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**THE UNIVERSITY OF NEBRASKA
DEPARTMENT OF CHEMISTRY**

**REACTIONS OF IODINE ACTIVATED BY THE NEUTRON
CAPTURE PROCESS IN LIQUID AND SOLID ALKANES
AND ALKENES**

A thesis by Robert L. Ayres

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**REACTIONS OF IODINE ACTIVATED BY THE NEUTRON CAPTURE
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Robert L. Ayres, Ph.D.

University of Nebraska, 1970

Adviser: Edward Paul Rack

A gas chromatograph was designed and constructed specifically for the analysis of the various organic halide products encountered in this research. The instrument was of a dual column design with temperature programming capabilities and a specially constructed flow-through window proportional counter for the detection of the products possessing a radioactive label. The radiation detector used in this instrument increased the flow sensitivity for the detection of the labeled ^{128}I products 200-fold over scintillation detectors.

The influence of exchange and other experimental parameters on the radiative neutron capture induced organic yields of iodine in "pure" alkyl iodides was investigated. The $^{127}\text{I}(n,\gamma)^{128}\text{I}$ induced yields of organically bound iodine in the liquid C_1 to C_4 alkyl iodides studied were found to exhibit, to varying degrees, a dependence on exchange reactions, accompanying γ -radiolysis, and phase. In the absence of and/or

corrected for the contributions of exchange and radiolysis the $^{127}\text{I}(\text{n},\gamma)$ ^{128}I induced organic yields in liquid methyl, ethyl, n-propyl, and n-butyl iodide are 57, 41, 48, and 48%, respectively. The corresponding yields of the polycrystalline alkyl iodide solids at 77° K are identical to the liquid state values; however, the yields for glassy normal propyl and butyl iodide are 8 to 12% higher than their corresponding polycrystalline and liquid state values.

The kinetics of the addition of iodine to 1-pentene, cis and trans-2-pentenenes, 2-methyl-1-butene and 2-methyl-2-butene were studied using ^{131}I labeled iodine. The data support the view that the observed stereospecific addition is the result of an attack of an iodine atom or molecule on a charge transfer complex between the olefin and either an iodine molecule or atom, respectively. For 1-pentene at 25° C it was found that the charge transfer equilibrium constant K_c is 1.0×10^{-1} mole $^{-1}$ liter. The rate constant, k_1 , for the reaction of the iodine atom or molecule with the complex was found to be 2.38×10^{-1} min $^{-1}$ mole $^{-1/2}$ liter $^{1/2}$. It was also found that the vicinal diiodides, which were the products of the addition, were reasonably stable in the dark if care was taken to remove all excess iodine. In addition, the dark reaction of iodine with the respective olefins was found to be negligible at low concentrations of added iodine.

Using the information accumulated in the previous studies, the radiative neutron capture induced yields of iodine and the resultant product distributions were determined in n-pentane, 1-pentene and the cis and

trans-2-penten_{es} as functions of additive concentration and irradiation time. The organic yields of the four C₅ isomers studied were found to decrease in the order 1-pentene = cis-2-pentene > trans-2-pentene > n-pentane. The radiolysis produced ¹³¹I products in these systems were determined and compared with the corresponding products produced by the nuclear activation process. Significant differences were found to exist between the observed product distributions resulting from the two dissimilar processes. As the "autoradiation hypothesis" would not account for these differences, it was concluded that these observed differences must be due to ion-molecule reactions occurring as a result of the internal conversion and subsequent Auger process accompanying the (n,γ) activation of iodine.

The organic yields of iodine resulting from the ¹²⁷I(n,γ)¹²⁸I reactions in polycrystalline n-hexane were studied as a function of I₂ concentration. Comparison with similar studies in cyclohexane and benzene show that under conditions of monomolecular dispersion, the three structurally dissimilar hydrocarbons possess approximately equal preference for either organic or inorganic combination. Constant organic yields in n-hexane between 0.001 and 0.02 mole percent I₂ indicate the formation of preferred (I₂)_n cluster sizes and/or similar numbers of molecules at sites in the polycrystalline n-hexane matrix. The solid state organic yields were found to be independent of isotope and mode of activation. Various re-purification procedures and additives were employed to determine the necessary and sufficient procedures required to obtain meaningful experimental data.

REACTIONS OF IODINE ACTIVATED BY THE
NEUTRON CAPTURE PROCESS IN LIQUID
AND SOLID ALKANES AND ALKENES

by

Robert Leroy Ayres

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Robert L. Ayres

To My Wife
Marylin Ann Slater Ayres

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CHAPTER I

INTRODUCTION

Definition of "Hot Atom" Chemistry

"Hot atom" chemistry is the study of high energy chemical reactions over a wide range of reactant energies that may be considerably greater than the minimum activation energies attained in thermal reactions. The initial hot atom can be produced by some kind of high energy beam method, photochemically, by ionizing radiation, or by nuclear transformations. Recent progress in hot atom chemistry has largely depended on the use of atoms produced by nuclear activation processes and, to a lesser extent, activation by the decay of a radioactive parent to its corresponding radioactive daughter nuclide. In fact the terms "hot atom chemistry" and "chemical effects of nuclear transformations" are often considered synonymous. Nuclear transformations may have chemical effects which are not only profound but quite varied in character. The energy released by the various nuclear transformations manifests itself in the kinetic energy of the particle formed, in electromagnetic radiation, in ionization, and in electronic and other excitations. Most of this energy is dissipated in the surrounding medium and produces normal radiolytic changes. But, in addition, the transformed nucleus is in itself a highly reactive specie capable of undergoing unique reactions.

Some of the various nuclear processes that have been employed in

studies of high energy chemical reactions are the (p,n) , $(n,2n)$, (n,p) , (γ,n) and (n,γ) nuclear activations and negatron, positron, electron capture, and isomeric transition nuclear decays. One of the most commonly employed nuclear activations is radiative neutron capture, (n,γ) , requiring a nuclear reactor, neutron generator, or other neutron source. The extensive use of this process is due to the relative availability of neutrons, the relative ease of using them under conditions where radiation damage and temperature effects are not serious, favorable cross sections for thermal neutron capture, and the fact that the (n,γ) process is capable of producing a number of radioactive species with chemical properties which are particularly suitable for the studies of interest.¹ Nuclear activations may yield a product nuclide in a metastable nuclear state. The decay of this state to the ground state (isomeric transition) may result in a second activation as a consequence of internal conversion and the associated Auger radiation process. In a number of nuclides the metastable nuclear state may be sufficiently long-lived to permit the chemical effects of the decay of the nuclide from this low level state to the ground state (isomeric transition) to be determined in the absence of other nuclear activation and/or decay processes. The criteria which must be met in the study of high energy reactions of this type are that the nuclear processes produce a radioactive nuclide and that the stable products which are formed by the transformed nucleus do not undergo thermal exchange with each other or with environmental molecules.

Historical Background

The chemical effects of nuclear transformations were first demonstrated by Szilard and Chalmers² in 1934 when they discovered that a portion of the ^{128}I produced in liquid ethyl iodide by the radiative neutron capture of stable ^{127}I splits off from the parent molecule and becomes stabilized in an inorganic form. They believed that the breaking of the C-I bond resulted from the physical process of momentum transfer from the neutron to the iodine atom. Shortly thereafter, Amaldi, Fermi, et. al.³, found the bond rupture to result from the recoil energy imparted by the emission of the capture gamma rays as the compound nucleus de-excites. Further investigation of the reactions of nuclear activated halogens with several alkyl halides demonstrated that the activation process could also result in the formation of carbon-halogen bonds.⁴

Since 1934 there have been over 300 papers published on the effects of nuclear transformations in organic systems. A number of review articles concerning the reactions of activated species in gaseous and condensed organic systems by Willard^{1,5-8}, Wolfgang^{9,10}, Maddock and Wolfgang¹¹, Filatov^{12,13}, Campbell¹⁴, and Wolf¹⁵ survey the field through 1967. Solid state reactions of nuclear activated species have been examined by Campbell¹⁶, Walton¹⁷, Mueller¹⁸, Harbottle¹⁹, and Anderson.²⁰ Other information includes a bibliography of publications in hot atom chemistry through 1962 by Suida²¹ and the proceedings of two symposia on the chemical effects of nuclear transformations sponsored by the

International Atomic Energy Agency.^{22,23}

There have been two main directions of thought regarding the mechanisms of hot atom reactions of halogens in the condensed state. One depicts the mechanism as a reaction between the activated atom and an undamaged target molecule; the other as a reaction between the hot atom and radicals, ions, or excited molecules which the hot atom produced in its deactivation process.

The first extensive attempt to explain the mechanism of hot atom reactions of halogens was made by Libby²⁴ in 1947. He developed the "billiard-ball collision" hypothesis to describe the incorporation of atoms possessing high translational energies into organic combination. Later, in co-authorship with Friedman²⁵, the "billiard-ball collision—epithermal collision" hypothesis was developed to explain the reactions of recoil atoms possessing lower (~ 10 ev) translational energies. They postulated that halogen atoms recoiling with a few hundred electron volts of kinetic energy in liquid or solid alkyl halides lose their energy by momentum transfer in elastic collisions with single atoms, and inelastic collisions with whole molecules when the energy of the recoil atom is reduced to approximately 10 e.v. by successive collisions. However, this hypothesis was oversimplified and could not give consistent correlation with the growing volume of experimental observations. In recent studies by Milman²⁶ and Mallison, *et. al.*²⁷, a molecular model was found to be consistent with the experimental data obtained in particular cases, but their model also fails to correlate with much of the existing data.

A more realistic and successful mechanistic theory of the hot atom

reactions of heavy halogens in the condensed state was the "random fragmentation", "brush heap", or "nest of radicals" hypothesis proposed by Willard.⁷ Condensed state reactions were treated in terms of kinetic energy dissipation and charge neutralization of the hot atom within a small volume element of the solution, which produces high concentrations of radicals, ions, and excited molecules in the region where the tagged atom decelerated to thermal energies. According to Willard, when a halogen atom bound to a molecule in a condensed system acquires several hundred e.v. of recoil energy it accelerates rapidly and breaks its chemical bonds, but having traveled less than a molecular diameter it encounters a solvent molecule backed by and surrounded by a close packed and often intertwined wall of other molecules. The result is that the energy is dissipated by breaking bonds in an indiscriminate fashion in the vicinity of the hot atom. When the energy of the atom has been reduced below bond-breaking energies it is in, or adjacent to, a pocket of high local concentration of organic radicals and inorganic atoms. It may combine with one of these in a hot atom reaction before becoming thermalized, or enter into chemical combination by thermal radical-molecule or radical-radical processes after thermalization and diffusion of the atoms escaping hot atom reactions. This approach was realistic, in that it explained the diversity of the observed products of hot atom reactions, but too qualitative and thus had limited quantitative applications.

One of the most significant studies was by Hornig, et. al.²⁸, who found hot atom reactions to occur in the gaseous state between ¹²⁸I

formed by radiative neutron capture of iodine in the presence of methane. This discovery led to more investigations in gaseous systems which until then had been assumed to involve no significant organic reactions with hot atoms. These investigations, especially those employing the ^3H hot atoms, resulted in the development of a mathematical model by Estrup and Wolfgang^{29,30}, based partially on the mathematics of neutron cooling, to describe the kinetics of hot atom reactions in the gas phase. Miller, et. al.²¹, developed a mathematical model for recoil reactions in liquids, using the same fundamental concept, but a specific reaction mechanism. the cage model of Libby^{24,32}, to evaluate the kinetic expressions. These efforts met with little success probably because of the inadequacy of the underlying mechanistic model. The Estrup-Wolfgang kinetic theory does not assume any model for the reaction itself. It is semi-empirical in nature and can provide a rigorous test of experimental data. The kinetic theory has been applied to reactions of hot tritium atoms with a number of gaseous hydrocarbon systems^{33,34} and with mixtures of hydrogen and methane.³⁵ It has also been used for the kinetic analysis of the hot atom reactions of ^{18}F with CF_4 , by Wolfgang, et. al.³⁶ Rack and Gordus were the first to demonstrate the applicability of the kinetic model to translationally "hot" heavy halogens by employing it to correlate the reactions of ^{80}Br with CH_4 ³⁷ and ^{128}I with CH_4 .^{38,39} Their investigations provided definitive evidence regarding the ratio of kinetic energy dependent reactions to those of translationally thermalized but electronically excited ions. In addition to the analysis of the effects of inert gas moderators Spicer and Wolfgang⁴⁰ have recently applied a modification of the kinetic theory to

the analysis of ^{39}Cl hot atom reactions with CH_4 to provide the first definite evidence for collisional decomposition of the resultant translationally excited product molecules.

Application of the kinetic theory to liquid systems has been difficult due to a lack of suitable nonreactive moderators. A recent effort was made by Milman to correlate data gathered in liquid organic halide systems⁴¹ and hot bromine atom reactions in various organic liquids²⁷ with the Estrup-Wolfgang theory. Although the data support the theory, they may not represent true results from a single type of hot atom process.⁴² Filatov, *et. al.*⁴³ have also made kinetic analyses of certain recoil halogen reactions in liquid systems. This work incorporates some assumptions of the reaction mechanism based largely on elastic collision models which appear to have limited applicability in condensed systems.

The currently accepted hypothesis as to the mechanism of hot atom reactions of halogens in liquid systems has been proposed by Geissler and Willard.⁴⁴ This concept is commonly called the "Auger electron reaction" or "Autoradiation" hypothesis. From their work with iodine and bromine, they noted that qualitatively similar products were formed by iodine or bromine atoms in a given solvent when activated by (n,γ) , (γ,n) , (d,p) , $(n,2n)$, or (IT) processes, and by irradiation with gamma-rays. Since the activations result in varying amounts of kinetic energy imparted to the hot atom and nearly zero energy imparted in an isomeric transition event, the fact that the products are qualitatively similar and quantitatively the same in many cases indicates that the hot atoms may pass through a stage common to all activations. "If all the nuclear processes produce

nuclei which pass through low-lying metastable levels which decay by internal conversion, the similarity of products could be explained in terms of the Auger radiation hypothesis."⁴⁴ The energies of the electrons emitted by ^{128}I would include the energy of the conversion electron, electrons with the energy of $L \rightarrow K$ transitions minus the L binding energy, i.e., about 20 kev., and in the case of highly charged ions, additional electrons in the range of a few kev. down. Each of these electrons, and to a lesser extent the accompanying x-radiation, would excite and ionize molecules of the solution in close proximity to the $^{128}\text{I}^{m+}$ ion from which they originated. Thus, a hot ion which has emitted several Auger electrons would be in the center of a highly localized concentration of radicals and ions, such as those found along the track of a Compton electron in a similar solution exposed to gamma radiation. The hot ion would then be neutralized rapidly by charge transfer with adjacent molecules if its ionization potential were higher than that of the solvent molecules. The probable fate of the atom thereafter would be combination with a radical or ion which was formed from the radiolysis of the surrounding solution by the conversion and Auger electrons.

Geissler and Willard's hypothesis was given added support by the work of Thompson and Miller⁴⁵ in their observations of the sequence of events following (n,γ) reactions in condensed phases. The initial recoil energy of the hot atom, resulting from the emission of high energy gamma-rays, was imparted to the atom in less than 10^{-13} sec after the neutron capture event. The high energy atom then followed a short and deviating path becoming chemically stabilized and/or thermalized only a few atomic

diameters from the site of activation. The ejection of one or more conversion electrons, followed by loss of other electrons by Auger radiation, occurred most frequently 10^{-12} to 10^{-5} sec. after neutron capture. Thus charge buildup could occur long after the hot atom was brought to thermal energies and had the opportunity to become chemically stabilized.

If the Auger electron hypothesis is valid, it implies that metastable nuclear states in hot atoms are sufficiently long-lived so that nuclear activation by internal conversion does not occur until after the atom has lost its initial recoil energy (as confirmed by Thompson and Miller⁴⁵ for the (n,γ) process) or that the length of the recoil path in the condensed phase is within the dimensions of the localized volume of high radical concentration produced by the electrons emitted in the nuclear activation process. Both possibilities are reasonable.

Recently, Fonseca et al.⁴⁶ have questioned the validity of the autoradiation hypothesis with respect to hot bromine atom reactions produced by various activation processes. The organically combined bromine product distributions as a function of different activation processes (e.g., $^{81}\text{Br}(n,2n)^{80}\text{Br}^m$, $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{80}\text{Br}^m(\text{IT})^{80}\text{Br}$, and radiolysis) were found to depend on the mode of activation, thus, the disparity between the product distributions from the different nuclear activation processes studied suggests that the yields are determined by effects characteristic of the activation event. Such would not be the case if the respective products were formed by the Auger electron radiolysis. These observations suggest that while the autoradiolysis theory may apply to a particular activation process it has no general validity.

There are several possible explanations for the observed similarity in the product distributions produced by radiolytic and nuclear activation processes in iodine systems⁴⁴ as compared to the dissimilarity observed between the various activation processes on the corresponding bromine systems.⁴⁶ It has been suggested⁴⁷ that after undergoing isomeric transition (or internal conversion) the daughter atom shares its charge among neighboring molecules, causing some to dissociate. The daughter atom may then recombine with a radical or ion formed by this process and if it avoids reaction at this stage it may then react with the more widely dispersed radicals produced by autoradiolysis. Thus the products arising from the charge neutralization of the activated species could differ from those produced by a radiolytic process. It is also known that the proportion of charged species produced by the various nuclear activation processes is greater for iodine than for bromine.^{48,49} Thus the dissimilarity in the nature and distribution of products formed by the various activation processes in the bromoethane-bromine system could result from the varying importance kinetic energy dependent reactions between the differing activations. In addition it is well known that ionizing radiation is capable of producing the same physical disruption of an atom by inducing the ejection of inner shell electrons as produced by the isomeric transition and internal conversion processes. In this instance the product distributions would be the result of identical processes initiated by differing modes of activation and would be identical. Because of the greater electron density of the iodine atoms as compared to bromine one would expect this process to be favored for

iodine. This could partially account for the great similarity of the product distributions reported⁴⁴ for the radiolytic and nuclear activation processes in iodine systems.

It should be noted that at least one mechanism other than that proposed by the "Auger radiation" hypothesis must contribute to the total organic yield observed in condensed iodine-scavenged systems.⁴⁴ This is the displacement type of reaction, which has been observed in the gas phase, by which the recoil iodine atom or ion replaces a substituent from an organic molecule in a bimolecular process. With the exception of the reactions of (n, γ) activated ^{128}I with CH_4 , the total organic yields of this type of process are only a few percent^{39,50}; however, it is not implausible that a change in phase may allow considerable contribution by this type of reaction to the total yields observed in condensed systems.

Nuclear Activation

When nuclei are subjected to a high neutron flux, there is a probability that a certain proportion of them (depending on the cross sections for neutron capture, magnitude of the neutron flux, and duration of exposure) will capture a neutron and become activated. The compound nuclei formed by the capture of a thermal neutron will obtain excitation energy equivalent to the binding energy of the neutron to the nuclei plus the kinetic energy of the captured neutron in the center of the mass system. The nuclear activation properties of the ^{127}I isotope used in this research are as follows: Nuclear activation process - ^{127}I

$(n,\gamma)^{128}\text{I}$; thermal neutron cross section - 5.6 Barns; neutron binding energy of product nucleus - 6.8 MeV; half-life of activated nucleus - 25.0 min.; positive charge acquired (minimum value) - 50%.⁴⁸

The compound nucleus, formed by thermal neutron absorption, is in an excited state. It is assumed from the compound nucleus model that the energy imparted by the incident particle is randomly distributed among all the nucleons in the compound nucleus such that none of the nucleons have enough energy to immediately escape. For thermal neutron captures the excitation energy supplied to the compound nuclei is too low to promote the escape of a nucleon and the excitation energy is, therefore, dissipated by gamma-ray emission (either singly or in a cascade) and/or internal conversion. The compound nucleus decays as a function of its energy, angular momentum, and parity, but not its mode of formation.⁵¹ Although detailed knowledge concerning the spins, parities, and energies of the low lying excited states of nuclides produced by neutron capture is known in only a limited number of cases, it may be stated generally⁵² that the (n,γ) reaction results in the population of low energy states with spins within a few units of the ground-state value. Transitions to the ground state from these levels have a high probability of occurring by internal conversion. The mean lifetimes of these low energy states is generally 10^{-12} sec. or longer, while states with energies in excess of about 1 Mev have lifetimes of 10^{-14} sec. or less.⁵³ Conservation of momentum requires that the recoil energies of the nuclei, resulting from gamma-emission, vary from zero to a maximum of $(537 B^2/M)$ ev for the

emission of a single gamma ray. Where B is the neutron binding energy and M is the atomic mass of the activated atom. For example, when an ^{127}I nucleus absorbs a neutron, the binding energy (6.8 Mev), if released in the form of a single gamma-ray of 6.8 Mev, would impart to the ^{128}I nucleus 182 ev of translational energy. Since the release of all the neutron binding energy in a single γ -quanta has not been observed (See Table I), the average recoil energy is estimated to be ~ 100 ev. Emission of more than one gamma-ray results in a spectrum of recoil energies ranging from zero (due to momentum cancellation by emission in opposite directions) to a maximum approaching the single gamma-emission value. The probable distribution of the recoil energy obtained by an atom as a result of nuclear processes has been discussed.⁵⁴ The capture γ -ray spectra of the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ reaction has been recently investigated by Archer, et. al.⁵⁵, using a high resolution Ge(Li) spectrometer. A total of 184 high- and low-energy γ -rays were observed for this reaction. The extremely complex nature of the thermal neutron capture γ -spectra of ^{127}I can be seen in Tables I and II.

Charge State and Electronic Excitation Energy

A certain percentage of recoil atoms will acquire a positive charge and electronic excitation energy as a result of internal conversion of several of the neutron capture excited levels of the nuclei and the subsequent vacancy cascade. Internal conversion is an interaction between the external electromagnetic field of the nucleus and the extranuclear

TABLE I
High-Energy Gamma-Rays from $^{127}\text{I}(n,\gamma)^{128}_{55}\text{I}$

Energy (kev)	Intensity (per 100 captures)	Energy (kev)	Intensity (per 100 captures)
6740	0.26	5985	0.41
6694	1.93	5945	0.23
6681	0.47	5887	0.35
6663	0.23	5793	0.47
6645	0.55	5742	0.64
6597	0.13	5728	1.48
6576	0.17	5633	0.22
6547	0.11	5577	1.79
6532	0.12	5562	2.54
6478	0.22	5527	0.58
6454	0.47	5486	1.05
6445	0.48	5462	1.33
6430	0.17	5450	0.47
6392	0.71	5412	0.19
6308	1.79	5386	0.46
6294	0.44	5365	0.27
6273	0.63	5328	0.38
6216	0.29	5300	1.29
6166	0.18	5291	0.90
6418	0.15	5277	0.36
5994	0.44	5200	1.44
5115	0.25	4587	0.23
5095	1.52	4546	0.45

TABLE I (continued)

Energy (kev)	Intensity (per 100 captures)	Energy (kev)	Intensity (per 100 captures)
5080	0.25	4518	0.45
5062	0.34	4502	0.22
5045	0.50	4465	0.11
5033	0.50	4398	0.33
5018	1.16	4347	0.33
5001	0.82	4312	0.21
4983	0.49	4284	0.23
4954	1.95	4156	0.35
4894	0.34	4100	0.31
4877	0.25	4075	0.27
4852	0.08	3997	0.13
4802	0.16	3979	0.27
4789	0.12	3810	0.60
4759	0.40	3659	0.26
4743	0.24	3595	0.39
4711	0.24	3486	0.26
4690	0.24		
4666	0.31		
4645	0.16		
4621	0.27		
4599	0.23		

TABLE II
 Low-Energy Gamma-Rays from $^{127}\text{I}(n,\gamma)^{128}_{55}\text{I}$

Energy (kev)	Intensity (per 100 captures)	Energy (kev)	Intensity (per 100 captures)
53	1.8	344	3.0
57	4.2	355	1.5
106	2.6	364	1.3
122	3.2	374	1.6
132	42.0	385	1.4
140	2.1	390	1.2
151	3.8	410	1.4
159	2.9	416	2.4
165	1.5	420	3.7
183	2.6	433	1.6
190	3.5	460	1.2
194	2.5	480	0.5
222	3.0	491	0.6
231	1.9	527	1.3
247	5.0	531	0.5
266	1.6	557	0.6
276	1.1	570	0.4
282	2.2	591	1.3
300	5.3	612	0.6
313	1.7	634	1.1
322	1.2	637	1.1
327	1.2	649	0.7
342	3.0	658	0.7

TABLE II (continued)

Energy (kev)	Intensity (per 100 captures)	Energy (kev)	Intensity (per 100 captures)
678	0.5	1127	0.5
682	0.5	1142	0.5
701	2.5	1150	0.4
716	0.4	1170	0.4
722	0.5	1218	0.4
740	1.5	1225	0.6
768	0.5	1241	0.4
786	1.2	1269	0.7
792	0.5	1293	1.5
814	0.7	1297	1.5
823	0.6	1356	0.3
839	0.7	1375	0.1
843	0.9	1400	0.5
853	0.8	1427	1.1
885	0.9	1433	0.1
911	0.5	1465	1.1
953	0.3	1477	1.0
965	0.7	1497	1.1
976	0.7	1511	0.6
1002	0.6	1519	0.9
1017	0.2	1538	1.2
1032	0.2	1663	1.1
1039	1.0	1582	1.8
1052	0.7	1598	1.1
1066	0.5	1614	1.6
1098	0.8	1641	1.1
1117	0.3	1660	1.1
		1665	0.1

electrons leading to nuclear de-excitation.⁵⁶ The lifetime of an excited nuclear state is on the order of 10^{-17} to 10^{-12} sec. However, many of the lower lying nuclear excited states may have a lifetime long enough to be measured, if the angular momenta of the excited state and the ground state are different. In fact, several of the lower excited states of the ^{128}I nucleus are reported to have lifetimes in excess of 8×10^{-7} sec.⁵⁷ The emission of these delayed low energy gamma-rays or the corresponding internal conversion electrons impart negligible recoil energy to the nuclides.

