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REACTIONS OF HALOGEN ATOMS ACTIVATED BY
NUCLEAR PROCESSES WITH ORGANIC MEDIA
AT 77° AND 298° K

A thesis by Richard M. Lambrecht

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REACTIONS OF HALOGEN ATOMS ACTIVATED

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University of Nebraska, 1969

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The chemical reactions initiated by the $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I and $^{82}\text{Br}^{\text{m}}$ (IT) ^{82}Br processes were investigated and compared with those induced by the ^{129}I (n, γ) ^{130}I + $^{130}\text{I}^{\text{m}}$, ^{127}I (n, γ) ^{128}I , ^{37}Cl (n, γ) ^{38}Cl and the ^{81}Br (n, γ) ^{82}Br + $^{82}\text{Br}^{\text{m}}$ nuclear transformations. The organic yields of ^{130}I + $^{130}\text{I}^{\text{m}}$ and ^{128}I activated by radiative neutron capture were compared to those of ^{130}I activated by isomeric transition in several liquid hydrocarbons ranging from n-pentane to n-nonane. The organic yields of (n, γ) activated $^{130}\text{I}^{\text{m}}$ + ^{130}I are consistently lower than the (IT) induced organic yields of ^{130}I and (n, γ) activated ^{128}I . Radiogas chromatography analysis has indicated the similarity of products, but differences in abundance of the relative product yields of ^{128}I , ^{130}I and ^{82}Br . Similarities in yields and product distributions between iodine and bromine isomeric transition induced reactions may indicate that radiohalogens mainly trace their chemical environment. The organic reactivity may be explained by the autoradiation hypothesis, which suggests the radiative neutron capture and isomeric transition processes should give similar products due to combinations of halogen species with radicals formed by localized radiation produced by the internal conversion and Auger electrons emitted by the recoil atom. The differences in individual product yields of iodine and bromine in a given hydrocarbon may reflect that in addition to the halogen atom tracing of isomeric

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transition produced radical debris, varying contributions of ion-molecule reactions characteristic of the halogen atom could occur. The (n, γ) and (IT) activated reactions of bromine were studied in various liquid hydrocarbons ranging from pentane to tridecane. The total organic yields of (n, γ) activated $^{80}\text{Br}^m$ were lower than the (IT) organic yields of ^{82}Br at all Br_2 concentrations studied. The organic yields were found to vary with the chain length and the target molecule structure. The lower reactivity of (n, γ) activated $^{130}\text{I} + ^{130}\text{I}^m$, as well as that of (n, γ) activated ^{82}Br and $^{82}\text{Br}^m$, could be due to a lower percent of ^{130}I , $^{130}\text{I}^m$, $^{82}\text{Br}^m$ and ^{82}Br born by the (n, γ) process in low-lying metastable states. If autoradiation effects with their accompanying iodine and bromine radical reactions, ion-molecule reactions, etc., accounts for only a part of the organic yields of (n, γ) activated $^{80}\text{Br}^m$, ^{82}Br and $^{130}\text{I} + ^{130}\text{I}^m$ reactions in liquid hydrocarbons, then the remaining organic yield may be the result of other processes such as those predicted by the random fragmentation hypothesis. The random fragmentation hypothesis would predict a radical mechanism and degradation products of the target molecule, as observed by radiogas chromatography.

The organic yields from I_2 , Br_2 and ICl source molecules activated by radiative neutron capture and isomeric transition were determined in polycrystalline n-hexane, cyclohexane, and 2,2-dimethyl butane, and in glassy 3-methyl pentane at 77°K . Specifically the influence of purity levels, neutron irradiation and post-irradiation procedures, the effect of halogen concentration, the influence of additives and nuclear transformation on the observed organic yields were investigated. The experiments with Br_2 , I_2 and ICl (in which either halogen atom may

acquire a radioactive label) have shown that the radiohalogens mainly trace their environment without chemical selectivity with regard to isotope and mode of activation. In glassy and polycrystalline halogen-hydrocarbon systems, the organic yields under the conditions of monomolecular dispersion are about $55 \pm 5\%$. In polycrystalline hydrocarbons containing I_2 , or ICl , rather constant organic yields of about 10% in n-hexane, and 2,2-dimethyl butane, and 25% in cyclohexane between 1×10^{-5} and 2×10^{-4} mf halogen suggests the formation of preferred $(X_2)_n$ cluster sizes and/or similar numbers of halogen molecules at sites in the hydrocarbon matrix. The organic yield plateaus indicate that the halogen clusters at the various sites in the organic matrix are larger in n-hexane than in cyclohexane. Similar clustering of I_2 and ICl does not occur in glassy 3-methyl pentane, rather the organic yields suggest that the halogen undergoes partial segregation during total crystallization.

The effects of phase change on $^{130}I^m(IT)^{130}I$ and the $^{82}Br^m(IT)^{82}Br$ induced organic yields were explored. The complicating role of isomeric transition induced reactions in neutron activation analysis for ^{82}Br and ^{130}I is discussed.

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by

Richard Merle Lambrecht

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To My Wife

Kathleen Joy McGill Lambrecht

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CHAPTER I

INTRODUCTION

Chapter I

Introduction

Hot atom chemistry is the study of chemical reactions which occur as a result of atoms having excess translational energy. Hot reactions may be observed through activation by ultraviolet radiation, crossed molecular beams, ionizing radiation, electrical discharge and nuclear transformations. The above methods for studying hot reactions provide different techniques and hence, different interpretations which give way to correlations of hot atom reactions. However, nuclear transformations which produce hot atoms by the (p,α) , $(n,2n)$, (n,p) , (n,γ) and (IT) nuclear reactions are the most commonly employed. Of these reactions, the radiative neutron capture, (n,γ) and isomeric transition, (IT) , are easily studied with the convenience of a neutron generator or nuclear reactor. Neutron sources are usually available, and may be used under conditions where radiation damage and temperature effects are not serious. Numerous isotopes have favorable capture cross sections for the (n,γ) process; and the (n,γ) and (IT) processes may produce a number of radioactive species with chemical properties which are desirable for a particular study. The nuclear activation methods employed in this research were the radiative neutron capture (n,γ) and isomeric transition (IT) processes. The remainder of this dissertation will refer to either or both of these processes.

The goal of hot atom chemistry is to determine the mechanism by which hot atom reactions occur. Two requirements¹ which must be met in order to study the mechanism of hot atom reactions are: (1) The

activated atom must result in a radioactive product, since only about one picomole or less of activated atoms are produced in a reaction system; and (2) Thermal exchange reactions with each other or with environmental molecules must be eliminated. Willard² in a recent review stated that dominant among the questions to which answers are being sought are: (1) The relative importance of kinetic energy and of charge in determining the chemical fate of the atoms studied; and (2) The effect of phase on the mechanisms which lead to chemical stabilization. This dissertation is concerned with the reactions of selected iodine, chlorine and bromine isotopes activated by either the radiative neutron capture and/or isomeric transition in several isomeric aliphatic hydrocarbons. Experiments were performed in liquid and solid media at 298° and 77° K.

Historical Background

As early as 1924 Lind and Bardwell³ discovered that an atom recoiling from alpha-particle emission could produce chemical radiolytic effects in solution. However, it was not until 1934 that Szilard and Chalmers^{4,5} investigated the chemical effects of the $^{127}\text{I} (n, \gamma) ^{128}\text{I}$ reaction in liquid ethyl iodide. They observed that a substantial fraction of the ^{128}I atoms were formed as inorganic species which could be extracted into aqueous solution. Szilard and Chalmers interpreted the breaking of the carbon-iodine bond as being due to transfer of the momentum of the neutron to the iodine atom. However, Fermi and his co-workers⁶ soon explained the bond breaking as being the result of the recoil energy resulting from the emission of gamma rays as the compound nucleus de-excites. Glueckauf

and Fay⁷ investigated the fate of recoil halogens in several alkyl halides and demonstrated that organic bonding of the recoil atom also occurred. Since these early experiments, the understanding of the chemical effects of nuclear transformations has served to reveal the richness of the field; however a thorough discussion of all historical aspects of the field is beyond the scope of this dissertation.

The different aspects of the chemical effects of nuclear transformations have been summarized through 1968 in several informative surveys. The kinetics and mechanism of hot reactions of carbon and tritium are discussed by Wolf,⁸ Wolfgang,⁹⁻¹¹ and Filatov.¹² Willard^{1,2,13-15} has reviewed advances in halogen hot atom chemistry. Wolf^{16,17} has discussed the labeling of organic and biological compounds by recoil methods. The chemical effects associated with several nuclear transformations of numerous isotopes in the solid state have been examined by Campbell,¹⁸ Walton,¹⁹ Mueller,²⁰ Harbottle²¹ and Anderson.²² Suida²³ has compiled the most complete bibliography of publications in hot atom chemistry through 1962. The area has been treated in two symposia²⁴ whose papers represent a broad cross section of current work.

Nuclear Activation

The nuclear activation properties of the isotopes used in this research are presented in Table I. When a nuclei is subjected to a neutron flux, the probability that a neutron will penetrate to the surface of the target nucleus is governed by the energy of the incident neutrons and the cross section for neutron absorption. As the neutron is absorbed a compound nucleus is formed which is in an excited quasi-stationary state. In the compound nucleus model it is assumed that the energy carried in 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 escape immediately.²⁵ The Heisenberg uncertainty principle suggests that the compound nucleus has a lifetime of about 10^{-14} to 10^{-15} second, which is long compared to the transit time 10^{-18} to 10^{-21} second of a thermal neutron across a nuclei used in this study. The decay of the compound nucleus depends only on its energy, angular momentum and parity, but not its mode of formation.

The compound nucleus is unstable with an energy equivalent to the neutron binding energy of the nuclei. (See Table I) The excitation energy is subsequently dissipated by the emission of a combination of gamma radiation emission and internal conversion processes. Conservation of momentum requires that the recoil energies of the nuclei resulting from gamma emission will vary from zero to a maximum of $(537 B^2/M)$ ev for the emission of a single gamma ray. B is the neutron binding energy and M is the atomic mass of the activated atom. However, the release of all the neutron binding energy in a single

Table I. Nuclear Properties of Halogen Isotopes

Nuclear Activation Process	(n,γ) Thermal Neutron Cross Section (Barns)	Neutron Binding Energy of Product Nucleus (Mev) ^a	Half-life of Activated Nucleus	Positive Charge of Activated Atoms (Minimum Values)
³⁷ Cl (n,γ) ³⁸ Cl	0.6	6.1	37.3 min	----
¹²⁷ I (n,γ) ¹²⁸ I	5.6	6.8	25.0 min	> 50 %
¹²⁹ I (n,γ) ¹³⁰ I	8.0	6.4	12.4 hr	----
¹²⁹ I (n,γ) ¹³⁰ I ^m	16.0	6.4	8.9 min	----
¹³⁰ I ^m (IT) ¹³⁰ I	---	---	12.4 hr	Approx. ^b 100 %
⁷⁹ Br (n,γ) ⁸⁰ Br	8.5	8.1	17.6 min	18 %
⁷⁹ Br (n,γ) ⁸⁰ Br ^m	2.9	8.0	4.5 hr	12 %
⁸¹ Br (n,γ) ⁸² Br	0.3	7.6	35.3 hr	25 %
⁸¹ Br (n,γ) ⁸² Br ^m	3.0	7.6	6.1 min	25 %
⁸⁰ Br ^m (IT) ⁸⁰ Br	---	---	17.6 min	Approx. ^b 100 %
⁸² Br ^m (IT) ⁸² Br	---	---	35.3 hr	Approx. ^b 100 %

^a Calculated from nuclear masses²⁵ and disintegration energies,²⁶ e.g. the neutron binding energy of ⁸²Br is equal to (mass ⁸¹Br + mass neutron - mass ⁸²Kr) X (931.6 Mev/amu) - 3.09 Mev (the disintegration energy of ⁸²Br).

^b The internal conversion coefficients, i.e., the ratio of conversion electrons to gamma rays emitted for ¹³⁰I^m, ⁸⁰Br^m and ⁸²Br^m isomeric transition processes are highly converted, 400 and 382 ± 75, respectively.^{27,28,29} Thus nearly all of the (IT) activated nuclides are charged.

γ -ray is a comparatively rare event. The most probable fluctuations will concentrate a fraction of the escaping energy on the escaping gamma ray. Emission of more than one gamma ray results in an energy spectrum ranging from zero (due to momentum cancellation by emission in opposite directions) to the maximum kinetic energy. The probable magnitude of the recoil energy transferred when the decay occurs in several steps has been discussed.³⁰ The gamma ray spectra following the absorption of individual neutrons for the isotopes used in this research are sparse, hence insufficient to calculate average recoil energies. However, the energy equivalent to the neutron binding energy of the nuclei serves as a representative measure of the expected maximum gamma-emission energy following neutron capture.

Charge State and Electronic Excitation Energy

After the activated nuclide has undergone the initial high energy gamma emission, it may still be in a low-lying energy state, or in a metastable (isomeric) nuclear state. An excited nucleus can change from one energy state to another as a result of internal conversion and the emission of gamma rays. Internal conversion is an electromagnetic interaction between the nucleus and the extranuclear transition and the electrons binding energy.³¹ Internal conversion competes with photon emission. The internal conversion coefficient, α , is the ratio of electrons to γ -rays. The lifetime of an excited state is, in general, extremely short and of the order of 10^{-17} to 10^{-12} second. However, if the angular momenta (spin) of the excited state and the ground state are different, the excited state may have a lifetime long enough to be measured.³² In the latter instances, de-excitation between two

isomeric pairs is called isomeric transition. There is no appreciable recoil energy associated directly with the isomeric transition gamma or the internal conversion (IC) radiations.

A most important point to understand is that isomeric transition processes result in chemical reactions which occur mainly as the result of a coulombic explosion caused by the production of a vacancy (hole) in the K (usually) or L shell of a nuclide. The factors leading to the coulombic explosion are the emission of an internal conversion electron which creates a vacancy and a single positive charge in the electron structure. This situation is very unstable because the energy by which an inner shell electron is held in the shell is much greater than the binding energy of the electrons in the outer shells. The energy difference between the two shells is subsequently emitted as an X-ray, or is transferred to another electron, i.e. Auger electron,³³ which will acquire enough energy to be emitted. At this point the atom is double charged as a result of two vacancies. (See Fig. 1) The vacancies may be filled by electrons from an outer shell, resulting in a higher positive charge on the excited ion. The initial internal conversion followed by the successive Auger electrons in cascade dissipates the energy of excitation towards the valence shell. A typical vacancy cascade of I^- as a result of the initial vacancy created by the IC electron is illustrated in Fig. 1. The time required for the Auger process to occur with the removal of the Auger electron from the atom is very short compared to the time required for a molecular vibration (10^{-14} sec). For example, a 100 ev electron will travel 60 Å in 10^{-15} second.

Carlson and White³⁵ have induced the Auger processes in the iodine

atom by bombarding CH_3I with X-rays. They observed that a subsequent charge build-up on the iodine of +5 was the most abundant, relative to a distribution of charges ranging from +1 to +10. The distribution of charge on a recoiling atom would be expected to be similar. The recoil energies as determined by mass spectrometry varied from 2 to 25 ev. The recoil energies of iodine ions would be expected to be smaller than those of bromine because of conservation of momentum requirements. Wexler³⁶ has shown for bromine that the charge may be as high as +13 with an average charge of +7. Kazanjian and Libby³⁷ have calculated the various recoil energies associated with the spectrum of charges on a bromine atom following isomeric transition. For example, by assuming the charge is evenly distributed between the bromine atom and its nearest neighbor, a charge of +8 results in a recoil energy of 40.3 ev.

In the condensed state the positive charge is spread over the neighboring molecules and virtually explodes as a result of the coulombic repulsion. Numerous recoiling fragments including free electrons and ions of varying velocities are produced as a result of the isomeric transition.³⁸ The various fragments will have high electron affinities and in the condensed phases will be rapidly neutralized by the environment either by free electrons or by electrons transferred from neutral species along their track.³⁷ The radioactive atom or ion which produced the ionic and radical debris reacts with the environment and also reacts by tracing the fragmented environment which was created as a result of the isomeric transition event. Hence an atom undergoing (IT) may react by virtue of the positive

charge and electronic excitation and the kinetic energy it may possess during the isomeric transition.

Wexler and Davies³⁹ have observed that 50% or more of ^{128}I atoms born by radiative neutron capture undergo internal conversion. Rack and Gordus⁴⁰ presented evidence that a fraction of the ^{128}I reactions in gaseous methane are electronically excited I ($^3\text{P}_2$, $^3\text{P}_1$ and/or $^3\text{P}_0$) atoms and I^+ ($^1\text{D}_2$) ions. Wexler and Davies⁴¹ reported a minimum of 12% of the $^{80}\text{Br}^{\text{m}}$, 18% of ^{80}Br and 25% of ^{82}Br become positively charged because of internal conversion and accompanying Auger electron effects that follow radiative neutron capture. It is of interest to note^{42,43} that the ^{82}Br that reacts as a result of isomeric transition in gaseous CH_4 is formed via 50% contributions of excess kinetic energy processes and 50% of the organic ^{82}Br is formed via thermal (kinetic-energy-independent) processes, probably involving Br^+ ($^3\text{P}_1$ and $^3\text{P}_0$) ions.

Thompson and Miller⁴⁴ examined the sequence of events following radiative neutron capture in the condensed phase. They observed that the initial recoil energy of the hot atom was due to photon (gamma) emission and was imparted to the recoil atom in less than 10^{-13} second after neutron capture. The high energy atom then followed a short and deviating path becoming stabilized chemically and/or thermalized only a few angstroms from the site of activation. The ejection of one or more IC electrons, followed by Auger radiation, occurred most frequently 10^{-12} to 10^{-15} second after neutron capture. Apparently charge build-up occurs after the hot atom has been thermalized and had the opportunity to undergo chemical reactions.

It is expected that the halogen isotopes employed in this research would be born with varying degrees of electronic excitation, which might be dependent on the amount of internal conversion and electronic rearrangement the nuclide experiences following the formation of the compound nucleus.

Final Chemical Stabilization

Since chemical bond energies are usually 2-3 ev, the recoil energies and positive charge build-up resulting from the radiative neutron capture and isomeric transition processes are greatly in excess of the energy required to break chemical bonds in neighboring molecules before becoming thermalized. An atom activated by a nuclear process will have the highest collision-efficiency leading to chemical combination at the lower end of the energy spectrum (10-5 ev). An atom that passes through the hot atom reaction zone without reacting will react as a thermal atom. Positively charged recoil atoms will be quickly neutralized in condensed media if the solvent has a lower ionization potential than the halogen.

Two probes which give useful information in the study of hot halogen reactions in organic media are: (1) The organic yield and, (2) The labeled product distribution.

Organic Yield Concept: The organic yield is an experimentally determined quantity relating the probability that a hot atom created by a nuclear transformation will become stabilized in organic combination. That is, the organic yield, OY, is the percent of radioactive atoms in organic combination relative to the total number of radioactive atoms present at the time of assay. The organic yields may

be different or similar for different species of hot atoms produced by the same or different nuclear transformations. The organic retention, which may be confused with the organic yield, historically refers to the resulting organic yield when the target atom is in organic combination prior to and following nuclear activation. For example, in the reaction,

the percent of $\text{C}_2\text{H}_5\text{I}^*$ formed represents the organic retention.

The organic yield is used extensively as a research tool for studying hot atom reactions, especially hot reactions of halogens, carbon and tritium in various organic matrices. Organic yields are relatively easily determined, and depend upon the chemical characteristics of the system.

Labeled Organic Product Distribution: A qualitative and quantitative identification of all of the products formed by hot atoms following a nuclear transformation is a prerequisite to the postulation of reaction mechanisms. Although the labeled organic product distribution may be readily determined by radio gas chromatography (RGC) and carrier distillations, it is essential that only labeled products formed by hot processes are assayed. Hence secondary reactions, i.e. thermal addition and exchange reactions must be eliminated prior to the identification of the labeled products. The organic yield of a given product is referred to as the product yield.

Statement of Problem

Various hypotheses, such as the autoradiation hypothesis,⁴⁵ the thermal spike model,⁴⁶ the intermediate complex model,⁴⁷ the modified impact model,⁴⁸ and the random fragmentation hypothesis,¹ have been presented in recent years to account for the chemical effects of nuclear transformations in condensed state organic media. The autoradiation hypothesis, which suggests that recoil atoms may react with radicals which are formed at high localized concentrations by reactions made possible by the radiation effects from its own electrons, has been the most successful in correlating halogen reactions activated by radiative neutron capture and isomeric transition. The recent discovery²⁷ of a metastable isomer of ^{130}I ($T_{1/2} = 9.2$ min) presented the opportunity to independently verify the half-life of $^{130}\text{I}^{\text{m}}$. In addition, the radiative neutron capture and isomeric transition chemistry of ^{130}I and $^{130}\text{I}^{\text{m}}$ had not been explored and provided a satisfactory means in which the autoradiation hypothesis could be further tested.

I found it extremely interesting and challenging that very little research on the interactions and reactions of halogens in solid hydrocarbons had been attempted and completed with any degree of success. Willard⁴⁹ had suggested that organic yields induced by nuclear transformations may give useful information on the state of aggregation of a solute and its tendency towards complexing in a solid hydrocarbon matrix.

The main purposes of this dissertation research were to:

1. (a) Verify the half-life of $^{130}\text{I}^{\text{m}}$ by an independent method, (b) to study the isomeric transition of $^{130}\text{I}^{\text{m}}$ and radiative neutron

capture reactions of $^{130}\text{I} + ^{130\text{m}}\text{I}$ and ^{128}I in several liquid $\text{C}_5\text{-C}_9$ aliphatic hydrocarbons, (c) to determine whether an isotope effect existed between the various isotopes of iodine activated by the two nuclear processes, (d) to compare the hot atom chemistry of iodine to that of bromine, and (e) to relate the organic yields and labeled product distributions to an acceptable mechanism.

2. Study the (n,γ) and (IT) reactions of bromine, iodine and iodine monochloride in selected hydrocarbon matrices at 77°K . In particular (a) to determine what experimental parameters must be considered to obtain meaningful experimental data, (b) if an isotope effect exists between (n,γ) and (IT) activation in solid hydrocarbon media, and (c) to determine how useful organic yields could be as a criteria of the state of aggregation, complexing, clustering, partial and total segregation during total crystallization of the halogen in the hydrocarbon matrices at 77°K .
3. Study the total organic yields of ^{82}Br activated by isomeric transition and $^{82}\text{Br} + ^{82\text{m}}\text{Br}$ activated by (n,γ) processes in selected liquid isomeric $\text{C}_5\text{-C}_{13}$ aliphatic hydrocarbons. Specifically, (a) to examine the effect of change of liquid to solid phase on (IT) induced organic yields, and (b) to determine the trends in the total organic yields with scavenger concentration, and mode of activation.
4. Discuss the complicating role that isomeric transition induced reactions may have in neutron activation analysis for ^{82}Br and ^{130}I .

CHAPTER II
EXPERIMENTAL

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, purity, and probable impurities for the high purity reagents. In addition, purification procedures, if employed, are presented.*

Br_2	Mallinckrodt, Analytical Reagent; following distillation the center fraction was taken and stored in a ground glass stoppered bottle placed in a desiccator with P_2O_5 drying agent
I_2	Mallinckrodt, reagent grade I_2 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.
ICl	Matheson, pure, M.P. $25-27^\circ \text{C}$.
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.
H_2O_2	Mallinckrodt, U. S. P. grade.

Na_2SO_3	Baker, reagent grade.
P_2O_5	Fisher, reagent grade.
Silica gel	Fisher, reagent grade.
Ammonia	Baker and Adamson, reagent grade.
He	Matheson, commercial grade.
O_2	Linde, commercial grade.
Iodine-129	Union Carbide, ORNL, obtained as Na^{129}I in basic sulfite solution of approximate pH 8. The iodine was extracted into the organic phase with H_2O_2 catalyzed with HNO_3 which was necessary for the oxidation of the $^{129}\text{I}^-$ to $^{129}\text{I}_2$. This solution was washed three times with distilled water, and dried over silica gel or CaCl_2 .
Iodine-131	Same as Iodine-129.
CH_3COCH_3	Fisher technical grade.
CCl_4	Fisher, reagent grade, if purified the CCl_4 was photobromated, extracted with aqueous sulfite solution, washed with distilled water, refluxed with 10% NaOH solution, washed with distilled water, dried over anhydrous CaCl_2 , and distilled on a Vigreux column with the center cut being retained.
CH_3Br	Eastman, white label.
$\text{C}_2\text{H}_5\text{Br}$	Eastman, white label.
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	Eastman, white label.

$\text{CH}_3\text{CHBrCH}_3$	Eastman, white label.
$\text{CH}_3(\text{CH}_2)_3\text{Br}$	Eastman, white label.
$\text{CH}_3\text{CHBrC}_2\text{H}_5$	Eastman, white label.
$(\text{CH}_3)_3\text{CBr}$	Eastman, white label.
$\text{CH}_3(\text{CH}_2)_4\text{Br}$	Eastman, white label.
$\text{c-C}_5\text{H}_9\text{Br}$	Eastman, yellow label.
$\text{n-C}_5\text{H}_9\text{Br}$	Eastman, white label.
$\text{n-C}_6\text{H}_{13}\text{Br}$	Eastman, white label.
$\text{c-C}_6\text{H}_{11}\text{Br}$	Eastman, white label.
$\text{CH}_3\text{CHBr}(\text{CH}_2)_3\text{CH}_3$	Matheson, Coleman, and Bell, practical grade.
$\text{C}_2\text{H}_5\text{CHBrC}_3\text{H}_7$	Matheson, Coleman, and Bell, practical grade.
$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{CH}_2\text{Br}$	Matheson, Coleman, and Bell, practical grade.
$(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{Br}$	Matheson, Coleman, and Bell, practical grade.
$\text{n-C}_7\text{H}_{15}\text{Br}$	Eastman, white label.
CH_3I	Eastman, white label.
CH_2I_2	Eastman, white label.
$\text{n-C}_3\text{H}_7\text{I}$	Eastman, white label.
$\text{i-C}_3\text{H}_7\text{I}$	Eastman, white label.
$\text{CH}_2\text{ICH}_2\text{CH}_2\text{I}$	Eastman, white label.
$\text{CH}_3\text{CI}(\text{CH}_3)\text{CH}_3$	Eastman, white label.
$\text{CH}_3\text{CH}_2\text{CHICH}_2\text{CH}_3$	K & K Laboratories, >95% purity.
$\text{CH}_2\text{I}(\text{CH}_2)_3\text{CH}_2\text{I}$	Eastman, white label.
$\text{CH}_2\text{I}(\text{CH}_2)_4\text{CH}_3$	Cal Bio Chem, white label.
$\text{CH}_3\text{CHI}(\text{CH}_2)_3\text{CH}_3$	K & K Laboratories, >95% purity.
$\text{CH}_3\text{CH}_2\text{CHI}(\text{CH}_2)_2\text{CH}_3$	K & K Laboratories, >95% purity.
$\text{CH}_2\text{I}(\text{CH}_2)_4\text{CH}_2\text{I}$	Baker, reagent grade.

