1(EH2(1),EH(19696))

COMMON AC,BC,CC,IX,IY

DATA EH1/25*6:740,193*6:694,47*6:681,23*6:663,55*6:645,13*6:597,

A 17*6:576,11*6:547,12*6:532,22*6:478,47*6:454,48*6:445;

B 17*6:430,71*6:392,17*6:308,44*6:294,63*6:273,29*6:216;

C 18*6:166,15*6:148,44*6:994,41*5:985,23*5:945,35*5:887;

D 47*5:793,64*5:752,142*5:728,22*5:633,179*5:462,254*5:562,

E 59*5:527,105*5:486,133*5:462,47*5:450,19*5:412,46*5:386;

F 27*5:365,38*5:339,129*5:300,90*5:291,36*5:277/

DATA EH2/144*5:200,25*5:115,152*5:095,25*5:080,34*5:062,50*5:045,

G 50*5:033,116*5:016,82*5:001,49*4:983,195*4:954,34*4:894,

H 25*4:877,2*4:452,16*4:802,12*4:789,40*4:759,24*4:743,

I 24*4:711,24*4:690,31*4:666,16*4:645,27*4:621,23*4:599,

J 23*4:587,45*4:546,45*4:518,22*4:502,11*4:465,33*4:398,

K 33*4:347,21*4:312,23*4:284,35*4:156,31*4:100,27*4:075,

L 13*3:997,27*3:979,60*3:810,26*3:659,39*3:595,26*3:486/

DATA EL1/10*1:665,110*1:660,110*1:641,160*1:614,110*1:598;

A 190*1:587,110*1:563,12*1:537,90*1:519,40*1:511,

B 110*1:497,100*1:477,110*1:465,10*1:433,110*1:427;

C 50*1:400,10*1:376,30*1:356,150*1:297,150*1:293,70*1:269,

D 40*1:241,60*1:225,40*1:218,40*1:170,40*1:150,60*1:142,

E 50*1:127,30*1:117,80*1:098,50*1:066,70*1:053,100*1:039,

F 20*1:032,20*1:017,60*1:002,70*0:976,70*0:965,30*0:953;

G 50*0:911,70*0:885,80*0:853,90*0:843,70*0:839,60*0:822,

H 70*0:814,50*0:792,120*0:786,50*0:768,150*0:740,50*0:722,

I 40*0:716,250*0:701/

DATA EL2/50*0:682,50*0:678,70*0:658,70*0:649,110*0:637,110*0:634,

J 60*0:612,130*0:591,40*0:570,60*0:557,50*0:531,130*0:527,

K 60*0:491,50*0:480,120*0:460,160*0:433,370*0:420;

L 340*0:416,140*0:410,120*0:390,140*0:385,160*0:374;

M 130*0:364,150*0:355,300*0:344,300*0:342,120*0:327,

N 120*0:322,170*0:313,530*0:300,270*0:282,110*0:276;

O 160*0:266,500*0:247,190*0:231,300*0:222,250*0:194;

P 350*0:190,360*0:183,150*0:165,270*0:159,380*0:151,

Q 210*0:147,420*0:132,320*0:122,260*0:106,420*0:057,

R 180*0:053/

DO 10 I=1,3

CALL RANDOM(IX,IY,F)

J=1+21661*F

AS(I)=EH(J)

10 IX=IY

DO 3 I=1,3

KM=I+1

IF (KM.EQ.4) GO TO 4

DO 3 J=KM,3

IF (AS(I).GT.AS(J)) GO TO 3

TEMP=AS(I)

AS(I)=AS(J)

AS(J)=TEMP

3 CONTINUE

4 AC=AS(1)

BC=AS(2)

CC=AS(3)

RETURN

4N IV G LEVEL 19

RANDU *

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SUBROUTINE RANDU(IY,YFL)

IY=1A*65539

IF (IY) 5,6,6

5 IY=IY+2147483647+1

6 YFL=IY

YFL=YFL*.4656613E-9

RETURN

END

Various cases for four unequal length steps *

Case	Conditions ^a
1	$A > (B+C+D)$ and $B > (C+D)$
2	$A > (B+C+D)$ and $(C+D) > B$
3	$(A+D) > (B+C)$, $(B+D) > A$, and $B > (C+D)$
4	$(A+D) > (B+C)$, $(B+C) > A$, $A > (B+D)$, and $B > (C+D)$
5	$(B+C+D) > A$, $A > (B+C)$, and $B > (C+D)$
6	$(A+D) > (B+C)$ and $(C+D) > A$
7	$(A+D) > (B+C)$ and $(B+D) > A > (C+D) > B$
8	$(A+D) > (B+C) > A > (B+D)$ and $(C+D) > B$
9	$(B+C+D) > A > (B+C)$ and $(C+D) > B$
10	$(B+C) > (A+D)$, $(B+D) > A$, and $B > (C+D)$
11	$(B+C) > (A+D)$, $A > (B+D)$, and $B > (C+D)$
12	$(B+C) > (A+D)$ and $(C+D) > A$
13	$(B+C) > (A+D)$ and $(B+D) > A > (C+D) > B$
14	$(B+C) > (A+D)$, $A > (B+D)$, and $(C+D) > B$