The ^{128}I isotope used in this study has been shown to have a high internal conversion coefficient, resulting in positive charge acquisition by a minimum of 50% of the activated iodine atoms.⁴⁸ The chemical reactivity of these species may be largely attributable to the production of a vacancy (hole) in the K- or L-shell as a result of conversion electron emission. The vacancy in the K-shell or L-shell is usually filled by an electron from an outer shell with the emission of a K or L x-ray respectively; however, the emission of an x-ray may be replaced by the ejection of an electron with a kinetic energy equal to the difference between the x-ray energy and the binding energy of the electron. This latter process may continue with the successive emission of x-rays and electrons (called "Auger" electrons after their discoverer) until the excess energy has been removed. This process will produce a high positive charge on the atom as shown schematically in Fig. 1. Carlson, Hunt, and Krause⁵⁸ have compiled extensive data on the charge build-up on an atom

Figure 1. Typical vacancy cascade in I^- as the result of an initial L vacancy. The X's represent electrons; O's, vacancies; and x's, the cases where a vacancy has been formed and then filled by a subsequent Auger process.⁵⁹

as a result of a sudden inner-shell vacancy such as that produced by conversion electron emission. They have devised a plot (Fig. 2) whereby the charge may be predicted as a function of shell level and nuclear charge, Z . Their studies indicate an unassociated iodine atom will acquire an average charge of +8 or +9. Other studies by Carlson and White⁵⁹ show that the charge induced by Auger processes in iodine atoms is dependent on the form of chemical combination of the iodine atom, i.e., the most abundant charge of iodine initially combined as CH_3I was +5, and that combined as HI was +7. These results suggest that the iodine ions formed by the internal conversion processes in ^{128}I may have an average charge of +4 or less if initially combined as I_2 and the higher energy gamma emission fails to promote bond rupture prior to the occurrence of the internal conversion; however, if the expected bond rupture has occurred then the expected average charge of the iodine atom would be +8. In addition bond rupture may occur as a result of the charge build-up on the combined iodine, which can produce recoil energies from coulombic repulsion as high as 25 ev.⁵⁹ Factors controlling the behavior of an iodine activated by Auger processes are system state (gaseous or condensed), chemical combination at the time of charging, and, if unassociated due to bond rupture following the emission of neutron capture gammas, its recoil energy at the time of charging.

In a definitive study of the effects of rare gas and various molecular additives on the radiative neutron capture induced reactions of ^{128}I with methane, Rack and Gordus^{38,39} have reported an overall organic

Figure 2. Estimated average charge as the result of a sudden vacancy in the K, L, and M shells as a function of the atomic number.⁵⁸

yield of 54.4%, of which 18.4% is formed via kinetic energy dependent processes, 25% by $I^+(^1D_2)$ ions, and 11% by thermalized excited iodine atoms and/or ions possessing less than 12.15 eV of electronic excitation. However, it is uncertain as to whether the 18.4%, found to depend on kinetic energy, is due to I atoms containing excess kinetic energy or to a combination of kinetic energy and electronic excitation.

Final Chemical Stabilization

After a nuclear activated atom is born with its high kinetic energy, positive charge, and electronic excitation, it cannot become stabilized in chemical combination until it reaches the "chemical energy" range (<100 eV). After loss of its excess energy by successive collisions with its surroundings it may then react and combine by a hot reaction. If it does not do so, it eventually reaches thermal energies (~0.025 eV) and reacts as a thermal atom.

There is an increasing amount of evidence showing that the formation of stable organically combined iodine species, via a recoil induced insertion into various hydrocarbon molecules, is improbable if not impossible. The low (~4%) organic yields of iodine reported for the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ induced reactions with CH_3I ³⁹ and the corresponding $^{127}\text{I}(n,2n)^{126}\text{I}$ study⁶⁰ illustrate the small contribution of kinetic energy to the observed organic yields in a system that would be expected to favor insertion of the recoil iodine, due to the comparable masses of the recoil iodine and the target molecule. In addition, Filitov¹² has shown that the formation of CH_3I by

^{128}I recoil atoms in methane would leave the product molecule with too much kinetic energy to survive collision with another molecule or atom in the system. This has been experimentally confirmed by Spicer and Wolfgang³⁵ in their study of the collisional dissociation of organic products formed by ^{39}Cl atoms possessing high translational energy in a gaseous methane environment.

Positively charged recoil ions will be quickly neutralized in condensed or gaseous systems if the solvent or additive(s) present have a lower ionization potential than the corresponding recoil ion. In such instances the neutralized specie would be expected to react as a neutral atom by virtue of kinetic energy processes. Two types of data which have proven valuable in recoil atom studies in organic media are (1) the organic yield and (2) the organic product distribution.

Organic Yield Concept

The organic yield is a measure of the percent or fraction of the total number of hot atoms, created by the nuclear activation process, which become stabilized in organic combination. The organic yield is used extensively as a research tool in hot atom studies because of the ease with which it can be determined experimentally and its independence of the specific activity of the hot atoms contained in the sample.

Organic Products Distribution

Recoil atoms and/or ions, by nature of their activation, can react

with organic molecules forming both inorganic and organic products. Even in the purest single-component system the recoil atoms are capable of forming many products. They may form inorganic products through either hot or thermal reactions. Because of the presence of a halogen scavenger in most reaction systems, rapid thermal exchange occurs between inorganic products, thus eliminating the study of inorganic product distributions as a useful tool. The organic products do not exchange as readily with scavengers and are formed by only "hot" reactions if enough scavenger is present to remove all thermalized hot atoms. The currently accepted means of determining hot atom product distributions is by means of gas chromatography. One of the first to recognize the applicability of gas chromatography was Evans, *et. al.*⁶⁸, in the study of some 15 products labeled with ^{82}Br by neutron irradiation of n-propyl bromide plus five mole percent borine. The yield of an individual product is expressed either as the percent or fraction of that product relative to the total organic products or relative to an arbitrarily selected product.

Statement of Problem

In the past nearly all the studies of the (n, γ) induced reactions of iodine in condensed systems have been carried out in various alkane and alkyl halide solvents. These solvents (target molecules), with the possible exception of some of the alkyl halides, would be expected to exhibit little or no chemical selectivity toward an ion or radical attack and, therefore, yield no useful information on the identity of the reactive iodine species. There have been a few studies, however, with aromatic systems liable to attack at particular ring positions by positive halogen ions, thus leading to more specific modes of reaction. Attempts to discover such effects have generally led to somewhat ambiguous conclusions.

Therefore, it would be desirable to find and employ a system which might be expected to exhibit a chemical selectivity toward either an ion or radical attack. In addition, this selectivity should be characterized by the preferential formation of a product or products characteristic of an attack by a particular species. Alkenes with their electron rich double bond might be expected to exhibit an internal chemical selectivity toward attack by an iodine ion or free radical.

The main objectives in this research were as follows:

- (1) to study the various experimental parameters effecting the radiative neutron capture induced yields of ^{128}I in pure alkyl iodides in order to evaluate their suitability as thermally non-reactive sources of "hot" iodine species in systems exhibiting

spontaneous thermal reactions with molecular iodine.

- (2) to determine the rate of addition of molecular iodine to a series of C_5 alkenes or a function of reactant concentrations in order to ascertain the mechanism of the thermal and/or photolytically induced addition of I_2 to the various pentenes.
- (3) to apply the above information in the study and evaluation of the radiative neutron capture induced yields and product distributions of iodine in various pentene solvents in an attempt to characterize the reactive iodine specie or species.
- (4) to apply the observed (n,γ) induced organic yield of iodine in polycrystalline n-hexane as an investigative tool in the determination of the states of aggregation of iodine in the solid iodine-hexane mixture as a function of iodine concentration.

CHAPTER II

EXPERIMENTAL

Chemicals Used in the Research

All of the chemicals which were used throughout this investigation are listed with the name of manufacturer, grade and purity. Standard purification procedures, if employed, are presented.

I_2	Mallinckrodt, reagent grade I, crystals were placed in a porcelain dish with equal volumes of CaO and KI and heated to sublime the I_2 . The I_2 was collected on a cold glass surface placed above the dish and stored in a ground-glass stoppered bottle.
KI	Baker, reagent grade.
CaO	Baker, reagent grade.
$CaCl_2$	Fisher, anhydrous technical grade.
H_2SO_4	Baker and Adamson, reagent grade.
HNO_3	Baker and Adamson, reagent grade.
HCl	Baker and Adamson, reagent grade.
$HClO_4$	Mallinckrodt, reagent grade.
H_2O_2	Mallinckrodt, U. S. P. grade.
Na_2SO_3	Baker, reagent grade.

$(\text{NH}_4)_2\text{SO}_3$	Matheson, Coleman and Bell, reagent grade.
P_2O_3	Mallinckrodt, reagent grade.
MgSO_4	Mallinckrodt, reagent grade.
Zn	Fisher, technical grade.
$\text{K}_4\text{Fe}(\text{CN})_6$	Baker and Adamson, reagent grade.
Magnesium	Baker, purified turnings.
Silica gel	Fisher, reagent grade.
Molecular Sieve	Analab, reagent grade.
CH_3COCH_3	Fisher, technical grade.
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	Mallinckrodt, reagent grade.
$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$	Mallinckrodt, reagent grade.
He	Air Products, commercial grade.
CO_2	Matheson Coleman, instrument grade, quoted purity 99.99% minimum.
O_2	Air Products, commercial grade.
NaOH	Fisher, reagent grade.
NH_4 (aq)	Dupont, reagent grade.
Iodine-131	New England Nuclear, obtained as Na^{131}I in 0.1 M NaOH. The iodine was extracted into the organic phase with H_2O_2 catalyzed with HNO_3 . This process converted $^{131}\text{I}^-$ to $^{131}\text{I}_2$. This solution was washed three times with distilled water, and dried over silica gel or CaCl_2 .
CCl_4	Baker and Adamson, technical grade.

CHCl_3	Mallinckrodt, reagent grade.
CH_3I	Matheson Coleman and Bell, reagent grade repurified either by extraction with aqueous sulfite, drying over silica gel, and distilla- tion or by stirring with concentrated H_2SO_4 for 5 min., extracting with aqueous sulfite, washing with water, drying over anhyd. MgSO_4 and distillation before use, taking the center cut for storage over copper turnings.
$\text{CH}_3\text{CH}_2\text{I}$	Fisher, reagent grade, purified by shaking with aqueous sulfite, drying over silica gel, and distillation taking the center cut fol- lowed by storage over copper turnings.
$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	Eastman, white label, purified as above for $\text{CH}_3\text{CH}_2\text{I}$.
$\text{CH}_3(\text{CH}_2)_3\text{I}$	Matheson Coleman and Bell, reagent grade, purified as above.
$\text{CH}_3(\text{CH}_2)_4\text{I}$	Eastman, white label.
CH_3CHCHI	Calbiochem, reagent grade.
$\text{CH}_3\text{CHI}(\text{CH}_2)_2\text{CH}_3$	Chemicals Procurement Laboratories, Inc.
$\text{CH}_3\text{CH}_2\text{CHICH}_2\text{CH}_3$	Eastman, white label.
CH_2I_2	Matheson Coleman and Bell, reagent grade.
CH_3OH	Baker and Adamson, reagent grade.
$\text{Hg}(\text{ClO}_4)_2 \cdot 9\text{H}_2\text{O}$	The G. Fredrick Smith Chemical Co.
Counting Gas	Matheson, P-10, 90% Ar + 10% CH_4 .

Anakrom	Analabs, 60/70 ABS diatomaceous earth.
Firebrick	Analabs, 50/60 C22A.
D.C. 550	Varian Aerograph, silicon oil.
Di(2-ethylhexyl)Sebacate	Analabs, Lot #006.
Propylene Glycol-Silver Nitrate 3:1	Analabs, Lot #010-8.
$(\text{CH}_3)_4\text{Si}$	Nuclear Magnetic Resonance Specialties, pure grade.
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	Phillips, research grade, 99.90 mole percent purity.
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	Phillips, research grade, 99.95 mole percent purity. Repurified by stirring with concentrated H_2SO_4 for 48 hrs.; washing with distilled water, drying over silica gel, and distillation taking the center cut.
$\text{CH}_3(\text{CH}_2)_2\text{CHCH}_2$	Phillips, research grade, 99.9+ mole percent purity.
<u>trans</u> - $\text{CH}_3\text{CH}_2\text{CHCHCH}_3$	Phillips, research grade, 99.53 mole percent purity.
<u>cis</u> - $\text{CH}_3\text{CH}_2\text{CHCHCH}_3$	Phillips, research grade, 99.94 mole percent purity.
$(\text{CH}_3)_2\text{CHCHCH}_3$	Phillips, research grade, 99.86 mole percent purity.
$(\text{CH}_3)_2\text{CHCHCH}_2$	Phillips, research grade, 99.87 mole percent purity.

Phillips, research grade, 99.91 mole percent
purity.

Preparation of Reaction Systems

Alkyl Halide Samples. The reactions of ^{128}I activated by thermal neutron capture were studied in liquid and solid C_1 to C_4 alkyl iodides. In particular the effects of accompanying radiolysis, dose rate, time between extraction and irradiation, increasing chain length, and purification were examined. All samples were prepared in 1-5 ml. quartz ampoules. The ampoules were attached with a constricted neck to a quartz stem having a tapered 10/30 ground-glass joint for connection to the vacuum line. The stem and ampoule were cleaned by washing twice with concentrated HNO_3 , dilute aqueous NH_3 and distilled H_2O followed by an additional rinse with distilled H_2O . The washing was accomplished by alternately cooling the ampoule in liquid N_2 , while introducing the wash solution, and then heating the ampoule to expel the liquid waste. The cleaning procedure removes any soluble contamination from the quartz surface. The ampoules were then attached to the vacuum line and flamed to a red glow to volatilize 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 soft glasses. Sodium-24, which is produced in the sodium containing glasses could be leached out in the chemical extractions, described later, and affect the radioactive assaying. Quartz also possesses a very desirable low coefficient of expansion which permits it to be subjected to the

extreme and sudden temperature changes encountered in the sample preparation procedures, without breakage.

At least quadruplicate samples were prepared for all experiments. The respective alkyl iodides were introduced into the ampoules by cooling the ampoule in liquid N_2 while introducing the liquid. The alkyl iodides were kept cool at all times to prevent volatilization of the sample. The samples in the ampoules were degassed four times by alternately freezing, evacuating and thawing and were then sealed while frozen under vacuum. All reaction systems were prepared in a dimmed room. The samples were wrapped in aluminum foil to eliminate light induced reactions, and stored under liquid N_2 to prevent any thermal reaction. The alkyl iodide samples were prepared from the reagent grade iodides as received or after repurification either by stirring with concentrated H_2SO_4 for five min. followed by extraction with aqueous sulfite, washing, drying over anhydrous $MgSO_4$, and distillation, or by the above procedure omitting the stirring with conc. H_2SO_4 . After purification the respective alkyl iodides were stored in dark bottles over copper turnings to minimize decomposition.

I_2 + Olefin Kinetic Systems. $^{131}I_2$ + Olefin Solutions for Rate Determinations. The extent of the addition of molecular iodine to a number of isomeric pentenes as a function of time (rate) and concentration of the reactants was followed using ^{131}I tagged I_2 . The $^{131}I_2$ was initially prepared by oxidizing the $^{131}I^-$ to molecular iodine with H_2O_2 , catalyzed with a trace of HNO_3 followed by extraction into CH_2Cl_2 . After separation

the CH_2Cl_2 solvent was removed by aspiration leaving ^{131}I tagged crystalline molecular iodine. Measured quantities of the tagged molecular iodine were then added to the respective olefin to initiate a kinetic run (zero time). Prior to the addition of the tagged iodine the pentene was equilibrated to $25 \pm 1^\circ \text{C}$ in an air bath and this temperature maintained throughout the duration of the run (typically one hr.). All runs, with one exception run in the dark, were performed with the samples in 25 ml. glass stoppered erlenmeyers illuminated by the ordinary white fluorescent lighting in the laboratory. Total sample volumes were 10-25 ml. Variation of the pentene concentration was accomplished by prior dilution with CCl_4 .

As shown in Chapter 5, the addition of iodine to the various pentenes as molecular iodine proved to be an unsatisfactory procedure. The preparation and addition of the ^{131}I tagged iodine was, therefore, modified by extracting the $^{131}\text{I}_2$ into CCl_4 and placing a measured volume of the solution directly into the pentene to initiate a kinetic run. Undesirable dilution of the olefin was prevented by addition of small (1-100 μl .) volumes of the iodine solution. The concentration of iodine in CCl_4 was determined spectrophotometrically. The final (stock) solution of ^{131}I tagged iodine in CCl_4 contained 3.07×10^{-5} moles/ml I_2 with a corresponding specific activity of $47,375,000 \text{ counts min}^{-1} \text{ ml}^{-1}$.

The olefins employed in this study (1-pentene, cis- and trans-2-pentene, 2-methyl-2-butene, and 2-methyl-1-butene) were Phillips research grade materials which were stated to be $> 99.53\%$ pure. They were used

without further purification. Iodine (Baker reagent grade) was sublimed before use. All other chemicals were reagent grade and were used without further purification.

Product Preparation for Qualitative Analysis. As the product identifications were performed by nmr spectroscopy the presence of the ^{131}I label was unnecessary. Thus the syntheses of the respective iodine addition products were accomplished by the gradual addition of stoichiometric quantities of unlabeled molecular iodine to the respective olefin. The olefin was contained in a large glass-stoppered flask in an ice bath during the addition of the large quantities of iodine in order to prevent the loss of the volatile olefin during the mildly exothermic addition of iodine. Upon completion (~ 1 hr.) of the addition of a stoichiometric quantity of iodine, the iodine-pentene-products solution was removed from the ice bath and the reaction allowed to proceed to completion at 25°C . The mixture was permitted to stand for several days to insure completion of the reaction. Typical quantities of reactants were 25 mls. of olefin and ~ 59 gm. of molecular iodine.

After completion of the reaction the excess iodine ($\sim 1\%$) was removed by extraction with aqueous sulfite solution and the reaction product dried over silica gel. In some instances, the extracted product was further purified by fractional distillation. A number of the analyses were, however, performed on the reaction mixture prior to any purification procedures.

Conversion of Products to Olefins. Aliquots of both the purified and

unpurified reaction products were reconverted to olefins. The conversion was accomplished by dehalogenation with zinc dust in methanol or magnesium turnings in ether. This was accomplished by the gradual addition of the products by syringe into a closed glass system which contained a constantly stirred solution of either zinc dust in methanol or magnesium turnings in ethyl ether. Any volatile reduction products were prevented from escaping by the use of a liquid N_2 cold trap. After removal of the inorganic materials (Zn, Mg and their respective diiodides) the hydrocarbon products (contained in both the reaction vessel and the cold trap) were separated from the solvent material by either distillation or preparative gas phase chromatography. Preparative GC separation of the products from the solvent was required when ethyl ether was used as a solvent media because of the small differences in the boiling points of the solvent and the respective product olefins. With the methyl alcohol solvent, distillation yielded satisfactory separation of the products from the solvent.

Iodine-Pentene Samples for Nuclear Activation I_2 + Pentene Samples

All pentene samples containing molecular iodine were prepared in a completely darkened room using a minimum of light from a nearby heat lamp (little or no UV radiation). Immediately after the addition of iodine the samples were placed in quartz ampoules, degassed three times, and sealed as described previously. Extra precautions were taken to minimize photo-induced reaction of the iodine with the various pentene solvents.

Such as performing all work in a room with all unnecessary light excluded and shielding the quartz ampoules containing the sample solution with aluminum foil during degassing. Immediately after encapsulation of the samples in the quartz ampoules, the ampoules were wrapped in aluminum foil and placed in liquid N_2 for storage.

The pentenes employed in this study (1-pentene, cis-2-pentene, and trans-2-pentene) were Phillips research grade materials which were stated to be $\geq 99.53\%$ pure. They were used without further purification. Quadruplicate samples were prepared on the vacuum line. The concentration of iodine was controlled by the addition of weighed quantities of molecular iodine to 5 ml. volumes of the pentene of interest. For iodine concentrations lower than $\sim 1 \times 10^{-3}$ mole fraction I_2 the solutions were prepared by dilution from a higher concentration stock solution. The sample solutions were maintained at $0^\circ C$ or lower during preparation to prevent loss of the volatile olefins and to minimize thermal reactions.

CH_3I + 1-Pentene Samples. The preparation of the 1-pentene samples containing CH_3I was, with two exceptions, identical to that employed in the previously described preparation of the I_2 + pentene samples. The two exceptions being (1) no special precautions were taken to exclude ambient light during sample preparation and (2) the addition of CH_3I was accomplished by volumetric addition to 5 ml. volumes of the 1-pentene. As in the case of the I_2 + pentene samples concentrations $< 1 \times 10^{-3}$ m.f. CH_3I in 1-pentene were prepared by dilution from higher concentrations.

Phillips research grade 1-pentene (quoted purity 99.9+ mole percent)

was used as received. A fresh shipment of Matheson, Coleman and Bell, reagent grade, methyl iodide was used as received and/or after purification by the procedures previously discussed. The majority of the samples were prepared with non-repurified CH_3I .

Iodine + Hexane Solid State Samples

Extensive experiments involving over 400 samples were performed to determine the necessary and sufficient repurification procedures required to obtain the highest possible purity of hydrocarbon and meaningful experimental data. Phillips research grade n-hexane (quoted purity 99.95 mole percent) was used as received or within 10 min. after various repurification procedures. The most consistent data were obtained by stirring the n-hexane with concentrated H_2SO_4 for 48 hrs., followed by washing, drying, fractional distillation and purging for 30-60 sec. with helium to remove any remaining volatile impurities. The impurities in the n-hexane could not be detected by gas chromatography using an Aerograph Model 1520 with a flame ionization detector having a sensitivity for 10^{-5} mole fraction of impurity, or by activation analysis for alkyl halides in the research grade n-hexane before and after repurification.

The freshly purified hydrocarbons showed negligible organic reaction with ^{131}I labeled I_2 after several hours standing in the dark. Organic additives were repurified, and H_2O redistilled before use. The inorganic additives were reagent grade and were used as received. Iodine was sublimed from a mixture of reagent grade I_2 , KI, and CaO. Iodine

concentrations were determined photometrically. Sample preparation and storage procedures were the same as those described previously for the alkyl iodide samples.

Neutron Irradiation

The thermal neutron irradiations were performed in the TRIGA Mark II "swimming pool" nuclear reactor at the U. S. Veteran's Administration Hospital at Omaha, Nebraska. An average flux of 1.1×10^{13} thermal neutrons $\text{cm}^{-2} \text{sec}^{-1}$ was present at an operating power of 15.5 kilowatts. Experiments designed to test for the occurrence of "fast" neutron reactions were negative within the limits of detection.⁶¹ Samples were placed either in the various ports of the "lazy susan" holder or the pneumatically operated "rabbit" facility. For irradiation times in excess of two minutes, the various ports of the "lazy susan" sample holder were employed and the assembly was rotated to insure that all samples received the same neutron flux and radiation dose. The radiation dose was approximately $3 \times 10^{17} \text{ ev g}^{-1} \text{ min}^{-1}$ as determined by Fricke dosimetry⁶², and ^{131}I organic pickup in irradiated $\text{c-C}_6\text{H}_{12}$.⁴² The effects of the accompanying radiolysis and dose rate on the observed ^{128}I organic yields of the various systems studied were determined by varying the reactor power from 1.7 kW to 17 kW and the total γ -dose received by the samples from 1×10^{14} to $1 \times 10^{17} \text{ ev g}^{-1}$. In most instances the organic yields were negligibly dependent on the accompanying radiolysis.

The quartz samples containing the reaction systems were sealed in plastic bags to prevent radioactive gases from escaping if the ampoules

were accidentally broken. The reaction systems were inserted into the TRIGA tubes or "rabbits" which were specially designed for the TRIGA reactor. Neutron irradiation times varied from 1 sec. to 2 hr.

Prior to irradiation, the reactive olefin systems were wrapped in carbon paper while frozen and then irradiated after liquefaction in the carbon paper wrapping in order to minimize light induced reactions. Immediately after removal from the reactor the samples were refrozen. Typical irradiation times for these samples were 1-10 sec.

Samples to be irradiated in the solid-state were removed from the liquid N_2 storage dewar and placed in the irradiation position within 15 sec. Irradiation times varied from 1-30 sec. The average temperature rise in the solid-state samples indicate that the maximum temperatures reached by the samples during the short irradiations employed in this study were insufficient to cause liquefaction.⁶¹ Remote handling equipment was employed whenever possible in order to minimize personal radiation hazards. Standard radiochemical techniques and practices were employed at all times.

Extraction of Organic and Inorganic Activities

Nuclear Activated Samples. The quartz ampoules containing the activated reaction systems were placed in specially designed separatory funnels. The reinforced separatory funnels contained aliquots of CCl_4 , with added I_2 carrier, and aqueous 0.5 M Na_2SO_3 , such that the volumes of

organic and inorganic phase were equal after the reaction system was added. The quartz ampoules were broken by vigorous shaking of the funnel. After mixing and equilibration, the CCl_4 phase contained the organically soluble labeled alkyl halides formed as a result of the nuclear transformation induced reactions.

The I_2 + hexane solid-state samples and the I_2 + pentene samples were broken in the extraction funnel while frozen to minimize any undesirable thermal processes in the respective samples. The extraction of the alkyl halide samples were timed from the mid-point of irradiation to breaking of the ampoule. In all cases the organic soluble portion was drained into an Erlenmeyer flask which contained anhydrous CaCl_2 as a drying agent. The flask was stoppered and shaken before equal volumes of each phase were pipetted into separate labeled counting tubes.

Olefin Samples for Kinetic Analysis. At timed intervals from the initiation of a kinetic run, 10 ml. aliquots of the reaction mixture were removed for analysis. The aliquots were removed ~ 10 sec. before extraction and the actual extraction was used as the timing mark. The extraction solutions were previously prepared by placing 5 ml. aliquots of either CCl_4 or CHCl_3 , containing added I_2 carrier, and 0.5 M Na_2SO_3 in a small (~ 10 ml.) separatory funnel. The reaction mixture was added to the extraction solution and vigorously shaken. After mixing and equilibration the organic phase containing the organically combined ^{131}I , was drained into an Erlenmeyer flask which contained anhydrous CaCl_2 as a

drying agent. Equal volumes of each phase were then pipetted into separate labeled counting tubes for assay.

Assaying Procedures

The radioisotopes were assayed with either a Tracerlab, Model SC-57, well scintillation detector with a two inch NaI(Tl) crystal in conjunction with a Tracerlab Spectromatic, Model SC-530, scaler-spectrometer, or a RIDL 400 channel pulse height analyzer with either a 2 in x 2 in well type NaI(Tl) crystal or two opposing 3 in x 3 in NaI(Tl) crystals with near 4 pi geometry. A description of the counting equipment, counting geometry and the lack of need for corrections due to counting coincidence losses and density have been adequately discussed in previous theses from this laboratory.^{42,62-64} The multichannel analyzer was used primarily for the assay of the ^{128}I isotope produced in the Szilard-Chalmers studies. The energies of the principle γ -radiation emitted by ^{128}I and ^{131}I are 0.441 and 0.364 Mev, respectively.⁶⁵ The difference between the gamma energies (0.077 Mev) of two isotopes is too small to permit the simultaneous assay of both isotopes by instrumental means. Therefore, in samples containing both isotopes it is necessary to count the sample within a few minutes after radiation (max. ^{128}I activity) and then allow at least four hours for the ^{128}I to decay and recount the samples. The latter count (^{131}I only) may then be used to correct the former for the ^{131}I activity present at the time of assay.