$\text{CH}_2\text{I}(\text{CH}_2)_5\text{CH}_3$	Eastman, white label.
$\text{CH}_2\text{I}(\text{CH}_2)_6\text{CH}_3$	Eastman, white label.
$\text{CH}_3\text{CHI}(\text{CH}_2)_5\text{CH}_3$	Eastman, white label.
$\text{CH}_2\text{I}(\text{CH}_2)_6\text{CH}_2\text{I}$	K & K Laboratories, > 95% purity.
$\text{CH}_2\text{I}(\text{CH}_2)_8\text{CH}_3$	Eastman, white label.
$\text{C}_2\text{H}_5\text{OH}$	Industrial Chemicals, absolute.
$\text{C}_6\text{H}_{13}\text{COOH}$	Eastman, white label.
$n\text{-C}_5\text{H}_{12}$	Phillips, research grade, 99.90 mole % purity, GLC indicates isopentane as impurity.
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$	Phillips, research grade, 99.99 mole % purity, probable impurity of n-pentane.
C_6H_6	Phillips, research grade, 99.89 mole % purity, probable impurity of toluene.
$n\text{-C}_6\text{H}_{14}$	Phillips, research grade, 99.95 mole % purity, GLC indicates methyl cyclopentane as impurity.
cyclo- C_6H_{12}	Phillips, research grade, 99.99 mole % purity, probable impurity of 2,4-dimethyl pentane.
$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{CH}_3$	Phillips, research grade, 99.95 mole % purity, probable impurity of 3-methyl pentane.
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	Phillips, research grade, 99.83 mole % purity, probable impurities of 2-methyl pentane, n-hexane and benzene.
$(\text{CH}_3)_3\text{CH}_2\text{CH}_3$	Phillips, research grade, 99.99+ mole % purity, probable impurity of 2,3-dimethyl pentane.

Phillips, research grade, 99.89 mole % purity, probable impurities of 2-methyl and 2,2-dimethyl pentane, 0.0068 weight % Dupont No. 6 inhibitor as anti-oxidant, removed by distillation.

Phillips, research grade, 99.92 mole % purity, probable impurities of 3-ethyl pentane and cis-1,2-dimethyl cyclohexane.

Phillips, research grade, 99.72 mole % purity, probable impurities of 2,2- and 3,3 dimethyl pentane.

Phillips, research grade, 99.91 mole % purity, probable impurity of toluene.

Phillips, research grade, 99.85 mole % purity, probable impurities of other n-paraffins and iso-paraffins in the same boiling range.

Phillips, research grade, 99.97 mole % purity, probable impurities of other C_8 paraffins.

Phillips, research grade, 99.52 mole % purity, probable impurities of other C_8 paraffins.

Phillips, research grade, 99.87 mole % purity, probable impurities of other dimethyl-cyclohexanes.

Phillips, research grade, 99.70 mole % purity, probable impurities of other dimethyl-cyclohexanes.

Phillips, research grade, 99.68 mole % purity.[#]

Phillips, research grade, 99.78 mole % purity.[#]

Phillips, research grade, 99.49 mole % purity.[#]

$n\text{-C}_{11}\text{H}_{24}$ Phillips, research grade, 99.90 mole % purity.[#] $n\text{-C}_{13}\text{H}_{28}$ Phillips, research grade, 99.78 mole % purity.[#]

[#] Probable impurities of C_8 and C_9 isoparaffins in the same boiling range.

- * The hydrocarbons were used as received or within 10 minutes after the repurification. The hydrocarbons were repurified by stirring with conc H_2SO_4 at 22°C for 48 hr. The H_2SO_4 was replaced if the acid turned yellow or discolored during the repurification treatment. The hydrocarbon was washed with aqueous NaHCO_3 , distilled water, dried over silica gel (in some instances anhydrous CaCl_2), and fractionally distilled through a 25 cm bubble-cap column. In most solid state studies the hydrocarbon solution was purged with He to remove trace gaseous impurities. The impurities in the systems could not be detected by gas chromatography, using an Aerograph Model 1520 with a flame detector having a sensitivity of 10^{-5} mf for impurity, or by activation analysis for alkyl halides in the Phillips research grade hydrocarbons before and after repurification. The freshly purified hydrocarbons showed negligible organic reaction with $\text{I}_2(^{131}\text{I})$ after several hours standing in the dark.

Sample Preparation

The reactions of ^{128}I , $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$, ^{38}Cl , $^{80}\text{Br}^{\text{m}}$, ^{82}Br and $^{82}\text{Br}^{\text{m}}$ activated by radiative neutron capture and the $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I and $^{82}\text{Br}^{\text{m}}$ (IT) ^{82}Br reactions were studied at 298°K and 77°K . Specifically, halogen concentration effects, impurity levels, the effect of phase and phase changes, the time between irradiation and extraction, and solvent effects were used as probes. All samples were prepared in 1-5 ml quartz ampoules. The ampoules were affixed with a constricted neck to a quartz stem equipped with a ground-glass joint for connection to a vacuum line. The stem and ampoule were cleansed by washing with concentrated HNO_3 , dilute aqueous NH_3 and distilled H_2O . The tedious washing procedure was repeated three times. The rinsing 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 and gaseous waste. The cleaning procedure removes soluble contamination from the quartz surface and eliminates the saliva (from the glassblower) from the reaction system. The ampoules were attached to the vacuum line and flamed to a red glow to volatilize any absorbed substances inside.

At least duplicate samples were prepared for all experiments. The reaction mixtures were introduced into the ampoules as a liquid in all instances. The solutions were sufficiently cooled in all cases to prevent volatilization of the solvent or solute. The samples in the ampoules were either degassed by the standard alternate freezing, evacuating and thawing procedure, or in some instances carefully sealed at atmospheric conditions. The bromine and iodine monochloride

systems were prepared in a dimmed room. The samples were wrapped in Al foil to eliminate ultraviolet radiation induced reactions. All samples were quick-frozen and stored under liquid N_2 to eliminate thermal exchange reactions. The ^{129}I and ^{131}I were obtained from Oak Ridge National Laboratory in aqueous $Na^{129}I$ or $Na^{131}I$ solution. The iodide salt was oxidized to iodine with H_2O_2 , catalyzed with a trace of HNO_3 , and extracted into the hydrocarbons. The solutions were washed and dried. Iodine concentrations were then determined photometrically with a Bausch and Lomb Spectronic 20.

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^{11} thermal neutrons $cm^{-2} sec^{-1}$ was present at an operating power of 15.5 kilowatts. For long irradiations the various ports in the lazy susan sample holder were employed, and the assembly was rotated to ensure that all samples received the same neutron flux and radiation dose. The assembly was not rotated for short irradiations, or the "rabbit" facility was employed. The radiation dose was approximately $3 \times 10^{17} \text{ ev } g^{-1} \text{ min}^{-1}$ as determined by using Frick dosimetry,⁵⁰ and ^{131}I organic pickup in irradiated $c-C_6H_{12}$.⁵¹ In most instances the organic yields were negligibly dependent upon the duration or irradiation. Appropriate corrections for radiation-induced reactions are required only in reaction systems containing a very dilute mole fraction of scavenger.

The quartz ampoules containing the liquid reaction systems were

sealed in plastic bags to prevent radioactive gases from escaping if the ampoules were accidentally broken. The reactions systems were inserted into TRIGA tubes or the "rabbit" capsules which were specifically designed for the TRIGA reactor. Neutron irradiation times varied between 1 and 1800 seconds.

Most samples to be irradiated at 77° K were inserted into plastic bags, filled with mineral oil and equilibrated to 77° K. Following the 10 sec, or less, thermal neutron irradiations, the ampoules were removed from the crystalline oil, washed with a series of halocarbon baths, and then broken under the extraction solution. If possible the post-reactor operations were performed before the sample liquefied. Other samples were removed from liquid N_2 and irradiated for 2-10 sec. Parks⁵² has determined the average temperature rise for the experimental conditions. The temperature rose to 80° K at 30 sec after removal from the liquid nitrogen, 83° K at 45 sec, and 103° at 55 sec.

The samples were taken from the reactor and transferred rapidly in order that the sample could be extracted and/or frozen and extracted at the appropriate time. Some of the samples were stored in a lead pig or liquid N_2 dewar and analyzed in the radiochemistry laboratory at the University of Nebraska. The first concern for all experiments was to minimize personal radiation hazards. Standard radiochemical techniques and practices were employed at all times.

Extraction of Organic and Inorganic Activities

The quartz ampoules containing the reaction systems were placed in specially designed separatory funnels. The reinforced separatory funnels contained the proper volumes of CCl_4 , halogen carrier and aqueous $0.5 \text{ M Na}_2\text{SO}_3$ such that the volumes of organic and inorganic phases were equal after the reaction system was added. The quartz ampoules were broken by vigorous shaking of the funnel. After a thorough mixing and equilibration, the CCl_4 phase contained the organically soluble labeled alkyl halides, etc. formed as a result of the nuclear induced reactions. The phases were separated rapidly (within 10-30 sec) after the interface appeared if isomeric transition induced reactions were occurring during the extraction process. 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.

Determination of Isomeric Transition Induced Organic Yields

When ^{129}I or ^{81}Br are subjected to a thermal neutron flux a large percentage of the activated nuclei are born in a metastable nuclear state.²⁷⁻²⁹ For example as shown in Fig. 2a, 67% of the ^{129}I atoms which absorb a neutron will result in $^{130\text{m}}\text{I}$; whereas 33% are born as ground nuclear state ^{130}I . The $^{130\text{m}}\text{I}$ decays to ^{130}I by isomeric transition and to ^{130}Xe by beta decay. Likewise, the percentage of $^{82\text{m}}\text{Br}$ (91%) and ^{82}Br , and the percentage of $^{82\text{m}}\text{Br}$ decaying by isomeric transition to ^{82}Br (99.8%) and by beta decay to ^{82}Kr are depicted in Fig. 2b.

Figure 2. Radiative neutron capture and subsequent decaying routes of (a) Iodine-129; (b) Bromine-81.

Merrigan^{51,53-55} developed a freeze-thaw technique for determining ⁸²Br isomeric transition induced organic yields independent of the radiative neutron capture organic yields. Essentially the technique consists of the neutron irradiation of a solid sample containing halogen and an aliphatic hydrocarbon. The solid state organic yields are usually less than 1% at concentrations of halogen where fractional crystallization or clumping of the halogen occurs during the freezing process. However, when the sample is liquefied following the neutron irradiation, the organic yields increase with the duration of time that isomeric transition reactions have occurred. Merrigan⁵³ developed an expression to calculate the (IT) organic yields based on information obtained with the freeze-thaw technique. Equation (1) is a general expression that is applicable to the determination of the organic yields of bromine and iodine isomeric transition induced reactions in liquid alkanes. Equation (1) is derived in Appendix I for the sake of completeness of this dissertation.

$$OY_{IT} \text{ liquid} = \left[R^{\infty} - \alpha R^0 / \beta \exp(-\lambda t) \right] - \left[(1 - \exp(-\lambda t)) R^0 / \exp(-\lambda t) \right] \quad (1)$$

The constants α and β are the fraction of the total activity produced directly by radiative neutron capture and the (IT) activated processes decaying in the liquid state, respectively. For ¹³⁰I^m systems α and β are 0.39 and 0.61 respectively;²⁷ but, for ⁸²Br^m systems α and β are 0.09 and 0.91 respectively.⁵⁶ R^{∞} is the organic yield produced in the liquid state when a sample is liquefied immediately ($\exp^{-\lambda t}$ describes the duration of time the sample was solid from mid-point of irradiation to liquefaction) after irradiation and after

99.9% of the metastable isomer has decayed to the ground state. R^0 is the organic yield produced in the solid state.

In instances where the solid state organic yields are less than 1% the correction for R^0 is nearly negligible. But if R^0 is appreciable, the above equation is valid only if the solid state organic yield is independent of the mode of activation, and does not change as a function of time following the neutron irradiation. These two restrictions have been tested, and were partially responsible for the motivation to perform the experiments described in Chapters IV and V.

Assaying Procedures

The radiohalogens 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 a 4 pi 2" x 2" NaI(Tl) crystal. A description of the counting equipment, the counting geometry and the lack of a need for corrections due to counting coincidence losses and density have been adequately discussed in previous theses from this laboratory.^{50,51,57,58} The multichannel analyzer examines the gamma-ray spectrum of the radioisotopes, and permits the qualitative identification and quantitative determination of the isotopes being analyzed. Representative spectra of the various isotopes used in this research are available.⁵⁹

The readout of the Tracerlab instrument was recorded manually; whereas, the output of the multichannel analyzer was stored on paper tape or typed-out on paper. The various calculations were performed either on the IBM 1620 or 360-65 computer, which was programmed to

calculate the organic yields corrected for background, radioactive decay and if necessary, Compton scatter.

The samples were assayed at the appropriate times which depended on the decay characteristics of the isotope(s) being analyzed. The timing procedures for assaying the various bromine isotopes has been discussed previously.⁵¹ The timing procedures employed for the assay of iodine isotopes are similar, with the appropriate modifications for the decay characteristics of the isotopes being analyzed. Spectrum stripping techniques were used to simultaneously determine ^{128}I and ^{38}Cl activities.

Determination of Labeled Product Distributions

The labeled product distributions of the radiohalogens in the hydrocarbons were determined by radiogas chromatography. A schematic diagram of the radiogas chromatograph is depicted in Fig. 3. The basic features of the radiogas chromatograph have been described elsewhere;^{51,60} however, R. L. Ayres,⁶¹ of this laboratory, recently improved several features by incorporating a Hewlett Packard D.C. power supply (Harrison 6202B), a Gilmont Instruments Inc. flowmeter, and Aerograph thermal conductivity cells and a four part backflush valve to facilitate elution of high boiling fractions which pass through the column slowly. A 2.1 m spiral column, 4-mm i.d., filled with 42-60 mesh Wilkens Instrumental firebrick coated with 40% of its weight of General Electric SF-81(50) silicone oil was used, with He as the mobile phase.

Silicone oil was chosen as the stationary phase because of its general separating characteristics, rather than selective abilities,

Figure 3. Schematic of the Radiogas Chromatograph

and for its proven ability to separate alkyl halides.⁵⁴ Since silicone oil is unselective to alkyl halides, they will elute from the column in a general order of increasing boiling point and/or molecular weight. The more compact the molecule the faster it travels through the column, i.e. tertiary > secondary > primary.

Ground firebrick was prepared as the solid support for the liquid phase by dissolving 40g of liquid silicon oil in 250 ml of chloroform, and suspending 100 g of firebrick in the solution. The chloroform was volatilized under vigorous mechanical stirring. The resultant firebrick coated with 40% of its weight of silicone oil was tightly packed in the coiled glass column.

The samples irradiated for radiogas chromatographic analysis were cooled to prevent evaporation of methyl halides, and extracted with 1 ml of the hydrocarbon solvent being investigated and 3 ml of 0.5 M Na_2SO_3 . Quantitative organic product distributions were initially determined in the absence of organic iodide or bromide carriers to prevent any exchange between carriers and labeled products at the elevated temperatures of the chromatograph. Subsequent runs employed carriers for product identification. The activities, which were corrected for background, flowrate and radioactive decay, were determined by planimeter readings of areas under individual peaks.

CHAPTER III

ISOTOPE EFFECTS OF IODINE REACTIONS ACTIVATED BY THE RADIATIVE NEUTRON CAPTURE AND ISOMERIC TRANSITION PROCESSES IN LIQUID HYDROCARBONS

Chapter III

Isotope Effects of Iodine Reactions Activated by the Radiative Neutron
Capture and Isomeric Transition Processes in Liquid Hydrocarbons

The recent discovery²⁷ of the $^{130\text{m}}\text{I}$ (IT) ^{130}I nuclear reaction ($T_{1/2} = 9.2$ min) has made it possible to compare isomeric transition induced reactions with the reactions of other iodine isotopes affected by other nuclear transformations. The (n, γ), (γ ,n), (d,p) and (IT) processes were reported to produce similar effects in several liquid alkyl halides.^{62,63} In iodine-hydrocarbon systems where iodine is not contained in the target molecule, Schuler and McCauley⁶⁴ suggested that the organic yields resulting from the (n,2n) processes were higher than those from the (n, γ) process due to a higher recoil energy of the (n,2n) transformation. Since isomeric transition activated ^{130}I undoubtedly has much less kinetic energy than the (n, γ)-activated ^{128}I , an isotope effect might be expected. None was found²⁷ in the n-hexane- I_2 system within $\pm 5\%$.

The moderation by rare gases of the ^{127}I (n, γ) ^{128}I gas phase reaction with CH_4 resembles the moderation by rare gases⁴⁰ of the $^{82\text{m}}\text{Br}$ (IT) ^{82}Br reaction with gaseous methane,⁶⁵ more so than the ^{79}Br (n, γ) ^{80}Br reaction with gaseous CH_4 .^{42,43} The similarity of ^{128}I reactions to those of (IT) activated bromine reactions suggests that ^{128}I gas phase reactions may be principally the result of internal conversion. The purpose of this research was (1) to determine the half-life of $^{130\text{m}}\text{I}$, (2) to investigate for possible isotope effects, especially between ^{128}I and (n, γ) activated $^{130}\text{I} + ^{130\text{m}}\text{I}$ in various

liquid hydrocarbons, (3) to compare the $^{129}\text{I} (n, \gamma) ^{130}\text{I} + ^{129}\text{I} (n, \gamma) ^{130\text{m}}\text{I}$, $^{127}\text{I} (n, \gamma) ^{128}\text{I}$, and $^{130\text{m}}\text{I} (\text{IT}) ^{130}\text{I}$ induced organic yields at several concentrations in selected hydrocarbons, (4) to compare the various radioiodine and radiobromine product distributions produced by the radiative neutron capture and isomeric transition induced reactions, and (5) to correlate the results with an acceptable mechanism.

Determination of the Half-Life of $^{130\text{m}}\text{I}$

The freeze-thaw technique⁵³ developed in the study of $^{82}\text{Br}^{\text{m}} (\text{IT}) ^{82}\text{Br}$ reactions is applicable without modification to the study of $^{130\text{m}}\text{I} (\text{IT}) ^{130}\text{I}$ reactions in aliphatic hydrocarbons. In addition the technique permits an independent method for determining the half-life of the recently discovered²⁷ $^{130\text{m}}\text{I}$.

The half-life of $^{130\text{m}}\text{I}$ was determined in cyclohexane containing 7.8×10^{-3} mf $^{129}\text{I}(\text{I}_2)$. The ^{130}I organic yield following a 30 sec thermal neutron irradiation was 2.8%. The low yield is ascribed to a phase separation of the iodine and hydrocarbon during the freezing process. As shown in Chapter IV, and V the solid state organic yields are constant and independent of the duration of time isomeric transition reactions have occurred in the solid state. However, when an identical sample was melted 20 sec after a thermal neutron irradiation at 77°K , and $^{130\text{m}}\text{I}$ allowed to decay in the liquid system, the yield was 21.7%. By use of equation (1) it is possible to calculate the organic yield due to isomeric transition. That is, by allowing for the fraction²⁷ (0.61) of ^{130}I born by (IT) reactions and the fraction of $^{130\text{m}}\text{I}$ which decayed while the sample was solid, the isomeric transition organic yield can be calculated.

The "growth" or increases in the ^{130}I organic yields in liquid cyclohexane are presented in Table II and are depicted in Figure 4. The intermediate points were determined by resolidifying the samples containing the $^{130}\text{I}^{\text{m}}$. The high rate of increase in the organic yield due to isomeric transition could be halted by freezing the sample in liquid nitrogen. That is, the freezing process produces clumping or total segregation of the $^{130}\text{I}^{\text{m}}(\text{I}_2)$.

Identical 1.0 ml samples in quartz ampoules were prepared from a single reaction mixture to eliminate random volume measurement errors between separate samples. Each sample was irradiated with neutrons for 30 ± 2 sec in the solid state and thawed quickly by immersing the ampoule in a hot water bath exactly 37 seconds after the beginning of the irradiation.

The timing procedure is necessary to insure that the ratio of $^{130}\text{I}^{\text{m}}$ present upon liquefaction to the total $^{130}\text{I}^{\text{m}}$ in the reactor was nearly identical in all samples. The time required for thawing was 4 ± 2 seconds. Approximately 4 ± 2 seconds were required if the liquid samples were refrozen again in liquid nitrogen. The duration of time the sample was liquid was recorded within 5 ± 2 seconds.

If the observed increases in the ^{130}I organic yields were only a result of $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I induced reactions, the rate of increase should be dependent only on $^{130}\text{I}^{\text{m}}$ decay, and hence related to its half-life. Then the growth of ^{130}I yields due to (IT) in the liquid state can be described by equation (2).

$$R^t - R_{\text{total}}^0 = R^{\infty} - R_{\text{total}}^0(1 - e^{-\lambda t}) \quad (2)$$

Table II. Growth of ^{130}I Organic Yields with
Duration of Time $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I Processes
Occurred in Liquid Cyclohexane^a

Time Liquid (Min)	R^{t} , Organic Yield ^b
1.0	3.9
2.0	5.0
3.0	6.8
4.0	7.9
7.0	10.2
8.0	11.0
9.0	12.2
10.0	13.2
12.0	13.7
13.0	14.5
14.0	15.6
15.0	14.8
16.0	16.1
17.0	16.9
18.0	17.1
19.0	17.1
20.0	18.9
21.0	19.0
23.0	19.5
26.0	19.8
30.0	20.5
40.0	20.8
50.0	21.2
70.0	21.7
90.0	21.7

^a Phillips research grade cyclohexane containing
 7.8×10^{-3} mf $^{129}\text{I}(\text{I}_2)$.

^b 30 sec neutron irradiation

Figure 4. Growth of ^{130}I organic yields by isomeric transition in liquid $\text{c-C}_6\text{H}_{12}$ —
 0.0078 mf I_2 following neutron irradiation of solid system.

Where: R^{∞} is the maximum organic yield obtainable in a liquid system after $^{130}\text{I}^{\text{m}}$ has decayed to ^{130}I . R°_{total} is the organic yield produced in the solid state. Since the fraction of $^{130}\text{I}^{\text{m}}$ which would decay in the time, Δt , between the initial liquefaction and subsequent re-freezing to halt further changes in the ^{130}I organic yields is $(1 - e^{-\lambda t})$, the organic yield, R^t , at any time, t , would be $(R^{\infty} - R^{\circ}_{\text{total}})(1 - e^{-\lambda t})$. The decay constant, λ , is for $^{130}\text{I}^{\text{m}}$. Equation (2) may be rearranged⁵³ with the result that a plot of $\log [(R^{\infty} - R^{\circ}) / (R^{\infty} - R^t)]$ vs Δt will give a straight line with a slope of $(0.693) / (2.303 \cdot T_{1/2})$. The half-life may be determined to a first-approximation. However, only a fraction, β , of the total activated atoms are born in a metastable nuclear state which can give organic combination as a result of isomeric transition. If α and β are the fractions of the total activity resulting from (n, γ) and (IT) , respectively, and since the contribution to the organic yield as a result of (IT) is dependent on the fraction of $^{130}\text{I}^{\text{m}}$ decaying in the solid state

$$R^{\circ}_{\text{total}} = \alpha R^{\circ}_{(n, \gamma)} + \beta R^{\circ}_{(\text{IT})}(e^{-\lambda t}) \quad (3)$$

Using the decay constant, as determined in the first approximation, and the improved R° , a better value of the half-life of $^{130}\text{I}^{\text{m}}$ may be determined.

With the appropriate plot (Fig. 5), the half-life of $^{130}\text{I}^{\text{m}}$ was determined to be 8.9 ± 0.3 min. The half-life determined by the freeze-thaw technique is consistent with the previously reported 9.2 ± 0.2 min²⁷ and the more recent value⁶⁶ of 8.8 minutes.

Figure 5. Determination of the half-life of $^{130}\text{I}^{\text{m}}$.

Determination of $^{130}\text{I} + ^{130\text{m}}\text{I}$ Organic Yields Activated by ^{129}I (n, γ)
 $^{130}\text{I} + ^{129}\text{I}$ (n, γ) $^{130\text{m}}\text{I}$ Processes

The liquid hydrocarbon systems containing dissolved $^{129}\text{I}_2$ at the various concentrations studied were irradiated with thermal neutrons, and subsequently frozen in liquid nitrogen at various time intervals after removal from the reactor. The ^{130}I organic yields increased with the duration of time $^{130\text{m}}\text{I}$ (IT) ^{130}I processes were allowed to occur in the liquid phase. Similar effects were reported for $^{82}\text{Br}^{\text{m}}$ -hydrocarbon systems,⁵⁴ where $^{82}\text{Br}^{\text{m}}$ (IT) ^{82}Br induced yields were greater than those of (n, γ) activated $^{82}\text{Br}^{\text{m}}$. Typical ^{130}I organic yield "growth" curves are shown in Fig. 6 and Tables III and IV for the n-hexane and n-nonane systems. It has been shown that changes in ^{82}Br organic yields due to (IT) activated reactions could be halted by freezing the systems in liquid nitrogen.^{53,54} The effect is discussed in detail in Chapter VI and has been shown for the iodine-hydrocarbons systems studied.