^aWhere $A > B > C > D$

* (See reference 44)

Probability distribution for four unequal length steps.*

R-range	Applicability - Case: ^a														$W_4(R)$
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
$0 \rightarrow (A-B-C-D)$	x	x													0
$0 \rightarrow (-A+B+C-D)$										x	x	x	x	x	$\frac{1}{8\pi ABC}$
$0 \rightarrow (-A+B+C+D)$					x				x						$\frac{-A+B+C+D}{16\pi ABCD}$
$0 \rightarrow (A-B-C+D)$			x	x		x	x	x							$\frac{(R-A+B+C+D)^2}{64\pi RABCD}$
$(A-B-C-D) \rightarrow (A-B-C+D)$	x	x													$\frac{8DR - (R+A-B-C+D)^2}{64\pi RABCD}$
$(-A+B+C+D) \rightarrow (A-B-C+D)$					x				x						
$(A-B-C+D) \rightarrow (-A+B+C+D)$					x			x							
$(-A+B+C-D) \rightarrow (A-B+C-D)$										x		x	x		
$(-A+B+C-D) \rightarrow (-A+B+C+D)$											x			x	
$(A-B-C+D) \rightarrow (A-B+C-D)$			x			x	x								$\frac{R-A+B+C}{16\pi RABC}$
$(-A+B+C+D) \rightarrow (A-B+C-D)$	x	x			x				x						
$(A-B+C-D) \rightarrow (-A+B+C+D)$			x				x	x		x				x	$\frac{4CD - (A-B)^2 - (R-C-D)^2}{32\pi RABCD}$
$(A-B+C-D) \rightarrow (A+B-C-D)$						x						x			

R-range	1	2	3	4	5	6	7	8	9	10	11	12	13	14	$w_4(R)$
$(A+B-C-D) \rightarrow (-A+B+C+D)$						x						x			$\frac{-[(R-A-B-C-D)(3R+A+B+C+D) + 4(A^2+B^2+C^2+D^2)]}{64\pi RABCD}$
$(A-B+C-D) \rightarrow (A+B-C-D)$		x						x	x					x	$\frac{8CD-(R-A+B-C-D)^2}{64\pi RABCD}$
$(A-B+C-D) \rightarrow (A-B+C+D)$	x			x	x						x				
$(-A+B+C+D) \rightarrow (A+B-C-D)$							x						x		
$(-A+B+C+D) \rightarrow (A-B+C+D)$			x							x					
$(A+B-C-D) \rightarrow (A-B+C+D)$		x					x	x	x				x	x	$\frac{4CD-(R-A)^2-(B-C-D)^2}{32\pi RABCD}$
$(A-B+C+D) \rightarrow (A+B-C-D)$	x		x	x	x					x	x				$\frac{1}{8\pi RAB}$
$(A+B-C-D) \rightarrow (A+B-C+D)$	x		x	x	x					x	x				$\frac{8CD-(R-A-B+C+D)^2}{64\pi RABCD}$
$(A-B+C+D) \rightarrow (A+B-C+D)$		x				x	x	x	x			x	x	x	
$(A+B-C+D) \rightarrow (A+B+C-D)$	x	x	x	x	x	x	x	x	x	x	x	x	x	x	$\frac{A+B+C-R}{16\pi RABC}$
$(A+B+C-D) \rightarrow (A+B+C+D)$	x	x	x	x	x	x	x	x	x	x	x	x	x	x	$\frac{(R-A-B-C-D)^2}{64\pi RABCD}$

*(See reference 44)

C CASE STUDY OF CLOSED GENERAL SOLUTIONS OF THE PROBABILITY DISTRIBUTION FOR ~~THREE~~ DIMENSIONAL RANDOM-WALK PROCESSES (4-STEPS)

