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REACTIONS OF SELECTED HALOGENS AND INTERHALOGENS
ACTIVATED BY RADIATIVE NEUTRON CAPTURE AND
ISOMERIC TRANSITION WITH CONDENSED STATE
CYCLOPENTANE AND AROMATIC HYDROCARBONS

A thesis by Ernest J. Kemnitz

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by

Ernest John Kemnitz, Jr.

A THESIS

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The Graduate College in the University of Nebraska
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REACTIONS OF SELECTED HALOGENS AND INTERHALOGENS
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Ernest John Kemnitz, Jr., Ph.D.

University of Nebraska, 1970

Advisor: Edward Paul Rack

Cyclopentane, benzene and selected alkylbenzenes were probed both in the liquid and solid phases with nuclear processes induced by the neutron activation of one or more of the following species: $^{127}\text{I}_2$, $^{129}\text{I}_2$, Br_2 , ICl and IBr . Of particular interest in each of the systems were the following: (1) isotope effects due to radiative neutron capture (n,γ) and isomeric transition (IT) processes; (2) individual and comparative scavenging effects in the liquid phase systems of the various halogens and interhalogens; (3) crystalline structure at 77° K, and; (4) product distributions of organic halides.

The organic yields due to the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ and $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ processes in liquid cyclopentane were about 1.2 times greater than those due to the $^{129}\text{I}(n,\gamma)^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ processes, whereas no differences were found when benzene and alkylbenzene were used as solvents. The product distribution was seemingly independent of the nuclear process in all

the solvents employed, which lends support to Willard's autoradiation hypothesis.

Using ICl in solid state systems, it was found that ^{38}Cl organic yields were useful in determining concentrations at which clustering or fractional crystallization occurred, while ^{128}I organic yields were seemingly misleading. In the Br_2 -benzene system at 77°K , two O.Y. plateaus appeared with the isotopes studied, producing different but parallel curves. The lower plateau region between 5×10^{-1} and 5×10^{-2} mf Br_2 has been interpreted as a region of uniform 1:1 complex plus pure solvent. The higher plateau region, generally below 5×10^{-4} mf Br_2 , was interpreted here to be a monomolecular dispersion of Br_2 in benzene. The constant $21 \pm 1\%$ organic yield of ^{38}Cl at all concentrations of ICl in benzene up to saturation supports this view.

The study of isotope effects in solid state systems was found to require extremely high purity components. Only the Br_2 -benzene gave reliable data for this reason. The $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br} + ^{82}\text{Br}^m$ and $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ processes each produced a different organic yield at a given concentration of Br_2 .

In the liquid state where organic yields were found to be much less sensitive to trace impurities, scavenging was found in mixed- and interhalogen-benzene systems but not in I_2 - and Br_2 -benzene systems. ^{38}Cl organic yields were not affected by phase or the presence of iodine while bromine organic yields lowered in the presence of iodine. ^{128}I organic yields were enhanced in the presence of chlorine and bromine, probably due to an increase in radical formation.

^{128}I and ^{38}Cl organic yields in solid state I_2 - and ICl -alkylbenzene systems resembled those in the analogous systems of benzene, indicating complex formation. The product distribution of the I_2 -alkylbenzene systems indicated that the alkyl side chains are quite vulnerable to attack by hot atom processes. Methyl iodide was the major product in the several alkylbenzenes studied except in the case of ethylbenzene where ethyl iodide was equally abundant. Interestingly, a large amount of unstable, unlabelled organic iodide was formed in the I_2 -ethylbenzene, -cumene and -tert-butyl-benzene systems.

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CHAPTER I
INTRODUCTION

Chapter I

Introduction

The study of the chemical consequences of nuclear transformations constitutes one of the major areas of hot atom chemistry. Nuclear transformations are usually produced by the (p,α) , $(n,2n)$, (n,p) , (n,γ) and (IT) reactions and the resulting species, "hot atoms", possess high kinetic energy or electrical charge or both. This initial energy normally far exceeds bonding energies and, thus, a hot atom may rupture many bonds in its immediate vicinity while losing its high kinetic energy or charge. Often the atom is made radioactive by the nuclear process which enables one to determine its chemical fate.

Although hot atoms are normally produced via nuclear transformations, they may also be produced by ultra-violet or visible light, by high-energy radiation, and by electrical discharges.

Radiative neutron capture, (n,γ) , is probably the most commonly employed mode of nuclear activation. The extensive use of this process is due to the relative availability of neutron sources, the relative ease of using them under conditions where radiation damage and temperature effects are not serious, favorable cross sections for the (n,γ) process, and the fact that the (n,γ) process is capable of producing a number of radioactive species with chemical properties which are particularly suitable for the studies of interest.¹

Radiative neutron capture often produces a sizeable percentage of

the product nuclide in a metastable nuclear state. Isomeric transition (IT) or the decay to the ground state produces a second nuclear process which occurs as a consequence of internal conversion and the associated Auger processes. These two nuclear activation processes were studied in this research.