As shown in Fig. 6 and Table V for 0.1 mole % ($^{129}\text{I}_2 + ^{127}\text{I}_2$) in n-hexane, the organic yields resulting from freezing samples left in the liquid phase 4 and 7 minutes prior to freezing and extraction from solid state at various times do not indicate any changes in the organic yields following the freezing of the sample. Apparently $^{130\text{m}}\text{I}$ organic yields behave similarly to those of $^{82}\text{Br}^{\text{m}}$ when frozen. The prior interpretation for the bromine systems⁵³ postulated that freezing the sample essentially separated organic and inorganic phases. Hence the portion of halogen which was in inorganic combination would remain inorganic; whereas, that which was in organic combination would be

Figure 6. Iodine-130 organic yields in n-hexane (0.1 mole % I_2), ●, and n-nonane (0.2 mole % I_2), ○, as a function of time in the liquid phase. Organic yields resulting from freezing samples left in the liquid phase 4 min., Δ, and 7 min., □, and extracting from the solid state at various times.

Table III. Iodine-130 Organic Yields in n-Hexane (0.1 mole % I_2) as a Function of Time in the Liquid Phase.

Time Liquid (Min)*	Organic Yield
0.5	33.2
1.0	34.6
2.0	33.8
3.0	36.7
6.0	38.4
7.0	38.0
10.0	39.0
12.0	40.2
15.0	41.6
20.0	40.8
25.0	42.5
30.0	43.1
40.0	43.8
45.0	43.9
60.0	44.2
70.0	44.8
80.0	43.0
90 +	43.8

* 15 second thermal neutron irradiation

Table IV. Iodine-130 Organic Yields in
n-Nonane (0.2 mole % I_2) as a Function of
Time in the Liquid Phase

Time Liquid (Min)*	Organic Yield
0.5	39.7
2.0	41.3
3.0	43.9
7.0	43.5
8.0	44.2
10.0	46.9
20.0	46.8
25.0	50.5
30.0	48.5
40.0	48.5
50.0	48.0
60.0	48.8
69.0	50.9
78.0	48.9
90 +	49.5

* 15 second thermal neutron irradiation

Table V. Iodine-130 Organic Yields Resulting From Freezing Samples Left in the Liquid Phase 4 and 7 Minutes, and Extracted From the Solid State at Various Times

Time (Min) in Solid State	Organic Yield* (Liquid 4 Min)	Organic Yield* (Liquid 7 Min)
5.0	38.3	
7.0		37.8
8.0		38.4
10.0	37.3	39.9
15.0	36.6	
20.0	37.5	
40.0	36.3	38.7
60.0	36.2	
90 +	36.7	38.8

* 15 second thermal neutron irradiation

dispersed in the organic phase in the solid state, and remain predominately in organic combination. Other recent evidence⁶⁷ indicates a similar behavior in liquid n-propyl bromide. About 85% of the $^{82}\text{Br}^m$ in organic combination will be stabilized as organic following isomeric transition; whereas, only 32% of the isomeric transition events of inorganic $^{82}\text{Br}^m$ produce organically bound ^{82}Br . It would not seem probable that organic halogen dispersed as an organic compound could be depended on to remain predominately in organic combination following isomeric transition. Hence a given halogen atom undergoing isomeric transition may not actually recombine with the fragment produced by isomeric transition, but may result in a new organic or inorganic product. Presumably by freezing the samples an averaging effect occurs and the final observed results are organic yields in the solid state which are nearly constant with respect to time of extraction. Freezing effects are discussed further in Chapter VI.

The extrapolated organic yields as shown in Fig. 6 correspond to the combined organic yields of (n, γ)-activated $^{130}\text{I}^m$ (which is formed in about 66% of the radiative neutron capture event)²⁷ and of (n, γ) activated ground-state ^{130}I . Table VI presents the increases in ^{130}I organic yields with the duration of time the $^{130}\text{I}^m$ (IT) ^{130}I processes occurred in the liquid phases at various I_2 concentrations in selected hydrocarbons. Evidence that thermal reactions did not contribute significantly to the increases in the observed organic yields is implied, since the organic yields did not increase if tracer quantities of ^{130}I (I_2) or ^{131}I (I_2) were added to the liquid hydrocarbons. Only impure reaction systems would be influenced by thermal reactions.

Table VI. Increases in ^{130}I Organic Yields with Duration of Time in the Liquid Phase at Various I_2 Concentrations in Selected Hydrocarbons

Solvent	mf I_2 $\times 10^3$	Time Liquid (Min)	Organic Yield ^{130}I
n-pentane	0.3	0.5	35.7
		1.0	37.6
	1.3	0.5	30.8
		1.0	33.8
	6.0	0.5	29.2
n-hexane	1.0	0.5	33.2
		3.0	36.7
		90+	43.8
	5.5	0.5	25.8
		10.0	28.8
		90+	31.7
cyclohexane	8.0	0.5	31.6
		90+	38.4
n-heptane	0.39	0.5	37.8
		5.0	41.0
	4.5	0.5	33.6
	7.0	0.5	30.3
	7.3	0.5	22.4
		5.0	23.5
n-octane	0.5	0.5	43.0
		1.0	45.4
	1.9	0.5	41.6
		0.5	41.9
	3.0	0.5	38.4
	7.0	0.5	33.5
		0.5	32.8

Table VI cont.

Solvent	mf I_2 $\times 10^3$	Time Liquid (Min)*	Organic Yield ^{130}I
n-nonane	2.1	0.5	39.7
		7.0	43.5
		90+	49.5
	7.0	0.5	36.0
		0.5	36.4
	7.5	0.5	30.1
		0.5	30.6
		5.0	33.0
	8.6	0.5	24.6
		0.5	26.0
		5.0	27.8

* The reaction systems were immersed in liquid N_2 to halt further changes in the $^{130}I^m$ (IT) ^{130}I organic yields.

The increases in the observed ^{130}I organic yields may be related to the half-life of $^{130}\text{I}^{\text{m}}$ and correspond to isomeric transition induced reactions of ^{130}I . Although present techniques do not permit an independent determination of radiative neutron capture organic yields of $^{130}\text{I}^{\text{m}}$ and ^{130}I , an isotope effect between the two species would not be expected. The values of $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ organic yields can be found by extrapolating a plot of the observed ^{130}I organic yields vs time kept in the liquid state to zero time. (See Fig. 6) In the hydrocarbons studied, $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I activated yields are greater than those of (n, γ) activated $^{129}\text{I} + ^{130}\text{I}^{\text{m}}$.

Comparison of ^{128}I and $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ Organic Yields to Those of Isomeric Transition Induced Organic Yields of ^{130}I

Presented in Table VII are representative organic yields of ^{128}I and $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ activated by the radiative neutron capture processes and ^{130}I activated by isomeric transition in various hydrocarbons as a function of dissolved I_2 concentration. The isomeric transition induced organic yields were determined by the freeze-thaw technique,⁵³ and represent organic yields due entirely to isomeric transition induced reactions. For example, Fig. 4 depicts the increases in the ^{130}I organic yields as a result of isomeric transition induced reactions in liquid cyclohexane containing 0.78 mole percent I_2 .

An alternate method for obtaining the ^{130}I isomeric transition organic yield was tested. An aqueous solution of Na^{129}I was irradiated with thermal neutrons to produce $(^{130}\text{I}^{\text{m}})^{-}$ which was oxidized with a trace of H_2O_2 catalyzed with a trace of HNO_3 . The $\text{I}_2 (^{130}\text{I}^{\text{m}})$ solution was extracted into n-hexane containing sufficient $\text{I}_2 (^{127}\text{I})$ to make

Table VII. Iodine Organic Yields Induced by (n, γ) and (IT) Processes in Liquid Hydrocarbons

Hydrocarbon	I_2 mf $\times 10^3$	^{128}I	Organic Yields ^a ^{130}I by (IT) ^b	$^{130}I^m + ^{130}I$ by (n, γ)
n-pentane	0.3	42 ^d	43.3	36.6
	1.3	38 ^d	38.7	32.0
	6.0	34.0	35.1	29.2
n-hexane	0.2		50.0	43.0
	1.0	42.5	44.0	33.0
	5.5	29.0	30.8	25.0
cyclohexane	8.0	37.5	36.5	31.0
	5.2	40.5	39.6	
n-heptane	0.4		58.0	37.8
	1.6	39.7	43.6	33.5
	4.5	37.5	38.7	31.0
	7.0	36.2	36.0	29.0
n-octane	0.5		55.5	44.2
	3.0	45.0	47.2	38.0
	7.0	38.5	41.1	32.5
n-nonane	2.1	46.0	47.7	39.0
	7.0		41.5	35.0
	7.5	37.3	38.5	30.0

^a Averages of at least 4 determinations; experimental error $\leq 1\%$.

^b Isomeric transition (IT) organic yields were obtained by irradiating the samples for 10 sec at 77° K, thawing exactly 35 sec after the beginning of the neutron irradiation and allowing $^{130}I^m$ to decay in the liquid systems at room temperature.

^c $^{130}I^m + ^{130}I$ organic yields in liquid hydrocarbons were determined by extrapolating a plot of ^{130}I organic yields vs time liquid to zero time. Samples were frozen in liquid N_2 at various times after neutron irradiation to halt further changes in the observed ^{130}I organic yields due to $^{130}I^m$ (IT) ^{130}I induced reactions. See text for discussion.

^d Data of Aditya and Willard,⁶⁸ $I_2 + 5$ mole % C_2H_5I in $n-C_5H_{12}$.

the resulting iodine concentration 1.2×10^{-3} mf. The reaction system was not dried or degassed. After 90 minutes essentially all the $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I processes had occurred. An aliquot was taken to be extracted and assayed as described in Chapter II. The appropriate corrections for the $^{130}\text{I}^{\text{m}}$ which had decayed prior to the mixing, and for 39% of the total ^{130}I activity being formed directly by radiative neutron capture were applied. The resulting isomeric transition organic yield was 42.6 as compared to 44.0 for the ^{130}I (IT) yield at 1.0×10^{-3} mf. (See Table VII) The agreement is considered very acceptable.

However, the $^{129}\text{I} (n, \gamma) ^{130}\text{I}^{\text{m}}$ and $^{129}\text{I} (n, \gamma) ^{130}\text{I}$ induced organic yields were determined by extrapolation of plots similar to Fig. 6. Hence, the quoted organic yields may represent an upper limit for the (n, γ) organic yields, due to experimental error in the extrapolated values. The ^{128}I data are similar to those reported by others.^{68,69} At all I_2 concentrations studied, ^{128}I and ^{130}I (by isomeric transition) organic yields were similar, within experimental error, as would be expected from previous results.²⁷ The $^{130}\text{I}^{\text{m}}$ and ^{130}I organic yields show the expected increases in organic yields with increases in the chain length of hydrocarbon solvent as shown for ^{128}I and ^{80}Br by Aditya and Willard.⁶⁸ However, in all systems studied the radiative neutron capture organic yields of $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ were consistently lower than the isomeric transition induced ^{130}I organic yields. The ratios of the ^{130}I organic yields due to isomeric transition to the $^{130}\text{I}^{\text{m}}$ organic yields resulting from radiative neutron capture were about 1.2 - 1.4.

Chang and Willard⁷⁰ report ^{128}I and ^{130}I organic yields in n-hexane of 34.0 and 35.5 at 0.6 mole % I_2 and 37.2 and 40.2 at 0.1 mole % I_2 . These data are quite similar to ours, but their ^{130}I data includes the (n, γ) organic yield plus a significant contribution of isomeric transition induced reactions which occurred prior to analysis. This appears to be the case since Chang and Willard's⁷⁰ ^{130}I organic yields at 0.1 mole % I_2 fall between our values for $^{130}\text{I}^{\text{m}}$ (by n, γ) and ^{130}I (by IT). The data differ in magnitude at 0.6 mole %; however, this does not effect either Professor Willard's or our interpretation of the data. Fig. 7 depicts the effect of I_2 concentration on the organic yields in n-hexane and compares the data reported here to that of Chang and Willard.⁷⁰ As shown, repurification of the Phillips research grade n-hexane did not affect the liquid state organic yields. Similar scavenger curves were observed in the other systems studied.

It is of interest to note that the total organic yield observed by irradiating a sample liquid and letting all the isomeric transition events occur in the liquid phase will result in an observed organic yield, which is within a few percent of the isomeric transition organic yield obtained by the freeze-thaw technique. Likewise, the similarity of (n, γ) + (IT) and (IT) organic yields is also characteristic of ^{82}Br . Table VIII presents a comparison of the organic yields of the ^{82}Br + $^{82}\text{Br}^{\text{m}}$ by (n, γ), the ^{82}Br by (n, γ) + (IT), the ^{82}Br by (IT), the ^{130}I (n, γ) + (IT) and ^{130}I by (IT) reactions in selected hydrocarbons containing 7.0×10^{-3} mf halogen. As expected from earlier results⁵¹ the ^{82}Br + $^{82}\text{Br}^{\text{m}}$ by (n, γ) organic yields are

Figure 7. Effect of I_2 concentration in n-hexane on ^{128}I , $\circ$, $\bullet$ and of $^{130}I + ^{130}I^m$, Δ , by (n, γ); ^{128}I , $\times$; and ^{130}I , $\ast$ by (n, γ) and (IT) (ref. 70); ^{130}I by (IT), $\blacksquare$, $\square$. Research or repurified ($\circ$, $\square$) n-hexane.

Table XVIII. Comparison of (IT), (n, γ) and (n, γ) + (IT) Organic Yields of ^{82}Br and ^{130}I in Selected Hydrocarbons^{a, b}

Solvent ^a	Organic Yields ^b					
	$^{82}\text{Br} + ^{82}\text{Br}^m$ (n, γ) 10 sec	^{82}Br (n, γ + IT) 10 sec	^{82}Br (n, γ + IT) 30 min	^{82}Br (IT) 10 sec	^{130}I (n, γ + IT) 30 min	^{130}I (IT) 10 sec
n-pentane	----	32.4	33.7	----	34.0	35.0
cyclohexane	26.3	36.3	35.9	37.4	36.3	36.5
2,2-dimethyl butane	24.9	37.0	38.5	32.4	35.2	----
n-heptane	18.8	40.5	41.5	39.5	35.7	36.0

^a Systems contained 7.0×10^{-3} mf Br_2 or I_2

^b Neutron irradiation times are given

substantially lower than the ^{82}Br isomeric transition. The fact that the length of neutron irradiation, i.e. either 10 or 1800 seconds did not have an appreciable effect, either the ^{130}I or the ^{82}Br (n, γ) + (IT) total organic yields suggests that the reaction systems for radiogas chromatography (as discussed later) have experienced a negligible fraction of radiation damage. However, the difference between the $^{130}\text{I} + ^{130}\text{I}^m$ and $^{82}\text{Br} + ^{82}\text{Br}^m$ radiative neutron capture versus the ^{130}I and ^{82}Br isomeric transition organic yields are markedly dependent on the average lifetime of the radioactive atoms in the liquid state. The data of Table VIII rather firmly confirm the suggestion that the lack of agreement between laboratories as to the existence of isotope effects between (n, γ) and (IT) activated reactions of various iodine and bromine isotopes is probably due to the differences in periods of irradiation and standing before the separation of organic and inorganic components.

The organic yields of ^{82}Br and ^{130}I activated by isomeric transition are compared to the radiative neutron capture organic yields of $^{80}\text{Br}^m$ and ^{128}I in cyclohexane in Table IX.

Table IX. Organic Yields of (IT)-Produced ^{130}I and ^{82}Br and (n, γ)-Produced ^{128}I and $^{80}\text{Br}^m$ in Cyclohexane

mf of I_2	^{130}I	^{128}I	^{82}Br	$^{80}\text{Br}^m$
7.8×10^{-3}	35.3	36.1	35.5	32.5
5.2×10^{-3}	39.6	40.5	39.2	25.4

The similarity of ^{130}I by (IT) and ^{128}I by (n, γ) organic yields may indicate a similarity of reactions independent of the initial kinetic energy of the activation atom. Their likeness to ^{82}Br isomeric transition yields would suggest that activated halogens may trace chemical processes which result from a similarity of environmental activation/or decomposition. The similarities were also observed between ^{130}I , ^{128}I and ^{80}Br formed by (IT), (n, γ) and (IT) processes respectively in n-hexane.²⁷ Merrigan et.al.⁵⁴ examined in detail the (n, γ) and (IT) activated reactions of bromine in the C_6 -alkanes and CCl_4 , and concluded that the isomeric transition yields are about 1.7 times greater than the radiative neutron capture organic yields of $^{80}\text{Br}^{\text{m}}$ and $^{82}\text{Br} + ^{82}\text{Br}^{\text{m}}$. Merrigan et.al.^{51,53,54} suggested that competition between processes which yield inorganic or organic combination, the types of organic radicals produced, and caging abilities of the system may have an appreciable influence on organic yields; and that the isomeric transition processes and associated internal conversion and Auger radiation result in a more reactive hot-atom zone than is produced by radiative neutron capture. The isotope effects of bromine reactions are again explored in Chapter VI and in the concluding section of this chapter.

Product Distribution of Radioiodine and Radiobromine Recoil Atoms in Liquid Hydrocarbons

Perhaps one of the best tests of the autoradiation hypothesis lies in qualitative and quantitative comparisons of the products formed by different halogen isotopes in a common media. If the autoradiation hypothesis is valid, one would expect similar products between radiative neutron capture and isomeric transition induced processes, even if only a part of the radiative neutron capture processes were the result of internal conversion and Auger electron reactions. Differences in abundances of individual products and total organic yields might be expected to occur as a result of ion-molecule, charge-transfer, ...etc., and other reactions characteristic of the halogen atom. Similarities between iodine and bromine were suggested by similar organic yields between ^{128}I , ^{82}Br by (IT) and ^{130}I by (IT) in liquid n-hexane²⁷ and cyclohexane.

The individual product yields were determined for the ^{127}I (n, γ) ^{128}I , the ^{129}I (n, γ) ^{130}I and $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I , and the ^{81}Br (n, γ) ^{82}Br and $^{82}\text{Br}^{\text{m}}$ (IT) ^{82}Br induced reactions in several liquid hydrocarbons. A typical radiogas chromatogram is illustrated in Fig. 8. Table X presents the product distributions and total organic yields observed when liquid samples of ^{127}I or ($^{127}\text{I} + ^{129}\text{I}$) in hydrocarbons ranging from n-pentane to several isomers of hexane to n-octane were irradiated with thermal neutrons for 30 min. Table XI depicts results obtained when liquid samples of 0.7 mole % of bromine in n-pentane, cyclohexane, 2,2-dimethyl butane, and n-heptane were irradiated for 30 min. The effect of duration of irradiation did not appear to influence the

Figure 8. Radiogas chromatogram of ^{128}I in n-pentane. See Table X for product distribution. Increasing time right to left.

Table X. Product Distributions^a Resulting From the ^{129}I (n, γ) ^{130}I , $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I and ^{127}I (n, γ) ^{128}I Processes in Liquid Hydrocarbons

Solvent	Isotope Assayed	Products ^b										Total Organic Yield
		mf I_2 $\times 10^3$	CH_3I to $\text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{I}$	$\text{C}_3\text{H}_7\text{I}$	$\text{C}_4\text{H}_9\text{I}$	$\text{C}_5\text{H}_{11}\text{I}$	$\text{C}_6\text{H}_{13}\text{I}$	$\text{C}_7\text{H}_{15}\text{I}$	$\text{C}_8\text{H}_{17}\text{I}$	Others ^c	
n-pentane	^{128}I	6.0	6.8	16.4	15.0	4.4	50.6				6.8	34.0
n-hexane	^{130}I	7.0	18.2 ^e		24.3	10.9	9.2	37.4			N.C.	31.7
	^{128}I	9.0	12.2	3.2	14.6	18.4	11.5	40.1			N.C.	29.5
cyclohexane	^{130}I	7.0	8.0 5.5	12.5 7.5	7.0 9.4			27.2 24.8 ^{f1} 32.3 35.4 ^{f2}			11.2 11.0 2.8 ^{c1} 3.5 ^{c1}	36.3
2-methyl pentane	^{130}I	7.5	11.6 14.0	6.6 7.9	14.0 28.6	g g	20.5 25.5	45.0 17.1			2.3 6.9	35.4
3-methyl pentane	^{130}I	7.5	25.1 25.5	27.0 33.0	g g	13.0 16.5	5.0 3.4	25.9 21.6			4.0 N.C.	34.0
2,2-dimethyl butane	^{130}I	7.0	33.2 25.2 27.6	23.9 34.7 30.0	g g g	3.2 ^h 2.6 ^h 2.0 ^h	8.4 ⁱ 5.6 ⁱ 6.4 ⁱ	29.3 31.5 34.0			N.C. N.C. N.C.	35.2

Table X cont.

Solvent	Isotope Assayed	mf I_2 $\times 10^3$	Products ^b								Others ^c	Total Organic Yield
			CH_3I to C_2H_5I	C_2H_5I	C_3H_7I	C_4H_9I	$C_5H_{11}I$	$C_6H_{13}I$	$C_7H_{15}I$	$C_8H_{17}I$		
n-heptane	^{130}I	7.0	12.8	6.2	17.4	12.0	14.0	j	37.3		N.C.	35.7
			11.8	4.8	13.5	9.8	19.6	j	40.5		N.C.	
			15.6	4.1	17.3	12.8	13.8	j	36.5		N.C.	
n-octane	^{130}I	7.0	10.0	6.4	15.8	22.9	10.2	3.3	17.0	14.4	N.C.	41.3

^a Averages of at least two determinations unless shown; duplicate runs of a given sample were in good agreement.

^b The values are the percent of individual products relative to the sum of the fractions collected.

^c Higher boiling fractions; N.C. = not collected; ^{c1} peak eluted before cyclohexyl iodide, but not identified.

^d 30 min neutron irradiation. ^e Methyl and ethyl iodides. ^{f1} Cyclohexyl iodide. ^{f2} Hexyliodides.

^g Peak not detected. ^h Tert-butyl iodide. ⁱ Tert-pentyl iodide

^j $C_5H_{11}I$ values are inclusive of $C_6H_{13}I$ products.

Table XI. Product Distributions^a Resulting From the ^{81}Br (n, γ) ^{82}Br and $^{82}\text{Br}^m$ (IT) ^{82}Br Induced Reactions Following 30 Min Neutron Irradiations of Liquid Hydrocarbons

Solvent	mf Br $\times 10^3$	Products ^b				C ₆ H ₁₃ Br	C ₇ H ₁₅ Br	Others ^c	Total ^d Organic Yield
		CH ₃ Br to C ₂ H ₅ Br	C ₂ H ₅ Br	C ₃ H ₇ Br	C ₄ H ₉ Br				
n-pentane	7.0	15.7	14.6	6.0	7.0	49.8		6.9	33.7
cyclohexane	7.0	9.1	6.4	4.5		21.3 ^f 40.3 ^g		14.1 ^e (4.3) ^e	35.9
2,2-dimethyl butane	7.0	17.6 26.4	20.8 9.9	h h	7.2 5.4	4.0 ⁱ 6.7 ⁱ	50.4 ^j 51.6 ^j	N.C. N.C.	38.5
n-heptane	7.0	9.8	9.6	9.2	12.5	6.7	11.5	40.7	41.5

^a Averages of at least 2 determinations unless shown; duplicate runs of a given sample were in good agreement.

^b The values are the percent of individual products relative to the sum of the fractions collected.

^c Higher boiling fractions; N.C. = not collected.

^d Observed organic yields of ^{82}Br following 30 min neutron irradiations. The ^{82}Br organic yield after a 10 sec irradiation was 32.4 in n-pentane; 37.0 in 2,2-dimethyl butane; and 40.5 in n-heptane.

^e Peak eluted before cyclohexyl bromide, but not identified. ^f Cyclohexyl bromide. ^g Hexyl bromides.

^h Peak not detected. ⁱ Tert-butyl bromide. ^j Tert-butyl bromide.

results, since similar organic yields were obtained for 10 sec and 30 min irradiations. (See Table VIII) Thermal exchange reactions would not be expected to be important, especially for the iodine systems since rapid exchange has been shown to occur only at very low I_2 concentrations.^{71,72} Bromine exchange reactions were minimized by exclusion of light prior to, during, and after the thermal neutron irradiations.

As can be seen in Table X, a definite structural effect exists with regard to certain products. For example at 0.7 mole % I_2 the relative yield, i.e. percent of total organic activity, of methyl iodide was less in cyclohexane than in the normal hydrocarbons (excluding n-pentane); but became more abundant as the branching of the molecules increased. Methyl iodide and ethyl iodide were particularly abundant in 2,2-dimethyl butane, and 3-methyl pentane; whereas, propyl iodides were formed readily in 2-methyl pentane. These data suggest that carbon to carbon bond breakages were most likely to yield labeled products when a highly branched site existed. Similar target molecule effects were observed for bromine recoil reactions in the isomers of hexane.⁵⁴

It is important to note that within the series of normal hydrocarbons studied, the number of labeled products formed increases with the chain length of the hydrocarbon. Experimentally we would expect to find more products as the number of C-C and C-H bonds increased if the relative importance of radical formation was dependent on random fragmentation or autoradiation effects. The labeled products formed are listed in Table X for n-pentane through n-octane. Normal nonane

was also investigated; however, the spectrum of products (five major broad peaks) were complex and yields of individual products could not be identified with certainty.

Within the experimental uncertainty, the product distribution and relative product yields of ^{128}I and ^{130}I are similar, as originally suggested by Chang and Willard.⁷⁰ By analysing samples which contained both ^{128}I and ^{130}I , and then analyzing again after the ^{128}I had decayed, no changes in either the formation or disappearance in the number of products assayed were observed. The labeled product distributions of iodine isotopes in n-pentane and n-hexane may be compared with earlier work. The agreement in product identification⁴⁵ and relative yields⁷⁰ is satisfactory considering the different conditions under which the experiments were performed.