COMMON AC,BC,CC,DC,IX,IY

IX=12345

207

8 DO 9 I=1,20000

CALL ABCD

SUM=AC+BC+CC+DC

IF ((SUM-6.826).GT.0.068.OR.(6.826-SUM).GT.0.068) GO TO 9

A=AC/SUM

B=BC/SUM

C=CC/SUM

D=DC/SUM

WRITE (6,888) A,B,C,D

888 FORMAT (2X,F10.3,2X,F10.3,2X,F10.3,2X,F10.3)

SUM1=A+D

SUM2=B+C

SUM3=B+D

SUM4=C+D

SUM5=B+C+D

S1=A+B+C+D

S2=A+B+C-D

S3=A+B-C-D

S4=A-B-C-D

S5=A-B+C+D

S6=A-B+C-D

S7=A-B-C+D

S8=A+B+C+D

S9=B-A+C+D

S10=B-A+C-D

C TEST FOR THE CONDITIONS 1 THROUGH 14

IF (A.GT.SUM5.AND.B.GT.SUM4) GO TO 101

IF (A.GT.SUM5.AND.B.LT.SUM4) GO TO 102

IF (SUM).GT.SUM2.AND.SUM3.GT.A.AND.B.GT.SUM4) GO TO 103

IF (SUM1.GT.SUM2.AND.SUM2.GT.A.AND.A.GT.SUM3.AND.B.GT.SUM4) GO TO

1104

IF (SUM5.GT.A.AND.A.GT.SUM2.AND.B.GT.SUM4) GO TO 105

IF (SUM1.GT.SUM2.AND.SUM4.GT.A) GO TO 106

IF (SUM1.GT.SUM2.AND.SUM3.GT.A.AND.A.GT.SUM4.AND.SUM4.GT.B) GO TO

1107

IF (SUM1.GT.SUM2.AND.SUM2.GT.A.AND.A.GT.SUM3.AND.SUM4.GT.B) GO TO

1108

IF (SUM5.GT.A.AND.A.GT.SUM2.AND.SUM4.GT.B) GO TO 109

IF (SUM2.GT.SUM1.AND.SUM3.GT.A.AND.B.GT.SUM4) GO TO 110

IF (SUM2.GT.SUM1.AND.A.GT.SUM3.AND.B.GT.SUM4) GO TO 111

IF (SUM2.GT.SUM1.AND.SUM4.GT.A) GO TO 112

IF (SUM2.GT.SUM1.AND.SUM3.GT.A.AND.A.GT.SUM4.AND.SUM4.GT.B) GO TO

1113

IF (SUM2.GT.SUM1.AND.A.GT.SUM3.AND.SUM4.GT.B) GO TO 114

GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITION1

101 WRITE (6,420)

420 FORMAT (' CONDITION1',30X,'R',15X,'PROB-DIST')

DO 311 M=1,100,5

E=M

R=E/100.0

IF (R.LT.S4) GO TO 301

IF (R.GE.S4.AND.R.LT.S6) GO TO 302

IF (R.GE.S6.AND.R.LT.S7) GO TO 303

```

      IF (R.GE.S7.AND.R.LT.S5) GO TO 304
      IF (R.GE.S5.AND.R.LT.S3) GO TO 305
      IF (R.GE.S3.AND.R.LT.S8) GO TO 306
      IF (R.GE.S8.AND.R.LT.S2) GO TO 307
      IF (R.GE.S2.AND.R.LT.S1) GO TO 308
      IF (R.GE.S1) GO TO 311
301 PD =0.0
      GO TO 421
302 PD=(R*((R-S4)**2))/(16.0*A*B*C*D)
      GO TO 421
303 PD=(R*(R-A+B+C))/(4.0*A*B*C)
      GO TO 421
304 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)
      GO TO 421
305 PD=(R/(2*A*B))
      GO TO 421
306 PD=((8.0*C*D)-((R-S3)**2))/(16.0*A*B*C*D)
      GO TO 421
307 PD=(R*(A+B+C-R))/(4.0*A*B*C)
      GO TO 421
308 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)
421 WRITE (6,422) R, PD
422 FORMAT (34X,F10.3,12X,F10.3)
311 CONTINUE
      GO TO 9
C. TEST FOR THE APPLICABILITY OF CONDITION2
102 WRITE (6,429)
429 FORMAT (' CONDITION2',30X,'R',15X,'PROB-DIST:')
      DO 318 M=1,100,5
      E=M
      R=E/100.0
      IF (R.LT.S4) GO TO 319
      IF (R.GE.S4.AND.R.LT.S6) GO TO 320
      IF (R.GE.S6.AND.R.LT.S7) GO TO 322
      IF (R.GE.S7.AND.R.LT.S3) GO TO 324
      IF (R.GE.S3.AND.R.LT.S5) GO TO 326
      IF (R.GE.S5.AND.R.LT.S8) GO TO 328
      IF (R.GE.S8.AND.R.LT.S2) GO TO 330
      IF (R.GE.S2.AND.R.LT.S1) GO TO 332
      IF (R.GE.S1) GO TO 318
319 PD=0.0
      GO TO 430
320 PD=(R*((R-S4)**2))/(16.0*A*B*C*D)
      GO TO 430
322 PD=(R*(R-A+B+C))/(4.0*A*B*C)
      GO TO 430
324 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)
      GO TO 430
326 PD=(R*((4.0*C*D)-((R-A)**2)-((B-C-D)**2)))/(8.0*A*B*C*D)
      GO TO 430
328 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)
      GO TO 430
330 PD=(R*(A+B+C-R))/(4.0*A*B*C)
      GO TO 430
332 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)
430 WRITE (6,431) R, PD
431 FORMAT (34X,F10.3,12X,F10.3)
318 CONTINUE

```


GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITION3

103 WRITE (6,438)

438 FORMAT (' CONDITION3',30X,'R',15X,'PROB-DIST')

DO 335 M=1,100,5

E=M

R=E/100.0

IF (R.LT.S6) GO TO 334

IF (R.GE.S6.AND.R.LT.S7) GO TO 336

IF (R.GE.S7.AND.R.LT.S10) GO TO 338

IF (R.GE.S10.AND.R.LT.S5) GO TO 340

IF (R.GE.S5.AND.R.LT.S4) GO TO 342

IF (R.GE.S4.AND.R.LT.S8) GO TO 344

IF (R.GE.S8.AND.R.LT.S2) GO TO 346

IF (R.GE.S2.AND.R.LE.S1) GO TO 348

IF (R.GE.S1) GO TO 335

334 PD=((R**2)-S10)/(4.0*A*B*C*D)

GO TO 439

336 PD=(R*((8.0*C*D)-((R+S6)**2)))/(16.0*A*B*C*D)

GO TO 439

338 PD=(R*((4.0*C*D)-((A-B)**2)-((R-C-D)**2)))/(8.0*A*B*C*D)

GO TO 439

340 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)