The readout of the Tracerlab instrument was recorded manually;

whereas, the output of the multichannel analyzer was stored on IBM-coded eight-channel paper tape. The activities represented by the photopeaks of the nuclide of interest were computed and the organic yield values calculated using an IBM 1620 computer. Programs 1 and 2 listed in Appendix I were written for this purpose using a paper tape read-in and editing routine previously prepared by Felix J. Kerrigan of the U.S.V.A. Hospital at Omaha, Nebraska. Attempts to consolidate the two programs were unsuccessful due to the limited core size (10 K) of the 1620 computer. These programs incorporate corrections for radioactive decay, residual background, and Compton scatter. In program 2 provision is made for direct hardcopy output of all input data and in program 1 all input data may be output on punched cards compatible with the University of Nebraska's IBM 360 system.

Determination of Organic Product Distributions

In characterizing the product distributions of the ^{128}I and ^{131}I isotopes in n-pentane and the various pentene systems, a variable temperature gas chromatograph employing a special detector for the determination of the radioactive labeled products was employed. The chromatographic column consisted of a 1/4" dia. by 10 ft. coiled stainless steel tube packed with 50/60 mesh Analabs C-22A firebrick coated with 5% of its weight with di-(2-ethylhexyl)-sebacate. Radioactive products were detected by a flow-through proportional counter, similar to discussed by Wolf, et. al.⁶⁶,

and shown in Appendix II. The activity of the effluent gas versus time was simultaneously recorded on one pen of a Dohrmann dual pen recorder and a Nuclear Data ND-110 128 channel analyzer. The multichannel analyzer was operated in the multiscaling mode with a dwell-time per channel of 10 sec. This allowed digital storage of chromatograms up to 1280 sec. duration and numerical integration of product peak areas. A more detailed description of the instrument employed in this research is located in Appendix II.

Product peaks were qualitatively identified by coincidental emergence with added carriers or by their characteristic retention times. The relative amounts of each product were determined by determining the counts under each peak from the ND-110 digital print-out after correction for background and decay. Relative product yields were determined by comparison of the activities of the individual products to the total organic activity detected. Absolute product yields could be determined by multiplying the relative values times the previously determined total organic yield of the sample analyzed. Any products of a polymeric nature could be detected by reversal of the directions of the carrier gas flow through the analytical column using a Varian four-part backflush valve, provided for this purpose.

CHAPTER III

RADIOGAS CHROMATOGRAPHY

The energetic iodine atoms produced in this study, resulting from the radiative neutron capture and internal conversion processes, possess kinetic energy and/or charge and other electronic excitation energy the value of which is determined by the nuclear process. Since these atoms are radioactive, their progress can be monitored by techniques used in tracer chemistry. After transferring most of their excess energy and charge to the immediate environment, hot atoms attain a stable state of combination in a great variety of chemical forms. The qualitative and quantitative distributions of these chemical species are perhaps the most important sources of information for interpretation of the behavior of hot atoms, determination of the reaction mechanism, and the evaluation of the charge and electronic excitation possessed by these atoms at the moment of formation. Radiochemical analysis of a system after irradiation or disintegration of an excited nucleus, is of fundamental importance due to the extremely small quantities of products ($< 10^{-13}$ g.) produced by the various nuclear processes.

One of the most extensively used radiochemical techniques for analyzing organic products tagged with radioactive halogens is gas chromatography. This is because gas chromatography is capable of permitting simultaneous separation, purification, and identification of the extremely

small quantities of chemical species under consideration. Another major factor in choosing gas chromatography for product analyses is that it does not generally require the use of carriers for quantitative determinations of products. Distillations, on the other hand require the addition of carriers to obtain proper results^{25,67}, thus permitting possible inaccuracies due to exchange occurring between the labeled products and the added carriers. Additional advantages of gas chromatography are its simplicity, which permits its application in most radiochemical laboratories, rapid separations, especially valuable when short-lived isotopes are involved, and its sensitivity. Evans and Willard⁶⁸ separated as little as 10^{-13} g. of $\text{CH}_3^{82}\text{Br}$ from a mixture of radiobromine labeled products obtained in the neutron irradiation of n-propyl bromide. The chief disadvantage of radiogas chromatography is that it requires the use of labeled compounds having rather high specific activities, although this problem has been alleviated to a certain extent by the recent introduction of a more sensitive detector. This requires the irradiations to be performed in a high neutron flux such as that present in a reactor or accelerator. This type of irradiation is often accompanied by radiolytic degradation processes.

Chromatographic methods have come into general laboratory use rather late compared with other separatory operations such as distillation, extraction, crystallization, etc. Chromatographic principles were mentioned as early as the beginning of the 16th century⁶⁹ but no real use of this amazing tool was made until the last two decades. The idea of

using a gaseous mobile phase was not apparently investigated thoroughly until 1952 by James and Martin.⁷⁰ Since 1952 gas chromatographic techniques have rapidly evolved into simple, rapid, and reliable methods of analyses used by researchers in all phases of chemistry and physics. The basic principles and practice of gas chromatography are now well known by nearly all practicing chemists.

Mobile and Stationary Phases

The chromatographic method used in this research was gas-liquid partition chromatography, employing helium as the mobile phase and a specially designed and constructed detector for the detection of the radioactively labeled products eluted. Various silicone oils, such as GE-SE-30, DC-550, and GE-SF-96, and di-(2-ethylhexane)-sebacate were employed as stationary phases because of their general separating characteristics, rather than selective abilities, and for their proven ability to separate the various alkyl halides.⁷¹⁻⁷⁴ The di-(2-ethylhexyl)-sebacate was found to produce the most desirable separation of the products of interest and was employed as the stationary phase in the majority of analyses. It was found to be unselective with regard to the various alkyl halides and alkenes; hence, the organic iodides were eluted from the column in a general order of increasing boiling points (Fig. 3). For the various branched alkyl iodide isomers, the more "compact" the molecule, the faster it diffused through the column, i.e., tertiary > secondary > primary. However, no separation of the iodoalkenes and iodoalkanes was achieved when

Figure 3. Adjusted retention volumes vs. boiling points of various alkyl halides. One-quarter in. by ten ft. SS column containing 5% di(2-ethylhexyl)-sebacate on 50/60 mesh firebrick @ 100° C.⁷⁵

the iodine was bonded to a saturated carbon in the respective iodoalkene. Those iodoalkenes which possess an iodine bonded to an unsaturated carbon generally have lower boiling points than their saturated analogs and thus were separated.

The column used in the majority of the analyses was a 5% by weight loading of di-(2-ethylhexyl)-sebacate on 50/60 mesh firebrick. The packing was prepared by dissolving 5 g. of the stationary phase in 250 ml. of acetone, suspending 100 g. of firebrick in the solution, and then volitizing the solvent under vigorous mechanical stirring. The resultant firebrick coated with the stationary phase (5% of its weight) was introduced into the coiled column and packed tightly using aspiration and vibration. No dead space was allowed in the column. Other column packings were prepared in a similar fashion.

The mobile phase (carrier gas) consisted of very pure helium. Helium was chosen because of its markedly higher thermal conductivity as compared to the various organic compounds of interest. Since a thermal conductivity cell was used as a detector for macroscopic (10^{-4} to 10^{-1} ml.) amounts of eluent, helium was one of the most favorable mobile phases with regard to sensitivity of the detector. Helium was chosen over hydrogen because of the fire hazards associated with the use of hydrogen. Both hydrogen and helium are practically insoluble in the various stationary phases used.

Apparatus

The first radiogas chromatograph utilized in this laboratory was constructed by Merrigan and Nicholas.^{42,76} This initial instrument was completely redesigned and extensively modified during the summer of 1967, resulting in improved reliability, sensitivity, and versatility of the chromatograph. The instrument has been in day-to-day use since it was placed in operation and has been used for all the product distributions determined in this research. Due to the construction of a new chromatograph a comprehensive description of the above instrument will not be presented here, but the reader is referred to Ref. 77 for a detailed description and Appendix II for a brief description.

After a year of extensive usage, a critical evaluation of the above instrument's performance suggested a number of improvements or modifications in the original design. On the basis of this evaluation a new chromatograph was constructed in order to incorporate the suggested modifications. Figures 4, 5, and 6 show the basic features of this chromatograph. The helium carrier gas is obtained from a pressurized steel cylinder and passed through a two-stage pressure regulator, shut-off valve, stream splitter, flow-meters, constant flow controllers, bulblet breaker and/or preheated injection ports, and into the reference and analytical columns. After separation in the analytical column, the eluted fractions enter the sensing portion of the thermal conductivity detector, where macroscopic amounts are detected. The signal from the thermal conductivity detector is routed through an attenuator to one pen

Figure 4. View of the Complete Instrument.

Figure 5. Block diagram of the radiogas chromatograph.

Figure 6. View of control console.

potentiometric strip chart recorder. After passage through the thermal conductivity cell the analytical and reference carrier gas streams are combined for passage through the radiation detectors. The radiation detector is a window-type proportional flow-counter, housed in a heated enclosure to prevent condensation of the products. Trace quantities ($\sim 10^{-13}$ g.) of eluted products are detected by monitoring the beta and/or gamma radiation emitted.

The signal from the proportional counter is directed through a pre-amp, amplifier, single-channel analyzer, ratemeter, and to a multichannel analyzer for digital storage of the output. The analog output of the count-rate meter is directed to the second pen of the strip chart recorder. From the proportional counter the eluted products flow through heated tubing to liquid N_2 cold traps, where the radioactive materials are removed from the carrier gas stream. After passage through the cold traps the carrier gas may be routed to a fume hood to insure that no radioactive species escape into the laboratory atmosphere.

The columns are housed in an insulated temperature controlled oven of a plenum chamber design. The temperature of the column oven is controlled by a 0-400° C potentiometric temperature controller possessing linear programming capabilities. The thermal conductivity cell, proportional counter, and bulblet breaker are located in a separate heated detector oven. The location of the detectors in an enclosure thermally isolated from the column oven, permits variation of the column oven temperature without any accompanying thermal effects in the various

detector signals.

Carrier Gas Measurement and Control

Figure 7 shows, in schematic form, the gas flow-through the instrument. Gas tank (A) and pressure reduction valve (B) furnish the supply of He carrier gas at a constant pressure of 50 psig. The carrier gas enters the flow control panel through shut-off valve (C) and is then split into two streams for entrance into the flow meters (F & G). The flow-meters are Brooks Sho-Rate "150" Purgemeters with direct reading scales, having a $\pm 1\%$ full scale accuracy for He at 50 psig and 25° C. These meters are protected from particulate contaminants by Brooks Model 1390 filters (D & E) attached to the inlets of the individual meters. After passage through the flow-meters the carrier gas streams pass through two Brooks ELF Flow Rate Controllers (H & I). These controllers provide valves for the control of the individual carrier gas flow rates and, after an initial flow rate has been set, automatically compensate for any increase in downstream pressure such as would be encountered in temperature programming. Individual (0-60 psig) pressure gauges (J & K) monitor the downstream pressures and are located between the flow controllers and the carrier gas exits from the control panel.

After exiting from the control panel the carrier gas streams are routed to the oven assembly. Here one stream enters a bulblet breaker assembly (1), housed in the detector oven and proceeds to the inlet of a

Figure 7. Instrument carrier gas flow.

separately heated injection port (M). The other carrier gas stream proceeds directly to the inlet of a matching injection port (N). The carrier gas streams then pass through interchangeable reference and analytical columns (O & P) located in the column oven. From there the carrier gases enter the detector oven and pass through the thermal conductivity cell (Q) and are recombined for passage through the radiation detector (R). After exiting from the radiation detector (and the detector oven) the carrier gas is routed through a series of two liquid N₂ cold traps (S & T) and then exited into the atmosphere.

All tubing and tubing fittings used prior to the entrance of the carrier gas into the various injection ports were of copper construction. Similarly all materials that would be contact with the sample gases were constructed of stainless steel, teflon, or glass. The use of direct reading flow meters greatly simplifies the determination of the carrier gas flow rates through the columns and the radiation detector. The inclusion of the constant flow controllers permits the automatic maintenance of the initial flow rate over a downstream pressure variation of 0-40 psig to within $\pm 0.3\%$ of the instantaneous rate. Thus providing the convenient and accurate flow control essential in radiogas chromatography due to the direct dependence of the hot product peak intensities on the rate of passage of the sample gases through the detector.

Injectors

Two different types of sample introduction techniques are employed.

Provision for the introduction of liquid samples is provided via two heated injection ports (Fig. 8), and quartz encapsulated gaseous systems are introduced directly into the carrier gas stream with a bulblet breaker (Fig. 9).

Measured quantities of liquid samples are introduced by syringe through a silicon rubber septum located in the injection ports. The individual injection ports were constructed using a bored through Swagelok fittings for the outlet connections to the columns and/or separate inserts. Thus either flash vaporization or direct on column injection of the sample is permitted by the selection of the appropriate column to injector connection and injector temperature. The injectors are heated by two 50 watt cartridge heaters and the temperature controlled by a Weathermeasure Corporation Model TPC-N potentiometric temperature controller with an accuracy of $\pm 0.5\%$ of the set point. A large brass heat sink is used to minimize rapid temperature fluctuation in the injectors and to simultaneously provide a heat source for preheating the carrier gas before entrance into the injectors. This is necessary to prevent condensation of the sample.

The capability of directly introducing gaseous samples, encapsulated in ~ 10 ml. quartz ampoules, into the carrier gas stream is provided by the specially constructed bulblet breaker shown in Fig. 9. In addition to the bulblet breaker itself a $1/4$ in. dia. by 5 in. removable stainless steel pre-column is located between the bulblet housing (Teflon) and the outlet of the assembly. This pre-column is packed with fine mesh

STAINLESS STEEL INJECTION PORT
(construct two)

BRASS HEAT SINK
(construct one)

Figure 8. Injection port assembly.

☒ TEFLON

☐ STAINLESS STEEL

potassium ferricyanide which removes inorganic halogens⁷⁸ from the sample prior to entrance into the analytical column; thus, preventing internal contamination of the instrument by the reactive inorganic products.

The bulblet breaker assembly is housed in the detector oven, thereby, eliminating the necessity of providing separate heating and temperature control.

Columns

The analytical columns, packed with an appropriate support and stationary phase, are coiled stainless steel or glass tubes 1/4 in. in diameter, 10 ft. in length, with a spiral diameter of 6 to 8 in. The diameter of the spiral is large enough to prevent loss of separating power attributable to the longer path which a gas has to transverse along the outer wall of the column. Either glass or stainless steel are used because of their relative inertness toward halogenated compounds as compared to other commonly used materials. The column inlets and outlets are connected to the chromatograph by way of 1/4 in. Swagelok fittings. When glass columns are used the stainless steel ferrules are replaced with teflon ferrules. As a result of the small separation between the injection ports, the individual columns must be coiled in opposite directions, i.e., the left column must be coiled in such a manner that its spiral extends to the left when connected and the right column such that its spiral extends to the right. Filling of the columns was accomplished by applying suction to the outlet end along with vibration during the

addition of the column packing to the inlet.

Detectors

Two detectors are present for the identification and quantitative treatment of fractions which elute from the column. A thermal conductivity cell was selected to detect macroscopic amounts of eluents because:

1. The measurements could be readily monitored with simple instrumentation.
2. The detector, because of its simplicity could be readily installed.
3. The sensitivity is high and adjustable.
4. The detector is sensitive to nearly all gases.
5. The wide operating temperature range of the cell.
6. The signal is linearly proportional to the concentration of the components eluting from the analytical column.

Since the thermal conductivity cell measures the presence of a component by a physical means, i.e., thermal conductivity, the sample was not destroyed and could be recovered for subsequent measurement of the component possessing a radioactive label.

The outlets of the individual columns are directed into the respective sensing and reference inlets of the thermal conductivity detector. The detector used is a Model 10-285, supplied by Gow-Mac, and consists of a stainless steel block with two matched sets of 48 ohm gold plated

tungsten filaments, one set each for the reference and sensing portions of the bridge. As a result of the gold plating on the tungsten filaments of this detector the filaments are insensitive to air oxidation when hot. This permits continuous operation when exposed to air, as can easily occur when using the bulblet breaker, thereby eliminating a serious source of instrument down time. Because the sensing and reference portions of the bridge are identical in all respects they may be readily interchanged; thus, in a dual column instrument either column may be used for the reference column simply by reversing the polarity of the bridge output. This provision has been included as shown in the complete thermal conductivity circuitry diagram (Fig. 10).

In this research, the thermal conductivity detector was used only for qualitative determinations of compounds so calibration of the detector output as a function of sample composition and operating conditions was ignored.

After passage through the thermal conductivity cell the reference and sensing carrier gas streams are recombined just prior to entrance into the radiation detector. Thus, fractions eluted from either column pass through the detector, again permitting either column to be employed as the analytical column for the quantitative and qualitative assay of the radioactively labeled products eluted.

The radiation detector is a cylindrical window flow-through proportional counter. The basic design of this counter and a number of its characteristics have been previously reported by Welch, *et. al.*⁶⁶ The

Figure 10. Circuit diagram of the thermal conductivity detector.

design and dimensions of our counter are shown in Figs. 11, 12 and 13. The design of the counter incorporates a number of modifications in the original, such that the counter may be placed in a heated enclosure and to improve its operation with the labeled halogen compound obtained in this research.

The principle modifications are as follows:

1. The counter was constructed so that it could be completely disassembled from one end, thus permitting easy access for repairs, when mounted in its oven enclosure.
2. A removable center support rod was employed in the window insert, thereby, permitting the window insert inlets and outlets to be modified in such a manner as to minimize any possible internal dead space in the flow assembly.
3. Use of stainless steel or titanium for construction of all components that are in contact with the sample because of their relative inertness to high temperatures and halogenated compounds.
4. Six equally spaced (60° apart) high voltage (0.0035 in tungsten wire) anodes, supported by Teflon insulators, were used to provide a uniform electrostatic field around the window containing the sample gases.

The previously reported⁶⁶ maximum operating temperature of the original design was 150°C . Since many of the possible products of systems under investigation by this laboratory have boiling points higher than

PROPORTIONAL COUNTER WINDOW MOUNTS AND INSERTION TOOL

Figure 12. Window insert and insertion-removal tool.

ASSEMBLY

Figure 13a. High voltage anode components and assembly.

Figure 13b. View of assembled high voltage anode assembly mounted in counter endcap.

150° C, several of the modifications on the original design, were implemented in an effort to increase the maximum operating temperature of the counter.

There are two restrictions placed on the maximum operating temperature of this type of counter. The first being the upper temperature limits of the materials used in the construction of the counter. This would be approximately 250° C due to the use of Teflon for the construction of several of the counter components. However, this physical temperature limitation can be readily increased by replacing the Teflon components with components constructed from materials possessing higher thermal stabilities such as a ceramic.

The second temperature limitation is imposed by maximum temperature at which a usable plateau may still be achieved. The usable plateau length decreases with increasing temperature of the counter as shown in Fig. 14. This is a result of increasing ease of ionization of the counting gas mixture (90% Ar + 10% CH₄) with increasing temperature, thus shifting the plateau to a lower voltage range and decreasing its length. Once the temperature has reached a certain point the length of the voltage plateau will decrease to zero, thereby restricting the counter to operation below this temperature. Although the counter may be operated at temperatures in excess of this limit by using a voltage in the sharply rising region prior to the onset of the plateau, the resulting accuracy would be poor because of large changes in sensitivity caused by small voltage fluctuations in the power supply.

Figure 14. Counter voltage plateaus as a function of temperature.

For a cylindrical counter the largest voltage gradient exists in the vicinity of the anode wires and is a function of e^{-r} , where r is the radius of the anode wire. Thus by using a larger diameter anode wire (3.5 mil.) and increasing the applied voltage the voltage gradient between the cathode (outer body) and the anodes would be reduced. This should result in a corresponding decrease in the sensitivity of the plateau region to the temperature of the counting gas.

Using the 3.5 ml. tungsten anode wires the voltage plateaus as a function of temperature were determined using a 5 mCi ^{137}Cs source located in the center of the counter and a mixture of 90% argon and 10% methane, at a flow rate of 10 ml. per minute, as the counting gas. As shown in Fig. 14 the plateau narrows from ~ 650 volts at 28°C to ~ 550 volts at a temperature of 155°C . Using the plateau voltage values given above, the decrease in the length of the voltage plateau with increasing temperature was found to be 0.8 volts per degree C. This would give an extrapolated maximum operating temperature of approximately 650°C for the proportional counter. However, as discussed previously, the present operation of the counter is limited to 250°C by the Teflon construction material.

In the operation of an earlier model counter, which contained a window insert identical in design to the original, problems with false efficiencies and contamination or sticking, with labeled halogen compounds possessing detected activities in excess of 10,000 counts per min., were encountered. This resulted in failure of the detector signal to return to the baseline after the illusion of the component possessing a high activity.

In an effort to determine the cause of this problem the counter was deliberately contaminated by introducing large quantities of ^{82}Br labeled organic bromides. The window insert was then dismantled and the individual components inspected for contamination. It was found that the stainless steel window, window support surfaces, and (to a greater extent) the exposed epoxy used to form and attach the window were contaminated. However, the degree of contamination of these surfaces was small in comparison to that observed during operation of the counter.

Examination of the design^{66,77}, and Appendix II of this window insert showed the existence of a small dead volume ($\sim 1-2$ ml.) between the entrance and/or exit gas ports and the window to insert seal. The trapping of a portion of the activity being detected in this dead volume would account for the appearance of contamination when high specific activity compounds are passed through the counter.

The counter contamination was observed to decrease at a rate independent of the half-life of the isotope responsible. This observation would support the contention that the principle cause of the observed "sticking" in the counter resulted from the trapping of a portion of the compound in these dead volumes rather than actual contamination of the counter surfaces. This could also contribute to the false efficiencies observed by Welch, *et. al.*⁶⁶, in this type of counter.

In an effort to correct these difficulties a new window insert (Fig. 12) was designed. By elimination of the counter support rod, which is unnecessary once the window insert is in place, the amount of

stainless steel surface exposed to the sample gases for possible contamination was reduced. In addition, a slight improvement in the counting geometry was obtained.

The elimination of the center support rod also permitted an improved inlet and outlet design, which minimizes or eliminates any dead volume associated with the detection volume in the earlier design, thus eliminating the suspected major source of contamination.

A new 0.5 mil. titanium window was used in this counter in place of the 1.0 mil. stainless steel window used previously, thereby, eliminating all exposed stainless steel surfaces in the counting volume. This window material was found to be more inert to organic halides than the previously used stainless steel and, in addition, the smaller attenuation coefficient, for the β -radiation detected, of this thinner and lower Z material window resulted in a two-fold increase in the detection sensitivity of the counter.

The use of high temperature silicon O-rings to seal the window to the insert (tested and found to form a gas tight seal of the thin window material to the stainless steel surfaces) eliminates the major portion of the epoxy surface on the inside of the window. The only remaining epoxy (Good year Pliobond HT-30) used in the construction of the window insert was that used to form the thin titanium foil into a cylinder. After joining the edges of the foil together to form the cylinder and allowing the adhesive to partially set, the interior of the cylinder was carefully cleaned with ethyl acetate solvent to remove any excess

adhesive. Thus, the maximum surface area of exposed epoxy in the window assembly consisted of a very thin line (< 0.05 in.) the length of the cylinder. Subsequent operation of the counter has shown these measures to be successful in eliminating or greatly reducing the contamination problems previously encountered with the earlier design.

The relative sensitivity of the proportional counter as compared to the NaI(Tl) scintillation well employed previously⁴² in the laboratory was determined for a number of halogen isotopes. The results are shown in Table III. As shown the relative sensitivities for the various isotopes differ greatly due to their dissimilar modes of decay; i.e. the ratio of the average number γ -photons emitted to the number of β^- particles (one) in a single decay. Since the proportional counter is relatively insensitive to γ -radiation ($\sim 1\%$ efficient) and close to 100% efficient for the detection of the β^- -radiation the sensitivity of the Wolf counter would not be expected to vary appreciably for the various isotopes tested. However, the scintillation well is insensitive to β^- particles and detects incident γ -radiation only (with $\sim 20\%$ efficiency); thus the large variation found for the relative sensitivity of the two counters can be largely attributed to the wide variation in the γ/β^- intensities (shown in Table III, column 5) for the three isotopes.

One of the most important results from the determinations of the relative sensitivities is the consistently higher sensitivity of the Wolf counter, particularly for the ^{128}I isotope of interest in this research. The greater counting efficiency, or sensitivity, of the proportional counter over that of the scintillation well, is the

TABLE III

Comparison of the Relative Sensitivities of the Wolf
and NaI(Tl) Well Counters for ^{38}Cl , ^{82}Br , and ^{128}I

Isotope	Activity Wolf Counter	Detected (C/M) NaI(Tl) Well Counter	Relative Sensitivity	Relative γ/β^- Intensity Ratio
^{82}Br	20527	4718	4.4	314
^{38}Cl	33952	973	35.0	85
^{128}I	28143	141	200.0	16

cumulative effect of a number of factors. A few of the more important ones are: (1) improved geometry ($\sim 4\pi$); (2) inherently greater static efficiency (a maximum of 5:1); and a larger active volume (~ 42 ml.) with a resultant increase in the flow counting efficiency. This greatly increased sensitivity has permitted the previously unobtainable analyses of low activity samples.

The efficiency of the flow-through proportional counter could be greatly improved by eliminating the window and passing the radioactive effluent directly through the counter, thereby eliminating all attenuation of the emitted β^- radiation by the window material. However, halogen containing compounds are effective quenching agents and preclude radioassay in a windowless counter.

The heating and temperature control of the counter is provided by the detector oven enclosure in which it is housed. The counter is shielded from background radiation by wrapping with eight turns of 1/8 in. thick sheet lead. The operating high voltage is supplied by a NIM Canberra Model 3002 high voltage power supply. Signal detection and amplification is provided by Canberra Models 1406 preamplifier and 816 amplifier, respectively. It was necessary to add a special diode protection network to the input FET transistor on the Model 1406 preamplifier in order to prevent destruction of the transistor by the input signals from the counter. After amplification the signal was routed to a Canberra Model 1431 single channel analyzer which was used to provide discrimination against low level instrument noise. The SCA output was

divided by a BNC "tee" connector and routed to a MecTronics Model 775 log/linear ratemeter and a Nuclear Data ND-110 128 channel analyzer. The output of the ratemeter is connected to one pen of a Dohrmann Instruments Model DC-120 dual pen strip chart recorder from which a permanent analog record of the counter output is obtained. The 128 channel analyzer is operated in the multi-sealing mode with a 10 sec. dwell time, thus the digital record of the counter output, over a time period of 1280 sec. in 10 sec. increments, is obtained for integration of product peak areas. A block diagram of the GC radiation detection system is shown in Figure 15.