Table XI presents the product distributions of ^{82}Br recoil atoms in several hydrocarbons. The products formed in the hexane isomers, excluding cyclohexane, are similar to those reported by Merrigan et.al.⁵⁴ The earlier investigation in cyclohexane at 7.0 mole % and higher concentrations did not detect the formation of low boiling bromides. However, a re-investigation has shown that methyl, ethyl and propyl bromides are formed at 0.7 mole % Br_2 . This result does not affect earlier interpretations. It is evident that a similar spectrum of products are formed by radioiodine and radiobromine atoms in the liquid hydrocarbons studied. Although the relative yields of iodine and bromine products in a given solvent are somewhat different in abundance, one might a priori expect this to be the case when chemically different halogen isotopes are compared.

The differences in individual product yields of iodine and bromine in a given hydrocarbon may reflect that in addition to the halogen atom tracing of isomeric transition produced radical debris, varying contributions of ion-molecule reactions characteristic of the halogen atom could occur. Additional evidence cited earlier suggests that halogen and tellurium⁷³ atoms activated by isomeric transition have a greater reactivity than is present during radiative neutron capture events.

Mechanistic Considerations

Although various hypotheses, such as the autoradiation hypothesis,⁴⁵ the thermal spike model,⁴⁶ the intermediate complex model,⁴⁷ the modified impact model⁴⁸ and the random fragmentation or "brush heap" model¹ have been presented in recent years to account for the chemical effects of nuclear transformations in condensed state organic media, the autoradiation hypothesis has been the most successful in correlating halogen reactions activated by radiative neutron capture and isomeric transition. The purpose and scope of this dissertation does not suggest that each of the various models should be discussed at length if they appear to be inapplicable.

According to the autoradiation hypothesis,⁴⁵ the radiative neutron capture and isomeric transition processes should give similar products due to combinations of halogen species with radicals formed by localized radiation produced by the internal conversion and Auger electrons emitted by the recoil atom. The hypothesis suggests the similarity of products may be explained if nuclear processes produce nuclei which pass through low-lying metastable states which decay by internal conversion.

Information regarding the detailed γ -ray structure resulting from the $^{127}\text{I} (n, \gamma) ^{128}\text{I}$ reaction is incomplete, extremely complex, and in some cases contradictory. A total of 184 high- and low- γ -rays have been observed,⁷⁴ with an enhancement of high energy intensity which appears to be related to a high-level density at low excitation energy. The proposed low-energy decay scheme includes 12 two-stage cascades. Kalinkin et.al.⁷⁵ found ^{128}I lines at 28 ± 2 , 135 ± 3 and 158 ± 4 kev with 23, 20 and 7.5 gamma quanta, respectively, emitted per 100 neutrons absorbed by ^{127}I . Measurements⁷⁶ of pulse height spectra satisfying the condition of prompt and delayed coincidence and at neutron resonances of iodine have established the presence and half-lives of excited states in ^{128}I . The predominate lines at 30, 137, and 90 Kev had lifetimes of 8.8 ± 1.0 , 8.0 ± 0.6 , and ≤ 0.7 nsec, respectively. (1 nanosecond = 10^{-9} sec) Lifetimes of low-lying states depend on specific nuclear mechanisms; whereas internal conversion processes are not expected to depend on nuclear structure.⁷⁷

Internal conversion is an alternate mode of de-excitation that competes with γ -ray emission. Various physical and chemical data suggest that a high percent percentage of ^{128}I atoms born by radiative neutron capture undergo internal conversion. Wexler⁴¹ has estimated that a minimum of 50% of the ^{128}I atoms are born with a positive charge. The energies of the electrons emitted by the ^{128}I will include the energies of IC electrons, electrons with the energy of the K $\rightarrow$ L transition minus the L binding energy, and in instances of highly charged ions there will be additional Kev and below electrons. In solution the electrons will induce excitation and ionization of the molecules in

close proximity to the ^{128}I ion which emitted them.

Willard² has pointed out that in a large variety of nuclides studied it has been shown that the excitation energy given to the nucleus by the (n,γ) process is normally lost by γ -ray cascades. As in the case of ^{128}I , relatively long-lived excited states are common in the 1-100 Kev energy range, and their decay is commonly accompanied by internal conversion and a vacancy cascade of Auger electrons. If the events last of the order of nanoseconds after the recoil from the initial, highly energetic gamma ray, the labeled atom will have time to enter into a stable combination prior to the charging process. In every instance it will be immediately surrounded by a relatively high concentration of ions, electrons, free radicals and excited molecules with a spectrum of species similar to that which would be produced by gamma irradiation of the bulk of the solution.² Because the Auger electrons have low-energy they will have a high linear energy transfer.* For example,⁷⁸ electrons of 0.1, 1, 10 and 20 kev, the linear energy transfer is 3.3, 1.2, 0.23 and 0.13 ev/ $\text{\AA}$, respectively. The recoil ion will find itself in the center of a high localized concentration of electrons, ions and radicals. In the case of a hot ion, it will be rapidly neutralized by charge transfer with adjacent molecules if its ionization potential is higher than that of the solvent. The most probable fate of the radioactive atom will be to

* Linear energy transfer is defined as the energy lost per unit length of path by the ionizing particle to the medium (for incident gammas, the ionizing particles are the Compton electrons).

react with a radical produced by its own internal conversion and Auger radiation.

The autoradiation hypothesis implies that the ^{128}I nuclei may be sufficiently long lived such that internal conversion does not occur until the atom has lost its kinetic energy of recoil. Recall that the measured⁷⁶ half-lives of the 30-, 137- and 90- Kev levels were $8.0 \leq 0.7$ nsec, and that the recoil energy due to gamma emission was imparted to the recoil atom in less than 10^{-13} sec after neutron capture.⁴⁴ Also, recall that the ejection of one or more internal conversion electrons, followed by loss of other electrons by Auger radiation, occurred frequently within 10^{-12} to 10^{-5} sec after the neutron capture. Hence hot reactions activated by neutron capture take place before the start of internal conversion and the associated avalanche charge increase processes. The autoradiation hypothesis also suggests that the length of the recoil path in the condensed phase may be within the dimensions of the localized volume of high radical concentration produced by the electrons emitted in the nuclear activation process.

The similarity of (n, γ) activated ^{128}I and ^{130}I activated by isomeric transition suggest that a high percentage of ^{128}I atoms born by radiative neutron capture undergo internal conversion. That is, the decay of $^{130}\text{I}^{\text{m}}$ and $^{82}\text{Br}^{\text{m}}$ are known to be highly converted.^{27,28,29} If isomeric transition activation of halogen atoms in liquid hydrocarbons results in atoms more reactive towards organic combination than those produced by radiative neutron capture, as suggested here and in previous studies^{54,79} similarities between ^{128}I and isomeric transition activated ^{130}I reactivities may suggest that nearly 100%

of the ^{128}I atoms are positively charged as a result of their nuclei passing through low-lying metastable states which decay by internal conversion.⁴⁵ However, attempts to find a short-lived isomer of ^{128}I ($T_{1/2} > 2$ sec) were unsuccessful.

The lower organic reactivity of (n, γ) activated $^{80}\text{Br}^{\text{m}}$, $^{82}\text{Br} + ^{82}\text{Br}^{\text{m}}$ and $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ could be ascribed to the possibility that the internal conversion accompanying the neutron capture event occurs before the recoil energy has been dissipated; thus it would be carried away from the center of the pocket of fragments caused by radiolytic effects. However, it seems more likely that the lower reactivity of (n, γ) activated $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$, as well as that of (n, γ) activated ^{82}Br and $^{82}\text{Br}^{\text{m}}$, could be due to a lower percent of ^{130}I , $^{130}\text{I}^{\text{m}}$, $^{82}\text{Br}^{\text{m}}$ and ^{82}Br born by the (n, γ) process in low-lying metastable states.⁷⁹

The differences in individual product yields of iodine and bromine in a given hydrocarbon may reflect that in addition to the halogen atom tracing of isomeric transition produced radical debris, varying contributions of ion-molecule reactions characteristics to the halogen could occur. If autoradiation effects with their accompanying iodine and bromine radical reactions, ion-molecule reactions, etc., account for only a part of the organic yields of (n, γ) activated $^{80}\text{Br}^{\text{m}}$, $^{82}\text{Br} + ^{82}\text{Br}^{\text{m}}$ and $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ reactions in liquid hydrocarbons, then the remaining organic yield may be the result of other processes such as those predicted by the random fragmentation hypothesis.

The random fragmentation (RF) hypothesis¹ postulates that when a halogen atom in a liquid phase environment acquires several kev of recoil energy it starts moving rapidly, but will travel less than a

molecular diameter before it encounters a solvent molecule. In the condensed phases the recoiling atom can not transfer momentum to the struck molecule in an elastic collision and continue on its way. The struck molecule is surrounded by a close packed and intertwined cage of other molecules. The RF hypothesis suggests that the energy of the recoiling atom is dissipated by breaking bonds in a rather random and indiscriminate manner in the vicinity of the energetic atom. When the energetic atom has lost sufficient energy that it can no longer break bonds, it will be confined to, or adjacent to, a pocket of high local concentration of organic radicals and inorganic atoms. The activated atom may react with one of the radicals before it has had the opportunity to diffuse through the system as a thermal atom; otherwise, it may enter chemical combination by a diffusion controlled thermal reaction with the medium. The "nest of radicals" approach is realistic, but too qualitative. The random fragmentation hypothesis would predict degradation products of the target molecule, as observed by radiogas chromatography. Previous data for (n,γ) activated reactions support, although indirectly, radical mechanisms.⁸⁰

Additional evidence as to the reactivity of ^{130}I activated by radiative neutron capture and isomeric transition is drawn from very recent gas phase experiments. Wilkey⁸¹ found the organic yields of the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ and $^{129}\text{I}(n,\gamma)^{130}\text{I}$ reactions in gaseous mixtures of CH_4 and I_2 are both 52% within experimental error. The similarity in the radiative neutron capture organic yields is not necessarily expected, and may be the result of radiolytic as well as hot atom effects. However, Wilkey also found that the $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ reactions

lead to an organic yield of 26%. Nicholas⁸² has recently found that the organic yield of ^{130}I resulting from the (n, γ) or the combined (n, γ) and (IT) processes is about 24.5%. The preliminary data⁸² suggest that of the 24.5 organic ^{128}I , about 9.4% forms as a result of hot ^{128}I reactions, 10.1% as a result of excited iodine atoms or I^+ ions in the $^3\text{P}_2$, $^3\text{P}_1$ and/or $^3\text{P}_0$ states, and 5.0% as a result of $\text{I}^+(\text{D}_2)$ ions. Rack and Gordus⁴⁰ examined the ^{127}I (n, γ) ^{128}I reaction in gaseous CH_4 and suggested that of the 54.5% organic ^{128}I , about 18.4% forms as a result of hot ^{128}I reactions, 11% as a result of excited iodine atoms or I^+ ions in the $^3\text{P}_2$, $^3\text{P}_1$ and/or $^3\text{P}_0$ states, and 25% as a result of reactions of $\text{I}^+(\text{D}_2)$ ions.

The lower organic reactivity of ^{130}I as compared to ^{128}I may be ascribed to a lower percent of the ^{130}I and $^{130}\text{I}^{\text{m}}$ being born in low lying excited states. Wilkey⁸¹ suggests the lower yield for the isomeric transition compared to that for (n, γ) activation may be explained if a smaller fraction of the (IT)-produced ^{130}I is produced with sufficient kinetic energy to react with CH_4 , and/or as a consequence of a lower excitation probability for I^+ ions from the isomeric transition.

The results obtained in this study do not give conclusive evidence of the mechanism. However, the autoradiation hypothesis appears to be the most satisfactory model for correlating the reactions of hot halogen atoms in liquid hydrocarbons. Additional experimental information on the nature and trends in hot halogen, i.e. bromine, reactions in liquid $\text{C}_5\text{-C}_{13}$ hydrocarbons is discussed in Chapter VI.

CHAPTER IV

EFFECT OF EXPERIMENTAL PARAMETERS ON BROMINE (n, γ) AND (IT) ORGANIC
YIELDS IN POLYCRYSTALLINE *n*-HEXANE AND CYCLOHEXANE

Chapter IV

Effect of Experimental Parameters on Bromine (n, γ) and (IT) Organic Yields in Polycrystalline n-Hexane and Cyclohexane

Recently it was shown that at 10^{-2} mole fraction of Br_2 in polycrystalline n-hexane at 77°K , the $^{80}\text{Br}^{\text{m}}$ isomeric transition induced organic yields were about 4%, suggesting clumping of the Br_2 in the organic matrix during freezing.⁸³ Employing the organic yields of the ^{79}Br (n, γ) $^{80}\text{Br}^{\text{m}}$ and the $^{80}\text{Br}^{\text{m}}$ (IT) ^{80}Br reactions in polycrystalline n-hexane at 77°K , Iyer and Willard⁴⁹ suggested that organic yields induced by nuclear transformations could give useful information about the state of aggregation of a solute and its tendency toward complex formation.

The purpose of this research was to explore in detail the reactor-irradiation technique for studying the radiative neutron capture (n, γ) and isomeric transition (IT) induced organic yields of bromine in polycrystalline n-hexane. Specifically, I investigated the influence of solvent purification, concentration of halogen and additive, neutron-irradiation and post-irradiation times, and nuclear transformation on the solid state organic yields.

Repurification and Neutron Irradiation Parameters

Iyer and Willard⁴⁹ have indicated that the organic yields of bromine induced by $^{80}\text{Br}^{\text{m}}$ isomeric transition in polycrystalline n- C_6H_{14} , are extremely sensitive to trace amounts of some additives. In this chapter the organic yields for bromine reactions with in-house purified hydrocarbons are compared to those observed in

research grade n-hexane. A few experiments were also performed using Br_2 in received Phillips research grade cyclohexane. The theme of the research discussed here is to evaluate the effects of various experimental parameters on the solid state organic yields.

The effects of impurities on raising the organic yields of halogens in alkyl halides and of halogens in hydrocarbons has been known for years. Criteria such as boiling point, freezing point depression and optical measurements may not detect; and hence, have difficulty in identifying the trace impurities in research grade hydrocarbons. Any repurification procedure that one uses may give a better quality of purity, but one must be careful that the repurification procedure does not introduce more impurity than it removes. Willard¹ has given three criteria that may indicate when the necessary and sufficient purity requirements have been met. The criteria are (1) identical results with reagents purified by different methods; (2) different, but related, compounds which might contain different types and amounts of impurities before repurification should give identical results when brought to the same purity; (3) the product distribution should be independent of any conceivable impurity.

Tables XII-XV present the organic yields of bromine isotopes as influenced by: (1) length of neutron irradiation, (2) time of extraction following neutron activation, (3) purification, (4) the presence of air and (5) length of time at 77°K prior to neutron irradiation. Table XVI presents the influence of additives on radiative neutron capture and isomeric transition organic yields of bromine isotopes in repurified n-hexane.

Tracer Br_2 (^{82}Br) indicated that contributions to the organic yield (OY) from dark reactions were nearly negligible. At 0.2 mole percent mf. Br_2 the pick-up observed by allowing the hydrocarbon solution to stand in the dark for two hours was 0.3% OY. An increase of about 0.1% was found in sample preparation by vacuum-line techniques. Calculations⁵⁵ did not predict radiation damage for the experimental conditions and the organic yields did not increase, within experimental error, with increased irradiation times. (See Table XII) However, when 0.3 mole percent Br_2 (^{82}Br) was added to liquid n-hexane previously irradiated as a glassy solid for 10, 45, 60 and 120 sec, the resulting organic yields were 0.6%, 1.0%, 3.0% and 3.7% respectively. The pick-up was probably due to bromine reactions with olefins formed by radiolytic reactions.⁸⁴ Neither the presence of air nor the duration of time the samples were frozen prior to irradiation had any observable effect, within experimental error, on the organic yields as also observed previously by Hahne and Willard⁸³ and Milman⁸⁵ respectively. (See Table XIV.)

As can be seen from the results depicted in Fig. 9, and in Tables XII-XV which present bromine organic yields as a function of mole fraction of Br_2 in n-hexane, in-house purification of research grade (99.99 quoted mole % purity) $\text{n-C}_6\text{H}_{14}$ substantially decreased the bromine organic yields. Since the organic yields of ^{82}Br and $^{80}\text{Br}^m$ are very sensitive to trace amounts of some additives, it may not be surprising that at concentrations lower than 4×10^{-3} mf Br_2 , the organic yields are somewhat higher than the previously reported values.⁴⁹ It may be difficult to attain the same degree of purity in hydrocarbons

Fig. 9 Organic Yields of Various Bromine Isotopes Induced by (n, γ) and (I. T.) Processes in Polycrystalline $n\text{-C}_6\text{H}_{14}$ at Various Mole Fractions of Bromine. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$ and ^{82}Br in research grade $\square$; and repurified research grade $\blacksquare$ $n\text{-C}_6\text{H}_{14}$; ^{80}Br by (I. T.), $\ominus$, of Iyer and Willard, see ref. 2. Tagged symbols indicate reaction systems not degassed.

Table XII. Influence of Length of Neutron Irradiation and Time of Extraction Following Neutron Irradiation of Bromine in Phillips Research Grade n-Hexane at 77° K.

mf Br ₂	Time Irrad. (Sec)	Time Till Extraction	Organic Yields		Averages	
			⁸² Br _m (n, γ)	⁸² Br (n, γ + IT)	⁸⁰ Br _m	⁸² Br
3.1 x 10 ⁻²	10	1 hr	4.9	2.9		
			5.2	3.8		
			4.9	2.4	5.0	3.0
	30	1 hr	2.7	2.7		
			5.7	4.9		
			3.0	2.9	3.6	3.5
	60	1 hr	6.0	5.5		
			4.9	3.1		
			2.7	2.9	4.5	3.8
5.3 x 10 ⁻³	10	1 hr	13.4	10.5		
			5.4	5.1		
			10.9	7.9	9.9	7.8
	30	1 hr	11.5	10.8		
			10.5	11.4		
			7.1	7.0	9.7	9.7
	60	1 hr	9.5	9.2		
			9.7	7.8		
					9.6	8.6
4.0 x 10 ⁻⁴	10	1 hr	36.5	38.2		
			34.2	37.4	35.3	37.8
	30	1 hr	---	40.4		
			38.1	38.8	38.1	39.6
	60	1 hr	29.8	36.0		
			41.6	40.5		
			38.9	28.3	36.8	35.9

Table XIII cont.

mf Br ₂	Time Irrad. (Sec)	Time Till Extraction	Organic Yields		Averages			
			⁸² Br ^m (n, γ)	⁸² Br (n, γ + IT)	⁸⁰ Br ^m	⁸² Br		
3.1 x 10 ⁻²	10	20 sec	4.3	3.1				
			7.5	4.8				
			6.1	3.4	6.0	4.0		
	60	20 sec	8.0	3.4	8.0	3.4		
			10	1 hr	6.7	3.0		
					7.2	3.5		
	7.0	3.5			7.0	3.3		
	5.3 x 10 ⁻³	10	20 sec	12.2	13.7			
				11.5	8.6			
11.9				9.7	11.8	10.7		
60		20 sec	10.3	10.2				
			9.8	10.1	10.1	10.1		
			10	1 hr	9.7	8.4		
8.9		10.6						
9.4		11.1			9.3	10.0		

Table XIII. Influence of Time of Extraction Following Neutron Irradiation of Bromine in Phillips Research Grade Cyclohexane at 77° K.

mf Br ₂	Time Till Extraction	Organic Yields		Averages	
		⁸⁰ Br ^m (n, γ)	⁸² Br ^m (n, γ + IT)	⁸⁰ Br ^m	⁸² Br ^m
1.4 x 10 ⁻²	20 sec	2.7	2.3		
		4.0	3.0		
		4.4	2.5	3.7	2.6
1.15 x 10 ⁻³	20 sec	---	20.6		
		---	20.5		
		---	29.6		23.6
	2 hr	32.7	25.9		
		12.4	26.3		
		19.8	16.1	18.6	22.7
7.00 x 10 ⁻⁴	20 sec	24.1	27.3		
		21.1	23.3	22.1	25.3
2.2 x 10 ⁻³	1 hr	7.5	7.9		
2.2 x 10 ⁻²	1 hr	2.1	2.1		

Table XIV. Effect of Duration of Time Bromine Samples* Were Frozen Under Liquid Nitrogen Prior to Irradiation at 77° K.

	Frozen 20 Sec		Frozen 24 Hr	
	$^{80}\text{Br}^m$ (n, γ)	$^{82}\text{Br} + ^{82}\text{Br}^m$ (n, γ)	$^{80}\text{Br}^m$ (n, γ)	$^{82}\text{Br}^m$ (n, γ + IT)
	7.2	7.2	7.5	7.9
	<u>10.0</u>	<u>13.1</u>	<u>10.8</u>	<u>10.2</u>
Avg.	8.6	10.1	9.1	9.0

* 4.8×10^{-3} mf Br_2 in Phillips research grade n-hexane used as received.

Table XV. Effects of Degassing and Repurification^a on Bromine (n,γ) and (IT) Organic Yields in n-Hexane at 77° K.

Extracted Immed. ^b			Extracted After (IT) ^c	
⁸⁰ Br ^m (n,γ)	⁸² Br + ⁸² Br ^m (n,γ)		⁸⁰ Br ^m (n,γ)	⁸² Br ^m (n,γ + IT)
6.4 x 10 ⁻⁴ mf Br ₂ in Phillips Grade n-Hexane: Degassed Samples				
18.5	----		17.2	15.9
21.2	18.3		16.9	20.1
18.0	19.4		18.9	20.5
			24.1	21.3
			15.8	22.8
Avg.	19.2	18.8	<u>18.8</u>	<u>19.3</u>
6.4 x 10 ⁻⁴ mf Br ₂ in Phillips Research Grade n-Hexane: Not Degassed				
			17.4	21.4
			19.9	22.1
			----	21.8
			19.3	17.5
Avg.			<u>18.8</u>	<u>21.2</u>
9.4 x 10 ⁻⁴ mf Br ₂ in N-Hexane, Repurified Research Grade: Not Degassed				
			----	10.7
			4.7	6.5
			----	10.5
			6.8	7.2
			5.2	15.7
			14.9	6.8
			10.8	6.8
Avg.			<u>8.5</u>	<u>9.2</u>

Table XV cont.

Extracted Immed. ^b		Extracted After (IT) ^c	
$^{80}\text{Br}^m$	$^{82}\text{Br} + ^{82}\text{Br}^m$	$^{80}\text{Br}^m$	$^{82}\text{Br}^m$
(n, γ)	(n, γ)	(n, γ)	(n, γ + IT)
<hr/>			
2.3 x 10 ⁻³ mf Br ₂ in Research Grade n-Hexane: Degassed			
	15.5	11.6	
	12.1	8.4	
	13.8	9.2	
Avg.	<u>13.8</u>	<u>9.7</u>	
2.9 x 10 ⁻³ mf Br ₂ in Research Grade n-Hexane: Degassed			
	8.8	8.1	9.3
	10.4	8.5	10.1
	7.4	9.9	13.6
	----	10.7	6.3
Avg.	<u>8.9</u>	<u>9.3</u>	<u>9.8</u>
2.9 x 10 ⁻³ mf Br ₂ in Research Grade n-Hexane: Not Degassed			
		7.2	7.1
		6.1	4.5
		6.8	7.2
		6.1	8.4
Avg.		<u>6.5</u>	<u>6.8</u>
2.8 x 10 ⁻³ mf Br ₂ in Research Grade n-Hexane: Degassed			
		8.3	7.4
		9.1	8.6
		7.4	10.3
Avg.		<u>8.3</u>	<u>8.8</u>

Table XV cont.

Extracted Immed. ^b		Extracted After (IT) ^c	
$^{80}\text{Br}^m$	$^{82}\text{Br} + ^{82}\text{Br}^m$	$^{80}\text{Br}^m$	$^{82}\text{Br}^m$
(n, γ)	(n, γ)	(n, γ)	(n, γ + IT)

2.8×10^{-3} mf Br_2 in Research Grade n-Hexane: Not Degassed

	8.5	6.7
	9.7	7.5
Avg.	<u>9.1</u>	<u>7.1</u>

5.2×10^{-3} mf Br_2 in Repurified Research Grade: Degassed

	5.8	4.5
	2.6	4.8
	5.2	5.5
Avg.	<u>4.5</u>	<u>4.9</u>

5.2×10^{-3} mf Br_2 in Repurified Research Grade: Not Degassed

	5.2	5.5
	4.8	5.2
	3.1	4.7
Avg.	<u>4.4</u>	<u>5.1</u>

5.1×10^{-3} mf Br_2 in Research Grade n-Hexane: Degassed

	8.7	7.4
	8.1	8.7
	7.1	8.2
	6.5	9.1
	8.3	7.0
Avg.	<u>7.7</u>	<u>8.1</u>

Table XV cont.

Extracted Immed. ^b			Extracted After (IT) ^c	
$^{80}\text{Br}^m$ (n, γ)	$^{82}\text{Br} + ^{82}\text{Br}^m$ (n, γ)		$^{80}\text{Br}^m$ (n, γ)	$^{82}\text{Br}^m$ (n, γ + IT)
9.7×10^{-3} mf Br_2 in Repurified n-hexane: Degassed				
			6.1	5.4
			2.4	4.8
			<u>4.2</u>	<u>5.1</u>
Avg.				
9.7×10^{-3} mf Br_2 in Repurified n-Hexane: Not Degassed				
			6.9	2.7
			2.2	3.9
			<u>4.5</u>	<u>3.3</u>
Avg.				

^a Repurified as described in Chapter II, but not purged with helium.

^b Samples extracted immediately were extracted 20 sec after removal from the reactor.

^c Samples extracted after (IT) were kept at 77° K, 1-2 hrs before extraction from the solid state.

between laboratories. Perhaps a characteristic of extremely pure $n\text{-C}_6\text{H}_{14}$ is that bromine organic yields are rather constant⁴⁹ in the range 1×10^{-2} to 5×10^{-4} mf Br_2 . However, the highly repurified systems tend to show data (Fig. 9) which decreases gradually in the concentration limits cited above.