GO TO 439

342 PD=(R/(2.0*A*B))

GO TO 439

344 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)

GO TO 439

346 PD=(R*((A*B*C)-R))/(4.0*A*B*C)

GO TO 439

348 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)

439 WRITE (6,440) R, PD

440 FORMAT (34X,F10,3,12X,F10,3)

335 CONTINUE

GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITION4

104 WRITE (6,447)

447 FORMAT (' CONDITION4',30X,'R',15X,'PROB-DIST')

DO 351 M=1,100,5

E=M

R=E/100.0

IF (R.LT.S6) GO TO 350

IF (R.GE.S6.AND.R.LT.S7) GO TO 352

IF (R.GE.S7.AND.R.LT.S5) GO TO 354

IF (R.GE.S5.AND.R.LT.S3) GO TO 356

IF (R.GE.S3.AND.R.LT.S8) GO TO 358

IF (R.GE.S8.AND.R.LT.S2) GO TO 360

IF (R.GE.S2.AND.R.LE.S1) GO TO 362

IF (R.GE.S1) GO TO 351

350 PD=((R**2)*S10)/(4.0*A*B*C*D)

GO TO 448

352 PD=(R*(R-A*B*C))/(4.0*A*B*C)

GO TO 448

354 PD=(R*((8.0*C*D)-((S5**2)))/(16.0*A*B*C*D)

GO TO 448

356 PD=(R/(8.0*A*B))

GO TO 448

358 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)

GO TO 448

360 PD=(R*(A+B+C-R))/(4.0*A*B*C)

GO TO 448

362 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)

448 WRITE (6,449) R, PD

449 FORMAT (34X,F10.3,12X,F10.3)

351 CONTINUE

GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITIONS

105 WRITE (6,455)

455 FORMAT (' CONDITIONS',30X,'R',15X,'PROB-DIST')

DO 365 M=1,100,5

E=M

R=E/100.0

IF (R.LT.S10) GO TO 364

IF (R.GE.S10.AND.R.LT.S6) GO TO 366

IF (R.GE.S6.AND.R.LT.S7) GO TO 368

IF (R.GE.S7.AND.R.LT.S5) GO TO 370

IF (R.GE.S5.AND.R.LT.S3) GO TO 372

IF (R.GE.S3.AND.R.LT.S8) GO TO 374

IF (R.GE.S8.AND.R.LT.S2) GO TO 376

IF (R.GE.S2.AND.R.LT.S1) GO TO 378

IF (R.GE.S1) GO TO 365

364 PD=((R**2)*S10)/(4.0*A*B*C*D)

GO TO 456

366 PD=(R*((R-S4)**2))/(16.0*A*B*C*D)

GO TO 456

368 PD=(R*(R-A+B+C))/(4.0*A*B*C)

GO TO 456

370 PD=(R*((8.0*C*D)-(55**2)))/(16.0*A*B*C*D)

GO TO 456

372 PD=(R/(2.0*A*B))

GO TO 456

374 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)

GO TO 456

376 PD=(R*(A+B+C-R))/(4.0*A*B*C)

GO TO 456

378 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)

456 WRITE (6,457) R, PD

457 FORMAT (34X,F10.3,12X,F10.3)

365 CONTINUE

GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITION6

106 WRITE (6,464)

464 FORMAT (' CONDITION6',30X,'R',15X,'PROB-DIST')

DO 381 M=1,100,5

E=M

R=E/100.0

IF (R.LT.S6) GO TO 380

IF (R.GE.S6.AND.R.LT.S7) GO TO 382

IF (R.GE.S7.AND.R.LT.S3) GO TO 384

IF (R.GE.S3.AND.R.LT.S10) GO TO 386

IF (R.GE.S10.AND.R.LT.S5) GO TO 388

IF (R.GE.S5.AND.R.LT.S8) GO TO 390

IF (R.GE.S8.AND.R.LT.S2) GO TO 392

IF (R.GE.S2.AND.R.LT.S1) GO TO 394

IF (R.GE.S1) GO TO 381

380 PD=((R**2)*S10)/(4.0*A*B*C*D)

211

```

GO TO 465
382 PD=(R*(18.0*D*R)-((R+S6)**2))/((16.0*A*B*C*D)
GO TO 465
384 PD=(R*((4.0*C*D)-((A-B)**2)-((R-C-D)**2)))/(8.0*A*B*C*D)
GO TO 465
386 PD=(R*((S1-R)*((3*R)+S1))-4.0*((A**2)+(B**2)+(C**2)+
1(D**2))))/(16.0*A*B*C*D)
GO TO 465
388 PD=(R*((4.0*C*D)-((R-A)**2)-((B-C-D)**2)))/(8.0*A*B*C*D)
GO TO 465
390 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)
GO TO 465
392 PD=(R*(A+B+C-R))/(4.0*A*B*C)
GO TO 465
394 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)
465 WRITE (6,466) R, PD
466 FORMAT (34X,F10.3,12X,F10.3)
381 CONTINUE
GO TO 9