Collection Devices

After gaseous fractions flow out of the counter, they are trapped in two tandem cold traps at -196°C . Radioactive compounds enter the top of the trap and are condensed on the sides. Stopcocks are arranged to permit removal of one trap while passing the effluent through the other, or, to pass the effluent through both traps in series. Over 98% of the radioactive compounds were shown experimentally to be trapped in the first cold trap. Even greater percentages were trapped when small amounts of glass wool are placed in the path of the carrier gas through the trap. After passage through the traps the carrier gas is expelled into the room or channeled to a fume hood where it is discharged if there is a possibility that all dangerous quantities of radioactivity

Figure 15. Block diagram of GC radiation detection system.

were not removed by the cold traps.

Oven Enclosure

The main oven enclosure consists of a 21 in. wide by 20 $\frac{3}{4}$ in. high by 16 $\frac{3}{8}$ in. deep box with the front enclosed by a removable 1 $\frac{3}{8}$ in. thick panel housing the injectors and column oven access door. The main enclosure and front panel were constructed by attaching $\frac{3}{8}$ in. thick high density asbestos board insulation to the inside of a 1 in. x 1 in. angle iron frame. Further insulation was provided by completely covering the exterior with a 1 inch thickness of fiberglas. After installation of all components the entire exterior was covered in with sheet metal. The interior of the insulated enclosure was then divided into two thermally isolated compartments (detector and column ovens) with provision for independent temperature control. The thermal barrier used to isolate the separate oven enclosures consisted of two $\frac{3}{8}$ in. thick sheets of asbestos board with a 1 $\frac{3}{4}$ in. space, filled with fiberglas, between the asbestos sheets. The larger of the two compartments (10" x 15" x 18") was used for the column oven and the smaller (5 $\frac{1}{2}$ " x 15" x 18") for the detector oven. A frontal view of the oven with the front panel and sheet metal column housing removed showing the location of several of the interiorly located components of the instrument is presented in Figure 16. The front panel is shown in Figure 17.

The column oven is a plenum chamber design as shown in Figure 18.

Parasitized

Figure 16a. Front view of partially assembled oven with front panel and sheet metal column housing removed.

Figure 16b. Dimensions and component locations.

Figure 17. Front panel with cover and insulation removed.

Figure 18. Side view of plenum chamber column bath.

This design was employed to insure uniform air velocity and has been reported⁷⁹ to provide a more uniform column temperature with a substantial reduction in column thermal gradients during temperature programming than other commonly employed oven designs. A three inch squirrel cage blower delivers air at high velocity to the plenum chamber, separated from the column compartment by a perforated metal sheet. The high velocity of the air and the flow resistance offered by the perforated sheet create a uniform pressure across the surface of the perforated sheet. This in turn promotes uniformity of air velocity over the entire cross section of the column compartment, minimizing temperature gradients on the column. A perforated sheet is also provided at the exit end of the column compartment to maintain nearly parallel lines of air flow through the column compartment.

Thin gauge stainless steel construction of the column compartment, low mass open wire heaters (two 800 watt, 110 v.), and a high velocity air circulation system permit rapid heating and cooling. Manually operated intake and exhaust dampers enhance the rate of cooling, and may be readily adapted to automatic control. Column temperature equilibrium is quickly achieved after cooling because the dampers permit the front closure of the bath to remain closed during the cooling phase.

In addition to its superior temperature characteristics, this design also provides convenience of use. The 12 in. x 12 in. x 10 in. oven can accommodate more than 50 ft. of 1/4 in. o.d. tubing. Column diameters

may be as large as 9 in. with only one sharp bend required. Convenient accessibility to the column compartment is provided by a 9 in. x 9 in. hinged door on the front panel of the oven enclosure, with a compressible silicon rubber gasket on its inner surface to prevent leakage of hot air.

Heat is supplied by two 800 watt, 100 volt A.C. open wire heaters wired in parallel. Individual gain (voltage) control is provided for each heater by a pair of General Electric Model S100C5 triac controllers. It is, therefore, possible to vary the heater power continuously from zero to a maximum of 1600 watts. The use of individual triacs was required in order to prevent damage to the controllers by excessive (~ 16 amp) current requirements at full power.

The detector oven is simply a tightly closed, thermally insulated, box with heat supplied by one 800 watt open wire heater. Provision for gain control of this heater was provided in a manner analogous to that described above. A simplified wiring diagram of the oven heater circuitry is presented in Figure 19. This circuit (four in all) was used for all heaters in the instrument.

Temperature Control and Measurement

Temperature control of the three individually heated areas (column oven, detector oven, and injection ports) was provided for by three Weather Measure Model TPC-I, type J potentiometric temperature controllers. The temperature set point was via a calibrated direct reading dial,

Figure 19. Basic heater wiring diagram.

spanning a 0-400° C temperature range with an accuracy of $\pm 0.5\%$ of the set point. Temperature sensing was performed by Iron-Constantan thermocouples with automatic cold junction compensation provided by the controller. The contacts in the internally located relay of the temperature controller were capable of handling a maximum current of 7.5 amps, since the two sets of oven heaters could exceed this amperage the controller relays for the detector and column ovens were used to operate heavier relays, which controlled the oven heater loads.

Provision for linear temperature programming the column oven was provided by introducing a linearly decreasing negative voltage into the positive thermocouple input of the temperature controller. A -10 to 0 v. D.C. voltage ramp was obtained from a Canberra Model 833 Baseline Sweep, associated with our nuclear counting instrumentation. The circuitry used in the construction of this programmer is shown in Fig. 20. The -10 to 0 v. output sweep of the Model 833 was reduced to a -51 to 0 mv. range by means of a voltage divider. The upper limit of the sweep range may be established at any value between zero and 51 mv by the ten-turn potentiometer incorporated in the voltage divider. This is sufficient to provide equivalent temperature ranges from 0 to greater than 400° C. This increasing (approaching zero from the negative direction) voltage range was then introduced into the positive thermocouple input as a bucking voltage as shown in Fig. 20.

Operation of the programmer is controlled by an in-out switch, the ten-turn range control, the sweep time setting of the baseline sweep,

Figure 20. Circuit diagram of the linear temperature programmer.

and the set point of the temperature controller. First the starting temperature of the column oven is established with the temperature controller. Then the heaters are momentarily switched off and the sweep is switched in and adjusted to provide the maximum (-10 v) output to the input of the voltage divider. The upper temperature limit of the program is then established by setting the temperature controller at the desired temperature. The range control is then adjusted in such a manner that the controller is maintaining the previously established initial temperature while set for the upper temperature limit of the program. This is determined by a zero reading on the deviation indicator of the temperature controller. The heaters are then switched back on. As the entire procedure outlined above can be performed in less than 15 sec., little or no deviation from the initial set point temperature will have occurred. The column oven may then be operated for an indefinite length of time at the initial temperature setting. The program may be initiated at anytime, with its previously established upper and lower limits, by turning the range setting of the baseline sweep to zero and pressing the start button. The sweep rate is established by the sweep time control on the baseline sweep. Presently total sweep times of 1, 3, 10, and 30 minutes are provided for by the sweep time control. However, a large number of other times may be readily obtained by changing the values of the resistors in the voltage input to the clock in the Model 833 sweep.

Direct temperature readout of the various points of interest is provided for by an Assembly Products, Inc., API, 0-400° C pyrometer.

The pyrometer is calibrated for iron-constantan thermocouples with an external resistance of 10 ohms. Adjustment of the thermocouple lead resistances to 10 ohms is accomplished by placing a one-turn 25 ohm trimpot between the positive input of the pyrometer and the thermocouple. The pyrometer has a 1% full scale accuracy and provides internal cold junction compensation.

An eight position selector switch having dual gold plated contacts was used to select a thermocouple located at one of the various points where temperature measurement is desired. The column oven, detector oven, injection ports, radiation counter, and thermal conductivity cell are presently provided with temperature readout, although additional locations may be readily added. The injection port and detector oven thermocouples provide temperature sensing for both measurement and control. Due to the additional circuitry associated with the column oven temperature control thermocouple a separate thermocouple is provided for measurement.

Chromatographic Analysis

Elution techniques were used in conjunction with a differential method of detection of radioactive compounds. An analog display of the differential response of the radiation analyzer showed any eluted activity at the instant of detection and the resultant signal was displayed on a potentiometric strip chart recorder as a nearly Gaussian-shaped elution curve. A typical chromatogram of products tagged with ^{128}I resulting from the neutron irradiation of CH_3I in the presence of 1-pentene is shown

in Fig. 21. The broken line represents the radiation detector signal and the solid trace that of the thermal conductivity detector. The "cold" iodo-products detected by the T. C. cell were added to the irradiated sample just prior to analysis to assist in the qualitative analysis of the "hot" products. The small difference in the recorded elution times of identical "hot" and "cold" compounds is a result of the differential flow time between the two detectors. The decrease in resolution observed for the "hot" peaks over that of the corresponding "cold" peak is a result of the much larger sensitive volume of the radiation detector (~ 40 ml.). There is no baseline drift in this temperature programmed run, since the detectors were operated at a constant temperature. If the proportional counter was improperly heated, some of the labeled products could adhere to the walls and increase the background counting rate, which appears to be a baseline drift. This could generally be rectified by increasing the counter temperature.

The number of theoretical plates or "plate equivalents" of the column was determined by the commonly accepted method⁸⁰ of measuring the retention time from the introduction of the sample, t_r , and the width of the peak base, Δt . The number of theoretical plates was given by the equation; $n = 16(t_r/\Delta t)^2$. The columns used had approximately 4100 plate equivalents. The height equivalent to theoretical plate (HETP) was obtained by dividing column length (10 ft.) by the number of plate equivalents. It was approximately 1.02 mm. The HETP generally decreased slightly with increasing retention time as generally would be expected.⁸⁰

Figure 21. Radiogas Chromatogram of ^{128}I labeled organic products obtained in a 0.1 mole % solution of CH_3I in 1-pentene. "hot" products, —; added carrier, ____.

Qualitative Identification of Radiocompounds

Since the labeled compounds produced by the nuclear activation were in such small quantities ($\sim 10^{-13}$ g.) that they could only be detected by virtue of their radioactive decay, their qualitative identification had to be determined by a type of carrier technique. This technique involved reverse isotope dilution methods in which cold (non-radioactive) carrier compounds, suspected to be identical to the labeled compounds produced by the nuclear activation, were added to the radioactive sample after removal of the inorganic activity by an aqueous sulfite extraction. Thus, in many instances, the qualitative identification could be made on the basis of the coincidental elution and detection (after correction for the time differential between the detectors) of the labeled product with its corresponding added carrier.

For the iodine-pentene systems studied in this research there were no carriers available for many of the unsaturated alkenyl iodides, thus, when possible, estimates of the identity of the peaks could be made on the basis of the boiling point of the compound. It was found that the alkenyl iodides having the iodine bonded to an unsaturated carbon would have a 5-15° C lower boiling point than its saturated analog and would, therefore, elute before the saturated iodide on the columns used. However, the alkenyl and alkyl iodides having the iodine bonded to a saturated carbon were not separated.

Several different techniques were employed in an effort to separate the unsaturated from the saturated C_3 to C_5 iodides. The first was the

use of a propylene glycol-silver nitrate (3:1), 5 % on Anakrom ABS 50/60 mesh, column packing. The silver nitrate loaded columns are well known for the selectivity towards unsaturated hydrocarbons. However, as determined by the analysis of 1-iodopropane and 3-iodo-propene, this column would not differentiate between the saturated and unsaturated iodides.

The work of Young, *et. al.*⁸¹ and Coulson⁸², in which mercuric perchlorate was found to selectively trap alkenes in a hydrocarbon mixture, suggested a possible alternative. A mercuric perchlorate-treated fire-brick column packing was prepared as described by Coulson⁸² and added as a 1/4 in. diameter by 6 in. long column between the analytical column and the detectors. We found, however, that this material removed not only the unsaturated iodides but also a considerable fraction of their saturated analogs. Thus, making this packing worthless for our purposes. It was therefore, not possible to completely isolate and identify all of the possible products of the reaction mixture; thereby, restricting the analysis of our experimental results to a certain extent.

Quantitative Determinations of Radiocompounds

Since the amounts of radioactive products were the only quantitative results desired, variance of the thermal conductivity cell with conductivity coefficients, temperature, flow rate, did not have to be determined. The radiation detector alone was the source of the

quantitative values obtained in this study. The chromatogram was recorded by a differential procedure employing the proportional counter and associated electronics, a potentiometric dual-pen recorder, and a digital integrater. Thus, the area under the resultant Gaussian type peaks in the count-rate versus time records was proportional to the quantity of radioactive compound present in the effluent gas stream (when the flow rate was held constant). Since nuclear decay does not significantly depend upon temperature, the chromatograph could be temperature programmed without any quantitative effects on the results due inherently to the temperature change. However, the flow rate of the carrier gas was seriously affected by changes of column temperature, requiring manual correction during temperature programming to prevent the introduction of error in the quantitative results as the magnitude of a peak resulting from a given amount of a radioactive compound was dependant on the length of time spent in the counter.

The detected radiation was the beta-ray emissions of ^{128}I and ^{131}I . The efficiency of detection was the same for all compounds and no corrections were needed in this regard. The ^{128}I gamma-ray emissions were sometimes monitored for the higher activity samples by a 5 ml. flow-through glass counting cell placed in a NaI(Tl) well counter. Because of the very much lower sensitivity of this detector (Table III) this data was seldom used.

The detector cell geometry was constant during a given run; background counting was relatively constant, and the flow was maintained at

a constant rate during the run. The only experimental parameter affecting the relative magnitudes of the detected peaks was the radioactive decay of the relatively short-lived (25 min.) ^{128}I . Thus, all peaks were corrected for the amount of iodine that had decayed prior to detection using the first peak eluted as the zero time marker. Such corrections were unnecessary for the longer-lived (8 day) ^{131}I product analyses. The area of each peak was determined by summing the total counts (in 10 sec. increments from the digital integrator) under the peak and then subtracting the background counts.

The product distributions of the individual samples were reported as the magnitude of the product peak relative to the total of all the organic products observed. Assuming all significant quantities of organic products were detected and measured, then the relative product distributions may be placed on an absolute basis by comparison with the previously determined organic yields of the respective samples.

CHAPTER IV
SZILARD-CHALMERS ORGANIC YIELDS IN
LIQUID AND SOLID ALKYL IODIDES

A number of conflicting values have been reported for the organic yields induced by various nuclear processes in pure alkyl iodides. For the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ activation process, the reported organic yield values range from 56-100%^{4,83-85}, 35-95%^{32,83, 85-87}, 41-55%^{83,85,88} and 41-53%^{85,89} for pure methyl, ethyl, n-propyl, and n-butyl iodide, respectively. Similar, but less scattered, values have been reported for the Szilard-Chalmers yields induced by other nuclear activation processes of iodine^{90,93} in these systems. A partial explanation for these varied results is suggested by studies of the exchange reactions of $^{131}\text{I}_2$ with the corresponding alkyl iodides.⁹⁴⁻⁹⁸

Svoboda⁹⁴ studied the exchange of $^{131}\text{I}_2$ in pure methyl, ethyl, n-propyl, and n-butyl iodide as a function of temperature and iodine concentration. He suggested that a pseudomonomolecular exchange of iodine with the alkyl iodides could be responsible for the higher values of organic yields reported in the literature. Cohen and Trumbore^{95,97} in a study of iodine exchange with ethyl iodide, confirmed the importance of exchange in the determination of Szilard-Chalmers yields in alkyl iodides. Both^{94,94} studies showed that, although the rate law is independent of iodine concentration, the apparent isotopic exchange (as

measured by organic retention of activity) is dependent on it. At the very low concentrations of iodine expected in the Szilard-Chalmers experiments, exchange was found to be very rapid. Thus, previously reported values of organic "retention", obtained in studies of Szilard-Chalmers reactions in alkyl iodides, are placed in doubt.

The purpose of this study was to investigate the influence of exchange, accompanying γ -radiolysis and dose rate, phase change, and degassing on the radiative neutron capture induced organic yields in "pure" alkyl iodides. Thus, by eliminating and/or correcting for any observed effects due to competing processes, the ^{128}I organic yields due solely to the nuclear activation process may be determined. This information is quite essential in order to employ the various alkyl iodides as sources of iodine in studies of the (n,γ) -activated processes of iodine in systems that are complicated by spontaneous thermal reactions with molecular iodine (See Chapter VI).

Liquid State Organic Yields

All neutron irradiations were carried out at $23 \pm 3^\circ \text{C}$ and the liquid samples maintained at this temperature, in the presence of normal interior illumination, for varying lengths of time prior to extraction. Irradiation, extraction, and assaying procedures have been described previously.

In order to determine the true $^{127}\text{I}(n,\gamma)^{128}\text{I}$ induced organic yields in the liquid methyl, ethyl, n-propyl, and n-butyl iodides studied, the following parameters were investigated: (1) the effects of exchange in

reactor irradiated samples by measuring the increase in organic yield as a function of time after irradiation, (2) the influence of accompanying γ -radiolysis and dose rate by varying reactor power and/or length of irradiation, and (3) compared degassed vs. air-saturated samples in order to determine the effect of oxygen scavenging on the observed organic yields.

Effects of Exchange. Shown in Tables IV, V, VI, and VII are the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ induced organic yields obtained for liquid methyl, ethyl, n-propyl, and n-butyl iodides, respectively, as a function of time of extraction following a 1 sec. irradiation. The midpoint of the irradiation was used as the zero time mark. The values in Tables IV to VII are summarized in Figure 22. The plotted experimental values as a function of time were used to obtain a graphical determination of the organic yields of the respective alkyl iodides at zero time (no exchange contribution). The respective liquid state organic yields were found to be 57, 41, 41, and 48%, after correction for any exchange which may have occurred by extrapolating the organic yields to zero time.

The exponential increase of organic yield with time illustrates the dependence of the observed organic yield on thermal exchange of the alkyl iodide with inorganic ^{128}I produced by the nuclear activation. This dependence of organic yield on time of extraction or extent of exchange decreases in the order $\text{MeI} > \text{EtI} > \text{n-PrI} = \text{n-BuI}$, consistent with the reported values⁹⁴⁻⁹⁸ for the exchange rates of the above alkyl iodides.

TABLE IV

Radiative Neutron Capture Induced Yields of ^{128}I
 in Liquid CH_3I as a Function of Elapsed Time,
 Δt , Between Irradiation and Extraction

Δt	Organic Yield %	Average Organic Yield
30 Sec.	64.99	62.34
	59.96	
	59.23	
	59.91	
	57.08	
	65.50	
	65.67	
	66.37	
1 Min.	61.76	69.65
	73.73	
	66.80	
	76.29	
2 Min.	73.93	76.12
	76.78	
	78.16	
	75.61	
4 Min.	80.02	81.37
	78.41	
	85.36	
	91.68	

TABLE IV (cont.)

At	Organic Yield %	Average % Organic Yield
8 Min.	89.92	88.67
	93.87	
	77.70	
	93.18	
15 Min.	99.19	91.49
	88.82	
30 Min.	98.49	96.58
	93.56	
	75.83	
	96.78	
	98.25	
45 Min.	97.70	98.29
	98.53	
	98.63	

TABLE V

Radiative Neutron Capture Induced yields of ^{128}I in
 Liquid $\text{CH}_3\text{-CH}_2\text{-I}$ as a Function of Elapsed Time,
 Δt , Between Irradiation and Extraction

Δt	Organic Yield %	Average % Organic Yield
30 Sec.	46.06 45.26 46.09 49.56	45.80
5 Min.	49.31 46.31 46.59 49.10	47.83
15 Min.	50.48 54.47 58.14 60.00 55.40	55.70
30 Min.	61.93 60.39 58.76 55.95	59.26

TABLE VI

Radiative Neutron Capture Induced Yields of ^{128}I
 in Liquid $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-I}$ as a Function of Elapsed
 Time, Δt , Between Irradiation and Extraction

Δt	Organic Yield %	Average % Organic Yield
30 Sec.	46.70	48.57
	48.24	
	50.39	
	48.42	
	49.07	
5 Min.	47.42	48.55
	44.44	
	50.94	
	57.36	
	49.82	
15 Min.	49.60	49.88
	51.41	
	51.60	
30 Min.	46.64	48.32
	48.64	
	46.58	
	49.61	
	47.67	
	49.18	
	48.22	

TABLE VII
Radiative Neutron Capture Induced Yields of ^{128}I
in Liquid $\text{CH}_3-(\text{CH}_2)_2-\text{CH}_2-\text{I}$ as a Function of Elapsed
Time, Δt , Between Irradiation and Extraction

Δt	Organic Yield %	Average % Organic Yield
30 Sec.	46.70	48.57
	48.24	
	50.39	
	48.42	
	49.07	
5 Min.	47.42	48.55
	44.44	
	50.94	
	47.36	
	49.82	
	49.60	
15 Min.	51.41	49.88
	51.60	
	46.64	
30 Min.	48.64	48.32
	46.58	
	49.61	
	47.67	
	49.18	
	48.22

Figure 22. Alkyl iodide organic yields as a function of time of extraction after irradiation. MeI, Δ ; EtI, $\bullet$; n-PrI, $\circ$; n-BuI, $\emptyset$. Solid points represent crystalline state values for the respective alkyl iodides.

The half-times for exchange were found to be 1.4×10^2 and 6.0×10^4 seconds for methyl and ethyl iodide, respectively. The rates of exchange for n-propyl and n-butyl iodide are equal within experimental error and are too small to permit a reasonable estimate of the exchange half-times. However, for the purpose of this study the rates of exchange are not of primary importance. The only necessary requirement is that the rate of exchange be small enough to permit a graphical determination of the organic yields at zero time.

Using the values of the exchange half-time obtained in this study and the values for the exchange rates reported by Svoboda⁹⁴ for methyl and ethyl iodide, respectively, the concentrations of I_2 present in our samples following the neutron activation may be estimated. In Table VIII, these values are compared with the concentration of iodine expected to be produced by the nuclear activation and accompanying radiolysis processes during irradiation. Since the concentration of iodine, predicted to be present in the samples by the observed exchange half-times, is one to two orders of magnitude greater than what would be expected to be produced during the nuclear activation, thus, iodine of approximately 5×10^{-6} mole/l concentration must have been present in the samples prior to irradiation. Iodine present at this very low concentration would not be expected to scavenge appreciably the (n, γ) activated iodine species, but to control the exchange rate of iodine with the alkyl iodide. The reported independence of organic yield

TABLE VIII

Concentrations of Molecular Iodine Calculated to be Present
and/or Produced by the Nuclear Activation

Alkyl Halide	Concentration of I_2^a Experimental ^c	Produced by Irradiation ^b	
		Nuclear ^d Activation	Radiolysis ^e
MeI	5.0×10^{-6}	5×10^{-12}	1.2×10^{-7}
EtI	7.2×10^{-6}	3×10^{-12}	1.8×10^{-7}

a In moles per liter.

b Calculated for the 1 sec. irradiations employed.

c Using Svoboda's values for the exchange rates of 6.0×10^{-19} mole l^{-1} sec^{-1} and 4.4×10^{-11} mole l^{-1} sec^{-1} for MeI and EtI at 20° C, respectively.

d Computed using the nuclear activation equation.

e Computed using the reported⁹⁹ G values of 1.4 and 2.0 for the production of I_2 in MeI and EtI, respectively.

between 2×10^{-5} and 2×10^{-7} mole fraction added iodine in methyl iodide after correction for exchange⁹³ supports this contention.

The values obtained in this study for the liquid state organic yields of n-propyl and n-butyl iodide are approximately 7% higher than the values reported in earlier studies.^{83,83,91} However the earlier determinations were performed with air-saturated samples; whereas, degassed samples were used in this study. McCauley, et. al.⁹², reported increase in the organic yields of n-propyl iodide for the ^{127}I (n,2n) ^{128}I activation, when samples were degassed. A corresponding decrease of 7% for the organic yields of n-butyl iodide was found, while employing air-saturated samples for the ^{127}I (n, γ) ^{128}I activation in this study. McCauley, et. al., suggested the lower yields observed for the air-saturated samples were a result of oxygen scavenging of the accompanying γ -radiolysis induced pick-up of the activated iodine.

Several conclusions can be drawn from the above results. (1) The observed organic yields for the alkyl iodides are dependent on the amount of exchange occurring prior to extraction. (2) The observed contribution to the organic yields by exchange reactions decreases in magnitude with increasing chain length of the alkyl iodide.

Influence of γ -dose and Dose Rate

The effects of the sample radiolysis during activation was studied by varying the reactor power to obtain a proportional change in the gamma dose rate received by the samples and the duration of irradiation to study the effects of the total gamma dose received by the samples. Only the n-propyl and n-butyl iodides were used in this study in order to avoid the complications of exchange reactions occurring in the methyl and ethyl iodides. However, the results obtained with the n-propyl and n-butyl iodides would be expected to be representative of the other alkyl iodides.

Investigating the effects of radiolysis on the observed ^{128}I organic yields of the alkyl iodides studied no evidence was found that the accompanying $5 \times 10^{15} \text{ eV. g}^{-1}$ radiation received by the samples contributed appreciably to the observed yields. The reactor power was varied from 1.7 Kw to 17 Kw and the total γ -dose received by the alkyl iodide samples from 1×10^{14} to $1 \times 10^{17} \text{ eV. g}^{-1}$. No dependence of the observed organic yields on dose rate and total dose received was found, when the gamma dose was less than $1 \times 10^{16} \text{ eV. g}^{-1}$. However, a ten-fold increase in total dose received by the samples from 5×10^{15} to $5 \times 10^{16} \text{ eV. g}^{-1}$ resulted in a 2 to 6% increase in the measured ^{128}I organic yields for normal propyl and butyl iodide. Similar results were reported for other n-propyl halides⁸⁸ and indicate that under certain conditions (i.e., total doses equal to or greater than $1 \times 10^{16} \text{ eV. g}^{-1}$) the observed organic yields in the alkyl

iodides studied are dependent on the accompanying γ -radiolysis.

Since no evidence was found that the reactor dose, accompanying the one second sample irradiations employed in this study, contributed to the organic yields of the alkyl iodides the increase in the respective organic yields of degassed samples as compared to air-saturated samples must result from oxygen scavenging of the radiative neutron capture induced yields of the ^{128}I . In this instance the values obtained for the degassed samples would be expected to reflect more closely the true organic yields of the activated iodine than would the air-saturated samples.

Solid State Organic Yields

All solid samples were irradiated for one second at 77° K and stored in liquid nitrogen immediately after irradiation. The stored samples were then extracted while frozen by previously described techniques.