Clustering of $(\text{Br}_2)_n$

Based on their experimental data, Iyer and Willard⁴⁹ have suggested that the region (5×10^{-4} to 1×10^{-2} mf Br_2) of constant organic yields indicate the formation of $(\text{Br}_2)_n$ clusters of nearly uniform size at all concentrations in the region. As shown in Fig. 9, the organic yields are "somewhat" constant, within experimental error, between 5×10^{-4} and 1×10^{-2} mf Br_2 in n -hexane. The data support the suggestion by use of independent techniques, that bromine is present as clusters of $(\text{Br}_2)_n$, where n is rather constant.

Influence of Additives

The results of a study of the influence of selected additives on the ^{79}Br (n, γ) $^{80}\text{Br}^m$, ^{81}Br (n, γ) $^{82}\text{Br}^m + ^{82}\text{Br}$, and the $^{82}\text{Br}^m$ (IT) ^{82}Br induced reactions in repurified n -hexane are presented in Table XVI. The effect of certain additives on raising the solid state organic yields may be rationalized, if the additive can lessen cluster formation by complexing the Br_2 . Evidence against an effect on the nature of the lattice sites in the crystals is derived from the fact that the yields are dependent on the ratio of the concentration of $n\text{-C}_3\text{H}_7\text{Br}$ to Br_2 rather than on the absolute concentration of $n\text{-C}_3\text{H}_7\text{Br}$.^{49,83}

Table XVI. The Influence of Additives on the ^{79}Br (n, γ) $^{80}\text{Br}^m$, ^{81}Br (n, γ) ^{82}Br + ^{81}Br (n, γ) $^{82}\text{Br}^m$ and the $^{82}\text{Br}^m$ (IT) ^{82}Br Induced Reactions in Repurified n-Hexane^a at 77° K.

	Extracted Immed. ^b		Extracted After (IT) ^c	
	$^{80}\text{Br}^m$ (n, γ)	^{82}Br + $^{82}\text{Br}^m$ (n, γ)	$^{80}\text{Br}^m$ (n, γ)	^{82}Br (n, γ + IT)
3-methyl pentane:				
	6.5	5.4	5.8	5.2
	5.2	5.0	5.2	4.6
	5.0	4.6	5.2	5.3
Avg.	<u>5.5</u>	<u>5.0</u>	<u>5.4</u>	<u>5.0</u>
2,2,4-trimethyl pentane:				
	5.5	4.4	4.3	4.7
	4.2	4.8	4.9	5.9
	5.2	5.5	4.3	4.4
Avg.	<u>5.0</u>	<u>4.9</u>	<u>4.5</u>	<u>5.0</u>
ethanol:				
	8.7	8.3	---	8.2
	7.6	7.6	---	7.0
	7.2	6.9		
Avg.	<u>7.8</u>	<u>7.6</u>		<u>7.6</u>
heptanoic acid:				
	7.7	8.1	---	8.0
	8.9	8.0	---	9.0
Avg.	<u>8.3</u>	<u>8.0</u>		<u>8.5</u>

Table XVI cont.

	Extracted Immed. ^b		Extracted After (IT) ^c	
	$^{80}\text{Br}^m$ (n, γ)	$^{82}\text{Br} + ^{82}\text{Br}^m$ (n, γ)	$^{80}\text{Br}^m$ (n, γ)	^{82}Br (n, γ + IT)
n-propyl iodide:				
	23.8	22.3	23.5	27.0
	----	20.9	22.9	20.4
	21.8	23.0	20.8	21.1
Avg.	<u>21.8</u>	<u>22.4</u>	<u>21.7</u>	<u>22.3</u>
benzene:				
	23.0	20.0	22.7	24.3
	20.7	24.1	22.5	20.3
	----	22.3	21.5	21.8
Avg.	<u>21.8</u>	<u>22.1</u>	<u>22.2</u>	<u>22.1</u>
bromobenzene:				
	22.3	22.4	24.4	22.9
	24.8	23.2	21.2	20.8
	24.6	24.7	23.4	23.1
Avg.	<u>23.9</u>	<u>23.4</u>	<u>23.0</u>	<u>22.3</u>
bromo-cyclohexane:				
	20.5	23.2	----	22.3
	22.5	22.9	----	21.8
Avg.	<u>21.5</u>	<u>23.0</u>		<u>22.0</u>

Table XVI Footnotes

- ^a 5×10^{-3} mf additive and 5×10^{-3} mf Br_2 with respect to n-hexane. The n-hexane was repurified as described in Chapter II, but was not purged with helium.
- ^b Samples were extracted within 20 sec after removal from the reactor to obtain yields which have less than a 5% contribution from isomeric transition.
- ^c Samples were extracted after 99.99% of the bromine isomeric transition had occurred, i.e. approximately 1-2 hrs after neutron irradiation.

The reactor irradiation technique was compared to the $^{80}\text{Br}^m$ isomeric transition method, by determining the $^{79}\text{Br} (n, \gamma) ^{80}\text{Br}^m$, $^{81}\text{Br} (n, \gamma) ^{82}\text{Br} + ^{82}\text{Br}^m$ and $^{81}\text{Br} (n, \gamma) ^{82}\text{Br} + ^{82}\text{Br}^m (\text{IT}) ^{82}\text{Br}$ induced organic yields in the presence of certain additives. The agreement with previous results⁴⁹ obtained by the $^{80}\text{Br}^m (\text{IT}) ^{80}\text{Br}$ reaction in the presence of 5×10^{-3} mf additive and 5×10^{-3} mf Br_2 was excellent. The additives investigated in Table XVI indicated that the organic yields are not affected by the presence of 3-methyl pentane and 2,2,4-trimethyl pentane. However, ethanol, heptanoic acid, n-propyl iodide, bromobenzene and bromocyclohexane would be expected to form charge-transfer complexes, and hence raise the organic yields as observed. In the studies of bromobenzene and bromocyclohexane a distinction has not been made between the organic yields resulting from bromine and R-Br. The fact that the organic yield in the presence of benzene is 22% as compared to 5% (in n-hexane) is consistent with the well-known complexing of bromine with benzene.⁸⁶

Isotope Effects

One objective of this research was to determine whether the radiative neutron capture organic yields of $^{80}\text{Br}^m$ and $^{82}\text{Br}^m + ^{82}\text{Br}$ in the polycrystalline state were the same or different than the $^{82}\text{Br} (n, \gamma) + ^{82}\text{Br}$ isomeric transition organic yields. In the latter case 91% of the total ^{82}Br activity will have resulted from $^{82}\text{Br}^m (\text{IT}) ^{82}\text{Br}$ induced reactions. The existence and validity of isotope effects between $^{80}\text{Br}^m$, ^{80}Br and ^{82}Br in the solid state has been debated between laboratories.⁸⁷⁻⁹¹ One would not a priori expect the isomeric transition yields to be greater than the radiative neutron capture

organic yields because of the greater recoil energy of the (n,Y) process. However, Iyer and Willard⁴⁹ reported that at 1×10^{-3} mf Br_2 and below the ^{79}Br (n,Y) $^{80}\text{Br}^{\text{m}}$ organic yields (1%) were substantially lower than the $^{80}\text{Br}^{\text{m}}$ (IT) ^{80}Br induced reactions (4%). Their results are unexpected and could not be verified in this study. As shown in Tables XII-XVI the $^{80}\text{Br}^{\text{m}}$ and $^{82}\text{Br}^{\text{m}} + ^{82}\text{Br}$ radiative neutron capture organic yields at all conditions and concentrations studied were similar to the yields of the ^{82}Br (n,Y) + ^{82}Br (IT) organic yields. It is particularly significant to note that even in the presence of additives (Table XVI) which affect the magnitude of the total organic yield, an isotope separation between (n,Y) and (IT) activations was not observed.

Although $^{80}\text{Br}^{\text{m}}$ organic yields induced by radiative neutron capture and ^{82}Br and ^{130}I organic yields induced by isomeric transition can readily be determined, it is necessary to study the organic yields as a function of post-irradiation time in order to determine the (n,Y) organic yield of ^{82}Br and likewise to distinguish between the organic yields of ^{130}I by the (n,Y) and (IT) processes as discussed in Chapter V.

It is difficult to determine organic yields that correspond to 100% (n,Y) processes for the isotopes where isomeric transition events are occurring simultaneously during the neutron activation process. The (IT) and (n,Y)-induced organic yields, if numerically different, would be observed as changes in the organic yield with the length of time that isomeric transition events were allowed to occur in the polycrystalline state prior to extraction.

If R_0° represents the organic yield before more than 5% of the (IT) has occurred in the polycrystalline state, and R_{∞}° represents the organic

yield achieved within the polycrystalline state after 99.9% of the (IT) events have occurred, the organic activity due to (IT) after all isomeric transition processes have occurred is $(R_{(IT)}/100)$ (total activity) (β).

$$R_{(IT)} = \int (R_{\infty}^0 - \alpha R_0^0) / \beta \quad (4)$$

where α is the fraction of atoms born in the ground nuclear state, and β is the fraction of activated atoms capable of reacting by (IT).

If experimentally

$$R_{\infty}^0 = R_0^0, \text{ then } R_{\infty}^0 = R_{(n,\gamma)}^0 = R_{(IT)}. \quad (5)$$

By varying the time of extraction after irradiation, from 20 sec to 1 hr and allowing the $^{82}\text{Br}^m$ (IT) ^{82}Br induced reaction to occur in repurified n-hexane at 77°K, the resulting organic yields of $^{80}\text{Br}^m$ and ^{82}Br were all within $4.5 \pm 0.7\%$ at 5×10^{-3} mf Br_2 . No isotope separation among $^{80}\text{Br}^m$ and ^{82}Br by (n, γ) and ^{82}Br by (IT) in either the repurified or research grade hydrocarbons studied in Fig. 9, or in systems containing additives were observed. These results are consistent with those reported earlier by this laboratory.^{53,54}

Summary

The data presented in this chapter confirm, by use of independent techniques, the suggestion of Iyer and Willard⁴⁹ that organic yields may be useful as a criteria for deducing the state of aggregation of a solute and its tendency toward complex formation. Chapter V represents an extension of the nuclear transformation technique to deduce information on state of aggregation, clustering, complexing, etc. of iodine and iodine monochloride in C_6 -hydrocarbon matrices at 77° K.

CHAPTER V

ORGANIC YIELDS AS AN INDICATION OF THE STATE OF AGGREGATION, COMPLEXING,
AND SEGREGATION DURING CRYSTALLIZATION OF ICl AND I₂ IN C₆-HYDROCARBON
MATRICES AT 77° K

Chapter V

Organic Yields as an Indication of the State of Aggregation, Complexing,
and Segregation During Crystallization of ICl and I_2 in C_6 -Hydrocarbon
Matrices at 77°K

The suggestion that organic yields induced by nuclear transformations could give useful information about the state of aggregation of a solute and its tendency toward complexing is expanded in this chapter. In particular four structurally different hydrocarbons, namely cyclohexane, n-hexane, 2,2-dimethyl butane and 2-methyl pentane were employed to determine the effects of iodine and/or iodine monochloride concentration, the influence of additives, and nuclear activation on the organic yields. The main purposes of this investigation were to look for halogen concentration ranges where uniform clustering of the halogen in the hydrocarbon matrix occurred, and to determine the organic yields under conditions of monomolecular dispersion of the halogen in the matrix.

Experimental Techniques

Two techniques were employed to determine the isomeric transition activated organic yields of ^{130}I in the polycrystalline hydrocarbons. Method (1): $^{129}\text{I}_2$ was added to the hydrocarbon and the solution washed, dried and the samples degassed prior to irradiation. The changes in the ^{130}I organic yields with the duration of time that the $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I processes were allowed to occur were determined. Method (2): The aqueous Na^{129}I was irradiated to produce $(^{130}\text{I}^{\text{m}})^-$ which was oxidized to $\text{I}_2(^{130}\text{I}^{\text{m}})$ as described above. The $\text{I}_2(^{130}\text{I}^{\text{m}})$ solution was trans-

ferred rapidly to a reaction vessel, containing known amounts of I_2 dissolved in the hydrocarbon being investigated, and immersed under liquid N_2 . The samples were not dried or degassed. After 90 minutes, essentially all of the ^{130m}I had decayed to the ground state, the solution was liquefied, and an aliquot taken to be extracted with CCl_4 containing I_2 carrier and 0.5 M aqueous Na_2SO_3 . A portion of the remaining solution was used to determine the exact iodine concentration for each experiment. The total time from the beginning of a 55 sec neutron irradiation until the sample was frozen was consistently 90 ± 5 sec. Activities were corrected for decay of ^{130m}I (IT) ^{130}I induced reactions occurring prior to mixing, or reaction in the liquid hydrocarbon prior to freezing to $77^\circ K$, and for 39% of the total ^{130}I activity being formed directly by radiative neutron capture.²⁷ The use of the method (2) for obtaining (IT) organic yields may be meaningless due to the influence of CO_2 and O_2 , (as air), H_2O , etc. not removed from the reaction vessel prior to freezing the sample to $77^\circ K$. The ^{130}I isomeric transition organic yields obtained by this technique would be expected to be high if in error.

Repurification

During the course of this investigation, R. L. Ayres⁶¹ of this laboratory was examining varied repurification procedures, and verified that the rigorous in-house repurification discussed in Chapter II gave good and consistent solid state data at most iodine concentrations. The H_2SO_4 treatment is a common method of repurification, and is particularly effective for the removal of olefinic impurities from the alkanes. However, Ayres⁶¹ was also able to show conclusively that

purging repurified n-hexane with helium for 30 seconds would remove trace gaseous impurities (presumably CO_2 and O_2) not removed by the rigorous H_2SO_4 treatment. Based on that result a number of experiments with iodine in polycrystalline cyclohexane were repeated using the He purging technique. However, all the experiments with ICl were in the rigorously repurified and helium purged hydrocarbons.

Fig. 10 and Tables XVII and XVIII present the organic yields of ^{128}I and ^{130}I in cyclohexane either used as received or after various repurification procedures. As expected, the organic yields are dependent on the purity of the solvent.

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 . One would not a priori expect the (IT) organic yields 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, no changes were observed in the ^{130}I organic yields.

An attempt was made to determine the organic yields of ^{130}I due only to isomeric transition in cyclohexane by employing method (2)

Fig. 10 Organic Yields of Various Iodine Isotopes Induced by (n,) and (IT) Processes in Polycrystalline $c\text{-C}_6\text{H}_{12}$ at Various Mole Fractions of Iodine. ^{128}I , $\circ$, and ^{130}I , Δ , in research grade; and ^{128}I , $\bullet$, in repurified research grade $c\text{-C}_6\text{H}_{12}$. Insert. Nature of Additives on ^{128}I Organic Yields: [1] C_6H_6 ; [2] $\text{CH}_3(\text{CH}_2)_5\text{COOH}$; [3] $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2$ and $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)_2$; [4] $n\text{-C}_6\text{H}_{13}\text{I}$; [5] $i\text{-C}_3\text{H}_7\text{I}$; [6] $n\text{-C}_3\text{H}_7\text{I}$.

Table XVII. Effect of I_2 Concentration on ^{128}I Organic Yields in Polycrystalline and Liquid Cyclohexane

mf I_2 $\times 10^4$	Organic Yields		
	^{128}I (Polycrystalline) ^a	^{128}I (Polycrystalline) ^b	^{128}I (Liquid) ^a
0.01	----	54	----
0.01	----	55	----
0.05	----	55	----
0.05	----	52	----
0.80	62.7	----	52.7
0.16	49.2	----	54.2
1.6	42.8	----	55.4
1.9	----	19.8	----
3.0	33.5	----	49.6
4.0	30.3	----	49.9
4.2	----	16.5	----
11.4	14.3	----	46.6
11.4	12.8	----	48.2
13.0	----	9.4	----
24.0	----	6.1	----
24.0	----	6.3	----
24.0	----	6.3	----
38.0	----	3.5	----
40.0	----	4.4	----
51.0	----	4.0	----
52.5	4.1	----	----
52.5	3.7	----	----
60.0	----	2.2	----
78.0	----	2.8	----
87.5	3.4	----	36.3
87.5	3.0	----	34.9
106.9	2.1	----	27.1
106.9	2.1	----	27.1
125.0	----	2.7	----
125.0	----	1.2	----

^a Phillips research grade cyclohexane used as received.

^b Repurified Phillips research grade cyclohexane, He purging did not affect the organic yields at high I_2 concentrations.

Table XVIII. Effect of I_2 Concentration on the Organic Yields of Various Iodine Isotopes in Polycrystalline Cyclohexane and n-Hexane

Solvent	mf I_2 $\times 10^4$	Organic Yields ^a			
		^{128}I (n, γ)	$^{130}I + ^{130}I_m$ (n, $\gamma + 5\% IT$)	^{130}I (n, $\gamma + IT$)	$^{130}I^b$ (IT)
cyclohexane	0.11 ^c	29	30	31	
	0.15 ^c	24	25	25	
	0.15 ^d	36			38
	2.5 ^c	26			27
	9.4 ^c	20			21
	23 ^c	4.5	3.1	3.2	
n-hexane	28 ^d	3.0	2.8	2.8	
	56 ^c	0.7	0.6	0.7	

^a Averages of several determinations. Error $\leq 1\%$.

^b See Chapter IV, page 87.

^c Repurified as outlined in experimental section, purged with He.

^d Repurified by distillation and purging with He.

outlined in the experimental techniques section of this chapter. In general the $^{130}\text{I}^m$ (IT) ^{130}I organic yields were generally similar to the ^{128}I and ^{130}I organic yields obtained by the in-reactor technique. Table XVIII and Fig. 10 show that the ^{128}I organic yields were similar to those of ^{130}I isotopes at all iodine concentrations studied. In the regions where the organic yields are low, differences in organic yields for the various isotopes would be difficult to detect. However, in cyclohexane and n-hexane the iodine organic yields were similar at all iodine concentrations studied. McCauley et.al.⁹⁰ 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 nuclear processes. The solid state iodine organic yields are apparently independent of isotope and mode of activation.

Influence of Additives on ^{128}I Organic Yields

Table XIX summarizes a study of the variations in organic yields in cyclohexane containing 5.5×10^{-3} mf I_2 and 5×10^{-3} mf additive. The point of interest was to determine the influence of additives on the organic yields in a region where partial segregation and clumping had occurred. Ethanol and the alkyl iodides would be expected to form Donor-Acceptor complexes with iodine;⁹² whereas saturated hydrocarbons would not be expected to have a significant complexing influence. Fig. 10 shows that the saturated hydrocarbons had little influence on the organic yields. Ethanol and the alkyl iodides resulted in higher ^{128}I organic yields. An attempt was not made to distinguish between the organic yields coming from I_2 and RI. Additives

Table XIX. Influence of Additives on ^{128}I Organic Yields in Poly-Crystalline Cyclohexane^a at 77° K.

Additive ^b	Organic Yield	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 5.0	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
Heptanoic Acid ^c	2.6 2.6 2.9	2.7 ± 0.1
1-Iodohexane	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

^a Phillips research grade cyclohexane repurified as described in the experimental section.

^b 5.5×10^{-3} mf I_2 , 5×10^{-3} mf additive.

^c In 1×10^{-5} mf I_2 containing 5.5×10^{-3} mf $\text{C}_6\text{H}_{15}\text{COOH}$ the organic yields were 5.6 ± 0.7 .

would not be predicted to have a large effect at I_2 concentrations where binary or ternary mixtures were formed.

The iodine systems containing additives have a multiplicity of colors that are different than the color of I_2 in the hydrocarbons. As suggested by Willard,⁴⁹ the color effects in the polycrystalline matrices suggest complex formation of halogen with additive and hydrocarbon. However, visual color effects are not reliable for predicting the organic yields and their variations at the concentrations studied. By comparison the influence of complexing agents on solid state bromine organic yields has been discussed previously in Chapter IV.

State of Aggregation of I_2 and ICl

In addition to the trends in the bromine organic yields in polycrystalline n-hexane (See Chapter IV), various types of physical measurements indicate the formation of $(X_2)_n$ clusters. Nuclear quadrupole moment measurements⁹³ suggest intermolecular bonding between halogen molecules in the solid state, and certain features of the absorption spectra of gaseous iodine and bromine suggest I_4 and Br_4 molecules.^{92,94} Passchier and Gregory⁹⁵ have given convincing evidence of the presence of molecular dimers of $(I_2)_2$ in iodine vapor. Ultraviolet absorption studies present evidence for the presence of I_2 , I_4 , I_6 and higher halogen polymers in liquid hydrocarbons.⁹⁶⁻⁹⁸ Electrical conductivity and ESR measurements indicate the presence of preferred site sizes of iodine and bromine in crystalline molecular complexes in polycyclic hydrocarbons.⁹⁹ The purpose of the research described in this section was to determine if iodine and chlorine

organic yields could be useful as a criteria of the state of aggregation of I_2 and ICl in polycrystalline cyclohexane, n-hexane, and 2,2-dimethyl butane (DMB), and in glassy 3-methyl pentane (3MP) at $77^\circ K$.

The study is unique in that ^{128}I yields from ICl and I_2 may be compared and the state of aggregation of ICl may be traced by both ^{38}Cl and ^{128}I formed by the radiative neutron capture processes. An interesting test for the nuclear transformation techniques as a valid indicator of the state of aggregation would be whether ^{128}I and ^{38}Cl from ICl gave similar results.

The determination of the organic yields of ^{128}I and ^{38}Cl is complicated by the reaction of ICl with products (probably olefins) of radiolysis formed by the reactor irradiations. The extent of this reaction was determined in separate experiments by irradiating the hydrocarbons at $77^\circ K$, liquefying, and adding ^{38}Cl and ^{128}I labeled ICl . The corrected organic yields are equal to the observed organic incorporation of ^{38}Cl and ^{128}I , reduced by the percent of activity that would have entered as a result of reaction with stable radiolysis products. When the small correction was applied, the ^{38}Cl and ^{128}I data from ICl were similar to the ^{128}I from I_2 data. Willard⁸⁴ has shown that I_2 does not react with stable radiolysis products formed by the reactor irradiations. Bromine solid state organic yields are also affected by the presence of stable unsaturated products formed by radiolysis.⁸⁴

A second factor that complicates the determination of solid state ^{38}Cl organic yields is the relatively small ^{37}Cl cross-section

for thermal neutrons. The natural relative abundance of ^{37}Cl is 24.5% and radiative neutron capture can lead to ^{38}Cl by two paths²⁶ as shown in Fig. 11.

Figure 11. Radiative Neutron Capture of ^{37}Cl and Subsequent Decay Routes

The 145-fold larger cross-section for the production of ^{38}Cl and the short irradiation times (10 sec) implies that most of the ^{38}Cl will be formed by (n, γ) rather than via 0.74 sec (IT). However, of the total activity produced in a short neutron irradiation of ICl , the formation of ^{128}I is favored by a 100% natural abundance of ^{127}I and a 6.4 b cross-section. Hence, the statistical error in determination of ^{38}Cl organic yields (due to low total activity of ^{38}Cl) is considerably greater than that of ^{128}I at dilute ICl concentrations.

Monomolecular Dispersion: Depicted in Figs. 12 and 13 are the results of the investigations of the $^{129}\text{I}(n, \gamma) ^{130}\text{I} + ^{130}\text{I}^m$, the $^{130}\text{I}^m(\text{IT}) ^{130}\text{I}$, the $^{127}\text{I}(n, \gamma) ^{128}\text{I}$, and the $^{37}\text{Cl}(n, \gamma) ^{38}\text{Cl}$ reactions in selected C_6 -hydrocarbons as a function of I_2 or ICl concentration.

Figure 12. The effect of ICl and I_2 mole fraction on ^{38}Cl and ^{128}I organic yields in polycrystalline n-hexane and cyclohexane at 77°K .

Figure 13. The effect of ICl and I_2 mole fraction on ^{38}Cl and ^{128}I organic yields in glassy 3-methyl pentane at 77°K .

In the aliphatic hydrocarbons studied the ^{128}I organic yields extrapolated to about $52 \pm 2\%$ at 10^{-6} mf halogen and below. One might expect the organic yields to be somewhat dependent on the media. However, under the conditions of monomolecular dispersion polycrystalline cyclohexane, n-hexane, and 2,2-dimethyl butane, and glassy 3-methyl pentane showed about equal preference for either organic or inorganic combination.

Evidence for the attainment of the conditions of monomolecular dispersion is drawn from recent results of Kemnitz.¹⁰⁰ In solid benzene the ^{128}I organic yields are rather constant at $59 \pm 3\%$ from 0.001 to 0.1 mole % I_2 . In benzene we would expect monomolecular dispersion of I_2 over an appreciable concentration range based on the well-known donor-acceptor complexing of iodine in solid benzene.⁸⁶ In two sets of experiments, I noted that the ^{128}I organic yields from a 5×10^{-5} and 5×10^{-6} mf ICl in polycrystalline benzene were comparable to the expected 55%. By comparison, Iyer and Willard⁴⁹ found that the $^{80}\text{Br}^m$ (IT) ^{80}Br organic yields in polycrystalline n-hexane were about 55% at 2×10^{-5} mf Br_2 and below.