```

C TEST FOR THE APPLICABILITY OF CONDITION7

```

107 WRITE (6,473)
473 FORMAT (' CONDITION7',30X,'R',15X,'PROB-DIST')
DO 397 M=1,100,5
E=M
R=E/100.0
IF (R.LT.S6) GO TO 396
IF (R.GE.S6.AND.R.LT.S7) GO TO 398
IF (R.GE.S7.AND.R.LT.S10) GO TO 500
IF (R.GE.S10.AND.R.LT.S3) GO TO 502
IF (R.GE.S3.AND.R.LT.S5) GO TO 504
IF (R.GE.S5.AND.R.LT.S8) GO TO 506
IF (R.GE.S8.AND.R.LT.S2) GO TO 508
IF (R.GE.S2.AND.R.LE.S1) GO TO 510
IF (R.GE.S1) GO TO 397
396 PD=((R**2)*S10)/(4.0*A*B*C*D)
GO TO 474
398 PD=(R*((8.0*D*R)-((R+S6)**2)))/(16.0*A*B*C*D)
GO TO 474
500 PD=(R*((4.0*C*D)-((A+B)**2)-((R-C-D)**2)))/(8.0*A*B*C*D)
GO TO 474
502 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)
GO TO 474
504 PD=(R*((4.0*C*D)-((R-A)**2)-((B-C-D)**2)))/(8.0*A*B*C*D)
GO TO 474
506 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)
GO TO 474
508 PD=(R*(A+B+C-R))/(4.0*A*B*C)
GO TO 474
510 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)
474 WRITE (6,475) R, PD
475 FORMAT (34X,F10.3,12X,F10.3)
397 CONTINUE
GO TO 9

```

C TEST FOR THE APPLICABILITY OF CONDITION8

```

108 WRITE (6,482)
482 FORMAT (' CONDITION8',30X,'R',15X,'PROB-DIST')
DO 513 M=1,100,5
E=M

```

R=E/100.0

IF (R.LT.S6) GO TO 512

IF (R.GE.S6.AND.R.LT.S10) GO TO 514

IF (R.GE.S10.AND.R.LT.S7) GO TO 516

IF (R.GE.S7.AND.R.LT.S3) GO TO 518

IF (R.GE.S3.AND.R.LT.S5) GO TO 520

IF (R.GE.S5.AND.R.LT.S8) GO TO 522

IF (R.GE.S8.AND.R.LT.S2) GO TO 524

IF (R.GE.S2.AND.R.LE.S1) GO TO 526

IF (R.GE.S1) GO TO 513

512 PD=((R**2)*S10)/(4.0*A*B*C*D)

GO TO 483

514 PD=(R*((8.0*D*R)-((R+S6)**2)))/(16.0*A*B*C*D)

GO TO 483

516 PD=(R*(R-A+B+C))/(4.0*A*B*C)

GO TO 483

518 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)

GO TO 483

520 PD=(R*((4.0*C*D)-((R-A)**2)-((B-C-D)**2.0)))/(8.0*A*B*C*D)

GO TO 483

522 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)

GO TO 483

524 PD=(R*(A+B+C-R))/(4.0*A*B*C)

GO TO 483

526 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)

483 WRITE (6,484) R, PD

484 FORMAT (34X,F10.3,12X,F10.3)

513 CONTINUE

GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITION9

109 WRITE (6,800)

800 FORMAT (1, 'CONDITION9', 30X, 'R', 15X, 'PROB-DIST')

DO 529 M=1,100,5

E=M

R=E/100.0

IF (R.LT.S10) GO TO 528

IF (R.GE.S10.AND.R.LT.S6) GO TO 530

IF (R.GE.S6.AND.R.LT.S7) GO TO 532

IF (R.GE.S7.AND.R.LT.S3) GO TO 534

IF (R.GE.S3.AND.R.LT.S5) GO TO 536

IF (R.GE.S5.AND.R.LT.S8) GO TO 538

IF (R.GE.S8.AND.R.LT.S2) GO TO 540

IF (R.GE.S2.AND.R.LE.S1) GO TO 542

IF (R.GE.S1) GO TO 529

528 PD=((R**2)*S10)/(4.0*A*B*C*D)

GO TO 801

530 PD=(R*((R-S4)**2))/(16.0*A*B*C*D)

GO TO 801

532 PD=(R*(R-A+B+C))/(4.0*A*B*C)

GO TO 801

534 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)

GO TO 801

536 PD=(R*((4.0*C*D)-((R-A)**2)-((B-C-D)**2.0)))/(8.0*A*B*C*D)

GO TO 801

538 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)

GO TO 801

540 PD=(R*(A+B+C-R))/(4.0*A*B*C)

GO TO 801

542 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)