The radiative neutron capture induced organic yields obtained for ^{128}I in the polycrystalline and/or glassy methyl, ethyl, n-propyl, and n-butyl iodides are shown in Table IX. As shown the ^{128}I organic yields were found to be 57, 41, 56, and 60% respectively, for the crystalline methyl and ethyl and glassy n-propyl and n-butyl iodides at 77° K. These values are in agreement, within experimental error, with the corresponding values previously reported in the literature.^{83,87,92}

TABLE IX

Radiative Neutron Capture Induced Organic Yields of ^{128}I
in Solid Alkyl Halides at 77°K^a

MeI^b	EtI^b	$n\text{-PrI}^c$	$n\text{-BuI}^c$	$n\text{-BuI}^b$
57.58	39.35	56.30	60.20	47.48
55.65	41.04	54.29	<u>60.22</u>	46.35
<u>58.16</u>	<u>40.73</u>	58.87	60.20	47.10
57.13	40.37	58.69		<u>46.83</u>
		55.25		<u>46.95</u>
		53.92		
		58.01		
		<u>55.56</u>		
		56.37		

a 1 sec. irradiation

b Polycrystalline solid

c Glassy solid

The solid state organic yields are the same as the corresponding liquid state values for the methyl and ethyl iodides but not for the n-propyl and butyl iodides which are higher by 8 to 12%. The methyl and ethyl iodides form a polycrystalline solid when rapidly frozen in liquid nitrogen; whereas, n-propyl and n-butyl iodide form glassy solids. The failure of the normal propyl and butyl iodides to follow the trend established by the methyl and ethyl iodides (i.e. solid and liquid state yields being equal) is due to the nature of the solid formed and not to structural differences as shown by the following. The polycrystalline form of n-butyl iodide was obtained by freezing the sample in liquid nitrogen, allowing it to warm slowly to its melting point (where the glass converts to the polycrystalline form), and cooling rapidly to 77° K. For the reactor irradiation of the polycrystalline form of the n-butyl iodide the organic yield was found to be 48%, identical to the liquid state value. Thus the differences reported earlier^{83,92} between the solid state and liquid state organic yields of the alkyl iodides containing more than two carbon atoms must be due to the type of solid formed and not to structural differences for the alkyl iodides studied.

Since the organic yields in the polycrystalline solid alkyl iodides were found to be the same as their respective liquid state yields, after correction of the latter for exchange, this direct correspondence between the liquid and polycrystalline state yields could then be used to simultaneously determine the polycrystalline yields and the corresponding liquid state yields in the absence of exchange and/or perhaps radiolysis.

This is demonstrated by the polycrystalline state alkyl iodide yields plotted in Figure 21 (solid points).

CHAPTER V
KINETICS AND MECHANISM OF IODINE
ADDITION TO VARIOUS PENTENE ISOMERS

Surrell, *et. al.*¹⁰⁰, and Skell and Pavlis¹⁰¹ have reported that contrary to information commonly found in the literature¹⁰²⁻¹⁰⁵, iodine readily adds to 1-pentene and C₄ alkenes, respectively. They have reported that in the presence of a liquid phase and an ordinary room illumination the reaction proceeds via a mildly exothermic reaction which goes essentially to completion:

In their study of the addition-elimination cycle of iodine to cis and trans-2-butenes, Skell and Pavlis¹⁰¹ proposed a radical chain mechanism, proceeding via a bridged radical intermediate. The basis for their hypothesis was the observed photoacceleration and stereospecific nature of the addition-elimination reactions of iodine with the corresponding 2-butenes.

Benson, *et. al.*¹⁰⁶ have reported that the I atom catalyzed elimination of iodine from vicinal diiodides must be a concerted process, proceeding by a single step elimination. They further concluded that if the decomposition reactions are concerted processes, then by the principle of

microscopic reversibility, the addition reactions also must be concerted processes. However, this microscopic reversibility argument has been shown to be invalid for reasons discussed by Burwell and Pearson.¹⁰⁷

This controversy over the sequence of the formation of the transition state has been summarized by Noyes, *et. al.*¹⁰⁸, without reaching a conclusion as to whether or not all present observations could be explained without assuming the existence of bridged radicals, as proposed by shell and co-workers to explain their stereochemical observations.^{101,109-111}

In order to study the radiative neutron capture induced reactions of ^{128}I in the various C_5 alkenes, (See Chapter VI) a knowledge of the rate and mechanism of the thermal reactions of iodine in these systems is essential. In view of the uncertainty in the rate and mechanism of the addition of iodine to various unsaturated hydrocarbons in the condensed phase, the kinetics of the addition process to various C_5 alkene isomers in solution at 25°C was investigated in an effort to shed additional light on the mechanism of the reaction.

Kinetic Experiments

As outlined previously a radiometric procedure was employed to follow the addition of iodine to the various pentene isomers studied. The individual kinetic runs were started by mixing known volumes of tagged iodine in CCl_4 with the pentene of interest. The reactions were initiated by the ordinary white fluorescent lighting of the laboratory. Prior to

the use of ^{131}I tagged I_2 in CCl_4 several runs were made by adding tagged molecular iodine directly to the liquid alkene to initiate a run. However, the dissolution time of the molecular iodine was found to affect the rate data obtained, particularly during the initial stages of addition. Thus, the procedure was modified, such that, the added I_2 was predissolved in carbon tetrachloride. The small mixing time of the two reactants was found to yield satisfactory results.

Reaction Order with Respect to Iodine

The addition of iodine to the double bond, in the various C_5 olefins studied, proceeds smoothly when the reaction is exposed to ambient light at 25°C . Several kinetic runs were made in which the concentration of iodine was varied and the initial velocity of the reaction as a function of iodine concentration was determined. A double-logarithmic plot of the velocity versus the concentration of the added I_2 yielded a straight line with the slope equal to the order of the reaction with respect to iodine. The reaction was found to be $3/2$ order with respect to iodine.

Since all kinetic runs were made with the respective alkene in excess, the rate of disappearance of iodine with respect to the concentration of iodine at time $\underline{t}$, can be expressed by

$$-d(\text{I}_2)_{\underline{t}}/d\underline{t} = k(\text{I}_2)^{3/2} \quad (1)$$

Integration of equation yields the following expression

$$\frac{1}{2}kt = 1/(\underline{a}_0 - \underline{x})^{\frac{1}{2}} - (1/\underline{a}_0^{\frac{1}{2}}) \quad (2)$$

where $\underline{a}_0$ is the initial concentration of iodine at zero time, $(\underline{a}_0 - \underline{x})$ the concentration of iodine at time $\underline{t}$, and $\underline{t}$ the time in minutes. Rate constants, $\underline{k}$, were determined from the slopes of the straight lines obtained by plotting the values of $1/(\underline{a}_0 - \underline{x})^{\frac{1}{2}}$ vs $\underline{kt}$. The data for a representative run in each of the five pentene isomers studied is presented in Table X to IV and summarized in Fig. 23. As demonstrated by the data, deviation of the reaction rates from equation 2 did not become serious until the reactions had proceeded to 75% completion or greater.

Within a few hours after the start of a reaction an equilibrium was established. At that point the reaction was 75-99% complete, depending on the original concentrations of the reactants and the nature of the alkene. This observed equilibrium could result from either or both of the following: (1) a true equilibrium established by the previously demonstrated¹¹² iodine atom catalyzed decomposition of the products, and/or (2) competition for the unreacted iodine via the formation of a charge transfer complex of iodine with the product, whose effect would be to decrease the concentration of uncombined iodine. The well-established photo-accelerated decomposition of various vicinal diiodides¹¹³⁻¹¹⁵ would suggest that the decomposition of the product predominantly accounts for the observed equilibrium.

Although the reactions become complex in their later stages, the kinetics can be studied readily up to at least 75% completion, as demonstrated by the data in Fig. 23.

TABLE X

Rate of Addition of Iodine to 1-Pentene at 25° C^a

Time (sec)	Organic Yield (%)	$\frac{1}{(a_0-x)^{1/2}}$ (moles ^{-1/2} l)	$(\text{min}^{-1} \frac{k \times 10^2}{\text{moles}^{-1/2} \text{ l}^{1/2}})^b$
30	14.2	28.1	13.8
120	37.0	32.8	11.3
300	65.1	44.1	12.0
600	82.7	62.6	12.2
900	88.7	77.6	11.5
1200	92.6	96.1	11.7
1800	95.5	122.9	10.8
2700	96.1	132.7	7.9
3600	96.7	143.5	6.5
4500	96.3	135.5	4.7

a Concentrations of I₂ and 1-pentene were 1.47×10^{-3} M and 8.78 M, respectively.

b Computed for each point using equation 2.

TABLE XI

Rate of Addition of Iodine to cis-2-Pentene at 25° C^a

Time (sec)	Organic Yield (%)	$\frac{1}{(a_0 - x)^{1/2}}$ (moles ^{-1/2} l)	$(\text{min}^{-1} \frac{k \times 10^2}{\text{mole}^{-1/2} \text{ l}^{1/2}})^b$
30	13.1	31.2	14.2
120	27.9	34.3	8.6
300	50.0	41.2	8.0
600	67.6	51.2	7.4
900	77.3	61.2	7.1
1200	83.5	71.6	7.0
1800	86.2	78.5	5.5
2700	90.1	92.4	4.7
3600	99.5	396.2	20.4
4500	99.5	400.0	16.5
39600	99.0	291.2	1.3

a Concentrations of I₂ and cis-2-pentene were 1.18 x 10⁻³ M and 8.99 M, respectively.

b Computed for each point using equation 2.

TABLE XII

Rate of Addition of Iodine to 2-Methyl-1-Butene at 25° C^a

Time (sec)	Organic Yield (%)	$\frac{1}{(a_0 - x)^{1/2}}$ (moles ^{-1/2} l)	$(\text{min}^{-1} \frac{k \times 10^2}{\text{moles}^{-1/2} \text{ l}^{1/2}})^b$
30	7.1	30.2	7.3
120	25.4	33.7	7.6
300	41.6	38.1	6.0
600	67.9	54.5	7.4
900	77.0	60.8	7.0
1200	83.7	72.1	7.2
1800	88.0	83.9	6.1
2700	88.5	85.9	4.2
3600	87.9	83.7	3.0
4500	88.8	86.8	2.6

a Concentrations of I₂ and 2-methyl-1-butene were 1.18 x 10⁻³ M and 8.92 M, respectively.

b Computed for each point using equation 2.

TABLE XIII

Rate of Addition of Iodine to 2-Methyl-2-Butene at 25° C^a

Time (sec)	Organic Yield (%)	$\frac{1}{(a_0-x)^{1/2}}$ (moles ⁻¹ l)	$(\text{min}^{-1} \frac{k \times 10^2}{\text{moles}^{1/2} \text{ l}^{1/2}})^b$
30	4.2	29.7	4.2
120	10.2	30.7	2.6
300	21.2	32.8	2.5
600	39.3	37.4	2.8
960	53.7	42.8	2.8
1200	59.0	45.5	2.7
1800	70.0	53.0	2.7
2700	79.3	64.0	2.6
3600	82.0	68.7	2.2
4500	84.6	74/3	2.0
5400	85.9	77/5	1.8
86400	82.4	69/4	0.1

a Concentrations of iodine and 2-methyl-2-butene were $1.18 \times 10^{-3} \text{ M}$ and 9.08 M , respectively.

b Computed for each point using equation 2.

TABLE XIV

Rate of Addition of Iodine to trans-2-Pentene at 25° C^a

Time (sec)	Organic Yield (%)	$\frac{1}{(a-x)^{1/2}}$ (moles ⁻¹ l)	(min ⁻¹ $\frac{k \times 10^2}{\text{moles}^{1/2} \text{ l}^{1/2}})^b$
30	6.5	26.8	5.0
120	13.6	28.0	3.3
300	20.4	29.2	2.1
600	34.9	32.3	2.1
900	47.1	35.9	2.2
1200	53.3	38.1	2.0
1800	63.5	43.2	1.9
2700	74.9	52.0	1.9
2660	78.9	56.8	1.7
4680	81.8	61.1	1.5
5400	84.8	66.8	1.5
7200	86.5	70.8	1.2
9000	84.4	66.1	.9
10800	88.5	76.9	.9
93600	84.3	65.8	.1

a Concentrations of iodine and trans-2-pentene were 1.18×10^{-3} M and 9.02 M, respectively.

b Computed for each point using equation 2.

Figure 23. Rate curves for the addition of iodine to olefins as a function of time. 1-pentene, O; *cis*-2-pentene, □; 2-methyl-1-butene, Δ; 2-methyl-2-butene, ◇; and *trans*-2-pentene, ○.

The reaction between the labeled iodine and 1-pentene was studied as a function of the initial concentrations of iodine and/or 1-pentene. The results of the individual runs are summarized in Table XV. The $2/3$ dependence of the reaction rate on the iodine concentrations is demonstrated by the results of runs 1-5.

Reaction Order with Respect to the Alkene. If the reaction was first order in 1-pentene concentration then the values of $(1\text{-pentene}/k)$ should have been independent of 1-pentene concentration. That this is not so is indicated in the last column of Table XV, runs 5-9. As the concentration of 1-pentene was decreased there was also a marked decrease in the ratio. This suggests that the order with respect to 1-pentene is more complex. A more complex order would be expected if a 1-pentene-iodine charge transfer complex was involved in the rate limiting step of the reaction (vide infra).

Additional evidence suggesting the importance of the iodine-olefin charge transfer complex, with respect to the addition of iodine to the double bond, was obtained by comparison of the reaction rates of a series of C_5 alkenes with their relative equilibrium constants for complex formation with iodine. Table XVI lists the rate constants obtained in this study along with the relative equilibrium constants obtained by Cvetanovic and his co-workers.¹¹⁶ It can be seen from the Table that there is a rough correlation between the rate of the reaction and the ability of the olefin to act as a donor toward iodine. Because of the

TABLE XV

Rate Constants for the Addition of Iodine to 1-Pentene
in Carbon Tetrachloride at 25° C

Run	(I ₂) mole/liter x 10 ³	(1-pentene) mole/liter	$\frac{k}{\text{min}^{-1}} \cdot \frac{\text{moles}^{-1/2} \text{liters}^{1/2}}{\text{x } 10^2}$	$\frac{(1\text{-pentene})}{k} \cdot \frac{\text{min} \text{ moles}^{3/2}}{\text{liters}^{-3/2}}$
1	21.89	9.12	10.9	83.26
2	8.83	9.13	10.9	83.26
3	0.076	9.11	11.5	79.2
4	0.152	9.10	12.1	75.2
5	0.147	8.78	11.2	78.4
6	1.18	7.02	9.7	72.6
7	1.18	5.27	8.0	65.8
8	1.18	3.51	6.4	54.8
9	1.18	1.76	4.01	44.1

TABLE XVI

Comparison of Rate Constants of Iodination with the Relative
Equilibrium Constants of Charge-Transfer Complexes

Olefin	k^a min moles $^{-1/2}$ l $^{1/2}$ $\times 10^2$	Relative K_c^b
1-pentene	11.0	12.7
<u>cis</u> -2-pentene	7.04	4.0
2-methyl-1-butene	6.74	.80
2-methyl-2-butene	2.59	.45
<u>trans</u> -2-pentene	1.03	.56

a Obtained with initial concentration of iodine of 1.8×10^{-3} mol/l.
in neat pentenes.

b Obtained from ref. 116. The values are relative to cis-2-butene,
which was taken as unity. It should be pointed out that Cvetanovic'
et. al. gave several values to choose from. The values quoted here
possibly the best values although the other choices showed the same
general trend. cf. W. E. Falconer and R. J. Cvetanovic', J. Chromat.,
27, 20 (1967).

complexity of the kinetic relationships one would not expect an exact correlation but it is gratifying that an overall trend in the anticipated direction is observed. This is precisely what would be expected if the iodine-olefin charge transfer complex was involved in the rate determining step.

However, as pointed out by Furuyama, *et. al.*¹²⁰, I atoms would also be expected to complex with the alkene π bond. Although there is no data on the relative equilibrium constants of the I-atom-olefin charge transfer complexes for the various pentene isomers studied, one might expect these constants to follow the same general trend as the corresponding molecular iodine complexes. Based on this assumption the earlier argument for the importance of the iodine-olefin charge transfer complex would be equally applicable to the I-atom-olefin complexes.

Mechanisms and Rate Laws

The effects of alkene concentration and complexing ability on the observed k values can be explained by the following reaction scheme in which steps 5 and 6, either singly or in combination, are rate determining

where $\underline{1}$ and $\underline{f}$ refer to the initiation and termination steps.

Examining the proposed reaction scheme a number of factors need to be considered:

- (1) The $I_2 \cdot$ olefin complex absorbs as well or better, than the free iodine, therefore, step $\underline{4}$ would be expected to contribute just as much, if not more, to the I atom formation as step $\underline{1}$;
- (2) I atoms probably form just as strong a π -complex with olefins as I_2 , so that the formation of the diiodide products from either step $\underline{5}$ or step $\underline{6}$ could be equally probably; (3) Both steps $\underline{5}$ and $\underline{6}$ lead to the same transition state $(C_5 I_3)$, thus the kinetic data would not be expected to distinguish between the two possibilities.

Assuming the rate determining step to be step $\underline{5}$ and that the $I_2 \cdot$ olefin complex contributes equally to the I $\cdot$ atom formation, then as shown in Appendix IIIA a mechanism of this type requires a rate law of the form

$$d(C_5 I_2)/dt = k_1 K_c (I_2)^{3/2} (C_5) / [1 + K_c (C_5)] \quad (3)$$

where K_c is the equilibrium constant for complex formation as defined by

$$K_c = (C_5 \cdot I_2) / (C_5)(I_2)_f \quad (4)$$

and where $(I_2)_f$ is the concentration of uncomplexed iodine. As shown in Appendix IIIA, the observed rate constant $\underline{k}$ should then be related to

k_1 by the expression

$$(C_5)/k = 1/(k_1 K_c) + (C_5)/k_1 \quad (5)$$

According to equation 5 a plot of the experimental values of $(C_5)/k$ vs. (C_5) should then yield a straight line, the slope and intercept of which should yield the values of K and k_1 , respectively. The data of Table XV were treated graphically according to equation 5. From the resultant plot (Fig. 24) values of $K = 1.0 \times 10^{-2}$ moles⁻¹ liters and $k_1 = 2.38 \times 10^{-1}$ min⁻¹ moles⁻¹ liters were obtained.

Alternately if step 6 is considered to be the rate determining step the required rate law (as shown in Appendix IIIB) is

$$d[C_5 I_2]/dt = k_1' K_c' [C_5][I_2]^{3/2}/(1 + K_c[C_5]) \quad (6)$$

where K_c' is the equilibrium constant for the I-atom-olefin complex formation as defined by

$$K_c' = [C_5 \cdot I]/[C_3][I] \quad (7)$$

The above rate expression, with the exception of K_c' in the numerator, is the same as the previously derived rate law for the $I \cdot + C_5 \cdot I_2 \rightarrow C_5 I_3$ mechanism. Thus the slope and intercept of the plot of $[C_5]/k$ vs. $[C_5]$ would be equal to $K_c/k_1' K_c'$ and $1/k_1' K_c'$, respectively. The value of k_1' is dependent on the value assumed for K_c' , but the value of K_c obtained from the solution of the two equations is independent of the value of K_c' . If $K_c' = K_c = 0.10$ moles⁻¹ l, then the value of k_1' is the same as that obtained previously.

One could also re-evaluate the first rate law, assuming that the

Figure 24. Plot used in the determination of K_c and k , according to equation 5.

$C_5 \cdot I_2$ complex does not contribute to the formation of I-atoms. This would require a rate law (as shown in Appendix IIIC) of the form

$$d[C_5I_2]/dt = k_1 K_c (I_2)^{3/2} (C_5) / (1 + K_c [C_5])^{3/2} \quad (8)$$

As shown in the Appendix IIIC, the observed rate constant k should then be related to k_1 by the expression

$$[(C_5)/k]^{2/3} = 1/(k_1 K_c)^{2/3} + K_c (C_5)/(k_1 K_c)^{2/3} \quad (9)$$

According to equation 9 a plot of the experimental values of $[(C_5)/k]^{2/3}$ vs. (C_5) should then yield a straight line, the slope and intercept of which should yield the value of K and k_1 , respectively. The data of Table XV were treated graphically according to equation 9. From the resultant plot (Fig. 25) values of $K = 7.07 \times 10^{-2}$ moles⁻¹ liters and $k_1 = 3.58 \times 10^{-1}$ min⁻¹ moles^{-1/2} liters^{1/2} were obtained.

Andrews and Keefer¹¹⁷ reported that the absolute value of the equilibrium constant for the cyclohexene/iodine complex was 0.34 mole⁻¹ liter. Ovetanović *et al.*¹¹⁶ gave a relative value for cyclohexene. Combining these data with the relative equilibrium constant for 1-pentene allows the calculation of the absolute value for 1-pentene. This comes out to be 9.0×10^{-2} mole⁻¹ liter. This compares very favorably with the independent value of 10.0×10^{-2} mole⁻¹ liter obtained in this study, assuming the iodine olefin complex contributes equally to the formation of I-atoms. The value of K_c obtained when the contribution of the complex is neglected (7.07×10^{-2} moles⁻¹ liters) results in poorer agreement, thus supporting the expected importance of the complex in contributing to the formation

Figure 25. Plot used in the determination of K_c and k_1 according to equation 9.

of I-atoms.

Equilibrium

A series of five solutions, containing varying concentrations of iodine between 1.0×10^{-2} and 1.0×10^{-3} moles liter⁻¹ in neat 1-pentene, were allowed to stand for 48 hrs. and the equilibrium concentrations of the respective reactants and products were determined. These values are listed in Table XVII. The expression for the overall equilibrium constant for step 5 assuming the reaction was reversible, would be

$$K = (C_5I_2)/(C_5 \cdot I_2) \quad (10)$$

and from equation 4. $(C_5 \cdot I_2)$ is equal to $K_c(C_5)(I_2)$. Then the expression for the observed equilibrium constant, K_{obs} , would be

$$K_{obs} = KK_c = (C_5I_2)/(C_5)(I_2) \quad (11)$$

Using equation 11, the average value of the observed equilibrium constant, K_{obs} , was found to be 2.51 ± 0.20 . Using this value and the value determined previously for K_c the value of K was found to be 25.10.

The observed deviation of the experimental values from the straight line plots in Fig. 23, which occur in the later stages of the reaction, and the subsequent attainment of an equilibrium suggest that the proposed mechanisms and the resultant kinetic expressions do not fully describe the iodine interaction with the alkene. For example step 5 would be more correctly expressed as follows

TABLE XVII

The Observed Equilibrium Constant, K_{obs} , for
the Addition of Iodine to 1-Pentene as a
Function of the Initial Reactant Concentration^a

$[I_2]_0$ (moles l^{-1})	$[1\text{-pentene}]_0$ (moles l^{-1})	Organic ^b Yield (%)	K_{obs}^c (moles ⁻¹ l)
9.07×10^{-3}	9.13	95.6	2.40
8.84×10^{-3}	9.13	95.8	2.48
1.47×10^{-3}	8.78	95.5	2.43
3.48×10^{-3}	8.28	95.4	2.52
6.40×10^{-3}	7.59	95.4	2.73
			Avg. 2.51 ± 0.2

a All runs performed in ambient light at 25° C.

b Determined $\geq$ 48 hrs. after addition of reactants.

c Calculated using equation 11.

allowing for the reversible decomposition of the products. Thus the kinetic expression should include an additional term allowing for the reversible step. Polissar,¹¹³ and others^{114,115} have shown that the decomposition of vicinal diiodides to proceed by an I atom catalyzed concerted process, i.e., essentially the reverse of the addition mechanism. Thus equation 3 could be rewritten to give:

$$d(C_5I_2)/dt = k_1 K_c (I_2)^{3/2} (C_5) / [1 + K_c (C_5)] - k_2 (C_5I_2) (I_2)^{1/2} \quad (13)$$

which includes the expression for the product decomposition. By the inclusion of the decomposition term in the overall kinetic expression the observed data should cover the entire range of the reaction. This, however, is not necessary in order to describe the addition mechanism. As demonstrated by the data the decomposition term may be neglected and sufficient data can be obtained from the initial stages of the reaction in order to identify the most probable rate determining step and, nature of the activated complex. A similar treatment of step 6 would be equally valid.

Stereochemistry of the Addition-Elimination Reactions

Identification of the products of addition of iodine to 1-pentene and cis and trans-2-pentene were made on the basis of their characteristic nmr spectra.¹¹⁸ A representative spectra of each of the pentene isomers and their corresponding diiodo products is shown in figures 26

Figure 26. NMR spectra of pure 1-pentene.

Figure 27. NMR spectra of the 1,2-diiodopentane.

Figure 28. NMR spectra of pure *cis*-2-pentene.

Figure 29. NMR spectra of *dl*-2,3-diiodopentane.

Figure 30. NMR spectra of pure trans-2-pentene.

Figure 31. NMR spectra of meso-2,3-diiodopentane.

to 31. The nmr spectra of the respective starting olefins were identical with the products of elimination of iodine from the corresponding diiodides. The 1,2-diiodopentane was readily converted to 1-pentene by stirring with zinc dust in methanol. Similar treatment of the dl- and meso-2,3-diiodopentanes, however, produced considerable quantities of pentane. The iodine catalyzed conversion of an alkene to its corresponding alkane has been reported previously.¹¹⁹ However, conversion of the 2,3-diiodopentanes back to their respective cis and trans-2-pentenenes was successfully accomplished by stirring with magnesium in ethyl ether. Although pentane was also produced in this reaction it was in a much smaller amount and sufficient quantities of the cis and trans-2-pentenenes were recovered to confirm the reported¹⁰¹ stereospecific nature of the addition and elimination of iodine.

Attempts to convert the respective diiodo-products back to their starting materials by thermal decomposition were also unsuccessful. When 1,2-diiodopentane and the 2,3-diiodopentanes were heated, without prior removal of the small quantities of excess iodine, decomposition occurred at ca. 35° which resulted in the formation of HI and a dark polymeric material of unknown composition. However, if the excess iodine was removed prior to heating by an aqueous sulfite extraction, the respective diiodides could be distilled at ca. 130° with little accompanying thermal decomposition.

Discussion

Assuming a mechanism based on either steps 5 or 6, it was possible to obtain reproducible experimental values for the rate constant consistent with the rate laws for either of the respective mechanisms. As both steps 5 and 6 require activated complexes having identical configurations, the kinetic measurements would not be expected to distinguish between the two proposed alternate reaction paths. In addition the expected correlation between reaction rates and complexing ability of the respective olefins was found. The value obtained for the charge transfer equilibrium constant for the 1-pentene/iodine complex was consistent with the reported value for the iodine-cyclohexene complex.¹¹⁷ It would therefore appear that, assuming similar complexing abilities of the olefins with I-atoms, either postulated mechanism is sufficiently justified by the experimental data.