Clustering: The organic yields resulting from the ^{127}I (n, γ) ^{128}I and the ^{37}Cl (n, γ) ^{38}Cl reactions as a function of ICl and I_2 concentration in polycrystalline n-hexane are depicted in Figs. 12 and 13 and Tables XVIII and XX. The ^{128}I data for I_2 in polycrystalline n-hexane were determined by R. L. Ayres⁶¹ and are presented here only for the purpose of comparison to the organic yields from ICl . The ^{128}I and ^{38}Cl organic yields from ICl are identical, within experimental error, to those of ^{128}I from I_2 over the concentration range

Table XX. Radiative Neutron Capture Organic Yields
as a Function of ICl Concentration in Crystalline
n-Hexane at 77° K

mf ICl	Organic Yields	
	³⁸ Cl	¹²⁸ I
5.0 x 10 ⁻³	3.2	1.3
	0.6	2.0
Avg.	<u>1.9</u>	<u>1.7</u>
1.0 x 10 ⁻³	8.5	3.6
	9.0	4.7
	4.1	3.0
	11.4	6.1
Avg.	<u>8.3</u>	<u>5.8</u>
5 x 10 ⁻⁴	19.3	6.3
	11.6	8.2
Avg.	<u>15.5</u>	<u>7.2</u>
4 x 10 ⁻⁵	7.8	11.8
	20.0	14.1
	13.6	16.7
Avg.	<u>13.7</u>	<u>14.2</u>
2 x 10 ⁻⁵	11.1	9.3
1 x 10 ⁻⁵	29.7 ^a	13.4
	16.4	17.8
	23.7	18.4
Avg.	<u>23.3</u>	<u>16.5</u>
8 x 10 ⁻⁶	28.8 ^a	25.5
	32.7	25.4
Avg.	<u>30.8</u>	<u>25.4</u>
1.6 x 10 ⁻⁶	a	51.0

^a Data inconclusive due to statistical error.

Table XXI. Radiative Neutron Capture Organic Yields as a Function of ICl Concentration in Crystalline 2,2-Dimethyl Butane at 77° K.

mf ICl	Organic Yields	
	^{38}Cl	^{128}I
5×10^{-4}	4.4	4.0
	5.6	4.4
	---	7.6
	Avg. 5.0	5.3
1×10^{-4}	11.2	7.2
	9.2	13.3
	----	8.7
	a	8.9
	Avg. 10.2	9.5
5×10^{-5}	9.0 ^b	14.9 ^b
1×10^{-5}	10.9 ^c	10.5 ^c

a $^{38}\text{Cl} = 23.3$ for 15 sec irradiation.

b $^{38}\text{Cl} = 29.1$ for 20 sec irradiation., $^{128}\text{I} = 23.1$.

c The ^{38}Cl and ^{128}I organic yields for 15 sec neutron irradiations were 37.0 and 51.0.

10^{-6} to 5×10^{-3} mf halogen. Since the organic yields are nearly constant at about 10% between 1×10^{-5} and 2×10^{-4} mf halogen, the most obvious interpretation is that the ICl and I_2 apparently form similar $(X_2)_n$ cluster sizes and/or are composed of similar numbers of halogen molecules at sites in the polycrystalline organic matrices. The ^{38}Cl and ^{128}I organic yields in polycrystalline 2,2-dimethyl butane were similar in trend and in magnitude to those observed in polycrystalline n-hexane. (See Table XX and XXI) This result is not surprising since Iyer and Willard⁴⁹ found the $^{80}\text{Br}^m$ (IT) ^{80}Br organic yields at 5×10^{-3} mf Br_2 in polycrystalline n-hexane and n-pentane to be similar (i.e., 4.7 and $4.2 \pm 1\%$, respectively).

However, in cyclohexane the organic yields drop from 53% to rather constant yields of about 25% (compared to about 10% for n-hexane and 2,2-dimethyl butane) between 2×10^{-5} and 2×10^{-4} mf I_2 . (See Fig. 12) Separation of the halogen from the matrix by partial segregation during total crystallization would result in a decrease in the observed organic yield with increasing total concentration of halogen, because the recoiling atoms would be shielded from reaction with the organic substrate by other halogen molecules in the matrix. Willard⁵² has suggested that the protection may be substantial, even for small bromine clusters where ^{80}Br is born on the surface, because exchange with Br_2 and scavenging of radicals by Br_2 as well as physical shielding are of importance.

Since the iodine organic yields in polycrystalline n-hexane, cyclohexane, and benzene and in glassy 3-methyl pentane extrapolated to zero mole fraction halogen are similar, the reactivity of iodine

atoms for organic product formation is apparently similar in the selected hydrocarbons. Therefore the iodine organic yield plateaus at 25% and 12% for cyclohexane and n-hexane and DMB 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 Willard⁴⁹ 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 $nX_2 \rightleftharpoons (X_2)_n$ in solution. The experimental evidence against the equilibrium is summarized in Table XXII. If an equilibrium was responsible for the lowering of the organic yield, one might expect to see the variation occur with the freezing point of the solvent. The iodine organic yields at 2×10^{-5} mf in polycrystalline benzene, cyclohexane, 2,2-dimethyl butane and n-hexane appear to roughly decrease with the freezing point of the "pure" solvent. However, at 5×10^{-3} mf Br_2 , in the case of ⁸⁰Br the yields in polycrystalline benzene, 25%, are larger than those of polycrystalline n-hexane, 4%, and n-pentane, 4%, even though the latter two freezing points differ by 40° K. If the organic yields in glassy 3-methyl pentane, 40% (fp ~ 120° K) are considered, the correlation with the temperature at which the solutions become rigid is rather meaningless. The hot atom chemistry of halogens is known to be different in glassy and polycrystalline alkyl halides.⁸³ The anomalously high yields in glassy 3-methyl pentane suggest a difference in

the state of aggregation in glassy and polycrystalline hydrocarbons, and argue against an equilibrium between the liquid and solid state. If such, an equilibrium prevailed it would be expected to favor more and possibly larger clusters at the lower temperature giving a yield less than, or equal to, that observed in polycrystalline n-hexane.⁴⁹

Table XXII. Freezing Points of Selected Hydrocarbons and Halogen Organic Yields at 77° K.

Solvent	Freezing Point °K	^{80}Br 5×10^{-3} mf Br_2	^{128}I 2×10^{-5} mf I_2	^{38}Cl 2×10^{-5} mf ICl
n-pentane	142	4 ± 1^a		
n-hexane	178	4 ± 1^a	10 ± 1^b	11 ± 2
2,2-dimethyl butane	185		10 ± 1	11 ± 2
cyclohexane	280		25 ± 1	
benzene	279	25 ± 1^a	58 ± 3^c	
3-methyl pentane	120	40 ± 1^a	40 ± 3	40 ± 3

^a Reference 49.

^b Reference 61.

^c Reference 100.

Different halogens would not necessarily be expected to form $(\text{X}_2)_n$ clusters and give the same or constant organic yields at comparable halogen concentrations. For example, in polycrystalline n-hexane, the $^{80}\text{Br}^m$ (IT) ^{80}Br organic yields are circa 5% between 5×10^{-4} and 1×10^{-2} mf Br_2 ; whereas, ^{127}I (n, γ) ^{128}I organic yields are about 10% between 1×10^{-5} and 2×10^{-4} mf I_2 .

Partial Segregation: The effect of I_2 and ICl concentration on the ^{128}I and ^{38}Cl organic yields in glassy 3MP are depicted in Fig. 13 and Table XXIII. The ^{128}I yields from I_2 in glassy 3-methyl pentane under the conditions of monomolecular dispersion (1×10^{-5} and below) are $59 \pm 3\%$ and are similar to those observed in polycrystalline hydrocarbons containing a very dilute concentration of halogen. However, between 1×10^{-5} and 1×10^{-3} mf halogen the organic yields decrease uniformly from 59% to less than 2%. The ^{128}I and ^{38}Cl organic yields are not constant over any appreciable halogen concentration range greater than 1×10^{-5} mf. Hence freezing the ICl or I_2 in glassy 3MP apparently results in a partial segregation of the halogen in the hydrocarbon matrix, rather than inducing the formation of preferred sizes of $(X_2)_n$ clusters in the glassy matrix. The ^{128}I and ^{38}Cl yields from ICl are the same within experimental error, and are similar in trend to the ^{128}I from I_2 as a function of halogen concentration. However, the ^{128}I and ^{38}Cl organic yields from ICl are a few percent higher than the corresponding ^{128}I from I_2 data at a comparable halogen mole fraction.

Total Segregation During Crystallization: The low organic yields (<2%) at the higher concentrations of halogen have in the past been ascribed to clumping or total segregation of the halogen species from the hydrocarbon during the freezing process.^{53,83} Hahne and Willard⁸³ found low ^{80}Br yields in n-hexane, and were the first to suggest the possibility of clumping of bromine during freezing so that relatively few bromine atoms resulting from $^{80}Br^m$ (IT) ^{80}Br processes were exposed to the solvent as they underwent the nuclear transformation. Low

Table XXIII. Radiative Neutron Capture Organic Yields as a Function of ICl and I₂ Concentration in Glassy 3-Methyl Pentane at 77° K.

mf Halogen	¹²⁸ I (I ₂)	Organic Yields			
		³⁸ Cl (ICl) (Obs)	(Cor)	¹²⁸ I (ICl) (Obs)	(Cor)
5 x 10 ⁻³		9.3 6.7		0.9 0.8	
	Avg.	8.0	1.0	0.8	
1 x 10 ⁻³	0.3	17.8 14.7 11.4 ----		3.0 3.8 3.5 4.3	
	Avg.	14.6	6.6	3.7	2.6
5 x 10 ⁻⁴	2.0 2.4 1.0 2.0 ----	21.0 19.3 9.9 19.4 ----		5.9 6.9 8.0 5.4 7.0	
	Avg.	18.4	8.4	6.6	5.6
1 x 10 ⁻⁴	----- 12.8 11.1 19.5	31.0 25.3 32.3 ----		11.0 9.8 19.4 11.9	
	Avg.	29.5	15.5	13.0	13.0
5 x 10 ⁻⁵	27.1 17.0 13.6 16.8 15.9	36.4 33.8 a a a		20.6 21.1 22.4 22.9 20.3	
	Avg.	35.1	22.0	21.5	
1.4 x 10 ⁻⁵	49.0	a			

Table XXIII cont.

mf Halogen	Organic Yields			
	^{128}I (I_2)	^{38}Cl (ICl) (Obs) (Cor)	^{128}I (ICl) (Obs) (Cor)	
1×10^{-5}	64.0	a	51.3	
	57.9		46.7	
	52.9		50.4	
	Avg. <u>55.4</u>		<u>50.8</u>	
5×10^{-6}	58.5			
	62.0			
	Avg. <u>60.2</u>			
2.5×10^{-6}	58.9			
	60.6			
	Avg. <u>59.7</u>			
1×10^{-6}		a	57.0	
			56.6	
	Avg.		<u>56.5</u>	

^a Data inconclusive due to statistical error.

organic yields (<1%) in $\text{Br}_2 + \text{C}_6$ -hydrocarbon systems were explained as clumping of the halogen during the freezing process.⁵³ Milman⁸⁵ reported that X-ray diffraction results in polycrystalline $\text{Br}_2\text{-C}_2\text{H}_5\text{Br}$ systems over a period of 5 min are consistent with the conclusion that the bromine is homogenously distributed. If appreciable aggregation occurred during freezing, fluctuations in the organic yields could be expected as a result of variation of bromine distribution resulting from chance variations in the rates of freezing. Milman¹⁰¹⁻¹⁰³ has attempted to rationalize erratic variations of the solid state ^{79}Br (n, γ) $^{80}\text{Br}^m$ organic yields in $1,2\text{-C}_2\text{H}_4\text{Br}_2$ with temperature in terms of phase transitions, as deduced from phase diagrams, and the heat capacity and dielectric constants as a function of temperature. Table XXIV presents the organic yields of ^{130}I under the conditions of total segregation of the iodine from the solvent in several selected alkanes. In addition, clumping effects on bromine solid state organic yields are discussed in Chapter VI.

Summary of Solid State Studies

The conclusions that can be drawn from this study are that:

- (1) The experiments with Br_2 , I_2 and ICl (in which the two different halogen atoms acquire a radioactive label) have shown that radio-halogens mainly trace their environment without chemical selectivity with regard to isotope and mode of activation. These results offer additional evidence that the nuclear transformation technique is useful as a criteria for obtaining qualitative information about the state of aggregation and tendency of a solute to complex in a solid hydrocarbon matrix.
- (2) In glassy and polycrystalline halogen-hydrocarbon systems,

Table XXIV. Effect of Total Segregation of Iodine on ^{130}I
Organic Yields in Selected Hydrocarbons *

System	mf I_2 $\times 10^3$	Organic Yield ^{130}I
n-pentane	1.3 6.0	1.6 1.4, 1.0
n-hexane	1.0 5.5	1.4, 0.7 0.4
cyclohexane	8.0	2.8
n-heptane	4.5 7.3	0.7, 0.9 1.1, 0.6
n-nonane	2.1 7.5 8.6	2.1 1.3, 1.1 0.9

* Phillips research grade hydrocarbons used as received.

the organic yields under the conditions of monomolecular dispersion are about $55 \pm 5\%$. (3) In polycrystalline hydrocarbons containing bromine,⁴⁹ iodine or iodine monochloride, rather constant organic yields over appreciable halogen concentration ranges, suggests the formation of preferred $(X_2)_n$ cluster sizes and/or similar numbers of halogen molecules at sites in the hydrocarbon matrix. (4) Similar clustering of iodine and iodine monochloride does not occur in glassy 3-methyl pentane, rather the organic yields suggest that the halogen undergoes partial segregation during total crystallization, (5) Very low organic yields ($<1\%$) can be attributed to total segregation of the halogen during crystallization.

CHAPTER VI

ISOTOPE AND PHASE EFFECTS OF BROMINE REACTIONS ACTIVATED BY RADIATIVE
NEUTRON CAPTURE AND ISOMERIC TRANSITION IN C_5-C_{13} HYDROCARBONS

Chapter VI

Isotope and Phase Effects of Bromine Reactions Activated by Radiative
Neutron Capture and Isomeric Transition in C_5-C_{13} Hydrocarbons

The autoradiation hypothesis⁴⁵ has given impetus to the study of halogen reactions activated by radiative neutron capture and isomeric transition in various organic solvents. According to the autoradiation hypothesis the (n, γ) and (IT) processes should give similar products due to combination of hot atoms with radicals formed by localized radiation induced by internal conversion and Auger electrons emitted by the recoil atom. Considerable support and extensions to the hypothesis were advanced in Chapter III.

Merrigan et.al.^{53,54} found similar products, but observed that isomeric transition induced organic yields were a factor of about 1.7 greater than the $^{80}\text{Br}^m$, ^{82}Br and $^{82}\text{Br}^m$ (n, γ)-activated organic yields in the C_6 -alkanes and CCl_4 . The authors suggested that the total organic yields for the (n, γ) process appeared to be proportional to the G-value for total radical production in the C_6 -alkanes. This suggested that predominately radical processes were contributing to the yield. However, the total organic yields from $^{82}\text{Br}^m$ (IT) ^{82}Br reactions were not proportional to the G-value and in all instances the isomeric transition organic yields were greater than the radiative neutron capture organic yields. The differences between the two processes were ascribed either to other processes, in addition to Auger radiation and/or differences in localized radical concentrations resulting from differing energies of the nuclear transformations.

The purposes of this research were: (1) to develop new variations in the methods for determining radiative neutron capture organic yields of ^{82}Br and $^{82}\text{Br}^m$. In particular to examine the overall effects of freezing a reaction system which had been irradiated with thermal neutrons in the liquid state, (2) to explore the (n, γ)- and (IT)-activated reactions of bromine with various $\text{C}_5\text{-C}_{13}$ alkanes, in an attempt to determine whether the (IT)- and (n, γ)- activated bromine reactions are similar or somewhat different as implied by the recent results, and (3) if possible to correlate the results with an acceptable mechanism.

Effect of Phase Change on $^{82}\text{Br} + ^{82}\text{Br}^m \text{-(n,}\gamma\text{)}$ and $^{82}\text{Br} \text{-(n,}\gamma\text{)} + \text{(IT)}$ Reactions in Liquid Hydrocarbons

Several laboratories^{53,83,104-107} have experimented with the effects of phase and phase change on the organic yields of halogens in hydrocarbons and alkyl halides. However, there are many unanswered questions as to the nature of the state of aggregation and agglomeration that occurs during the freezing process. Chapter IV and V have shown that the organic yields of Br_2 , I_2 and ICl may be useful as a criteria of the state of aggregation of dilute concentrations of halogens in hydrocarbons at 77°K . However, if the halogen concentration is sufficiently high, the organic yields are very low as a result of total segregation of the halogen during freezing. This research is aimed at investigating the overall effects on the organic yields when a liquid sample is frozen in liquid N_2 after a short thermal neutron irradiation.

Merrigan⁵⁴ applied a freezing technique to deduce the radiative neutron capture organic yields of ^{82}Br and $^{82}\text{Br}^m$ independent of the

$^{82}\text{Br}^m$ (IT) ^{82}Br induced reactions. It was suggested that freezing the reaction systems after a neutron irradiation stopped increases in ^{82}Br yields rather than promoted decreases.

This conclusion was reached on the basis that the ^{82}Br organic yields (as obtained by freezing the sample in liquid N_2 immediately after irradiation and keeping the sample solid until extraction 1-2 hrs after the neutron irradiation), were within experimental error of the $^{80}\text{Br}^m$ (n, γ) organic yields. If the length of irradiation was increased, the average lifetime of $^{82}\text{Br}^m$ in solution was increased, and hence the observed ^{82}Br organic yield increased with a function of time the sample was in the liquid state. (See Table VIII, Chapter 3)

Cessation of the increase or decrease in ^{82}Br organic yields upon freezing is not easily explained. A qualitative interpretation⁵³ was postulated that freezing the sample essentially separated the organic and inorganic phases. Hence that portion of halogen which was born in inorganic envelope of bromine molecules would remain inorganic, whereas that which was in organic combination would be dispersed in the organic phase in the solid state, and remain predominately in organic combination following isomeric transition. Hence a given halogen atom undergoing isomeric transition may not actually recombine with the fragment produced by the isomeric transition, but could result in a new organic or inorganic product.

The change of phase from liquid to solid might either: (a) completely halt any changes in the organic yields. This possibility is very reasonable in the case of $^{82}\text{Br}^m$ that is entrapped within a cluster or clump of bromine molecules. (b) enhance the yield of

products being formed by fragments restricted in a Franck-Rabinowitch¹⁰⁸ "cage" of solvent molecules. In this case the radioactive atoms may lose their energy to the cage walls and immediately recombine, or (c) the labeled atoms may recombine by diffusion after having escaped only a few molecular diameters from each other.¹⁰⁹

In Chapter III it was shown that for 0.1 mole percent ($^{129}\text{I}_2 + ^{127}\text{I}_2$) in n-hexane, the organic yields resulting from freezing samples left in the liquid phase 4 and 7 min prior to freezing and extraction from the solid state at various times do not indicate any changes in the organic yields following the freezing of the samples. Presumably in $^{130}\text{I}^m$ reaction systems by freezing samples an averaging effect occurs and the final observed results are organic yields in the solid state which are nearly constant with respect to time of extraction. An interesting test of the freezing technique for determining the $^{82}\text{Br} + ^{82}\text{Br}^m$ radiative neutron capture organic yields independent of $^{82}\text{Br}(n, \gamma) + (IT)$ organic yields would be to determine whether the total organic yield varied in any manner with the duration of time the sample was in the solid state.

The decision was made to study the radiative neutron capture organic yields of $^{82}\text{Br} + ^{82}\text{Br}^m$ and the combination $(n, \gamma) + (IT)$ ^{82}Br organic yields in n-pentane and isopentane. The C_5 hydrocarbons are representative of the $\text{C}_5\text{-C}_{13}$ hydrocarbons investigated later in this chapter. The liquid state $^{80}\text{Br}^m$ organic yields were not determined, because an isotope effect between (n, γ) activated bromine isotopes is neither expected in liquid aliphatic hydrocarbons, nor observed in the $\text{C}_6\text{-alkanes}$ and CCl_4 . The experiments were generally performed at high

concentrations (0.1 mf and greater) of Br_2 where the solid state organic yields are very low.

Figure 14 depicts the increase in the ^{82}Br organic yield in 0.3 mf Br_2 in n-pentane with the duration the sample was liquid following the neutron irradiation of the liquid system. Extrapolation of the organic yields to zero time gives the radiative neutron capture organic yield of $^{82}\text{Br} + ^{82}\text{Br}^{\text{m}}$, as shown in Table XXV. The organic yields increase from about 9.5% to 17%. The organic yield due to isomeric transition only (as determined by the freeze-thaw technique) was 15.0%.

Likewise, if 0.1 mf Br_2 in isopentane was irradiated with thermal neutrons for 7 sec and immersed in liquid nitrogen at various times after removal from the reactor, the ^{82}Br organic yields would be dependent on the length of time $^{82}\text{Br}^{\text{m}}$ (IT) ^{82}Br reactions were allowed to occur before freezing the reaction system. The variations in the organic yields are described in Table XXVI and are shown in Fig. 15, and are similar to those which would be observed had the reaction system merely been extracted from the liquid state at various times. The change in the organic yield, in both instances varies in a manner that can be related to the half-life of $^{82}\text{Br}^{\text{m}}$. (See p. 33)

These experiments are the first illustration and direct experimental evidence that the chemical separation of inorganic $^{82}\text{Br}^{\text{m}}$ from the reaction system will result in the same result that one obtains by employing the freezing procedure and performing chemical separations after the $^{82}\text{Br}^{\text{m}}$ has completely decayed in the frozen system.

However, the instances in which the chemical extraction is

Figure 14. Variations in ^{82}Br organic yields in n-pentane and 0.3 mf Br_2 as a function of time in the liquid phase before extraction, ●, or immediate freeze and extracted at various times, □.

Table XXV. Variations in ^{82}Br Organic Yields*
as a Function of Time in the Liquid Phase
Before Extraction

Time Liquid (Min)	Organic Yield ^{82}Br
0.5	9.8
3.0	13.6
9.0	14.8
12.0	11.9
13.0	15.4
18.0	14.2
24.0	15.7
30.0	17.1
45.0	17.5
60.0	17.4

* 7 sec neutron irradiation of 0.30 mf Br_2 in
Phillips research grade n-pentane.

Table XXVI. Variations in ^{82}Br Organic Yields as a Function of Time in the Liquid Phase,^a Followed by Freezing^b and Extraction^c After the $^{82}\text{Br}^m$ (IT) ^{82}Br Processes

Time Liquid (Min)	Organic Yield ^{82}Br
0.3	12.8
3.0	13.4
6.0	14.7
9.0	16.5
11.0	16.1
30.0	20.6
60.0	22.2

^a 7 sec neutron irradiation of 0.11 mf Br_2 in Phillips research grade isopentane.

^b The samples were usually solidified within 0.2 min after immersing in liquid N_2 .

^c The samples were kept frozen until the actual extraction.

Figure 15. Variations in ^{82}Br organic yields of isopentane and 0.1 mf Br_2 as a function of time in the liquid phase, followed by freezing and extraction after the $^{82}\text{Br}^{\text{m}}$ (II) ^{82}Br processes.

performed before the $^{82}\text{Br}^m$ (IT) ^{82}Br processes have decayed out in the solid state does not give equivalent results. For example, after a short neutron irradiation of 0.1 mf Br_2 in isopentane, the reaction systems were frozen in liquid nitrogen within 15 sec, or after 6.0 min following their removal from the reactor. If the polycrystalline samples were removed from the liquid N_2 and extracted from the solid state as a function of time the sample had been frozen, the organic yields were not constant and independent of the duration of time the samples were in the solid state. This result is depicted in Fig. 16. The yields obtained by the extraction of the solid reaction system soon after the neutron irradiation are considerably higher than obtained by extraction of a similar sample that had not been frozen (cf. Figs. 14 and 16.) In the case of the samples of 0.11 mf Br_2 in isopentane frozen immediately upon removal from the reactor, and extracted at various times the yields decreased uniformly from 14.5% to 10.8%. The organic yield obtained by an immediate extraction, without freezing procedures was 11%. If the reaction system was liquid for 6.0 min before freezing, the average lifetime of $^{82}\text{Br}^m$ in solution was increased, with a corresponding increase in the ^{82}Br (n, γ) + (IT) organic yield. The extraction of the frozen reaction system at various times produced a decrease in the observed organic yields from 19.9% to about 16%. See Table XXVII. Similar effects were noted in 0.3 mf Br_2 -n-pentane reaction systems as shown in Table XXVIII.

Although $^{82}\text{Br}^m$ appears to behave differently than $^{130}\text{I}^m$ when frozen into a polycrystalline matrix after a liquid state neutron irradiation and extracted from the solid state as a function of time,

Figure 16. Variations in ^{82}Br organic yields of isopentane and 0.1 mf Br_2 following freezing the reaction system 0.5 min, ●, or 6.0 min, ▲, after irradiation and extraction from solid state at various times.

Table XXVII. Variations in ^{82}Br Organic Yields Following Freezing the System,^a and Extraction as a Function of Time the Sample Was Solid^b

Time Liquid (Min)	Time Solid (Min)	Total Time Lapse Till Extraction (Min)	Organic Yield ^{82}Br
0.2	5.0	5.2	14.5
0.2	10.0	10.2	13.9
0.2	15.0	15.2	13.0
0.2	20.0	20.2	12.3
0.2	25.0	25.2	12.4
0.2	30.0	30.2	11.0
0.2	40.0	40.2	10.9
0.2	50.0	50.2	11.1
0.2	60 +	60 +	10.8
6.0	3.0	9.0	19.9
6.0	6.0	12.0	20.2
6.0	12.0	18.0	17.9
6.0	18.0	24.0	17.5
6.0	30.0	36.0	15.2
6.0	60.0	66.0	16.2

^a 0.11 mf Br_2 in Phillips research grade isopentane.

^b The samples were kept frozen until the actual extraction

Table XXVIII. Bromine-82 Organic Yields^a
Resulting From Liquid Irradiation,^b Freezing^c
and Extraction of the Solid System at Various
Times

Time Solid (Min)	Organic Yield ⁸² Br
3.0	12.2
12.0	12.1
24.0	8.9
30.0	8.5
60.0	9.0

^a 0.30 mf Br₂ in Phillips research grade n-pentane.

^b 7 sec thermal neutron irradiation.