801 WRITE (6,802) R, PD

802 FORMAT (34X,F10.3,12X,F10.3)

529 CONTINUE

GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITION10

110 WRITE (6,600)

600 FORMAT (' CONDITION10',30X,'R',15X,'PROB-DIST')

DO 545 M=1,100,5

E=M

R=E/100.0

IF (R,LT,S9) GO TO 544

IF (R,GE,S9,AND,R,LT,S7) GO TO 546

IF (R,GE,S7,AND,R,LT,S10) GO TO 548

IF (R,GE,S10,AND,R,LT,S5) GO TO 550

IF (R,GE,S5,AND,R,LT,S3) GO TO 552

IF (R,GE,S3,AND,R,LT,S8) GO TO 554

IF (R,GE,S8,AND,R,LT,S2) GO TO 556

IF (R,GE,S2,AND,R,LE,S1) GO TO 558

IF (R,GE,S1) GO TO 545

544 PD=(R**2)/(2.0*A*B*C)

GO TO 601

546 PD=(R*((8.0*D*R)-((R+S6)**2)))/(16.0*A*B*C*D)

GO TO 601

548 PD=(R*((4.0*C*D)-((A-B)**2)-((R-C-D)**2)))/(8.0*A*B*C*D)

GO TO 601

550 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)

GO TO 601

552 PD=(R/(2.0*A*B))

GO TO 601

554 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)

GO TO 601

556 PD=(R*(A+B+C-R))/(4.0*A*B*C)

GO TO 601

558 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)

601 WRITE (6,602) R, PD

602 FORMAT (34X,F10.3,12X,F10.3)

545 CONTINUE

GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITION11

111 WRITE (6,609)

609 FORMAT (' CONDITION11',30X,'R',15X,'PROB-DIST')

DO 577 M=1,100,5

E=M

R=E/100.0

IF (R,LT,S9) GO TO 576

IF (R,GE,S9,AND,R,LT,S10) GO TO 578

IF (R,GE,S10,AND,R,LT,S7) GO TO 580

IF (R,GE,S7,AND,R,LT,S5) GO TO 582

IF (R,GE,S5,AND,R,LT,S3) GO TO 584

IF (R,GE,S3,AND,R,LT,S8) GO TO 586

IF (R,GE,S8,AND,R,LT,S2) GO TO 588

IF (R,GE,S2,AND,R,LE,S1) GO TO 590

IF (R,GE,S1) GO TO 577

576 PD=(R**2)/(2.0*A*B*C)

GO TO 610

578 PD=(R*((8.0*D*R)-((R+S6)**2)))/(16.0*A*B*C*D)

GO TO 610

580 PD=(R*(R-A+B+C))/(4.0*A*B*C)

GO TO 610

582 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)

GO TO 610

584 PD=(R/(2.0*A*B))

GO TO 610

586 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)

GO TO 610

588 PD=(R*(A+B+C-R))/(4.0*A*B*C)

GO TO 610

590 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)

610 WRITE (6,611) R, PD

611 FORMAT (34X,F10.3,12X,F10.3)

577 CONTINUE

GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITION12

112 WRITE (6,618)

618 FORMAT (' CONDITION12',30X,'R',15X,'PROB-DIST')

DO 593 M=1,100,5

E=M

R=E/100.0

IF (R.LT.S9) GO TO 592

IF (R.GE.S9.AND.R.LT.S7) GO TO 594

IF (R.GE.S7.AND.R.LT.S3) GO TO 596

IF (R.GE.S3.AND.R.LT.S10) GO TO 598

IF (R.GE.S10.AND.R.LT.S5) GO TO 700

IF (R.GE.S5.AND.R.LT.S8) GO TO 702

IF (R.GE.S8.AND.R.LT.S2) GO TO 704

IF (R.GE.S2.AND.R.LT.S1) GO TO 706

IF (R.GE.S1) GO TO 593

592 PD=(R**2)/(2.0*A*B)

GO TO 619

594 PD=(R*((8.0*D*R)-((R+S6)**2)))/(16.0*A*B*C*D)

GO TO 619

596 PD=(R*((4.0*C*D)-((A-B)**2)-((R-C-D)**2)))/(8.0*A*B*C*D)

GO TO 619

598 PD=(R*((S1-R)*((3*R)+S1)+(4.0*((A**2)+(R**2)+(C**2)+

1(D**2)))))/(16.0*A*B*C*D)

GO TO 619

700 PD=(R*((4.0*C*D)-((R-A)**2)-((R-C-D)**2)))/(8.0*A*B*C*D)

GO TO 619

702 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)

GO TO 619

704 PD=(R*(A+B+C-R))/(4.0*A*B*C)

GO TO 619

706 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)

619 WRITE (6,620) R, PD

620 FORMAT (34X,F10.3,12X,F10.3)

593 CONTINUE

GO TO 9

C TEST FOR THE APPLICABILITY OF CONDITION13

113 WRITE (6,627)

627 FORMAT (' CONDITION13',30X,'R',15X,'PROB-DIST')

DO 709 M=1,100,5

E=M

R=E/100.0

IF (R.LT.S9) GO TO 708

IF (R.GE.S9.AND.R.LT.S7) GO TO 710

```

IF (R.GE.57.AND.R.LT.S10) GO TO 712
IF (R.GE.510.AND.R.LT.S3) GO TO 714
IF (R.GE.53.AND.R.LT.S5) GO TO 716
IF (R.GE.55.AND.R.LT.S8) GO TO 718
IF (R.GE.58.AND.R.LT.S2) GO TO 720
IF (R.GE.52.AND.R.LE.S1) GO TO 722
IF (R.GE.S1) GO TO 709