The mechanism in step 5 is also in complete agreement with other studies which suggested that a concerted addition mechanism was required for the addition of iodine to alkenes. Most of these studies dealt with the reverse of the addition reaction^{113,114} and with isomerization of olefins by iodine.^{111,112,119,120} Agreement with the reported stereospecific nature of the iodine addition and elimination, found in this study and reported previously by Skell, *et. al.*¹⁰¹, is also consistent with the proposed mechanism, as the pi-complex would be expected to collapse stereospecifically. Although our observations can be explained

without assuming the existence of bridged radicals we can offer no definitive evidence to either prove or disprove the importance of the $C_5I\cdot$ radical in the formation of the diiodo products. However, the stereospecific nature of the iodine addition and elimination require the iodine atom to bridge the two carbons.

As discussed previously the diiodoproducts were converted back to their respective olefins and the stereospecific nature of the addition-elimination cycle of iodine was confirmed. The dependence of the thermal stability of the products on the presence of iodine and the conversion of the pentenes to their respective pentanes, while interesting were not pursued further.

CHAPTER VI
CHEMICAL EFFECTS OF THE (n, γ)-ACTIVATION OF IODINE
IN LIQUID ALKENE-IODINE SYSTEMS

The chemical effects of the (n, γ) induced reactions in condensed systems may involve a large number of factors, the relative importance of which is not well understood as yet. The currently accepted hypothesis employed in the interpretation of the chemical effects of the nuclear transformation induced reactions of heavy halogens in condensed systems is the "Auger Electron Hypothesis",⁴⁴ This hypothesis suggests that the recoil halogens react with the solvent radicals which are formed at high localized concentration in their immediate vicinity by reactions such as $RX + e^- \rightarrow R + X^-$ and $EX + H \rightarrow R + HX$, made possible by the localized radiation chemistry induced by the internal conversion and Auger electrons emitted by the recoil atoms.

Because of the complicated nature of radiation chemistry itself, such as the well known production of approximately equal quantities of radicals and ionized species, the "Auger Electron Hypothesis" proposed by Willard⁴⁴ fails to predict the identity of the reactive species responsible for the incorporation of the halogen into the solvent molecule and/or one of its fragments. In fact, the "Auger Electron Hypothesis" does not even consider the activated iodine species is directly participating

in the formation of the observed products. For instance the formation of organic iodides could proceed via charged and/or excited iodine atoms, as found to occur in the gas phase^{38,38,50}, or by radicals produced by the internal conversion and Auger processes. However, the previously described hypothesis would not be expected to differentiate between the formation of products by either process.

In the past nearly all studies of the (n, γ) induced reactions of iodine in condensed systems have been carried out in various alkane and alkyl halide solvents. These solvents (target molecules), with the possible exception of some of the alkyl halides, would be expected to exhibit little chemical selectivity toward an ion or radical attack and, therefore, yield no information on the identity of the reactive species. There have been a few studies, however, with aromatic systems liable to attack by positive halogens at particular positions, thus leading to more specific modes of reaction.¹¹ Attempts to discover such effects have generally led to somewhat ambiguous results.

It would therefore be desirable to find and employ a system which would exhibit a chemical selectivity toward either an ion or a radical attack that could be detected by the formation of a product or products characteristic of an attack by a particular species. Alkenes with their electron rich double bond, could exhibit an internal chemical selectivity to attack by a positive iodine ion. If such is the case one would expect the ion to attack the molecule at the position of the double bond and as result observe an increase in the formation of products with the labeled

iodine attached to this position, as compared to the product distribution of the corresponding alkane. Thus by studying the (n, γ) induced reactions of iodine in liquid alkenes, it may be possible to determine if ionic precursors are important to the incorporation of iodine into the solvent molecules in condensed media.

Although there exists little information with respect to the ion-molecule reactions of alkenes and halogens, the thermal (iodine free radical) reactions of iodine with alkenes in both the gas^{106,121} and liquid^{100,101,122} have been investigated in some detail. Golden and Benson¹²¹ in a recent review of the gas phase reactions have shown that these reactions do not lead to the incorporation of iodine into the alkene. Similar studies in the liquid state show that the formation of the respective 1,2-diiodo- products occurs rapidly when illuminated by ordinary white fluorescent light.^{100,101} As discussed in Chapter V, it was found that the addition to the alkene double bond proceeds through a I atom catalyzed concerted addition process. It has been noted however, that negligible addition occurs in the absence of light^{101,122} as would be expected for a free radical process. Thus, the (n, γ) induced hot atom studies of the addition of iodine to olefins may be performed in the dark, in either the gaseous or condensed state, with little or no interference expected from thermal addition reactions.

If, contrary to what would be expected, significant interference with the "hot atom" studies by thermal processes did occur, then a less reactive source of iodine such as CH_3I could be employed. The feasibility

of using methyl iodide as a source of "hot" iodine has been demonstrated.^{123,124} Although this would not permit the effects of I_2 scavenger to be determined and complicate the product determinations, no other experimental problems would be expected.

Organic Yields

Previous studies (Chapter V and Refs. 100,101,122) have shown that, while molecular iodine readily adds to the double bond in a number of simple olefins when in the presence of light, the addition reaction is negligible in the dark. In fact less than 10% addition was found to occur after three hrs. of standing in the dark for a 1.5×10^{-5} M solution of I_2 (^{131}I) in 1-pentene at 25° C. Therefore, all the iodine-olefin samples, for subsequent neutron activation, were prepared in a completely darkened room with only a dim red light present to supply the necessary illumination. Quadruplicate one ml. samples of each concentration were prepared immediately (≤ 1 min.) after mixing of the I_2 with the pentene isomer of interest. After placing the samples in individual quartz ampoules, the ampoules were shielded with an aluminum foil shroud to further protect them from any incident light during the degassing procedure described previously. Immediately after preparation the samples were wrapped in foil and frozen in liquid N_2 . Just prior to activation of the individual samples in the reactor they were removed from the liquid N_2 and wrapped in carbon paper and then allowed to liquify. The carbon paper wrap was employed to shield the samples from any incident

light during irradiation as the more durable aluminum foil wrap, used previously, would present an unnecessary radiation hazard as a result of its high cross section for thermal neutrons. Immediately after activation the samples were refrozen, unwrapped, and then extracted while solid. Thus, throughout the sample preparation, activation, and extraction procedures, little or no photo-induced addition reactions would be expected.

The $^{127}\text{I}(n,\gamma)^{128}\text{I}$ induced yield of iodine in 1-pentene, trans-2-pentene, and cis-2-pentene were determined as a function of I_2 concentration. The results are tabulated in Table XVIII and represented graphically in Fig. 32. It was found that the organic yields of 1-pentene and cis-2-pentene were the same within experimental error and, that the trans-2-pentene yields were slightly lower than the corresponding 1-pentene and cis-2-pentene yields.

The organic yields of 1-pentene as a function of added CH_3I were then determined to test for any thermal contribution to the observed organic yields in the I_2 -1-pentene system. Of the three olefins used, 1-pentene possesses the fastest rate of thermal iodine addition¹²², and was, therefore, selected as the system for this comparison.

Since CH_3I would not be expected to react thermally, with the various olefins studied the radiative neutron capture induced organic yields of dilute CH_3I -1-pentene solutions would be expected to reflect the organic yield in an iodine-1-pentene system in the absence of any thermal reactions and iodine scavenger effects. Thus, if there exists no contribution by thermal processes to the observed organic yields in very dilute iodine-olefin systems (where scavenger effects would be expected to be negligible)

TABLE XVIII

Radiative Neutron Capture Induced Yields of ^{128}I in Various
 C_5 Isomers as a Function of Additive Concentration

<u>Additive</u>	<u>Concentration</u>	<u>Organic Yield</u>			
		<u>Pentane</u>	<u>1-pentene</u>	<u>trans-2-pentene</u>	<u>cis-2-pentene</u>
I_2	4.8×10^{-2}				29.02
					29.11
					32.13
					29.19
					29.86
I_2	1×10^{-2}		36.78	31.58	40.88
			38.35	31.61	42.63
			40.25	32.47	37.41
			39.03	32.18	38.50
			38.60	31.96	39.86
I_2	1×10^{-3}	39.39	46.58	38.57	46.55
		40.45	47.82	41.97	48.26
		41.88	44.66	38.42	49.18
		40.88	43.71	35.02	42.90
			45.69	38.50	46.72
I_2	1×10^{-4}	45.42	49.30	45.77	58.73
		45.54	46.34	44.74	54.85
		50.65	48.48	43.46	56.79
		42.07	47.68	44.66	
			47.95		

TABLE XVIII (cont.)

Additive	Concentration	Pentane	1-pentene	trans-2-pentene	cis-2-pentene
I ₂	5 x 10 ⁻⁵		53.35		
			52.54		
			55.76		
			53.88		
I ₂	1 x 10 ⁻⁵	48.53	54.05	54.04	60.66
		54.62	51.95	51.41	60.03
		47.95	55.87	64.26	60.30
		55.91	58.60	64.21	57.83
			55.12	61.71	59.71
				59.36	
				59.17	
I ₂	5 x 10 ⁻⁶			69.82	86.39
				66.84	80.52
				69.78	88.66
				73.67	77.99
				66.20	75.07
					41.49
I ₂	1 x 10 ⁻⁶	86.52	81.37	74.50	66.97
		88.51	66.69	59.68	71.82
		90.45	71.43	73.39	90.05
			88.59	89.55	91.73
				92.99	91.83
				90.46	85.24
				65.24	
				59.82	
CH ₃ I	1 x 10 ⁻¹	53.28			
		54.58			
		57.65			

TABLE XVIII (cont.)

Additive	Concentration	Pentane	1-pentene	trans-2-pentene	cis-2-pentene
		61.62			
		56.78			
CH ₃ I	1 x 10 ⁻²	56.55			
		57.39			
		58.11			
		58.44			
		58.56			
		59.17			
		59.91			
		62.78			
		58.86			
CH ₃ I	1 x 10 ⁻³	56.55			
		60.00			
		60.52			
		63.53			
		64.37			
		66.11			
		62.15			
CH ₃ I	1 x 10 ⁻⁴		57.80		
			59.95		
			61.91		
			62.73		
			63.30		
			65.13		
			62.48		

TABLE XVIII (cont.)

Additive	Concentration	Pentane	1-pentene	trans-2-pentene	cis-2-pentene
CH ₃ I	1 x 10 ⁻⁵		54.95		
			56.15		
			61.76		
			61.92		
			64.51		
			70.52		
			72.06		
			<u>63.12</u>

Figure 32. $^{127}I(n,\gamma)^{128}I$ induced organic yields in pentane and various pentene isomers as a function of I_2 or CH_3I concentration.

the radiative neutron capture induced yields of iodine in both the dilute CH_3I -olefin and I_2 -olefin systems would be expected to be the same.

The experimentally determined organic yields obtained in the CH_3I -1-pentene system as a function of the methyl iodide concentration are presented in Table XVIII and compared with the I_2 -1-pentene system in Fig. 32. After correction for the reported¹²³ 1.09% failure to bond rupture for the CH_3I , the CH_3I + 1-pentene organic yields were found to ca. 3 per cent higher than the corresponding I_2 + 1-pentene organic yields at 1×10^{-5} mole fraction added I_2 or CH_3I . The slightly lower yields for the I_2 + 1-pentene system can be attributed to the scavenging effect of the small amount of I_2 present; as comparison of the organic yields (and the trend of the yields with concentration) of the two systems at even lower additive concentrations suggest that they are identical for infinitely dilute solutions, as would be expected if there was no contribution to the observed I_2 + 1-pentene yields from thermal processes. However, the extremely low activities and radiolytic damage accompanying the longer irradiation times (~ 1 min.) preclude any accurate experimental values below 1×10^{-5} mole fraction additive.

The ^{128}I organic yields in the I_2 + pentane system, as a function of iodine concentration, were determined for comparison with the corresponding yields obtained in the pentene systems. The results of this study are also reported in Table XVIII and compared with the pentene systems in Fig. 32. The ^{128}I organic yields were consistently lower than the

corresponding pentene values and showed a smaller dependence on added iodine (scavenger) concentration. This smaller dependence on scavenger concentration indicates the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ induced organic yields in the pentane system are less dependent on diffusive radical reactions than those in the unsaturated pentene systems.

The most important information obtained from the study of the organic yields in these varied C_5 isomers is the great similarity in the observed yields under identical conditions. Although the four C_5 isomer studied possess widely varying thermal reactivities with molecular iodine, varying from essentially zero to nearly complete addition in one hour, the radiative neutron capture induced yields vary less than 10 per cent over the entire concentration range studied. However, this information is not particularly useful in terms of any mechanistic interpretations; but, merely reflects the high energy nature of the nuclear activation process.

The higher pentene yields do suggest, however, that the more thermally reactive double bond possessed by these isomers, also exhibits a greater reactivity toward the activated iodine species. The slightly smaller values obtained for the organic yields of the trans-2-pentene isomer could be the result of increased steric inhibition to attack at the position of the double bond by the reactive iodine species or compared to the 1-pentene and cis-2-pentene isomers. The importance of steric factors in the inhibition of $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ induced yields has been previously demonstrated in halocarbon systems.¹²⁵

Product Distributions

As discussed previously, the organic yields of a system as a function of various parameters are insufficient, by themselves, for any adequate interpretation of the mechanism of product formation. As in any type of chemical reaction, it is essential that the final reaction product or products are known before any reasonable consideration can be given to the mechanism of their formation. Therefore, the I_2 + pentane, CH_3I + 1-pentene and I_2 + 1-pentene, cis-2-pentene, and trans-2-pentene systems were analyzed by radiogas chromatography in order to identify and measure the relative quantities of the various products formed by the nuclear activation of ^{127}I in these systems. With the exception of increased irradiation times, the preparation and irradiation of the various systems for product analyses was identical to the procedures employed for the organic yield samples.

The qualitative and quantitative product analyses for the various systems studied were determined as functions of additive (I_2 or CH_3I), additive concentration, and irradiation time. The product distributions obtained for the various C_5 isomers as functions of these parameters are tabulated in Table XIX. The yields of the individual products are reported relative to the total organic activity detected. The qualitative identification of the saturated and unsaturated C_1 - C_5 iodides and the relative abundances of these products were determined by the radiogas chromatography procedures as discussed in Chapter III.

TABLE XIX

Relative Yields^a of Organic ^{128}I Products Formed by the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ Activation
of Iodine in Solutions of Various C_5 Hydrocarbon Isomers^b

Isomer	I_2 mole fraction	Irrad. Time				<u>1-</u> and <u>n-</u>	<u>1-</u> and <u>n-</u>			2- and 3-	1-	CH_2I_2
			CH_3I	$\text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{I}$	$\text{C}_3\text{H}_7\text{I}$	$\text{C}_3\text{H}_7\text{I}$	$\text{C}_4\text{H}_9\text{I}$	$\text{C}_5\text{H}_9\text{I}$	$\text{C}_5\text{H}_{11}\text{I}$	$\text{C}_5\text{H}_{11}\text{I}$	
Pentane ^d	1×10^{-2}	10 min.	6.4	2.0	13.7	1.8	12.3	3.1	0.8	34.8	25.0	--c
	1×10^{-3}	10 min.	11.2	3.4	8.2	1.7	9.6	3.1	2.3	30.1	27.8	--c
1-pentene ^d	1×10^{-3}	10 min.	5.0	4.6	10.5	0.9	7.7	2.8	3.7	35.3	27.1	2.6
	1×10^{-2}	10 min.	5.7	4.4	13.3	2.2	4.8	5.5	6.1	23.6	34.2	--c
	1×10^{-2}	30 sec.	7.4	6.3	8.8	0.8	6.3	5.5	5.3	23.8	31.6	4.4
	d	10 min.	40.4	2.6	5.2	--c	3.9	--c	--c	14.6	10.6	20.8
	e	10 min.	28.1	3.7	6.8	1.5	5.9	2.4	2.9	24.7	18.8	5.3
	f	10 min.	21.8	5.4	10.1	1.0	6.3	2.8	4.0	18.6	24.9	5.1
<u>trans</u> -2-pentene	1×10^{-3}	10 min.	21.0	4.1	11.3	1.0	8.0	5.4	--c	38.9	6.3	4.1
	1×10^{-2}	10 min.	17.3	4.2	10.7	2.1	6.8	1.5	2.2	41.7	10.9	2.0
	1×10^{-2}	30 sec.	21.6	4.2	11.1	1.6	4.7	5.3	--c	34.5	6.3	7.2
<u>cis</u> -pentene	1×10^{-3}	10 min.	17.2	3.9	10.5	2.8	7.9	2.3	2.6	37.0	12.1	3.7
	1×10^{-2}	10 min.	21.1	4.7	10.6	1.1	5.8	--c	--c	43.8	12.9	--c
	1×10^{-2}	30 sec.	25.9	4.7	10.3	1.1	7.4	5.2	--c	31.1	4.3	6.6

a Expressed as the percent total organic activity.

c no peak detected.

b All irradiations performed at 25° C in carbon paper wrapped ampoules.

d reference 75.

As shown in Table XIX the 128 product distributions for the various C_5 isomers exhibit considerable differences from isomer to isomer, particularly with respect to the relative quantities of methyl and the various C_5 iodides. The product distributions of the cis and trans-2-pentene isomers are, however, identical within experimental error as might be expected.

Assuming that all positions were equally liable to attack by the reactive iodine species one would then expect a statistical distribution of the observed 1-, 2-, and 3-iodopentanes and/or pentenes. In this case the relative product distributions for the C_5 iodides would be 2:1:2 for the 1-, 3-, and 2-iodo products respectively. As the 2- and 3-iodopentanes were not separated in this study then the observed relative product distributions assuming a statistical distribution, would be 1.5:1 for the combined 2- and 3-iodopentanes and the 1-iodopentane, respectively.

Examining of experimental data in Table XIX, the values for the relative product distributions for combined 2- and 3-iodo products and the 1-iodo product were found to be ca. 1.4, 0.7, 7.2, and 5.8 for pentane, 1-pentene, trans-2-pentene, and cis-2-pentene respectively. Thus, the I_2 + pentane system possesses a nearly statistical distribution of the respective C_5 iodides as would be expected due to the uniform bonding throughout this molecule. However, the 1- and 2-pentene isomer exhibit considerable deviation from a statistical distribution of iodination of the respective pentene molecules, with the 1-pentene isomer favoring iodination at the 1-position and the 2-pentene isomer favoring

iodination at the 2- and/or 3-positions. This is precisely the expected result if the respective pentene isomers possessed an internal chemical selectivity towards attack by the reactive iodine species at the position of the double bond.

The greater CH_3I yields observed for the 2-pentene isomers over that found for 1-pentene and pentane systems could be the result of cleavage of the carbon to carbon single bond containing the methyl group adjacent to the double bond with the subsequent attachment of the attacking iodine species, contained in the activated complex, to the methyl radical produced. The lower total C_5 iodide yields for the 2-pentene isomers as compared to the pentane and 1-pentene systems would seem to support this hypothesis.

Comparison with Radiolysis Produced Products

The currently accepted hypothesis used to account for the chemical distribution of the active atoms produced by the nuclear activation is the autoradiolysis theory proposed by Geissler and Willard.⁴⁴ This hypothesis is based upon the observed similarity between the yields of radioactive products formed either by neutron capture in the system: aliphatic iodide + iodine + pentane, or by radiolysis of the same system tagged with $^{131}\text{I}_2$ with ^{60}Co γ -rays.⁴⁴

In order to test the validity of the "autoradiation hypothesis" in describing the observed ^{128}I product distributions in our systems, the

^{131}I product distributions produced by radiolytic processes in similar systems, are required for purposes of comparison with the product distributions resulting from the nuclear activation process. Therefore 1-pentene, trans-2-pentene, and cis-2-pentene samples containing 1×10^{-3} mole fraction of ^{131}I tagged molecular iodine were prepared for irradiation. These samples were then irradiated in the "lazy susan" of the TRIGA reactor for a period of two hours, during this time they received an accumulated γ -dose of 3.6×10^{19} e.v. g^{-1} per sample. Little or no ^{132}I , produced by the nuclear activation of ^{131}I in the reactor, would be expected because of the extremely small quantity of ^{131}I in the sample (~ 1 mCi or $< 4 \times 10^{-11}$ moles) and the small thermal neutron cross section of 0.7 barns for the ^{131}I . Thus, after allowing ≥ 4 hours for the ^{128}I produced in these samples to decay, the only labeled products remaining would be the desired ^{131}I labeled products produced by the γ -radiolysis during the sample irradiation.

The results obtained from the radiogas chromatographic analyses of the respective I_2 (^{131}I)-pentene systems are reported in Table XX and compared with the corresponding ^{128}I product distributions. For the purposes of comparison with the ^{131}I labeled radiolysis products the ^{128}I product distributions obtained in the short irradiation time, high iodine scavenger concentration systems were chosen, as they would be expected to possess the smallest contribution to the ^{128}I products formed by the accompanying radiolysis of the sample.

TABLE XX

Comparison of the Radiolysis Produced ^{131}I Organic Products^a from the Reactor Irradiation of I_2 (^{131}I) Solutions of the Various C_5 Hydrocarbon Isomers with the Corresponding ^{128}I Products^a Produced by the Nuclear Activation of ^{127}I ^b

System	CH_3I	$\text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{I}$	$\frac{1-}{\text{C}_3\text{H}_5\text{I}}$ and $\frac{n-}{\text{C}_3\text{H}_5\text{I}}$	$\frac{1-}{\text{C}_3\text{H}_7\text{I}}$ and $\frac{n-}{\text{C}_3\text{H}_7\text{I}}$	$\text{C}_4\text{H}_9\text{I}$	$\text{C}_3\text{H}_9\text{I}$	$\frac{2-}{\text{C}_5\text{H}_{11}\text{I}}$ and $\frac{3-}{\text{C}_5\text{H}_{11}\text{I}}$	$\frac{1-}{\text{C}_5\text{H}_{11}\text{I}}$	CH_2I_2
Pentane- $^{131}\text{I}^{\text{c,h}}$	6.1	— ^d	14.1	— ^d	10.9	1.0	— ^d	51.0	17.0	— ^d
— $^{128}\text{I}^{\text{i,h}}$	6.4	2.0	13.7	1.8	12.3	3.1	0.8	34.8	25.0	— ^d
1-pentene- $^{131}\text{I}^{\text{f,h}}$	3.0	2.7	7.8	0.5	5.6	3.2	7.6	42.2	25.5	1.7
— $^{128}\text{I}^{\text{e,h}}$	7.4	6.3	8.8	0.8	6.3	5.5	5.3	23.8	31.6	4.4
cis-2-pentene- $^{131}\text{I}^{\text{f}}$	9.3	0.6	5.2	— ^g	4.0	0.8	— ^g	58.3	15.6	6.3
— $^{128}\text{I}^{\text{e}}$	25.9	4.7	10.3	1.1	7.4	5.2	— ^g	31.1	4.3	6.6
trans-2-pentene- $^{131}\text{I}^{\text{f}}$	10.1	— ^g	4.9	— ^g	4.3	1.3	— ^g	60.8	15.8	1.4
— $^{128}\text{I}^{\text{e}}$	21.6	4.2	11.1	4.2	4.7	5.3	— ^g	34.5	6.3	7.2

TABLE XX (cont.)

- a Expressed as per cent of total organic activity detected.
- b All ^{128}I organic yields determined with 1×10^{-2} mole fraction of I_2 present and 30 sec. irradiation time to minimize any radiolytic contributions.
- c Obtained from ref. 44.
- d No peak reported.
- e 1×10^{-2} mf I_2
- f 1×10^{-3} mf I_2 (^{131}I)
- g No peak detected.
- h Reference 75
- i 1×10^{-2} mf I_2

The comparison of the ^{131}I radiolytic product distributions with the ^{128}I product distributions from the (n,γ) activation of ^{127}I in Table XX shows two major differences between the relative quantities of the various products produced by the dissimilar processes. The major difference being a considerable decrease in the total quantity of the various observed fragmentation products ($\text{C}_4\text{-C}_1$ iodides) for the radiolysis produced products as compared to the ^{128}I product distributions, produced by the nuclear activation. In addition, the C_5 iodides produced by the radiolysis process tend to favor a more statistical distribution over those produced by the nuclear activation.

The increase in fragmentation products observed for the (n,γ) activation would suggest that the product formation proceeds through a higher energy process than the corresponding radiolysis processes. While the increased randomness in the formation of the various C_5 iodide isomers for the radiolytic process could be the result of decreased chemical selectivity in the formation of radicals by ionizing radiation and/or rearrangements occurring after the formation of the various hydrocarbon radicals.

These differences between the product distributions of the organic iodides produced by radiolysis and the radiative neutron capture of ^{127}I , clearly indicate that the "autoradiation hypothesis" does not adequately explain the total product distributions for the (n,γ) activation of iodine in the various pentene systems studied. Therefore, other processes must account, either partially or completely, for the formation of the

observed products in these systems.

Discussion

As discussed previously, the (n,γ) activation of ^{127}I produces chemical effects which are not only profound but quite varied in character. The energy released in the transformation manifests itself in the kinetic energy of the particle formed, in electromagnetic radiation, in ionization, and in electronic and other excitations. Most of this energy is dissipated in the surrounding medium, along tracks of primary and secondary particles, and produces normal radiolytic changes in the system. However, the iodine ion or atom incorporating the transformed nucleus is in itself a highly reactive entity and should not be neglected in an overall consideration of the mechanism or mechanisms of final product formation. Thus the number of reactive species capable of participating in the formation of products are many and varied.

The "autoradiation hypothesis" attributes the formation of all products to reactions between the activated halogen and solvent radicals which are formed by the localized radiation chemistry induced by the internal conversion and Auger electrons emitted by the recoil atoms; thereby, completely neglecting any possible contribution to the overall product formation by the potentially reactive iodine atom or ion produced by the nuclear transformations.

Two other possible processes, not considered by the "autoradiation

hypothesis", are displacement reactions whereby the iodine atom or ion replaces a hydrogen atom or radical from a solvent molecule in a bimolecular process by virtue of its excess kinetic energy and the formation of products through ion-molecule reactions with ions produced by the vacancy cascade associated with the internal conversion of the activated iodine and/or the subsequent neutralization of this highly charged specie by charge exchange with the surrounding media.

Gas phase studies have shown^{38,39,50,126} the bimolecular replacement reactions of species attacked by ^{128}I to result in total organic yields of only a few percent, except in CH_4 systems. Thus this type of process would not be expected to contribute, appreciably to the total yields observed in condensed systems unless the probability for this type of reaction is greatly altered by the change in phase. The reactions of iodine atoms at elevated temperatures with various saturated and unsaturated hydrocarbons do not lead to the production of organic iodides but instead produce HI by a hydrogen abstraction mechanism.^{106,121,127} In addition, the studies^{101,122} of the photo and thermochemical reactions of iodine atoms and molecules in the various liquid pentenes of interest reveal no formation of the various mono-iodo products found in this study. On the basis of the accumulated evidence presented above the formation of the organic products observed in this study via bimolecular displacement reactions would appear to be unimportant.