^c The systems were frozen in liquid N₂ within 0.3 min
after irradiation.

the result is not necessarily unexpected. It is important to recall the same organic yield is observed, if the sample is not frozen and is extracted from the liquid state, or if the sample is frozen upon removal from the reactor and extracted 1-2 hr after the short neutron irradiation. Merrigan⁵⁴ has shown that within experimental error, there is not an isotope effect between (n, γ)-activated $^{80}\text{Br}^m$, $^{82}\text{Br}^m$ and ^{82}Br . The most obvious conclusion is that the postulate⁵³ that freezing the reaction systems essentially clumps or fractionally crystallizes the bromine and hydrocarbon and shields against further reaction is a valid suggestion. That is, $^{82}\text{Br}^m$ born in the inorganic, reacts with inorganic fractions and $^{82}\text{Br}^m$ present in the organic remains predominately in organic combination. Hence, only those $^{82}\text{Br}^m$ (IT) ^{82}Br reactions which occur on the interface of the clump have about a 25% chance to react with the organic phase. (i.e. under the conditions of monomolecular dispersion about 55% of the $^{80}\text{Br}^m$ (IT) ^{80}Br reactions will yield labeled organic products. See Chapter V and reference 49 for details.)

The observation that the organic yields are not always constant at various extraction times from the solid state might be expected. If the $^{82}\text{Br}^m$ (IT) ^{82}Br process results in the formation of long-lived pockets of radicals, etc., melting and extraction of the reaction system prior to the decay of the radicals could promote rapid chemical reactions of the radioactive bromine with the solvent. Willard and co-workers^{83,107} have noted differences in the electron spin resonance spectrum in the trapped radical production and stable product production in γ -irradiation of glassy and polycrystalline alkyl bromides con-

taining Br_2 and have discussed the formation of "trapped" free radicals produced in the solid state by ionizing radiation.

Influence of Molecular Parameters on the ^{81}Br (n, γ) ^{82}Br + $^{82}\text{Br}^m$ and $^{82}\text{Br}^m$ (IT) ^{82}Br Reactions in $\text{C}_5\text{-C}_{13}$ Hydrocarbons

Perhaps one of the most revealing probes used in investigating hot halogen atom reactions in the liquid phase has been the addition, prior to neutron irradiation, of substances which scavenge (i.e. react readily) with thermalized halogen atoms. Bromine and Iodine are effective radical scavengers. The variations of organic yield with the concentration (usually mole fraction) of scavenger is called a scavenger curve or scavenging effect.^{1,11} A general feature of bromine organic yield curves is a rapid decrease in yield caused by the addition of small quantities of scavenger. At low concentrations (less than 0.1 mf Br_2 in this study) the chances of a tagged bromine atom reacting by thermal and diffusion controlled reactions with radicals produced by the recoil and/or de-excitation of the atom are increased. If the organic yield is relatively insensitive to small variations in scavenger concentration, then the yields are usually considered to have resulted from hot reactions. Under the conditions of high Br_2 concentration (0.1 mf) radicals produced by a hot atom would react with bromine in the immediate vicinity and the labeled atom which formed the radicals would have little chance of reacting thermally with a radical even if it escaped high energy reaction. Elemental Br_2 is an effective scavenger of thermalized Br atoms. The extent of the hot atom reaction can be estimated by extrapolation to zero mole fraction bromine. In general radiolytic effects are completely suppressed at high bromine concentrations.

The shape of scavenger curve in the region of high bromine concentration is useful in the interpretation of the mechanism involved in the hot atom reaction. If the curve is linear, the reaction is probably predominately radical in nature. The effect of adding Br_2 would be to dilute the organic radical concentration in the hot atom region, and hence the organic yields is reduced because of the increased probability that radicals produced by hot atoms would react with the Br_2 scavenger rather than the labeled atom. If the scavenging effect is non-linear, a molecular type of reaction is implied. Molecular reactions depend on the impact of a recoil atom and hence on the relative cross section for reaction with either organic substrate or bromine scavenger. In addition to diluting organic molecules, the higher concentration of Br_2 presents a larger inorganic target, and hence, the resultant scavenger curve may depend on differences in area presented to the recoil atom by Br_2 and the organic substrate and differences in momentum transfer from the recoil atom to either target. It is not possible to obtain a scavenger curve with iodine scavenger out to unit mole fraction, because of the limited solubility of I_2 in the aliphatic hydrocarbons.

The scavenger curves for the ^{81}Br (n, γ) ^{82}Br + $^{82}\text{Br}^m$ and $^{82}\text{Br}^m$ (IT) ^{82}Br reaction in the liquid state have been determined for fifteen isomeric $\text{C}_5\text{-C}_{13}$ alkanes and for heptanoic acid. Figures 17 through 30 illustrate the general shape of the scavenger curves and trends in the bromine solid state organic yields in several isomeric $\text{C}_5\text{-C}_{11}$ hydrocarbons. Each of the normal chain alkanes was examined. In addition to the five branched chain compounds, three substituted

Figure 17—Organic retentions of reactions of Br_2 with n-Pentane. ^{80}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ^{82}Br from (N, γ) at 298° K., ^{82}Br from (I.T.) at 298° K., ●

Figure 18. Organic retentions of reactions of Br_2 with isopentane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K, ■; ^{82}Br from (N, γ) at 298° K, ○; $^{80}\text{Br}^m$, $^{82}\text{Br}^m$ from (N, γ) at 298° K, ○; ^{82}Br from (I.T.) at 298° K, ●.

Figure 19—Organic retentions of reactions of Br_2 with n-Heptane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ) , ^{82}Br from (I.T.) at 77° K., $\blacksquare$; $^{82}\text{Br}^m$, ^{82}Br from (N, γ) at 298° K., $\circ$; ^{82}Br from (I.T.) at 298° K., $\bullet$.

Figure 20—Organic retentions of reactions of Br_2 with 2,4-dimethyl pentane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N,γ); ^{82}Br from (I.T.) at 77° K., ■; $^{82}\text{Br} + ^{82}\text{Br}^m$ (N,γ) at 298° K., ○; ^{82}Br from (I.T.) at 298° K., ●.

Figure 21—Organic retentions of reactions of Br_2 with Methyl cyclohexane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ) , ^{82}Br from (I.T.) at 77°K , ■ ^{82}Br , $^{82}\text{Br}^m$ (N, γ) at 298°K , ○ ; ^{82}Br from (I.T.) at 298°K , ● .

Figure 22 —Organic retentions of reactions of Br_2 with n-octane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ^{80}Br , ^{82}Br (N, γ) at 298° K., $\bullet$; ^{82}Br from (I.T.) at 298° K., $\bullet$

Figure 23 — Organic retentions of reactions of Br_2 with 2,2,4-trimethyl pentane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., $\blacksquare$; ^{82}Br from (N, γ) at 298° K., $\circ$; ^{82}Br from (I.T.) at 298° K., $\bullet$.

Figure 24 —Organic retentions of reactions of Br_2 with 2,3,4-trimethyl pentane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■; $^{82}\text{Br} + ^{82}\text{Br}^m$ (N, γ) at 298° K., ○; ^{82}Br from (I.T.) at 298° K., ●.

Figure 25.—Organic retentions of reactions of Br_2 with Cis-1,2-dimethyl cyclohexane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., $\blacksquare$; $^{80}\text{Br}^m$, $^{82}\text{Br}^m$ (N, γ) at 298° K., $\circ$; ^{82}Br from (I.T.) at 298° K., $\bullet$.

Figure 26 Organic retentions of reactions of Br_2 with trans-1,2-dimethyl cyclohexane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N,γ), ^{82}Br from (I.T.) at 77° K., ■ ; $^{82}\text{Br} + ^{82}\text{Br}^-$ (N,γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ●

Figure 27 —Organic retentions of reactions of Br_2 with n-nonane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., $\blacksquare$, ^{82}Br from (I.T.) at 298° K., $\circ$, ^{82}Br from (I.T.) at 298° K., $\bullet$.

Figure 28 -Organic retentions of reactions of Br_2 with 2,2,5-trimethyl hexane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■; $^{82}\text{Br} + ^{82}\text{Br}^m$ (N, γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ●

Figure 24—Organic retentions of reactions of Br_2 with n-decane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■; $^{82}\text{Br} + ^{82}\text{Br}^m$ (N, γ) at 298° K., ○; ^{82}Br from (I.T.) at 298° K., ●.

cyclohexanes were examined. In all instances studied, the liquid state scavengers are linear between 0.1 and 1.0 mf Br_2 , which suggests that the mechanism of both the isomeric transition and radiative neutron capture activated reactions may be primarily radical in nature. Another significant feature of the curves is that in all instances, save one, the $^{82}\text{Br}^m$ (IT) ^{82}Br organic yields in the liquid state were greater than the complementary $^{82}\text{Br} + ^{82}\text{Br}^m$ radioactive neutron capture organic yields. The liquid and solid state organic yields at the various concentrations of Br_2 are shown in Table XXIX. The magnitude of the isotope effect in the liquid state varies from 2.2 to 1.3 for the $\text{C}_5\text{-C}_{13}$ normal hydrocarbons, and from 2.2 to 1.0 for the various isomeric alkanes.

^{82}Br organic yields produced by isomeric transition to $^{80}\text{Br}^m$ and $^{82}\text{Br}^m$ yields following radiative neutron capture was approximately 1.7 at any given concentration of Br_2 in the C_6 alkanes and CCl_4 . The data rather firmly support earlier investigations on the isotope effects of bromine reactions in the hexane isomers. Isotope effects between bromine reactions activated by radiative neutron capture and isomeric transition in liquid hydrocarbons and alkyl halides have recently been reported and examined by a number of other laboratories.^{46,47,67,105,110-112.}

The solid state organic yields were very low in most systems. The tailing-up at dilute mole fractions of Br_2 is probably due to the presence of gaseous impurities in the Phillips research grade hydrocarbons. As discussed in Chapters IV and V the solid state organic yields are extremely sensitive to the presence of some impurities.

Table XXIX. Organic Yields Induced by ^{81}Br (n, γ), $^{82}\text{Br} + ^{82}\text{Br}^m$ and $^{82}\text{Br}^m$ (II) ^{82}Br Processes at Various Concentrations of Br_2 in Solid and Liquid Hydrocarbons

mf Br_2	Solid ^b		Liquid (n, γ) ^c	Liquid (II) ^d
	$^{80}\text{Br}^m$	$^{82}\text{Br}^m$	$^{82}\text{Br}^m + ^{82}\text{Br}$	^{82}Br
<u>$n\text{-C}_5\text{H}_{10}$</u>				
0.050	2.4	2.9	11.1	22.2
0.095	0.8	0.8	9.5	20.5
0.174	0.8	0.7	8.0	18.6
0.297	0.6	0.5	3.5	15.0
0.613	0.5	0.4	5.3	7.5
0.725	0.2	0.2	2.5	6.2
<u>$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$</u>				
0.108	1.3	1.4	11.1	19.0
0.194	0.6	0.7	8.7	18.6
0.617	0.8	0.7	3.5	7.3
0.784	0.3	0.2	3.0	4.1
<u>$n\text{-C}_7\text{H}_{16}$</u>				
0.0135	7.0	6.3	18.8	----
0.063	1.0	1.1	14.8	25.2
0.118	0.9	0.9	13.2	20.9
0.215	0.3	0.5	9.7	17.8
0.392	1.3	0.4	7.9	13.1
0.606	0.4	0.4	6.0	7.6
0.800	0.2	0.2	3.6	4.9
<u>$n\text{-C}_7\text{H}_{15}\text{COOH}$</u>				
0.18	----	2.8	13.6	22.2
0.37	----	1.2	10.0	14.2

Table XXIX cont.

mf Br ₂	Solid ^b $^{80}\text{Br}^m$ $^{82}\text{Br}^m$ ^{82}Br		Liquid (n, γ) ^c $^{82}\text{Br}^m + ^{82}\text{Br}$	Liquid (IT) ^d ^{82}Br
<u>(CH₃)₂CHCH₂CH(CH₃)₂</u>				
0.064	2.6	2.1	17.7	25.6
0.120	1.4	1.6	12.4	19.7
0.214	---	---	10.3	16.6
0.343	0.2	0.3	8.8	11.9
0.618	0.9	0.6	6.6	7.8
0.803	0.1	0.1	3.4	5.0
<u>CH₃-cyclo-C₆H₁₁</u>				
0.054	3.1	3.4	25.1	32.1
0.103	2.5	2.4	16.0	20.9
0.216	1.7	1.5	12.6	17.6
0.364	0.7	0.7	10.1	13.7
0.496	1.0	0.9	6.6	10.6
0.774	1.2	0.5	2.0	5.9
<u>n-C₈H₁₈</u>				
0.069	---	---	17.3	25.2
0.129	1.6	1.4	13.3	20.2
0.229	0.7	0.6	11.7	18.1
0.426	1.3	1.7	10.0	13.9
0.639	0.4	0.3	6.1	8.0
0.817	0.6	0.6	4.2	4.9
<u>(CH₃)₃CCH₂CH(CH₃)₂</u>				
0.0021	16.6	18.5	30.4	46.0
0.0106	13.8	15.1	22.3	42.8
0.0219	8.7	9.1	23.4	38.7

Table XXIX cont.

0.131	0.9	0.9	15.0	22.9
0.232	0.4	0.4	12.8	19.1
0.668	0.9	0.8	6.0	8.1
0.833	0.3	0.3	3.9	4.8
<u>$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$</u>				
0.128	5.7	4.8	17.9	26.8
0.267	1.9	1.9	13.6	16.3
0.636	1.1	1.0	8.3	10.3
0.763	1.2	1.1	2.0	6.2
<u>cis-1,2-$(\text{CH}_3)_2$-cyclo-C_6H_{10}</u>				
0.061	0.4	3.0	17.9	26.4
0.114	2.1	2.2	15.3	22.0
0.205	1.6	1.6	11.8	17.0
0.564	0.7	1.2	6.7	8.9
0.795	---	---	3.3	---
0.244	1.1	1.1	10.7	16.7
<u>trans-1,2-$(\text{CH}_3)_2$-cyclo-C_6H_{10}</u>				
0.062	5.6	5.4	16.3	23.2
0.117	5.0	4.6	14.2	---
0.209	1.8	1.8	10.8	17.2
0.415	1.1	1.1	10.1	13.2
0.702	1.3	1.1	5.7	7.2
0.850	1.1	1.1	2.4	4.9
<u>n-C_9H_{20}</u>				
0.140	3.1	3.5	15.3	21.8
0.246	0.8	0.8	12.6	17.0
0.551	0.6	0.6	7.9	11.2
0.767	0.9	0.7	5.0	6.6

Table XXIX cont.

<u>$(\text{CH}_3)_3\text{C}-(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$</u>				
0.144	8.7	9.0	23.5	23.0
0.294	4.4	4.6	17.9	18.0
0.556	2.0	1.7	11.0	11.9
0.723	1.3	1.0	6.9	6.3
<u>$n\text{-C}_{10}\text{H}_{22}$</u>				
0.151	3.3	3.4	---	24.0
0.263	0.9	0.8	10.5	20.5
0.572	0.2	0.6	7.0	10.9
0.789	0.4	0.3	2.9	6.1
<u>$n\text{-C}_{11}\text{H}_{24}$</u>				
0.126	1.1	1.2	17.0	26.7
0.225	0.8	0.8	14.5	22.5
0.548	0.4	0.4	9.1	12.9
0.778	0.3	0.5	5.6	8.5
<u>$n\text{-C}_{13}\text{H}_{28}$</u>				
0.14	---	0.7	16.4	27.6
0.25	---	0.5	14.2	21.6
0.58	---	---	9.9	13.3
0.81	---	0.4	5.9	7.1

^a Experimental error about ± 0.5 .

^b Samples were irradiated in the reactor for 10 sec at 77° K and were kept frozen until $^{82}\text{Br}^{\text{m}}$ had decayed.

^c Samples were irradiated for 10 sec at 298° K and frozen within 20 sec after irradiation to prevent further changes in observed ^{82}Br organic yield due to $^{82}\text{Br}^{\text{m}}$ (II) ^{82}Br activations.

Table XXIX Footnotes cont.

d ^{82}Br organic yields induced by $^{82}\text{Br}^{\text{m}}$ (II) ^{82}Br processes were obtained by irradiating the samples for 10 sec at 77°K . Following irradiation the samples were thawed, in a water bath at approximately 360°K , in exactly 35 sec. The $^{82}\text{Br}^{\text{m}}$ decayed in the liquid system at 298°K and the observed ^{82}Br organic yield minus the corrected solid state ^{82}Br yield was multiplied by 1.17.

The possibility also exists that the solid state yields have started to show tendencies to form aggregates or clusters of preferred size, clustering of bromine in n-hexane was discussed in Chapter IV. An isotope effect between (n, γ) activated $^{80}\text{Br}^m$ and $^{82}\text{Br}^m + ^{82}\text{Br}$ or ^{82}Br (n, γ) + (IT) was not observed.

Table XXX presents a summary of the data obtained in the investigation of the reactions of hot bromine atoms with the various isomeric target molecules. Zero mole fraction organic yields were obtained by extrapolating the linear portion of the scavenger curve to the intercept. The error in the extrapolated value is about $\pm 1\%$. An examination of the extrapolated organic yields in the normal $\text{C}_5\text{-C}_{11}$ hydrocarbons is depicted in Figs. 31 and 32. The extrapolated values for the $^{82}\text{Br}^m$ (IT) ^{82}Br reaction increase in the order of increasing chain length. Although not shown, the scavenger curve for n-tridecane is very similar to that of n-undecane. (See Table XXX) It is of further interest to note that the isomeric transition and radiative neutron capture organic yields in heptanoic acid (i.e. n- $\text{C}_7\text{H}_{15}\text{COOH}$) are nearly superimposable over the scavenger curve in n-heptane. The latter observation is qualitative evidence that the organic yield is more dependent on the structure of the target molecule than on its mass (i.e. molecular weight). However, it is interesting to note that within experimental error cis- and trans-1,2-dimethyl cyclohexane gave the same total organic yields at all concentrations of Br_2 studied. Fig. 32 depicts the zero mole fraction $^{82}\text{Br} + ^{82}\text{Br}^m$ radiative neutron capture in the normal hydrocarbons ranging from pentane through undecane. The extrapolated values

Table XXX. Zero Mole Fraction Br₂ Organic Yields of Bromine-82
(n,γ) and (IT) Reactions in Liquid Hydrocarbons

Hydrocarbon	Organic Yields		G-Value* (Total Radical)
	⁸² Br ^m + ⁸² Br (n,γ)	⁸² Br (IT)	
n-pentane -	10.0	21.6	8.7
isopentane	10.6	20.3	7.9
n-heptane ✓	14.0	21.0	9.1
heptanoic acid	14.0	21.0	---
2,4-dimethyl pentane	14.5	20.5	9.3
methyl-cyclohexane	17.8	21.6	6.9
n-octane -	17.0	22.0	8.3
2,3,4-trimethyl pentane	17.0	28.0	8.1
2,2,4-trimethyl pentane	17.6	25.2	8.9
<u>cis</u> -1,2-dimethyl cyclohexane	17.5	22.0	6.7
<u>trans</u> -1,2-dimethyl cyclohexane	17.0	22.0	6.7
n-nonane	17.5	24.3	9.4
2,2,5-trimethyl hexane	28.0	28.0	8.9
n-decane	15.8	28.0	8.9
n-undecane	19.0	30.5	---
n-tridecane	19.5	30.5	---

* Reference 113

Figure 31. Comparison of isomeric transition scavenger curves in $\text{C}_5 - \text{C}_{11}$ normal hydrocarbons.

Figure 32. Comparison of radiative neutron capture scavenger curves in C_5 - C_{11} normal hydrocarbons.

appear to increase with chain length, with the exception of n-decane which lies between n-heptane and n-octane. As in the case of the ^{82}Br isomeric transition, the organic yields of $n\text{-C}_{13}\text{H}_{28}$ and $n\text{-C}_7\text{H}_{15}\text{COOH}$ are similar to n-undecane and n-heptane, respectively.

For the (n, γ) process there appears to be a structural influence within any series of isomers studied. The total organic yields follow the general order for molecular structure:

normal $\simeq$ cyclic < single secondary group $\simeq$ two
secondary groups < branched methyl alkane < tertiary.

Hardwick¹¹³ confirmed Dewhurst's¹¹⁴ observation that the extent or radical formation (the radiation G-value* for total radical formation) from C-C bond scission is clearly related to chemical structure. It appears that the greater the branching of the chain hydrocarbon, the greater the number of radicals formed by C-C bond scission. Cycloalkanes as a group show similar G-value trends. Merrigan⁵⁴ has suggested that if the hot atom reactions were radiation-induced by localized interactions of Auger electrons with the surrounding environment, forming reactive organic radicals, the yield of organic products could perhaps be proportional to the G-value for radical production by gamma radiation since hot electrons are involved in radiation-induced reactions.⁵⁴ Unfortunately, G-values determined under the conditions of these experiments are not available. Hence, one can presently only speculate as

* The G-value is a quantitative measure of the efficiency of a radiation-induced chemical effect, i.e. the number of molecules destroyed or produced per 100 ev of energy absorbed.

to any correlation that might exist between the zero mole fraction organic yields and the G-value for radical production of the various isomeric hydrocarbons. The fate of the tagged atom is dependent upon a competition between processes which will stabilize it in organic form and those which will stabilize it in inorganic competition. However, one must be cautioned that in using hydrocarbons containing 10 mole percent and higher concentrations of bromine one is working in media drastically different from the hydrocarbon systems for which the G-values of Hardwick¹¹³ were determined. In the reaction systems discussed here and previously,⁵⁴ 20% or more of the absorbed energy is absorbed by bromine rather than by the hydrocarbon. If only for the purposes of comparison, G (radicals) as determined by EPR are presented along with the zero mole fraction organic yields in Table XXX.

Figure 33 depicts the relationship between the zero mole fraction Br₂ organic yields in the normal C₅-C₁₃ hydrocarbons versus the number of carbon atoms in the target molecule. It is interesting to note that the radiative neutron capture organic yields increase rather linearly between n-pentane and n-nonane and then level off. If one extrapolates the linear portion between C₅ and C₉ it appears that the radiative neutron capture organic yield might be proportional to the number of carbon atoms in the chain. However, the same trend does not hold in the case of the ⁸²Br isomeric transition organic yields. If the (n,γ)-activated organic yields are proportional to the chain length of the target molecule, then, the trend could be suggestive of the relative importance of degradation of the target molecule and subsequent radical reactions as predicted by the random fragmentation hypothesis.¹ The

Figure 33. Zero mole fraction organic yields in $\text{C}_5\text{-C}_{13}$ normal hydrocarbons. $^{82}\text{Br} + ^{82}\text{Br}^m$ by (n, γ), ○; ^{82}Br by (IT), ●.

increase in (IT) organic yields with chain length, but a lack of correlation with the chain length of the target molecule could suggest that processes in addition to radical reactions are operative in bromine isomeric transition chemistry. The scavenger curves suggest, the $^{82}\text{Br}^m$ (IT) ^{82}Br and ^{81}Br (n, γ) ^{82}Br + $^{82}\text{Br}^m$ organic yields are primarily radical in nature. If the organic yields for isomeric transition reactions are strictly radical in nature, it would be expected that the (IT) organic yields would parallel the (n, γ)-activated yields. Hence one is lead to the conclusion that while (n, γ) reactions may be the result of random fragmentation and autoradiation effects, the (IT) reaction may be due in part to other processes, i.e. ion molecule, charge transfer, excited molecule, ...etc. that are occurring in addition to internal conversion and Auger electron radiation reactions. Hence the autoradiation hypothesis seems to be a satisfactory model to explain the reactions of hot halogen atoms in liquid organic media. Additional evidence from radiation chemistry and ion-molecule chemistry will undoubtedly be of value in deducing the mechanism of radiative neutron capture and isomeric transition chemistry.

• CHAPTER VII

COMPLICATING ROLE OF REACTIONS INDUCED BY ISOMERIC TRANSITION IN NEUTRON-
ACTIVATION ANALYSIS FOR ^{82}Br AND ^{130}I

Chapter VII

Complicating Role of Reactions Induced by Isomeric Transition in Neutron-Activation Analysis for ^{82}Br and ^{130}I

Neutron-activation analysis has been generally employed in the analysis of numerous elements in a large variety of inorganic, organic, biological and pharmaceutical materials.¹¹⁵⁻¹¹⁸ In activation analysis the sample is exposed to a thermal or fast neutron flux and the element to be analyzed acquires a radioactive tag. Meinke¹¹⁹ has emphasized that the proper use of activation analysis adds to the demand on other techniques rather than diminishes them, and requires the extension of old techniques and new concepts.

Lyon, et.al.¹¹⁸ have recently reviewed the enormous amount of literature that has been published on neutron activation analysis techniques to analyze specific elements in given matrices. However, they also emphasized that many investigators have given a "long hard look" at established methods to eliminate systematic errors and interferences to improve accuracy and precision. The instance in which the activated atoms are born in metastable isomeric states and decay to a longer-lived isotope is the principle concern of this discussion.

In the analysis for ^{82}Br and ^{130}I , which have isomeric states,^{27,28,29} it is important to take cognizance of possible isomeric transition induced reactions of the ^{82}Br and ^{130}I in the sample (and possibly the sample container),¹²⁰ and with solvent and solute, if the sample must be transferred from the sample vessel, in which it was irradiated, in order to carry out wet chemical procedures to remove interferences. Although numerous analytical techniques have been developed for the

analysis of bromine and iodine, it is now apparent and necessary that the analyst consider the possible influence of isomeric transition induced reactions on his results. Radiative neutron capture of ^{81}Br results in 91% of the activated atoms being born as $^{82}\text{Br}^m$ ($T_{1/2}^1 = 6 \text{ min}$) which decays by isomeric transition to ^{82}Br ($T_{1/2}^1 = 35.3 \text{ hr}$). (See Fig. 2) Consider as an example, the scheme of Blekas and Souliotus¹²¹ for the simultaneous determination of iodine and bromine in urine by neutron-activation-analysis. If ^{82}Br separation is begun immediately after removal of the sample from the reactor, considerable ^{82}Br activity may be discarded prior to assay, because of (IT) reactions of ^{82}Br with CCl_4 used in subsequent solvent extractions. That is, hot-atom (IT) reactions may incorporate halogen into chemical forms that do not lend themselves to desirable chemical separation. The hot atom chemistry of ^{82}Br and ^{130}I reactions in several organic solvents has been discussed previously^{27,49,51-54} and in this thesis, evidence is clearly presented to indicate that at least 50% of the activity resulting from $^{82}\text{Br}^m$ (IT) ^{82}Br reactions at dilute bromine concentrations will react with CCl_4 . However, by waiting until the short-lived metastable isotope has decayed (about 10 $T_{1/2}^1$'s) before performing any chemistry with the sample, complicating isomeric transition induced reactions are eliminated. In the case of long-lived metastable isomers, e.g. $^{80}\text{Br}^m$, ($T_{1/2}^1 = 4.5 \text{ hr}$) contributions from (IT) reactions are minimized by performing operations with the sample in a time interval that is short compared to the half-life of the metastable species being analyzed.