```

```
708 PD=(R**2)/(2.0*A*B*C)
```

```
GO TO 628
```

```
710 PD=(R*((8.0*D*R)-((R+S6)**2)))/(16.0*A*B*C*D)
```

```
GO TO 628
```

```
712 PD=(R*((4.0*C*D)-((R-A)**2)-((R-C-D)**2)))/(8.0*A*B*C*D)
```

```
GO TO 628
```

```
714 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)
```

```
GO TO 628
```

```
716 PD=(R*((4.0*C*D)-((R-A)**2)-((B-C-D)**2)))/(8.0*A*B*C*D)
```

```
GO TO 628
```

```
718 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)
```

```
GO TO 628
```

```
720 PD=(R*(A+B+C-R))/(4.0*A*B*C)
```

```
GO TO 628
```

```
722 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)
```

```
628 WRITE (6,629) R, PD
```

```
629 FORMAT (34X,F10.3,12X,F10.3)
```

```
709 CONTINUE
```

```
GO TO 9
```

C TEST FOR THE APPLICABILITY OF CONDITION14

```
114 WRITE (6,636)
```

```
636 FORMAT (' CONDITION14',30X,'R',15X,'PROB-DIST')
```

```
DO 725 M=1,100,5
```

```
E=M
```

```
R=E/100.0
```

```
IF (R.LT.S9) GO TO 724
```

```
IF (R.GE.S9.AND.R.LT.S10) GO TO 726
```

```
IF (R.GE.S10.AND.R.LT.S7) GO TO 728
```

```
IF (R.GE.S7.AND.R.LT.S3) GO TO 730
```

```
IF (R.GE.S3.AND.R.LT.S5) GO TO 732
```

```
IF (R.GE.S5.AND.R.LT.S8) GO TO 734
```

```
IF (R.GE.S8.AND.R.LT.S2) GO TO 736
```

```
IF (R.GE.S2.AND.R.LE.S1) GO TO 738
```

```
IF (R.GE.S1) GO TO 725
```

```
724 PD=(R**2)/(2.0*A*B)
```

```
GO TO 637
```

```
726 PD=(R*((8.0*D*R)-((R+S6)**2)))/(16.0*A*B*C*D)
```

```
GO TO 637
```

```
728 PD=(R*(R-A+B-C))/(4.0*A*B*C)
```

```
GO TO 637
```

```
730 PD=(R*((8.0*C*D)-((R-S5)**2)))/(16.0*A*B*C*D)
```

```
GO TO 637
```

```
732 PD=(R*((4.0*C*D)-((R-A)**2)-((B-C-D)**2)))/(8.0*A*B*C*D)
```

```
GO TO 637
```

```
734 PD=(R*((8.0*C*D)-((R-S3)**2)))/(16.0*A*B*C*D)
```

```
GO TO 637
```

```
736 PD=(R*(A+B+C-R))/(4.0*A*B*C)
```

```
GO TO 637
```

```
738 PD=(R*((R-S1)**2))/(16.0*A*B*C*D)
```

```
637 WRITE (6,638) R, PD
```

```
638 FORMAT (34X,F10.3,12X,F10.3)
```

V G LEVEL 19

MAIN

DATE = 71320

17/46/21

725 CONTINUE

9 CONTINUE

STOP

END

SUBROUTINE ABCD

DIMENSION AS(4),EH1(2535),EH2(1766),EL1(4100),EL2(13260),

217

IEH1(21861)

EQUIVALENCE (EL1(1),EH(1)),(EL2(1),EH(4101)),(EH1(1),EH1(17361)),

IEH2(1),EH1(19896))