In the I_2 + pentene liquid systems employed in this study, the highly

charged iodine atom produced by the nuclear activation process will first share its charge with the molecule to which it is attached and then abstract electrons from the surrounding solvent molecules producing considerable ionization and fragmentation of these molecules in close proximity to the activated iodine. During this stage chemical combination would be improbable between the activated iodine and the charged solvent molecules, and will occur only after the charge density has been reduced by neutralization or by diffusion of the ions away from each other. Because of their lower mass, protons dissociated from the solvent molecules by this process would be expected to diffuse further than any other groups under the action of the field, so that the center of the ionic cluster containing the activated iodine would be rich in hydrogen deficient species with which the active atom may react. This type of mechanism, previously advanced by Mia and Shaw⁴⁷ to explain the product distributions associated with neutron capture processes in liquid bromoethane systems, could be expected to produce both ionic and radical iodine and hydrocarbon precursors leading to the eventual organic combination of the activated iodine species.

In a recent study of the ion-molecule reactions of various simple olefins, Henis¹²⁸ was able to account for the observed products distributions in all of the reactions studied by assuming the following selection factors:

1. no significant rearrangement of parent ions;
2. positive charge located at a secondary carbon in the parent ion;

3. site of the unpaired electron may be considered the active or attacking site on the ion;
4. addition occurs at either double-bond site (steric factors may favor primary sites when they are available);
5. fragmentation involving more than one bond is not possible;
6. fragmentation occurs most favorably at the tertiary carbon in the intermediate;
7. loss of CH_3 radicals generally will not occur (possibly due to unfavorable thermo-chemistry).

Assuming these qualitative rules also apply to ion-molecule reactions between iodine atoms or ions with olefin ions or atoms, respectively, the observed product distributions found for the (n, γ) induced reactions of ^{128}I in the C_5 pentene isomer could be accounted for. In particular rules 3 and 4 would account for the preferential addition of iodine at the double bond site and rule 5 for the extremely small quantities of di-iodo products observed. Although rule 7 conflicts with the large quantities of methyl iodide found in our systems, particularly for the 2-pentene systems, the potentially higher energy nature of the ion-molecule reactions in our systems could account for this violation. In fact, the high $\text{CH}_3\text{I}^{128}$ yields obtained in the 2-pentenenes show a strong preference for loss of CH_3 radicals adjacent to the double bond. It would therefore seem that the ionization associated with the nuclear activation of the iodine leads to subsequent ion-molecule reactions between the activated iodine and the solvent or its fragmentation products; thereby, accounting for the differences found between products distributions produced by nuclear activation and radiolytic processes found in this study.

CHAPTER VII
IODINE ORGANIC YIELDS IN HYDROCARBON MATRICES
AS AN INDICATION OF CLUSTERING, COMPLEXING,
AND FRACTIONAL CRYSTALLIZATION AT 77° K

Employing the organic yields of the $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$ and the $^{80}\text{Br}^m$ (IT) ^{80}Br reactions in polycrystalline n-hexane at 77° K, Iyer and Willard¹³⁰ suggested that organic yields induced by nuclear transformations could give useful information about the state of aggregation of a solute and its tendency toward complexing. By investigating three structurally different hydrocarbons, the influence of varied repurification procedures on the organic yields, the effect of iodine concentration, the influence of additives, and nuclear activation on the organic yields was determined. The main purpose of this study was to look for I_2 concentration ranges where the iodine organic yields were constant, which would indicate uniform clustering of iodine in the hydrocarbon matrix. In addition, an accurate knowledge of the effects of varying iodine concentration on the organic yields of iodine, produced by various nuclear transformations, in polycrystalline hydrocarbon matrices is required for the successful application of the freeze-thaw technique¹²⁹ developed in this laboratory.

Influence of Additives and Solvent Repurification

Phillips research-grade hydrocarbons (99.83 to 99.99 quoted mole %

purities) and Phillips technical grade (95 mole % purity) were used. The research grade hydrocarbons were used as received and/or after rigid in-house repurification. All technical grade n-hexane was repurified before use.

The rigid in-house repurification consisted of stirring with concentrated H_2SO_4 for 48 hours, washing, drying over silica gel, and distilling, using a 12 section bubble-cap distillation column, taking the middle fraction. The hydrocarbon solvents were purged with helium for 30 - 90 sec. to remove carbon dioxide. All samples, prepared from purged solvent, were prepared within 10 min. after purging and were then degassed 5 times, regardless of prior treatment.

The solid state organic yields of ^{128}I and ^{130}I , induced by radiative neutron capture and isomeric transition reactions, were shown to be extremely sensitive to trace amounts of some impurities (See Table XXI). It was found that repurification of Phillips research grade hydrocarbons lowered the solid state organic yields. However, the impurities could not be detected by gas chromatography, using an Aerograph Model 1520 with a flame ionization detector having a sensitivity of 10^{-12} g. or by activation analysis in either the Phillips research grade, used as received, or the repurified Phillips research grade hydrocarbons.

Carbon dioxide is known to be an impurity present in many solvents. Thus, it was concluded that carbon dioxide was the most probable impurity that was removed by purging the hydrocarbon solvent with helium immediately prior to sample preparation. It was necessary to use this procedure since

the normal degassing technique fails to completely remove all the carbon dioxide and other volatile impurities that may be present due to the low temperatures of the liquid nitrogen used during the degassing on the vacuum line. The removal of carbon dioxide was shown to have a significant effect on the solid state organic yields, particularly for mole fractions of iodine of 6×10^{-5} or lower. Repurification and distillation just prior to sample preparation could remove substantial quantities of dissolved CO_2 and other gaseous impurities from the prepared sample.

After the removal of carbon dioxide, the solid state organic yields were the same within experimental error, for both the repurified and non-repurified Phillips research grade hydrocarbons as shown in Table XXI at dilute I_2 concentrations.

Table XXII shows the results of the various methods employed, both physical and chemical, to remove carbon dioxide from n-hexane. The physical methods of carbon dioxide removal attempted were, bubbling helium through the solvent, distillation, and degassing the n-hexane solution in the liquid state using a degassing apparatus described by Randeau.¹³¹ As can be seen in Table XXII, helium bubbling prior to sample preparation appears to give the most consistent results.

In addition to the H_2SO_4 treatment, outlined previously, chemical removal of carbon dioxide attempted by various treatments with solid and aqueous sodium hydroxide gave poor and inconsistent results as shown in Table XXII. These poor results with sodium hydroxide could be attributed to the deactivation of the sodium hydroxide with respect to reaction with

TABLE XXI

Organic Yields Induced by the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ Process at Various Concentrations of I_2
 in Polycrystalline n-hexane Using Various Repurification Procedures
 on Phillips Research and Technical Grade Reagent

mf I_2 $\times 10^4$	Research Grade ^a After Repurification	Research Grade ^a Used as Received After He Bubbling	Research Grade ^a Used After Repurification and He Bubbling	Tech. Grade ^b Used After Repurification
87.4	0.65 1.90 0.63 0.27 <hr/> avg. 0.87			
65.0	0.30 0.27 0.51 0.60 <hr/> avg. 0.42			
34.0				0.48 0.71 0.69 0.74 <hr/> avg. 0.66

TABLE XXI (cont.)

mf I_2 $\times 10^4$	Research Grade ^a After Repurification	Research Grade ^a Used as Received After He Bubbling	Research Grade ^a Used After Repurification and He Bubbling	Tech. Grade ^b Used After Repurification
23.6	1.41 0.82 0.98 <hr/> avg. 1.07	0.81 0.67 0.81 <hr/> avg. 0.76		
18.4			1.28 0.65 0.73 <hr/> avg. 0.89	
10.0	4.45 4.67 2.09 <hr/> avg. 3.74	1.30 1.67 1.76 <hr/> avg. 1.58	1.83 2.81 1.78 1.23 <hr/> avg. 1.91	4.30 3.28 2.30 <hr/> avg. 3.29
5.0	4.41 4.78 5.85 <hr/> avg. 5.01	2.84 2.67 <hr/> avg. 2.76	2.73 3.81 4.22 <hr/> avg. 3.59	

TABLE XXI (cont.)

mf I ₂ x 10 ⁴	Research Grade ^a				Tech. Grade ^b	
	After Repurification	Used as Received After He Bubbling	Used After Repurification and He Bubbling		Used After Repurification	
2.6			5.48			
			7.30			
			7.47			
			avg. 6.75			
1.3			7.93			
			11.33			
			9.79			
			avg. 9.68			
1.0	14.19	10.19	7.54		8.06	
	14.30	8.78	9.00		8.16	
	9.57	9.70	7.02		6.04	
	15.48		10.29			
	13.45	avg. 9.56	avg. 8.46		avg. 7.42	
	9.64					
	9.60					
	8.71					
	13.48					
	13.05					
	11.39					
	11.87					
	10.03					

TABLE XXI (cont.)

mf I_2 $\times 10^4$	Research Grade ^a After Repurification	Research Grade ^a Used as Received After He Bubbling	Research Grade ^a Used After Repurification and He Bubbling	Tech. Grade ^b Used After Repurification
	19.22 14.81 14.56 — avg. 13.56			
0.76			13.44 17.23 — avg. 15.33	
0.50	29.85 28.01 — avg. 28.96	16.76 13.57 17.40 14.29 — avg. 15.51	13.06 10.91 13.64 — avg. 12.53	28.27 28.13 29.28 17.93 — avg. 25.90
0.10	38.33 17.23 37.98 38.29 39.69 — avg. 34.30	29.10 30.93 29.82 26.85 — avg. 29.18	13.51 14.22 8.42 — avg. 12.05	29.78 33.22 34.60 35.63 36.03 — avg. 33.77

TABLE XXI (cont.)

mf I ₂ x 10 ⁴	Research Grade ^a		Research Grade ^a		Tech. Grade ^b	
	After Repurification		Used as Received After He Bubbling		Used After Repurification	
0.050		53.14				
		31.29		41.35		
		49.47		30.00		
		35.80		32.45		
		30.43				
			avg.	38.57		
	avg.	40.03				
0.010		61.03		37.25		33.67
		42.25		31.91		50.00
		46.60		38.10		46.51
		31.51		42.81		
					avg.	43.39
			avg.	37.53		
	avg.	45.35				

Footnotes:

a Phillips research grade n-hexane 99.99 mole percent quoted purity.

b Phillips technical grade n-hexane 95.00 mole percent quoted purity.

TABLE XXII

Comparison of the Relative Abilities of Various Techniques of
 CO_2 Removal from Liquid n-Hexane Based on Organic Yields
 Resulting from the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ Process in
 Polycrystalline n-Hexane^a

Process used to remove CO_2	O.Y.	Average
Degassed liquid ^b	11.23 19.26 16.35 17.44 13.56 16.02	16.47
Boiling of liquid	15.50 11.99 16.39 12.93	14.20
Distilled with NaOH_s	12.27 11.39 9.60 10.16	10.86
Shaken with NaOH_s	12.64 16.05 12.18 17.49	14.59
Distilled and used immediately ^c	13.54 14.17 12.70	13.47
Repurified and used immediately ^c	13.48 13.05 11.39 11.87 10.03 14.81 14.56	12.74

TABLE XXII (cont.)

Process used to remove CO ₂	O.Y.	Average
Repurified and shaken with NaOH _s	9.40 9.94 9.26 12.63	10.32
Repurified and distilled over NaOH _s	9.18 11.78 13.22 7.35	10.38
Shaken with NaOH _s for 48 hours	13.00 23.62 15.65 9.87	15.54
Shaken with aqueous NaOH	19.59 10.08 15.36 13.75	14.70
Helium bubbled	10.19 8.78 9.70 7.54 9.09 7.02 10.29	8.94

- a Phillips research grade n-hexane containing 1×10^{-4} mf I₂.
- b Use of apparatus described in reference 50.
- c Samples were prepared with 10 min. after distillation.

carbon dioxide by coating the surface of the NaOH pellets with a film of hydrocarbon.

As shown in Table XXIII carbon dioxide does not have a significant effect on the liquid state organic yields. This experimental result indicates that CO_2 probably is involved in the structure of the halogen-hydrocarbon matrix at 77°K and that CO_2 is not strongly associated as a complex at 298°K .

Depicted in Tables XXIV and XXV are data that indicate that the iodine organic yields are extremely sensitive to small concentrations of some impurities. Table XXIV represents a study to specifically determine the influence of additives which might be common laboratory contaminants. Carbon dioxide and acetone tend to raise the organic yields more than the other additives in n-hexane. Table XXV represents a study to determine the influence of additives which might complex with iodine and/or cyclohexane or influence the structure of the halogen-hydrocarbon matrix at 77°K .^{132,133} Ethanol and the hydrocarbons used had no appreciable effect on the organic yields; whereas, heptanoic acid and benzene slightly lowered the organic yields. The presence of alkyl iodide additives resulted in higher ^{128}I organic yields. Perhaps alkyl iodides complex⁴⁸ with the I_2 and result in smaller clusters in the organic matrix; while, benzene and heptanoic acid apparently enhanced fractional crystallization within the organic matrix. The data suggests that small polar molecules with an electropositive carbon give larger increases in solid state organic yields, i.e. $(\text{CH}_3)_2\text{CO}$, CO_2 , and the alkyl halides, than do

TABLE XXIII

The Effect of CO₂ Removal on ¹²⁷I(n,γ)¹²⁸I Induced
 Organic Yields in Liquid Phillips Research
 Grade n-Hexane at 298° K Containing
 1.08×10^{-4} mf I₂

Comments	O.Y.	Average
He bubbled to remove CO ₂	45.56	46.17
	46.65	
	44.01	
	48.45	
Used as received	48.27	46.95
	48.53	
	45.10	
	45.92	

TABLE XXIV

The Effects of Additives on the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ Induced
Organic Yields in Polycrystalline n-Hexane

mf I_2 $\times 10^{4a,b}$	Additive	mf Additive $\times 10^4$	O.Y.	Average
1.0	CO_2	Saturated	5.58 8.74 12.86 18.37 16.21	12.35
1.0	H_2O	14.1	13.76 11.59 11.77	12.36
10.0	H_2O	10.0	1.28 3.28	2.28
1.0	H_2SO_4	4.77	13.46 12.56 11.96 13.11	12.77
10.0	HNO_3	10.0	1.49 2.05 1.93	1.82
10.0	NH_3	10.0	1.35 1.19 2.86	1.80
1.0	$(\text{CH}_3)_2\text{CO}$	3.47	39.40 25.79 28.74	31.31

a 1×10^{-4} mf I_2 in Phillips research grade repurified n-hexane.

b 1×10^{-3} mf I_2 in Phillips research grade n-hexane used as received after He bubbling.

TABLE XXV

Organic Yields of the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ Reaction in Polycrystalline
Cyclohexane at 0.55 Mole Percent I_2 in the Presence
of 0.55 Mole Percent Added Impurity^{132,133}

Additive	O.Y.	Average
None	3.8 4.1	3.9 ± 0.2
Ethanol	5.8 4.2 3.9	4.5 ± 0.7
2-Methyl Pentane	3.6 4.0	4.3 ± 0.6
2,4-Dimethyl Pentane	4.0 3.7 1.8	3.2 ± 0.6
2,2,4-Trimethyl Pentane	4.4 4.2 4.0	4.2 ± 0.2
Benzene	1.5 1.9 1.9	1.8 ± 0.2
Heptanoic Acid	2.6 2.6 2.9	2.7 ± 0.1
n-Nonane	3.0 2.4 1.8	2.4 ± 0.6
1-Iodoheptane	12.1 10.6	11.4 ± 0.8
n-Propyl Iodide	22.5 18.4 14.5	18.4 ± 2.7
2-Propyl Iodide	14.6 16.4 13.6	14.9 ± 1.0

the larger non-polar molecules.

This increase in solid state organic yields, by these small polar molecules, can be attributed to the formation of charge transfer complexes, and other types of intermolecular non-bonding interactions between the iodine molecules and the additive. This interaction can possibly reduce the size of the iodine clusters until monomolecular dispersion of the iodine molecules in the polycrystalline hydrocarbon matrix is attained. The extreme sensitivity of the systems to impurities makes it difficult to obtain consistent experimental results. The principle uncertainty in the samples is believed to be the dissolved carbon dioxide content of the hydrocarbon. However, Fig. 33 indicates the solid state organic yields resulting from nuclear transformations of halogen atoms can give useful information about the relative impurity content of the hydrocarbon solvent.

The effects of impurities on raising the organic yields of halogens in alkyl halides and halogens in hydrocarbons has been known for years. Since the repurification of research grade hydrocarbons (quoted purities greater than 99.8 mole percent) resulted in iodine organic yields lower than those of the untreated hydrocarbon, the preceding investigation of repurification procedure was required.

At 0.001 mole percent I_2 in untreated $n-C_6H_{14}$ the ^{128}I organic yields were 42%; however, if helium was bubbled through the hydrocarbon prior to sample preparation, the organic yields were reduced to 30%. If the hydrocarbons was stirred with H_2SO_4 for 48 hr., washed, dried, fractionally

Figure 33. Organic yields of ^{128}I vs. log mole fraction of iodine in various purities of polycrystalline n-hexane. Phillips research grade used as received, O; used after purging with helium, Δ; used after rigid repurification and purging with helium, □.

distilled, and then purged with helium, the solid state organic yields were about 12%. Figure 33 summarizes the effects of these repurification procedures on the ^{128}I organic yields in n-hexane as a function of I_2 concentration. As can be seen from Fig. 33, at I_2 concentrations greater than 0.01 mole percent I_2 , helium purging of the untreated research grade n-hexane and extensive repurification of the n-hexane followed by He purging resulted in similar organic yields. It is interesting to note that while rigorous repurification of n-hexane resulted in an organic yield plateau, similar but higher plateaus were observed for the untreated hydrocarbon and the helium purged hydrocarbon.

Since helium purging was obviously removing gaseous impurities, perhaps CO_2 and/or O_2 several tests were performed on the systems. At 1×10^{-4} mf I_2 , the ^{128}I organic yields in untreated n-hexane were 16.5%. Rigorous repurification and He purging resulted in a 9.5% organic yield. When the rigorously repurified hydrocarbon solutions were saturated with CO_2 gas, (Matheson Coleman Instrument Grade, quoted purity 99.99% min.) the organic yields were the same or higher than those in the research grade hydrocarbon. However, if the research grade hydrocarbon were treated with H_2SO_4 , washed, dried and distilled over NaOH pellets, the organic yields were reduced to only 10.4%. The above results suggest that CO_2 may be a main gaseous impurity. Since distillation over NaOH resulted in slightly higher organic yields than obtained by rigorous repurification and He purging, either He is more effective than NaOH for removal of CO_2 , or the He purging removes one or more gaseous impurities such as O_2 in addition to CO_2 .

Isotope Effects

One objective of this study was to determine whether the radiative neutron capture organic yields of ^{128}I and $^{130}\text{I} + ^{130\text{m}}\text{I}$ in the polycrystalline state were the same or different than the isomeric transition induced organic yields of ^{130}I . The (IT) organic yields would not a priori be expected to be greater than the (n, γ) organic yields due to the greater recoil energy of the (n, γ) process. If (n, γ) and (IT) induced organic yields were numerically different, the differences would be observed as changes in the organic yield with the length of time that isomeric transition processes were allowed to occur in the polycrystalline state prior to extraction. By varying the time of extraction and allowing the $^{130\text{m}}\text{I}$ (IT) ^{130}I processes to occur in the polycrystalline state for 90 minutes, Lambrecht¹³² found no changes in the ^{130}I organic yields. (See Table III.) In general the $^{130\text{m}}\text{I}$ (IT) ^{130}I organic yields were reported to be similar to the ^{128}I and ^{130}I organic yields obtained by the in-reactor technique. McCauley, et. al.¹³⁴ investigated the (n, γ) and (n,2n) iodine reactions in solid alkyl iodides, and concluded that the ultimate chemical fate of the radioactive nucleus is not dependent on the initial energy of the recoiling atom or on other variations which might be expected to result from different nuclear processes. This suggests that the solid state iodine organic yields are independent of isotope and mode of activation.

State of Aggregation of Iodine

Depicted in Fig. 34 are the results of the investigation of the $^{129}\text{I}(\text{n},\gamma)^{130}\text{I} + ^{130}\text{I}^{\text{m}}$, the $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ and/or the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ reactions in n-hexane, cyclohexane¹³² and benzene¹³⁵ as a function of iodine concentration. In the aliphatic hydrocarbons studied the ^{128}I organic yields extrapolated to about $55 \pm 3\%$ at zero mole fraction I_2 . The ^{128}I organic yields in benzene extrapolated to a somewhat higher value of $59 \pm 3\%$.¹³⁵ The organic yields would be expected to be somewhat dependent on the media. However, under the conditions of monomolecular dispersion, that the three structurally dissimilar hydrocarbons (benzene, cyclohexane and n-hexane) were found to show about equal preference for either organic or inorganic combination.

By comparison, Iyer and Willard¹³⁰ found that the $^{80}\text{Br}^{\text{m}}(\text{IT})^{80}\text{Br}$ organic yields at 77°K in n-hexane are also about 55% at concentrations of 0.002 mole percent Br_2 and below. However, in general, the solid state organic yields would not be expected to be similar for bromine and iodine isotopes at a given concentration in a common solvent.

In solid benzene the ^{128}I organic yields are rather constant at 59% from 0.001 to 0.1 mole percent I_2 .¹³⁵ In benzene monomolecular dispersion of I_2 would be expected to occur over an appreciable concentration range based on the donor-acceptor complexing of iodine in solid benzene.^{136,137} At 0.1 mole percent I_2 the organic yields decrease gradually to 11% at 8.7 mole percent I_2 indicating segregation of iodine during total crystallization. However, in cyclohexane and n-hexane the organic yields drop

Figure 34. Organic yields of various iodine isotopes vs. log mole fraction iodine in polycrystalline organic matrices. Iodine-128 in n-hexane, O; in cyclohexane, Δ; in benzene, □; Iodine-131 by (IT) only, Δ; by in reactor technique, Δ.

from 55% to regions of rather constant organic yields of 25% and 12%, respectively. The plateau regions for n-hexane and cyclohexane between 0.001 and 0.02 mole percent I_2 appear to indicate the formation of preferred cluster sized and/or similar numbers of iodine molecules at sites in the polycrystalline organic matrices.

Since the iodine organic yields in polycrystalline n-hexane and cyclohexane extrapolated to zero mole fraction I_2 are similar, the reactivity of iodine atoms for organic product formation is similar in the two hydrocarbons. Therefore the iodine organic yield plateaus at 25% and 12% for cyclohexane and n-hexane, respectively, indicate that the clusters of iodine molecules or numbers of iodine molecules at the various sites in the organic matrix are larger in n-hexane than in cyclohexane. Iyer and Willard¹³⁰ reported a constancy of bromine organic yields over an appreciable concentration range in polycrystalline n-hexane at 77° K. They suggested that the formation of $(Br_2)_n$ clusters appeared to be dependent upon a preferred size of bromine aggregate in the crystal lattice, rather than an equilibrium of the type $X_2 \rightleftharpoons (X_2)_n$ in solution.

The observed behavior of the organic yields beyond the plateau region in n-hexane and cyclohexane (concentrations greater than 0.02 mole percent I_2) may be explained by segregation of the iodine during total crystallization. This effect has been discussed previously.¹³⁸⁻¹⁴⁰

APPENDIX I^a

Program 1.