The neutron-activation analysis of fission-produced ^{129}I in the atmosphere and in biological systems as a result of atomic testing

fallout, has been of recent interest.¹²²⁻¹²⁴ Since ^{129}I subjected to a neutron flux results in 61% of the activated atoms being born as $^{130\text{m}}\text{I}$ ($T_{\frac{1}{2}} = 9 \text{ min}$), many of the techniques developed for the neutron-activation analysis of ^{128}I (formed directly by neutron capture) may not be applicable without making proper modification to the analysis of ^{130}I ($T_{\frac{1}{2}} = 12.4 \text{ hr}$).

Integrating Summary

The chemical reactions initiated by the $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I and $^{82}\text{Br}^{\text{m}}$ (IT) ^{82}Br processes were investigated and compared with those induced by the ^{129}I (n, γ) ^{130}I + $^{130}\text{I}^{\text{m}}$, ^{127}I (n, γ) ^{128}I , ^{37}Cl (n, γ) ^{38}Cl and the ^{81}Br (n, γ) ^{82}Br + $^{82}\text{Br}^{\text{m}}$ nuclear transformations. The organic yields of ^{130}I + $^{130}\text{I}^{\text{m}}$ and ^{128}I activated by radiative neutron capture were compared to those of ^{130}I activated by isomeric transition in several liquid hydrocarbons ranging from n-pentane to n-nonane. The organic yields of (n, γ) activated $^{130}\text{I}^{\text{m}}$ + ^{130}I are consistently lower than the (IT) induced organic yields of ^{130}I and (n, γ) activated ^{128}I . Radiogas chromatography analysis has indicated the similarity of products, but differences in abundance of the relative product yields of ^{128}I , ^{130}I and ^{82}Br . Similarities in yields and product distributions between iodine and bromine isomeric transition induced reactions may indicate that radiohalogens mainly trace their chemical environment. The organic reactivity may be explained by the autoradiation hypothesis, which suggests the radiative neutron capture and isomeric transition processes should give similar products due to combinations of halogen species with radicals formed by localized radiation produced by the internal conversion and Auger electrons emitted by the recoil atom. The differences in individual product yields of iodine and bromine in a given hydrocarbon may reflect that in addition to the halogen atom tracing of isomeric transition produced radical debris, varying contributions of ion-molecule reactions characteristic of the halogen atom could occur. The (n, γ) and (IT) activated reactions of bromine were studied in various liquid hydrocarbons ranging from pentane to tridecane. The total

organic yields of (n,γ) activated $^{80}\text{Br}^m$ were lower than the (IT) organic yields of ^{82}Br at all Br_2 concentrations studied. The organic yields were found to vary with the chain length and the target molecule structure. The lower reactivity of (n,γ) activated $^{130}\text{I} + ^{130}\text{I}^m$, as well as that of (n,γ) activated ^{82}Br and $^{82}\text{Br}^m$, could be due to a lower percent of ^{130}I , $^{130}\text{I}^m$, $^{82}\text{Br}^m$ and ^{82}Br born by the (n,γ) process in low-lying metastable states. If autoradiation effects with their accompanying iodine and bromine radical reactions, ion-molecule reactions, etc., accounts for only a part of the organic yields of (n,γ) activated $^{80}\text{Br}^m$, ^{82}Br and $^{130}\text{I} + ^{130}\text{I}^m$ reactions in liquid hydrocarbons, then the remaining organic yield may be the result of other processes such as those predicted by the random fragmentation hypothesis. The random fragmentation hypothesis would predict a radical mechanism and degradation products of the target molecule, as observed by radiogas chromatography.

The organic yields from I_2 , Br_2 and ICl source molecules activated by radiative neutron capture and isomeric transition were determined in polycrystalline n-hexane, cyclohexane, and 2,2-dimethyl butane, and in glassy 3-methyl pentane at 77°K . Specifically the influence of purity levels, neutron irradiation and post-irradiation procedures, the effect of halogen concentration, the influence of additives and nuclear transformation on the observed organic yields were investigated. The experiments with Br_2 , I_2 and ICl (in which either halogen atom may acquire a radioactive label) have shown that the radiohalogens mainly trace their environment without chemical selectivity with regard to isotope and mode of activation. In glassy and polycrystalline halogen-hydrocarbon systems, the organic yields under the conditions of monomolecular dispersion are about $55 \pm 5\%$. In polycrystalline hydrocarbons containing

I_2 , or ICl , rather constant organic yields of about 10% in n-hexane, and 2,2-dimethyl butane, and 25% in cyclohexane between 1×10^{-5} and 2×10^{-4} mf halogen suggests the formation of preferred $(X_2)_n$ cluster sizes and/or similar numbers of halogen molecules at sites in the hydrocarbon matrix. The organic yield plateaus indicate that the halogen clusters at the various sites in the organic matrix are larger in n-hexane than in cyclohexane. Similar clustering of I_2 and ICl does not occur in glassy 3-methyl pentane, rather the organic yields suggest that the halogen undergoes partial segregation during total crystallization.

The effects of phase change on $^{130}I^m(II)^{130}I$ and the $^{82}Br^m(II)^{82}Br$ induced organic yields were explored. The complicating role of isomeric transition induced reactions in neutron activation analysis for ^{82}Br and ^{130}I is discussed.

APPENDIX

Appendix

General Expression for Obtaining Isomeric Transition Organic Yields

An expression for obtaining isomeric transition induced organic yields, based on the use of the "freeze-thaw technique", was derived by Merrigan.^{51,54} Subsequently Merrigan and Parks obtained a more general expression (Eq. 4).

In a freeze-thaw type experiment the observed organic yield, OY, may be described

$$OY_{obs} = \frac{\text{Org. Act.}_{IT}^{liquid} + \text{Org. Act.}_{IT}^{sld} + \text{Org. Act.}_{n,y}^{sld}}{\text{Total Activity}} \quad (1)$$

The organic yield (R^0) due strictly to isomeric transition induced reactions in the liquid state is defined as the organic activity introduced into the liquid organic phase by (IT) reactions divided by only that fraction of total activity produced by the decay of the metastable isomer in the liquid state. This result is obtained by dividing Eq. 1 by the term, $\beta e^{-\lambda t}$, where β is the fraction of the total activity (TA) born by (IT)-activated processes decaying in the liquid state, and $e(-\lambda t)$ describes the duration of time the sample was solid from midpoint to irradiation to liquefaction.

$$\frac{OY_{obs}}{\beta e^{-\lambda t}} = \frac{\text{Org. Act.}_{IT}^{liq}}{\beta e^{-\lambda t}(TA)} + \frac{\text{Org. Act.}_{IT}^{sld}}{\beta e^{-\lambda t}(TA)} + \frac{\text{Org. Act.}_{n,y}^{sld}}{\beta e^{-\lambda t}(TA)} \quad (2)$$

Rearranging

$$OY_{IT}^{liq.} = \frac{\text{Org. Act.}_{IT}^{liq.}}{\beta e^{-\lambda t} (TA)} = \frac{OY_{obs}}{\beta e^{-\lambda t}} - \frac{\text{Org. Act.}_{IT}^{sld} + \text{Org Act.}_{n,\gamma}^{sld}}{\beta e^{-\lambda t} (TA)} \quad (3)$$

The solid state organic activity induced by (IT)-activation is equal to $(1 - e^{-\lambda t})\beta$ times the observed solid state organic yield. The solid state organic activity induced by (n,γ) -activation is equal to α times the observed solid state organic yield, (R^0) where α is the fraction of the total activity produced directly by radiative neutron capture. For $^{82}\text{Br}^m$ systems α and β are 0.09 and 0.91, respectively;⁵⁶ but in $^{130}\text{I}^m$ systems α and β are 0.39 and 0.61 respectively.²⁷ By making the proper substitutions and rearranging a general expression (4) is obtained for systems where the freeze-thaw technique is applicable.

$$OY_{IT}^{liq} = \left[R^0 - \alpha R^0 / \beta e^{-\lambda t} \right] - \left[(1 - e^{-\lambda t}) R^0 / e^{-\lambda t} \right] \quad (4)$$

LITERATURE CITED

Literature Cited

1. J. E. Willard, Ann. Rev. Nucl. Sci., **3**, 193 (1953).
2. J. E. Willard, Symposium on Chemical Effects Associated with Nuclear Reactions and Radioactive Transformations, Vol. 1, p. 221, IAEA, Vienna (1965).
3. S. C. Lind and D. C. Bardwell, J. Amer. Chem. Soc., **46**, 2003 (1924).
4. L. Szilard and T. A. Chalmers, Nature, **134**, 462 (1934).
5. L. Szilard and T. A. Chalmers, Nature, **134**, 494 (1934).
6. E. Amaldi, E. Fermi, B. Pontecorvo, F. Rasetti, and E. Segre, Proc. Roy. Soc. (London), **A 149**, 522 (1935).
7. E. Glueckauf and J. Fay, J. Chem. Soc., 390 (1936).
8. A. P. Wolf in "Advances in Physical Organic Chemistry" Vol. 2, V. Gold, ed., Academic Press, New York, 1964, p. 202-277.
9. R. Wolfgang in "Progress in Reaction Kinetics" Vol. 3, G. Porter, ed., Pergamon Press, Oxford, 1965, p. 99-169.
10. C. MacKay and R. Wolfgang, Science, **148**, 899 (1965).
11. R. Wolfgang, Ann. Rev. Phys. Chem., **16**, 15 (1965).
12. E. S. Filatov, Russ. Chem. Rev. **34**, 680 (1965).
13. J. E. Willard, Ann. Rev. Phys. Chem., **6**, 141 (1955).
14. J. E. Willard, Nucleonics, **19**, No. 10, 61 (1961).
15. J. E. Willard, Proceedings of the 1960 Prague Symposium on Chemical Effects of Nuclear Transformations, Vol. 1, p. 215, IAEA, Vienna (1961).
16. A. P. Wolf, Ann. Rev. Nucl. Sci. **10**, 259 (1960).
17. G. Stocklin and A. P. Wolf, "Preparation and Biomedical Application of Labelled Molecules", Brussels, Euratom, p. 437 (1964).
18. I. G. Campbell, Advan. Inorg. Chem. Radiochem., **5**, 135 (1963).
19. G. N. Walton, Radiochimica Acta, **2**, 201 (1964).

20. H. Muller, Angewandte Chemie, (English Edition) 6, 133 (1967).
21. G. Harbottle, Ann. Rev. Nucl. Sci., 16, 89 (1966).
22. T. Anderson, "Experimental Investigations of Chemical Effects Associated With Nuclear Transformations in Some Inorganic Solids," Aarhus University, Denmark, 1968.
23. A. Suida, Information Center of the Polish Atomic Energy Commission, Report No 6 (1963).
24. Proceedings of Symposia on the Chemical Effects of Nuclear Transformations held in Prague, October, 1960, and published in two volumes; and Chemical Effects Associated with Nuclear Reactions and Radioactive Transformations held in Vienna, December, 1964, and published in two volumes by the International Atomic Energy Commission (IAEA).
25. G. Friedlander, J. Kennedy, J. Miller, "Nuclear And Radiochemistry," 2 nd Ed., John Wilery & Sons Inc., New York, 1964.
26. D. T. Goldman, "Chart of the Nuclides," 8 th Ed., General Electric Company, New York, 1965.
27. D. D. Wilkey and J. E. Willard, J. Chem. Phys., 44, 970 (1966).
28. J. F. Emery, J. Inorg. Nucl. Chem., 27, 903 (1965).
29. O. U. Anders, Phys. Rev., 138, B1 (1965).
30. See for example: C. Hsiung, H. Hsiung and A. A. Gordus, J. Chem. Phys., 34, 535 (1961).; H. C. Schweinler, Ref. 15, Vol 1, P. 63.; J. W. Cobble and G. E. Boyd, J. Amer. Chem. Soc., 74, 1282 (1952).
31. B. G. Harvey, " Introduction to Nuclear Physics and Chemistry," Prentice-Hall, Inc., New Jersey, 1962. P. 116.
32. L. R. B. Elton, "Introductory Nuclear Theory," 2 nd Ed., Sir Isaac Pitman & Sons, Ltd., London, 1965. P. 16.
33. E. H. S. Burhop, "The Auger Effect," Cambridge University Press, Cambridge, England, 1952.
34. J. T. Waber and D. T. Cromer, J. Chem. Phys. 42, 4116 (1965).

35. T. A. Carlson and R. M. White, J. Chem. Phys., 44, 4510 (1966).
36. S. Wexler, J. Chem. Phys., 36, 1992 (1962). Also see Science, 156, 901 (1967).
37. A. R. Kizanjian and W. F. Libby, J. Chem. Phys., 48, 2778 (1965).
38. W. F. Libby, "Isomeric Transition Chemistry," a paper presented at the 152 nd National Meeting of the American Chemical Society, New York, September, 1966. R-29.
39. S. Wexler and H. Davis, J. Chem. Phys., 20, 1588 (1952).
40. E. P. Rack and A. A. Gordus, J. Chem. Phys., 34, 1855 (1961).
41. S. Wexler and T. H. Davis, J. Chem. Phys., 20, 1688 (1952).
42. J. B. Nicholas, J. A. Merrigan and E. P. Rack, J. Chem. Phys., 46, 1996 (1967).
43. J. B. Nicholas and E. P. Rack, J. Chem. Phys., 48, 4085 (1968).
44. J. L. Thompson and W. W. Miller, J. Chem. Phys., 38, 2477 (1963).
45. P. R. Geissler and J. E. Willard, J. Phys. Chem., 67, 1675 (1963).
46. P. F. D. Shaw, Radiochimica Acta, 1, 177 (1963); ibid, 6, 150 (1966).
47. N. A. Katsanos and M. I. Stamouli, Radiochimica Acta, 7, 126 (1967); ibid, 7, 177 (1967).
48. M. Milman, Radiochimica Acta, 1, 15 (1962); ibid, 2, 180 (1964).
49. R. M. Iyer and J. E. Willard, J. Amer. Chem. Soc., 88, 4561 (1966).
50. W. K. Ellgren, Jr., M. S. Thesis, The University of Nebraska, 1965.
51. J. A. Merrigan, Ph. D. Thesis, The University of Nebraska, 1966.
52. N. J. Parks, Private Communication, This Laboratory, 1967.
53. J. A. Merrigan, W. K. Ellgren, Jr., and E. P. Rack, J. Chem. Phys., 44, 174 (1966).
54. J. A. Merrigan, J. B. Nicholas and E. P. Rack, Radiochimica Acta, 6, 94 (1966).

55. J. A. Merrigan and E. P. Rack, J. Phys. Chem., 69, 3795 (1965).
56. R. M. Iyer and J. E. Willard, J. Amer. Chem. Soc., 87, 2494 (1965).
57. F. J. Bryant, M. S. Thesis, The University of Nebraska, 1966.
58. J. B. Nicholas, M. S. Thesis, The University of Nebraska, 1967.
59. O. U. Anders, "Gamma Ray Spectra of Neutron Activated Elements," 3rd Printing, Dow Chemical Company, Midland Michigan, 1964.
60. J. A. Merrigan, J. B. Nicholas and E. P. Rack, J. Chem. Ed., 43 543 (1966).
61. R. L. Ayres, Private Communication, This Laboratory, 1967.
62. R. H. Schuler, J. Chem. Phys., 22, 2026 (1954).
63. G. Levey and J. E. Willard, J. Amer. Chem. Soc., 74, 6161 (1956).
64. R. H. Schuler and C. E. McCauley, J. Chem. Phys., 25, 1080 (1956).
65. E. P. Rack and A. A. Gordus, J. Phys. Chem., 65, 944 (1961).
66. Oak Ridge National Laboratory, Report No 3994, (1966). P. 1-26.
67. N. A. Katsanos and M. I. Stamouli, Radiochimica Acta, 5, 148 (1966).
68. S. Aditya and J. E. Willard, J. Amer. Chem. Soc., 79, 3367 (1957).
69. J. E. C. Macrae and P. F. D. Shaw, J. Inorg. Nucl. Chem., 24 1327 (1962).
70. H. M. Chang and J. E. Willard, J. Phys. Chem., 71, 3576 (1967).
71. H. Behrens and A. G. Maddock, Jr. J. Chem. Phys., 22, 1139 (1954).
72. N. V. Lassen and A. P. Boerg, Can. J. Chem., 42, 2684 (1964).
73. H. J. Riedel and E. Merz, Radiochimica Acta, 6, 144 (1966).
74. N. P. Archer, L. B. Hughes, T. J. Kennett and W. V. Prestwoch, Nuclear Physics, 83, 241 (1966).
75. L. F. Kalinkin, A. S. Melioranski and I. V. Estulin, J. Exptl. Theort. Phys., (U.S.S.R.) 36, 1613 (1959). [Translation: Soviet Physics. JETP 9, 1146 (1959).

76. S. J. Dutoit and L. M. Bollinger, Phys. Rev., 123, 629 (1961).
77. M. G. Mayer and J. H. D. Jensen, "Elementary Theory of Nuclear Shell Structure," John Wiley & Sons, Inc., New York, 1957. p. 207.
78. D. E. Lea, "Actions of Radiations on Living Cells," Cambridge Univ. Press, 1955, p. 24.
79. R. M. Iyer and J. E. Willard, Radiochimica Acta, 7, 175 (1967).
80. For examples and references, see references 1, 2, 15, 45, 53 and 54.
81. D. D. Wilkey, Ph.D. Thesis, University of Wisconsin, (1968).
82. J. B. Nicholas, Private Communication, This Laboratory, 1969.
83. R. M. A. Hahne and J. E. Willard, J. Phys. Chem., 68, 2582 (1964).
84. R. M. Iyer and J. E. Willard, J. Phys. Chem., 71, 3070 (1967).
85. M. Milman, J. Amer. Chem. Soc., 80, 5592 (1958).
86. O. Hassel and K. O. Stromme, Acta. Chem. Scand., 12, 1146 (1958).
87. A. N. Nesemeyanov, E. S. Filatov, E. A. Borisov and B. M. Shukla, Ref. 15, Vol 2. p. 259.
88. P. C. Capron and E. Crevecœur, J. Chem. Phys., 21, 1843 (1953).
89. F. S. Rowland and W. F. Libby, J. Chem. Phys., 21, 1495 (1953).
90. C. E. McCauley, C. J. Hilsdorf, P. R. Geisler and R. H. Schuler, J. Amer. Chem. Soc., 78, 3245 (1956).
91. G. Harbottle and N. Sutin, "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeleus and A. G. Sharp, eds., Academic Press, New York, 1959. p. 268.
92. R. M. Keefer and T. L. Allen, J. Chem. Phys., 25, 1059 (1956).
93. C. H. Townes and B. P. Dailey, J. Chem. Phys., 20, 35 (1952).
94. E. A. Ogryzlo and B. C. Sanctuasy, J. Phys. Chem., 69, 4422 (1965).
95. A. A. Passchier and N. W. Gregory, J. Phys. Chem. 72, 2697 (1968).
96. D. F. Evans, J. Chem. Phys., 23, 1424 (1955).
97. J. Groh and S. Papp, Z. Physik. Chem., A149, 153 (1930).

98. G. Kortun and G. Friedheim, Z. Naturforsch., 2A, 20 (1947).
99. H. Akamatu, et. al., Bull. Chem. Soc. Japan, 29, 213 (1956);
Ibid, 30, 618 (1957); Ibid, 34, 1015 (1961).
100. E. J. Kemnitz, Private Communication, This Laboratory, 1968.
101. M. Milman, J. Amer. Chem. Soc., 86, 3567 (1964).
102. J. Stevovic, K. Tanaka, M. Milman, Inorg. Nucl. Chem. Letters, 3,
415 (1967).
103. Z. Abendinzadeh, S. Grillet, J. Stevovic, K. Tanaka and M. Milman,
Radiochimica Acta, (In Press), 1969.
104. M. Milman, J. Amer. Chem. Soc., 88, 1578 (1966).
105. M. Milman, J. Chimie, Phys., 64, 658 (1967).
106. Z. Abedinzadeh, R. Radicella, K. Tanaka and M. Milman, Radiochimica
Acta (In Press), 1969.
107. T. O. Jones, R. H. Luebbe, Jr., J. R. Wilson and J. E. Willard,
J. Phys. Chem., 62, 9 (1958).
108. J. Franck and E. Rabinowitch, Trans. Faraday Soc., 30, 120 (1934).
109. R. M. Noyes, J. Chem. Phys., 18, 999 (1950).
110. A. Lal, Indian J. Physics, XLI, 39 (1967).
111. M. D. Mia and P. F. D. Shaw, Radiochimica Acta, 6, 172, (1966).
112. T. Shiokawa, T. Sato, K. Kondo and K. Sato, Nippon Kagaku Zasshi,
87, 922 (1966).
113. T. J. Hardwick, J. Phys. Chem., 66, 1611 (1962).
114. H. A. Dewhurst, J. Amer. Chem. Soc., 80, 5607 (1958).
115. W. W. Meinke, Anal. Chem., 28, 736 (1956); Ibid, 30, 686 (1958);
Ibid, 32, 104R (1964).
116. G. W. Leddicotte, Anal. Chem., 36, 419R (1964).
117. W. S. Lyon, E. Ricci and H. H. Ross, Anal. Chem., 40, 168R (1968).
118. W. S. Lyon, E. Ricci and H. H. Ross, Anal. Chem., 38, 215R (1966).

119. W. W. Meinke, "Activation Analysis" in the Proceedings of the R. A. Welch Foundation Conferences on Chemical Research, November 18-20 (1963), Houston, Texas.
120. H. R. Lukens, F. M. Grabes and D. M. Settle, Trans. Amer. Nucl. Soc., 9, 88 (1966).
121. E. P. Belkas and A. G. Souliotis, Analyst, 91, 199 (1966).
122. M. H. Studier, C. Postmus, J. Mech, R. R. Walters and E. N. Sloth, J. Inorg. Nucl. Chem., 24, 755 (1962).
123. R. R. Edwards, Science, 137, 851 (1962).
124. J. T. Watson, D. K. Roe, H. A. Selenkow, Radiation Research, 26, 159 (1965).

Publications and Papers Presented

Publications

1. "Isomeric Transition Induced Reactions of Iodine-130 in Cyclohexane." with H. A. Merrigan, J. B. Nicholas, N. J. Parks and E. P. Rack. J. Phys. Chem. **70**, 2417 (1966).
2. "Isotope Effects of Iodine Reactions Activated by the Radiative Neutron Capture and Isomeric Transition Processes in Liquid Hydrocarbons." with E. P. Rack. J. Chem. Phys. **48**, 3735 (1968).
3. "Complicating Role of Reactions Induced by Isomeric Transition in Neutron-Activation Analysis for ^{82}Br and ^{130}I ." with E. P. Rack. The Analyst. **93**, 550 (1968).
4. "Iodine Organic Yields in Hydrocarbon Matrices as an Indication of Clustering, Complexing and Fractional Crystallization at 77°K ." with R. L. Ayres, E. J. Kemnitz and E. P. Rack, Radiochimica Acta (In Press).
5. "Radiative Neutron Capture Organic Yields as an Indication of the State of Aggregation of ICl and I_2 in C_6 -Hydrocarbon Matrices at 77°K ." with H. K. J. Hahn and E. P. Rack, (submitted to J. Phys. Chem.).
6. "Deuteration and Heavy Atom Effects on the Scintillation Lifetime of p-terphenyl in Liquid Benzene." based on work during the summer of 1968 at Eastman Kodak Company with J. A. Merrigan and T. M. Kelly. (To be submitted to J. Chem. Phys.).
7. "Isomeric Transition Chemistry: An Experiment Using the $^{82}\text{Br}^m$ Isomer." with E. P. Rack. (To be submitted for consideration to J. Chem. Ed.).

Papers Presented at National Meetings

1. "Influence of Molecular Parameters on the ^{79}Br (n, γ) $^{80}\text{Br}^m$ and the $^{82}\text{Br}^m$ (IT) ^{82}Br Processes in Liquid Hydrocarbons." with E. P. Rack, Division of Nuclear Chemistry and Technology, American Chemical Society, Miami Beach, Florida, April 9-14, 1967. N-75.

2. "Radiative Neutron Capture and Isomeric Transition Induced Reactions of Iodine with Chloromethanes." presented by N. J. Parks, with R. M. Lambrecht, J. B. Nicholas, E. P. Rack and A. A. Gordus. Division of Nuclear Chemistry and Technology, American Chemical Society, Miami Beach, Florida, April 9-14, 1967. N-77.
3. "Isotope Effects of Iodine Reactions Activated by the (n, γ) and (IT) Processes in Liquid Hydrocarbons." with E. P. Rack. Division of Nuclear Chemistry and Technology, American Chemical Society, San Francisco, California, April 1-5, 1968. O-87.
4. "Iodine Organic Yields in Hydrocarbon Matrices as an Indication of Clustering, Complexing and Fractional Crystallization at 77° K." submitted to be presented by R. L. Ayres, with E. J. Kemnitz, R. M. Lambrecht, and E. P. Rack, The Division of Nuclear Chemistry and Technology, American Chemical Society, Minneapolis, Minn., April, 1969.
5. "Deuteration and Heavy Atom Effects on the Scintillation Lifetime of p-Terphenyl in Liquid Benzene." Submitted to be presented by J. A. Merrigan with R. M. Lambrecht and T. M. Kelly at the Division of Physical Chemistry, American Chemical Society, Minneapolis, Minn., April, 1969.