COMMON AC,BC,CC,DC,IX,IY

DATA EH1/26*6,740,193*6,694,47*6,681,23*6,663,55*6,645,13*6,597,

A 17*6,576,11*6,547,12*6,532,22*6,478,47*6,459,48*6,445,

B 17*6,430,71*6,392,179*6,308,44*6,294,63*6,273,29*6,216,

C 18*6,166,15*6,148,44*5,994,41*5,985,23*5,945,39*5,887,

D 47*5,793,64*5,752,148*5,728,22*5,633,179*5,462,254*5,562,

E 58*5,527,105*5,486,133*5,462,47*5,450,19*5,412,46*5,386,

F 27*5,365,38*5,338,129*5,300,90*5,291,36*5,277

DATA EH2/144*5,200,25*5,115,152*5,095,25*5,080,34*5,062,50*5,045,

G 50*5,033,116*5,018,82*5,001,49*4,983,195*4,954,34*4,894,

H 25*4,877,8*4,852,16*4,802,12*4,789,40*4,759,24*4,743,

I 24*4,711,24*4,690,31*4,666,16*4,645,27*4,621,23*4,599,

J 23*4,587,45*4,546,45*4,518,22*4,502,11*4,465,33*4,398,

K 33*4,347,21*4,312,23*4,284,35*4,156,31*4,100,27*4,075,

L 13*3,997,27*3,979,60*3,810,26*3,659,39*3,595,26*3,486,

DATA EL1/10*1,665,110*1,660,110*1,641,160*1,614,110*1,598,

A 180*1,582,110*1,563,120*1,538,90*1,519,60*1,511,

B 110*1,497,100*1,477,110*1,465,10*1,433,110*1,427,

C 50*1,400,10*1,375,30*1,356,150*1,297,150*1,293,70*1,269,

D 40*1,241,60*1,225,40*1,218,40*1,170,40*1,150,50*1,142,

E 50*1,127,30*1,117,80*1,098,50*1,066,70*1,053,100*1,039,

F 20*1,032,20*1,017,60*1,002,70*0,976,70*0,965,30*0,953,

G 50*0,911,90*0,885,80*0,853,90*0,843,70*0,839,60*0,822,

H 70*0,814,50*0,792,120*0,786,50*0,768,150*0,740,50*0,722,

I 40*0,716,250*0,701

DATA EL2/50*0,682,50*0,678,70*0,658,70*0,649,110*0,637,110*0,634,

J 80*0,612,130*0,591,40*0,570,60*0,557,50*0,531,130*0,527,

K 60*0,491,50*0,480,120*0,460,160*0,433,370*0,420,

L 340*0,416,140*0,410,120*0,390,140*0,385,160*0,374,

M 130*0,364,150*0,355,300*0,344,300*0,342,120*0,327,

N 120*0,322,170*0,313,530*0,300,220*0,282,110*0,276,

O 160*0,266,500*0,247,190*0,231,300*0,222,250*0,194,

P 350*0,190,360*0,183,150*0,165,290*0,159,380*0,151,

Q 210*0,140,420*0,132,320*0,122,260*0,106,420*0,057,

R 180*0,053

DO 10 I=1,4

CALL RANDU(IX,IY,F)

J=1+21461*F

AS(I)=EH(J)

10 IX=IY

DO 3 I=1,4

KM=1+I

IF (KM.EQ.5) GO TO 4

DO 3 J=KM,4

IF (AS(I).GT.AS(J)) GO TO 3

TEMP=AS(I)

AS(I)=AS(J)

AS(J)=TEMP

3 CONTINUE

4 AC=AS(1)

BC=AS(2)

CC=AS(3)

DC=AS(4)

G LEVEL 19

RANOU

DATE = 71320

17/46/21

SUBROUTINE RANOU(IX,IY,YFL)

IY=IX*65539

218

IF (IY) 5,6,6

5 IY=IY+2147483647*1

6 YFL=IY

YFL=YFL*.4656613E-9

RETURN

END

PERSONNEL, PUBLICATIONS, TALKS AND MEETINGS

A. PERSONNEL LISTING:

1. Project Director

E. P. Rack

2. Graduate Students

O. Gadeken

R. Helton

D. Oates

J. B. Nicholas (Ph.D. June, 1971)

R. Pettijohn

K. Schwartz

M. Yoong

3. Undergraduate Students

F. E. Ming

4. Technician

W. M. Grauer

B. PUBLICATIONS:

1. R. L. Ayres, C. J. Michejda, and E. P. Rack, "Reactions of Iodine with Olefins. I. Kinetics and Mechanism of Iodine Addition to Pentene Isomers", J. Am. Chem. Soc. 93, 1389 (1971).
2. R. L. Ayres, O. C. Gadeken, and E. P. Rack, "Reactions of Iodine with Olefins. II. Radiative Neutron Capture Induced Reactions of Iodine-128 with Various C₅ Isomers: Evidence for a Mechanism other than Autoradiolysis in the Condensed State", J. Phys. Chem., 75, 2880 (1971).
3. R. W. Helton, M. Yoong, and E. P. Rack, "Kinetic Energy Isotope Effects of Bromine Reactions Activated by Radiative Neutron Capture in Gaseous CH₃F and CD₃F", J. Phys. Chem., 75, 2072 (1971).

C. TALKS:

1. R. W. Helton (with E. P. Rack), "Isotope and Pressure Effects of (n,γ)-Activated Bromine Reactions in Gaseous CH₃F". Los Angeles, California, March, 1971. Division of Nuclear Chemistry and Technology, Am. Chem. Soc.
2. M. Yoong (with E. P. Rack), "Decomposition Probabilities for Products Formed by (n,γ) and (I.T.) Activated Iodine in CH₄, CD₄ and Halomethanes", Los Angeles, California, March, 1971. Division of Nuclear Chemistry and Technology, Am. Chem. Soc.
3. E. P. Rack, Lead Lecture, "Liquid Phase Hot Atom Chemistry, Organic and Inorganic", 6th International Hot Atom Chemistry Symposium, Upton, New York, September 9, 1971.

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$$\left(\frac{E}{EN}\right)_{\max} = \frac{4 MaMn}{(Ma+Mn)^2} \text{ where } Ma = \text{mass of hot atom and } Mn = \text{mass of target-molecule.}$$