C Program 1
C
C
C This program integrates the peak of interest and the
C subtracts the background value (which is obtained from the
C first tape total) and then proceeds to compute the organic
C yields using these values.
C
C Compile using special subroutines so that paper tape may
C be read using the rcd routine and the presence of a record
C mark may be ascertained using the rtc routine
C
C Sense switch 1 on calls for channels on tape to be punched
C out
C
C Sense switch 2 on calls for the partial relisting of headings,
C starting with (scavenger) and ending with (mole fraction).
C
C Sense switch 3 off provides for a pause after each tape total
C
C To relist headings turn sense switch 2 on after the execu-
C tion of the pause provided by sense switch 3)
C
C Branch to (4911068) to enter bkg if other than the value on
C the first tape total. If this is used also branch to loca-
C tion (4910998) to enter the proper deck number in order to
C have the following tape total properly labeled.
C This will allow the order of org vs aq to be changed (i.e. if
C 0001 is entered the sum of the following tape will be labeled
C bkg, or if 0002 is entered the following sum will be labeled
C org, or if 0003 is entered the following sum will be labeled
C aq.
C
C Branch to (4909570) to have stored channel numbers punched
C on cards
C
C Branch to (4908456) to enter data group. (5 digits)
C
C Branch to (4910998) to enter deck number. (4 digits)

Program 1 (continued)

```

C
C   Header cards should contain the following-
C   First card - (1) no. of channels to be read (4 digits) (2)
C   the decay constant (a blank or + sign, a digit, a decimal
C   pt., and then 4 digits) (3) the no. of minutes the background
C   is to be divided by (a blank, 3 digits, and a decimal pt.)
C   Second card- number of totals to be taken from each tape.
C   (4) digits)
C   Third and following cards-channel numbers to be integrated
C   over (two 4 digit fields)
C
C
C   All branch statements providing for the entrance of data
C   calls for the data to be entered on the typewriter.
C
C
C   Dimension X(400), NA(15), NB(15), A(10), B(8)
C   DX = CDS(5.)
215 DX = .3003 + 0.0
C   DX = UNL(2991.)
C   DX = PAS(29728101.)
C   Read 13, itest, decay, tbkg
13  Format (14,F7.4, F5.0)
C   Decay = ((1.0)/(decay))
C   KD = 1
1  Read 5, NN
C   DO 10 I=1, NN
10  Read 11, NA(1), NB(1)
11  Format (214)
C   DO 500 I=1,400
500 X(I)=0.0
22  Type 33
33  Format (//6H date-, 10X,12H background-, 10X,9Hcounter-,10X,
19H voltage-,//37H irradiation facility-Omaha VA Triga,11X,
217H flux- 1.1*10**11,/)
400 Type 420
420 Format (//10H channels-, 6X,4H to-,6X,13H calibration-,//)
36  Type 55
55  Format(11H scavenger-,15X,10H additive-, 15X,8H amount-,10X,/,
17H phase-,15X,15H counting time-,10X,/,14H purification-,25X)
66  Type 77
77  Format(1H target-, 15X,8H amount-, 10X,/,8H source-,15X,18H
amount-,/,12H extraction-,/,10H comments-,/,15H mole fraction-,
230X, 9H isotope-,/)

```

Program I (continued)

```

102  I = 1
C
C   Tape read-in block
199  DO 212 I=1,
200  DX = PAS (11151101.)
      DX = RCD (51.)
      DX = CMP (11151101.)
      IF (DX) 191, 190, 191
191  Print 192
192  Format (25HCHAN missed, restart tape)
      Go to 300
190  DX = RTC(501)
      If(DX) 204, 201, 204
202  Control 102
      Control 108
      Type 240, 1, KD
240  Format (4HCHAN, 14,5H tape, 14,3h is)
      Accept 241, DZ
241  Format (F5.0)
      DX = PAS (12052020.)
      Go to 212
201  If (I -1) 202, 200, 202
204  DX = RTC(504.)
      If (DX) 220, 203, 220
203  ICK = GET(50330.) + 1.
      If (I -ICK) 210, 210, 210
C   Channel number from tape could be checked
210  DX = RCD(51.)
      DX = RTC(506.)
      If (DX) 202, 211, 202
211  DX = GET(50550.)
      Go to 212
220  DX = RTC(507.)
      If (DX) 230, 221, 230
221  DX = CMP(28150601.)
      If (DX) 222, 211, 222
222  DZ = GET(50660.)
      Go to 212
230  DX = CMP(28150901.)
      If (DX) 202, 231, 202
231  ICK = GET(50330.) +1.
      If (I -ICK) 232,232,232
232  DZ = GET(50850.)
212  X(1) = DZ
C
C

```

Program I (continued)

```

      If (sense switch 1) 703, 335
703 DO 704 I=1, itest, 8
704 Punch 705, X(I), X(1+1),X(1+2),X(1+3),X(1+4),X(1+5),X(1+6),
      X(1+7)
705 Format (8F 10.0)
      Pause
335 Continue
      DO 88 I=1, NN
      NLOW = NA(1)
      NHI=NB(1)
      B=0.0
      DO 40 J= NLOW, NHI
40    B=B+X(J)
88    Continue
340 Go to (4,2,3),KD
4    Bkg=B
      Bkg=((bkg)/(tbkg))
      KD=2
      Print 400, bkg
400 Format (5H bkg-,F7.0/)
      Go to 102
2    Org=B
      KD=3
      Go to 102
3    Aq=B
      Aq=((Aq)*(Decay))
      KD=2
15    OY=((org-bkg)/))org+aq)-2.*bkg))*100.
      Print 100, org, aq, oy
100 Format (//12H sample no.-,//10X,4HORG=,F10.0,/10X,4H aq=,
      F10.0,1//15X, 3HOY=F7.2)
      If(sense switch 3) 102,136
136 Pause
      If (sense switch) 44, 102
44    Print 420
      type 55
      Type 77
      Go to 102
300 Accept 5, KD
      Go to 102
5    Format (14,14,14,14)
317 Accept 6, bkg
6    Format (F7.0)
      Go to 102
      End

```

Program 2

C Program number 2
C
C
C This program utilizes 3 sums--the first and last sums being
C used to compute the compton edge correction for the integrated
C peak (2 ND sum)
C
C Extract NN channel sums from decks or tapes
C
C Compile using special subroutines so that paper tape may be
C read using the RCD routine and the presence of a record mark
C may be ascertained using the RTC routine
C
C Sense switch 1 on calls for channels on tape to be typed out.
C
C Send switch 2 on calls for the partial relisting of headings,
C starting with (scavenger) and ending with (mole fraction).
C
C Sense switch 3 off provides for pause after each tape total.
C
C To relist headings turn sense switch 2 on after the execution
C of the pause provided by sense switch 3)
C
C Branch to (4909474) To enter data group. (5 digits)
C
C Branch to (4911158) to enter deck number. (4 digits)
C
C Header cards should contain the following-
C First card- (1) No. of channels to be read (4 digits) (2)
C No of channels containing the peak (4 digits and a decimal pt.)
C (3) the sum of the no. of channels to be read on each side of
C the peak (4 digits and a decimal pt.) (4) decay constant (
C blank, a digit, a decimal pt., and then 4 digits)
C Second card- number of totals to be taken from each tape.
C (4digits)
C Third and following cards-channel numbers to be integrated
C over. (two 4 digit fields)
C
C
C
C All branch statements providing for the entrance of data
C calls for the data to be entered on the typewriter.
C
C
C

Program 2 (continued)

```

      Dimension X(400), NA(15), NB(15), A(10), B(8)
      DX = CDS(5.)
215  DX = .3003 + 0.0
      DX = PAS (29728101.)
      Read 13, itest, Q,P, decay
13   Format (14,2F5.0,F7.4)
      Decay=((1.0/decay))
      KD = 1
1    Read 5, NN
      DO 10 I=1, NN
10   Read 11, NA(1),NB(1)
11   Format(214)
      DO 500 I=1,400
500  X(I)=0.0
22   Type 33
33   Format (//6H date-, 10X,12H background-, 10X,9H counter-,
      10X, 19H voltage-, //37H irradiation facility - Omaha VA
      TRIGA, 11X, 217H flux- 1.1*10**11,/)
400  Type 420
420  Format (//0H channels)
55   Format (11H scavenger-, 15X,10H additive-, 15X,8H amount-,
      //,17H phase-,15X,15H, counting time-,10X//14H purification-,
      230X, 9H isotope-,//)
102  I = 1
C
C    Tape read-in block
199  Do 212 I = 1, itest
200  DX = PAS (11151101.)
      DX = RCD (51.)
      DX = CMP (11151101.)
      IF (DX) 191,190,191
191  Print 192
192  Format (25HCHAN missed, restart tape) go to 300
190  DX = RTC(501.)
      If (DX) 204, 201, 204
202  Control 102
      Control 108
      Type 240,1,KD
240  Format (4HCHAN, 14 5H tape, 14,3H 1S
      Accept 241,DZ
241  format (F5.0)
      DX = PAS (12052020.)
      Go to 212
201  If (I - 1) 202, 200, 202

```

Program 2 (continued)

```

204 DX = RTC(504.)
    If (DX) 220, 203, 220
203 ICK = GET(50330.) + 1.
    If (1 - ICK) 210, 210, 210
C   Channel number from tape could be checked
210 DX = RCD (51.)
    DX = RTC(506.)
    If DX 202, 211, 202
211 DZ = GET(50550.)
    Go to 212
220 DX = RTC(507.)
    If (DX) 230, 221, 230
221 DX = CMP (28150601.)
    If (DX) 22, 211, 222
222 DZ = Get(50660.)
    Go to 212
230 DX = CMP(28150901.)
    If (1 - ICK) 232, 232, 232
232 DZ = Get(50850.)
212 X(1) = DZ
C
C
    If (sense switch 1) 70,355
700 DO 701 1=1, itest, 10
701 Print 702, X(1), X(1+1), X(1+2), X(1+3),X(1+4),X(1+5),X(1+6),
    1X(1+7),X(1+8),X(1+9)
702 Format (10F7.0)
    Pause
335 Continue
    DO 88 1=1,NN
    NLOW = NA(1)
    B = 0.0
    DO 40 J=NLOW,NHI
40  B=B+X(J)
    Go to 345
88  Continue
345 Go to (7,8,9,12,14,17),KD
7   A=B
    KD=2
    Go to 88
8   org=B
    KD=2
    Go to 88
8   org=B
    KD=3
    Go to 88

```


Program 2 (continued)

```

9      C=B
      KD = 4
      Go to 102
12     D=B
      KD=5
      Go to 88
14     AQ=B
      KD=6
      Go to 88
17     E=B
      KD=1
      Org=(org)-(((A+C)/P)*Q)
      Aq=(((Aq)-(((D+E)/P*Q))* (decay))
15     OY+((org)/(org+aq))*100.0
      Print 100,org,aq,oy
100    Format (//12H sample no.-,//10X,4HORG=,510.0,/,10.0,/,10X,
4H aq=, F10.0, 1//15X,3HOY=,F7.2)
      If (sense switch 3) 102, 136
136    Pause
      If (sense switch 2) 44, 102
44     Print 420
      Type 55
      Type 77
      Go to 102
300    Accept 5, KD
      Go to 102
5      Format (14,14,14,14)
      End

```

a Tape read-in block and special subroutines prepared by

F. J. Kerrigan, U. S. V. A. H., Omaha, Nebraska.

APPENDIX II
DESCRIPTION OF INITIAL RADIOGAS CHROMATOGRAPH
CONSTRUCTED AND EMPLOYED IN THIS RESEARCH

As pointed out in Chapter III, the majority of the product determinations carried out in the course of this research were performed with an earlier version of the instrument described in that chapter. Because of the extensive use of this chromatograph in this research a brief description of the instrument will be presented here. As shown by comparison of the following description with that given for the newer version in Chapter III the new chromatograph is simply a more sophisticated version of the one described below.

Figures 35, 36 and 37 show the basic features of the gas chromatograph used in this research. The helium carrier gas is supplied by a pressurized steel cylinder, and passed through a pressure-regulating valve, flow controller, pre-heating column, the reference side of the thermal conductivity detector, 4-way backflush valve, and into the column. After being separated in the column, the eluted fractions enter the sensing portion of the thermal conductivity detector, where macroscopic amounts ($\sim 1 \times 10^{-3}$ ml.) are detected. The signals from the thermal conductivity cell are routed through an attenuator, D.C. operational amplifier, and then to one pen of a Texas Instruments (Model PDR) dual pen recorder. From

Figure 35. Block diagram of radiogas chromatograph.

Figure 36a. Main console.

Figure 36b. Main console component locations.*

*Control and Indicator Functions

1. Detector oven	16. Fine Attenuation Control
2. Column oven	17. Bridge Balance Control
3. Recorder	18. Signal Selector Switch
4. Master Switch and Pilot Light	19. Detector Oven Heater Selector Switch
5. D.C. Power Supply	20. Detector Oven Pilot Light
6. Galvanometer	21. Detector Oven Heater Switch
7. Detector Oven Powerstat	22. Fan Switch
8. Counting Cell Powerstat	23. Fan Pilot Light
9. Column Oven Powerstat	24. D.C. Discharge Detector
10. Column Oven Fan	25. Calibrated Flow Meter
11. Column Oven Temperature Control	26. Injection Port
12. Operational Amplifier	27. Pyrometer
13. Recorder Selector Switch	28. Meter Illumination
14. Amplifier Output Jacks	29. Thermocouple Selector
15. Course Attenuation Switch	
-

Figure 37. View of assembled instrument.

the thermal conductivity cell, the effluent passes through a helium discharge detector which can be used in lieu of or concomitantly with the thermal conductivity cell for the detection of macroscopic amounts of eluant. The effluent then passes through a window-type proportional flow-counter, maintained at a temperature greater than the ambient oven temperature where trace quantities ($\sim 10^{-15}$ g.) of eluted products are detected by monitoring the beta and/or gamma radiation emitted.

The signal from the proportional counter is directed through a scaler, ratemeter, and to the second pen of the dual pen recorder. From the proportion counter the eluted products flow through a heated capillary tubing to a well-type NaI(Tl) scintillation detector. The signal from the scintillation detector is routed to a radiation analyzer and from there to a Texas Instruments (Model #PWS) single pen recorder. The signals from either radiation detector can be monitored by a scaler for simultaneous determination of total activity.

The effluent fractions issuing from the second radiation detector, are collected in cold traps. The carrier gas is routed from the traps into a flow meter, and then to a fume hood to prevent the escape of radioactive species into the laboratory atmosphere.

The column, injecting parts, warm-up coil, and back-flush valve are housed in an insulated heating oven controlled by a cenco powerstat and a thermostat. The thermal conductivity cell and helium discharge detector are located in a separately heated detector oven. The location of the thermal conductivity detector in a separate enclosure permits the column to be temperature programmed without excessive baseline drift of the

conductivity trace due to heating of the detector.

Carrier Gas Control. The chromatograph was designed to allow atmospheric pressure at the end of the column. The flow rates can be varied between 20 and 180 ml. min.⁻¹. These flow rates may be obtained by applying an excess pressure of ca. 20 psi to the column head. Variability of the column head pressure is necessary in order to obtain constant flow rates, as column temperature is changed, and to achieve a given flow rate with differing column packings of varying density.

Since the helium carrier gas is at room temperature upon entering the chromatograph, it is necessary to pre-heat it to the temperature of the injectors and column to prevent condensation of sample gases when introduced into the carrier gas stream. A copper warm-up coil, 2 meters long and 1/8 inch I.D., is located inside the column oven in front of the injection ports for this purpose.

A "Valco" 4-port backflush valve is located in the column oven as shown in Fig. 1. This permits the reversal of carrier gas flow in the column and permits the elution of any high boiling sample components having excessive retention times after separation and analysis of all low boiling constituents. In the flush position this valve permits material introduced into the injection ports to bypass the column, allowing rapid determination of the time delay between succeeding detectors. This is necessary to correlate relative retention times indicated by each detector. Additionally, the backflush position may be employed for the

introduction of large quantities of solvent to flush out any contamination occurring in one or more of the detectors without destroying the column packing.

The flow rate of the helium carrier gas is continuously indicated by an RGI calibrated flowmeter (size #1), with a flow range of 0-260 ml. per minute. The flow meter is located immediately after the cold trap to prevent contamination of the meter by eluting materials. The location of the flow meter after the cold traps affects the accuracy of the measurements obtained during the elution of macroscopic amounts of solvent vapors as a result of their condensation before reaching the flow meter. This does not affect the actual flow rate of the gases past the detectors, and does not introduce any measurement errors except for an improper reading during the short periods of macroscopic component elution and subsequent condensation.

Injectors. Two different types sample introduction techniques are employed. One is a rubber septum injection port, most commonly used for the introduction of liquid samples, and the other is a bulblet breaker which allows the introduction of quartz encapsulated gas samples directly into the helium stream.

Gaseous samples are encapsulated in quartz ampoules, irradiated, then crushed in the bulblet breaker, shown in Fig. 38. The bulblet breaker introduces the sample gases into the carrier gas stream prior to passage through a three-inch pre-column.

Column. The analytical column, packed with an appropriate support

and stationary phase, is a coiled glass tube 4 mm. in diameter, 2.1 meters in length, and a spiral diameter of 190 mm. The column is connected to the chromatograph by way of 1/4" Swagelok fittings using teflon ferrules.

Detection. Four detectors are employed in various combinations for the identification and quantitative treatment of fractions which are eluted from the column. A thermal conductivity cell and a helium discharge detector can be used singly or in tandem for the qualitative and quantitative detection of macroscopic amounts of non-radioactively labeled fractions.

Figure 38. Bulblet breaker.

The most frequently used detector for the detection of non-radioactive species is the thermal conductivity cell. The detector consists of a stainless steel block with two matched pairs of 30 ohm. tungsten rhenium filaments, one pair each for the reference and sensing portions of the bridge. The circuitry for this detector is shown in Fig. 39. Filament current is supplied by a Hewlett-Packard Model 6202B DC power supply.

The helium discharge detector employed is similar to that developed by Karmen and Bowman which was based on a low current electric discharge in argon or helium in the presence of a high-intensity electrostatic field.

Figure 39. Thermal conductivity detector circuitry.

Fractions eluted from the column, after passing through the thermal conductivity and helium discharge detectors, are channeled into a heated capillary tube which leads to the radiation detectors for radioassay of the labeled products. The first of the radiation detectors is a cylindrical window flow proportional counter. The basic design of this counter and its characteristics have been previously reported by Wolf, et. al.⁶⁶

The basic design and dimensions of the counter are shown in Figs. 40, 41 and 42. The design of this counter closely follows that discussed by Wolf, et. al.⁶⁶, except for a few important modifications.

The principle modifications were the use of a stainless steel window and flow insert, because of its relative inertness to high temperatures and halogenated compounds, and a complete redesign of the high voltage anodes.

The high voltage anodes differ from Wolf's⁶⁶ design in the following ways:

1. Teflon insulators are used for the anode supports.
2. 0.0035 inch tungsten wire is used as the high voltage anodes.
3. The mounting arrangement of the individual anode wires differs, as shown in Fig. 42.
4. Six anodes spaced 60° apart are used in order to furnish a more uniform electrostatic field.

Presently the maximum operating temperature of the counter is limited by the high temperature deterioration of the epoxy (Goodyear Plibond

Figure 40a. Counter body.

Figure 40b. Schematic of counter body.

Figure 41a. Assembled window and window insert.

Figure 41b. Window insert design.

Figures 42a, 42b. Views of high voltage anode assembly.

Figure 42c. Design of high voltage anode assembly.

HT-30) at 225° C.

The counter is heated by wrapping completely with a heating tape, with the temperature regulation supplied by a Cenco-Powerstat. The counter is shielded by stacking lead bricks around it. The high voltage, signal detection, and amplification are supplied by a TracerLab 131-N Model Scaler. The amplified signal is then routed to a Picker ratemeter for analog conversion of the signal to a strip chart recorder.

The signal from the scaler is simultaneously relayed to a Nuclear Data ND-110 Multichannel Analyzer, operated in the multiscaling mode, for digital peak integration. Under our conditions, the background of the counter is 100 cpm at 100° C, rising slightly as temperature is increased.

Fractions eluted from the proportional counter are channeled into

Figure 43. Scintillation counting cell.

a heated capillary tube which leads to a 5-ml. heated counting cell (Fig. 43). The counting cell is set in the well of a Nuclear-Chicago DS-5, scintillation detector which is connected to a Nuclear-Chicago-1810 radiation analyzer where the signal is recorded as counting rate versus time. A TracerLab 131-N scaler is connected to the analyzer to serve as an integrating unit. A detailed description of the detector and its operating characteristic is given in Ref. 42.

Collection Devices. After gaseous fractions flow out of the counting cell, they are trapped in two tandem cold traps at -196°C . Radioactive compounds enter the top of the trap and are condensed on the sides. Stopcocks are arranged to permit removal of one trap while the effluent passes through the other, or, to pass through both traps. The carrier gas is subsequently channeled through a gas flowmeter, to a fume hood where it is discharged.

Heating Ovens. A modified Boekel, 110 volt 660 watt heating oven is used for the column oven. Insulation (0.75 inch) coated with reflective aluminum foil was attached to the inner walls of the oven to prevent excessive heat dissipation due to conduction and radiation. The original oven temperature control was disconnected and oven temperature control is now maintained by a Hotpoint Model 276 C485 P9 thermostat with heater gain controlled by a Cenco-Powerstat and air circulation provided by a circulating fan to eliminate temperature gradients in the oven enclosure.

Temperature can be controlled within $\pm 3^{\circ}\text{C}$, and can be varied between room temperature and 300°C .

Temperature programming is accomplished by timed settings of the column oven powerstat with the thermostat control set at the upper temperature limit of the program. The oven may be cooled at a rate of 50°C per minute.

A separate oven was constructed to provide constant temperature regulation for the thermal conductivity and helium discharge detectors. This oven was constructed in the form of a rectangular box, measuring 14 x 14 x 12 inches, with a hinged access door in the front. The oven enclosure is insulated with 0.75 inch fiberglass and heated by two 500 watt cone heaters regulated by a cenco powerstat.

Temperature monitoring. Direct temperature readout is provided by an Assembly Products, Inc., API, 0 - 400°C pyrometer. The pyrometer is calibrated for iron-constantan thermocouples with an external resistance of 10 ohms. The meter has an accuracy of 1% full scale.

A twelve-position selector switch, having dual gold plated contacts, is used to select one of the various thermocouples which are located at the various points where temperature measurements are desired, such as the column oven, individual detectors, and the detector oven.

APPENDIX III^a

The derivations of the rate expressions for the three possible mechanisms, discussed in Chapter V, are based on the following overall mechanism:

A. The following rate expressions are similar to the one arrived at by Keefer and Andrews in a study of the exchange reactions between organic halides and iodine monochloride. cf. R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc., 75, 543 (1953); ibid, 76, 253 (1954).

For the purpose of this derivation it was assumed that equation 4 was rate determining and irreversible. In addition, equation 3 was assumed to contribute to the production of iodine atoms in a manner similar to equation 1.

The rate of formation of product according to equation 4 is given by

$$d[C_5I_2]/dt = k_1 [C_5 \cdot I_2][I_2]_{\text{eff}}^{\frac{1}{2}} \quad \underline{8}$$

where $[I_2]_{\text{eff}}$ is the effective iodine concentration leading to the production of iodine atoms, which includes the contribution from equation 3, is expressed by

$$[I_2]_{\text{eff}} = [I_2]_f + [C_5 \cdot I_2] \quad \underline{9}$$

and

$$[I_2]_f = \text{concentration of uncomplexed iodine} \\ = [I_2] - [C_5 \cdot I_2] \quad \underline{10}$$

thus

$$[I_2]_{\text{eff}} = [I_2] \quad \underline{11}$$

The charge transfer equilibrium constant is defined by

$$K_c = \frac{[C_5 \cdot I_2]}{[C_5][I_2]_f} \quad \underline{12}$$

Substituting the expression for $[I_2]_f$ into equation 12 and rearranging we obtain the expression for the concentration of the complex

$$[C_5 \cdot I_2] = \frac{K_c [C_5][I_2]}{1 + K_c [C_5]} \quad \underline{13}$$

Substituting equation 13 into equation 8 and rearranging we get:

$$[I_2]^{-3/2} d[C_5I_2]/dt = \frac{k_1 K_c [C_5]}{1 + K_c [C_5]} \quad \underline{14}$$

Since the observed rate constant is given by equation 15

$$d[C_5I_2]/dt = k[I_2]^{3/2} \quad 15$$

it can be rewritten in terms of equation 14 to give equation 16.

$$\frac{[C_5]}{k} = \frac{1}{k_1 K_c} + \frac{[C_5]}{k_1} \quad 16$$

According to equation 16 a plot of $[C_5]/k$ versus $[C_5]$ would give a straight line whose slope would be equal to $1/k_1$ and the intercept equal to $1/k_1 K_c$.

B. If, instead of equation 4, equation 17 is the rate determining step

then the rate of formation of product according to equation 17 is given by

$$d[C_5I_2]/dt = k'_1 [C_5 \cdot I][I_2]_f \quad 18$$

where $[I_2]_f$ are previously defined.

The charge transfer equilibrium constant for the iodine atom-olefin complex then defined by

$$K'_c = \frac{[C_5 \cdot I]}{[C_5][I]} \quad 19$$

Again assuming the rate of production of iodine atoms by equations 1 and 3 to be the same, then

$$[I]_{eff} = [I_2]^{1/2} \quad 20$$

By substituting equation 20 in equation 18 and rearranging an expression

for the concentration of the complex is obtained

$$[C_5 \cdot I] = K'_c [C_5] [I_2]^{\frac{1}{2}} \quad 21$$

Substituting 21 into equation 18 and rearranging equation 22 is obtained

$$\frac{d[C_5 I_2]}{dt} = k_1' K'_c [C_5] [I_2]^{\frac{1}{2}} [I_2]_f \quad 22$$

Substituting equation 10 into equation 22 then

$$\frac{d[C_5 I_2]}{dt} = k_1' K'_c [C_5] [I_2]^{\frac{1}{2}} ([I_2] - [C_5 \cdot I_2]) \quad 23$$

By substituting the value previously obtained in equation 13 for the concentration of $C_5 \cdot I_2$ into equation 23 and rearranging then

$$\frac{d[C_5 I_2]}{dt} = \frac{k_1' K'_c [C_5] [I_2]^{3/2}}{1 + K_c [C_5]} \quad 24$$

Since the observed rate constant is given by equation 15, equation 24 may be rewritten to give equation 25.

$$\frac{[C_5]}{k} = \frac{1}{k_1' K'_c} + \frac{K_c [C_5]}{k_1' K'_c} \quad 25$$

According to equation 25 a plot of $[C_5]/k$ versus $[C_5]$ would give a straight line whose slope would be equal to $K_c/k_1' K'_c$ and the intercept equal to $1/k_1' K'_c$.

- C. Alternately, if the contribution to the iodine atom contribution from equation 3 had been neglected in the derivation of the rate expressions in part A, then the concentration of iodine would be defined by

$$[I_2] = [I_2]_f + [C_5I_2] \quad \underline{26}$$

and the rate expression by

$$\frac{d[C_5I_2]}{dt} = k_1 [C_5 \cdot I_2] [I_2]^{\frac{1}{2}} \quad \underline{27}$$

The charge transfer equilibrium constant is defined by

$$K_c = \frac{[C_5 \cdot I_2]}{[C_5][I_2]_f} \quad \underline{28}$$

Solving for $[I_2]_f$ and substituting into equation 27 then

$$d[C_5I_2]/dt = k_1 [C_5 \cdot I_2]^{3/2} / [C_5]^{\frac{1}{2}} K_c^{\frac{1}{2}} \quad \underline{29}$$

By substitution of $[I_2]_f$ in equation 28 and rearrangement an expression for the concentration of the complex is obtained

$$[C_5 \cdot I_2] = \frac{K_c [C_5] [I_2]}{1 + K_c [C_5]} \quad \underline{30}$$

Substitution of 30 into equation 29 and rearrangement then:

$$[I_2]^{-3/2} d[C_5I_2]/dt = \frac{k_1 K_c [C_5]}{(1 + K_c [C_5])^{3/2}} \quad \underline{31}$$

Since the observed rate constant is given by equation 32

$$d(C_5 I_2)/dt = k[I_2]^{3/2} \quad \underline{32}$$

it can be rewritten in terms of equation 31 to give equation 33

$$\frac{[C_5]^{2/3}}{k} = \frac{1}{(k_1 K_c)^{2/3}} + \frac{K_c [C_5]}{(k_1 K_c)^{2/3}} \quad \underline{33}$$

According to equation 33 a plot of $([C_5]/k)^{2/3}$ versus $[C_5]$ would give a straight line whose slope would be equal to $K_c/(k_1 K_c)^{2/3}$ and the intercept equal to $(k_1 K_c)^{-2/3}$.

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PUBLICATIONS AND PAPERS PRESENTED AT MEETINGS

Publications

1. "Iodine Organic Yields in Hydrocarbon Matrices as an Introduction of Clustering, Complexing, and Fractional Crystallization at 77° K" with E. J. Kemnitz, R. M. Lambrecht, and E. P. Rack, Radiochim. Acta, 11, 1 (1969).
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5. "Reactions of Iodine with Olefins: I. Kinetics and Mechanism of Iodine Addition to Pentene Isomers" with C. J. Michejda and E. P. Rack, J. Am. Chem. Soc. (In Press).
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Papers Presented at National Meetings

1. "Iodine Organic Yields in Hydrocarbon Matrices as an Indication of

Clustering, Complexing and Fractional Crystallization at 77° K"
with E. J. Kemnitz, R. M. Lambrecht, and E. P. Rack. Division of
Nuclear Chemistry and Technology, American Chemical Society,
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2. "Reactions of Iodine-128 Induced by Radiative Neutron Capture in
Homologous Gas-Phase Halomethane Systems" presented by N. J. Parks,
with R. L. Ayres, D. W. Oates and E. P. Rack. Division of Nuclear
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