The mechanisms involved in hot atom reactions are not easily elucidated but are of prime importance. A number of review articles¹⁻⁷ discuss the various models proposed and their limitations. The two requirements in mechanistic hot atom studies are: (1) The activated atom must produce a radioactive product, since the number of activated atoms is extremely small; and (2) thermal exchange reactions with each other or with other molecules cannot be allowed. The reactions studied in this research include ~~iodine~~ iodine, bromine, and chlorine isotopes activated by either radiative neutron capture and/or isomeric transition in cyclopentane and selected aromatic hydrocarbons. The systems were studied at room temperature and at (or near) liquid nitrogen temperature (77° K).

Historical Background

In 1934, Szilard and Chalmers⁸ initiated the study of the chemical effects of nuclear transformations with their study of the chemical effects of the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ reaction in liquid ethyl iodide. They found that part of the ^{128}I , which was produced by radiative neutron capture, escaped from the parent ethyl iodide molecule and became stabilized as an inorganic species. The scission of the C-I bond was thought to result from a momentum transfer from the neutron to the iodide

atom. Later, Amaldi⁹, et al., found that the recoil energy imparted by the emission of gamma rays as the target nucleus de-excites was responsible for the breaking of the C-I bond. In a subsequent study, Glueckauf and Fay¹⁰ found that the activated atom could also undergo organic bonding as well. The number of workers and the papers presented in hot atom chemistry since this time reflects the richness of the field and places any comprehensive survey beyond the scope of this dissertation. A very complete bibliography of publications in hot atom chemistry through 1962 has been compiled by Suida.¹¹ Review articles covering various aspects of hot atom chemistry have been written by Anderson¹², Campbell⁵, Filatov⁶, Harbottle¹³, Mueller¹⁴, Walton¹⁵, Willard^{1,2,18-20}, Wolf^{16,17}, and Wolfgang.^{3,4} Willard's^{1,18,19} review articles and the proceedings of two symposia^{2,20} on the chemical effects of nuclear transformations sponsored by the International Atomic Energy Agency cover the literature concerning the reactions of activated halogen atoms through 1963.

The evolution of hot atom reaction mechanisms of halogens in the condensed state is of particular importance. Libby²¹, in 1947, was the first to propose a detailed mechanism, which was called the "billiard-ball collision" hypothesis. The model was expanded somewhat with Friedman²² as co-author and referred to as the "billiard-ball collision--epithermal collision" hypothesis. The basic idea pictured the halogen atoms as recoiling with several hundred electron volts of energy (in liquid or solid alkyl halides) and losing their energy by momentum transfer in elastic collisions with single atoms, and inelastic collisions with whole molecules when the energy of the recoil atom is reduced by

successive collisions to the order of ten electron volts. This oversimplified hypothesis could not correlate the large volume of experimental data with any real consistency. Mallison²³, et al., and later Milman²⁴ proposed a molecular model which was good for specific cases but had severe limitations, in general, correlating all the existing data.

The "random fragmentation", "brush heap", or "nest of radicals" hypothesis proposed by Willard¹⁹ was a more realistic and applicable mechanistic theory for condensed state hot atom reactions. Simply stated, this theory treats the reactions in condensed states in terms of kinetic energy dissipation and charge neutralization of the hot atom within a small volume element, which produces a high concentration of ions, radicals, and excited molecules. Thus, when the excited atom returns to thermal energies it is surrounded by a high concentration of organic radicals and inorganic atoms. If the hot atom does not combine with one of these species in a hot atom reaction before reaching thermal energies, it may enter into chemical combination by diffusion. Although realistic, Willard's model was too qualitative in nature, which limited its applicability in quantitative studies.

A mathematical model for hot atom reactions in the gaseous state was developed by Estrup and Wolfgang.²⁵ This theory assumes no model for the reaction itself and is semi-empirical in nature. It has been applied successfully to a number of systems. The application of this theory to liquid systems is very difficult since no suitable, non-reactive moderator is available. However, Milman²⁶ recently made an effort to apply the theory to systems in which hot bromine atoms were produced in a number of organic liquids. The data was successfully applied in supporting the

theory, but may not represent a single type of hot atom reaction and thus, oversimplify the results. Filatov²⁷, et al., have also made a similar study of recoil halogen reactions in liquid systems. They incorporated some assumption of the mechanisms of reactions based largely on elastic collision models, which seem to limit their applicability in liquid systems.

More recently Geissler and Willard²⁸ proposed another mechanism for hot atom halogen reactions in liquid systems. This model is referred to as the "Auger electron reaction" or "Auger radiation" hypothesis. Their work with bromine and iodine revealed similar products from the various nuclear activation processes and gamma ray irradiation. Due to the fact that the various nuclear activations (and gamma irradiation) impart varying amounts of kinetic energy to the hot atom and nearly none in an isomeric transition, and since the products are qualitatively similar or actually the same in some cases suggests that the activated atoms pass through a common stage during de-excitation. Geissler and Willard²⁸ suggest that all the nuclear processes produce nuclei which pass through low-lying metastable levels which decay by internal conversion. As an example of this process, ^{128}I emits a conversion electron, electrons with the energy of $L \rightarrow K$ transition minus the L binding energy, approximately 20 Kev., and in the case of highly charged ions, additional electrons in the range of a few Kev. on down. These emitted electrons would excite or ionize molecules adjacent to the forming ^{128}I ion. The hot ion would then be surrounded by a highly localized concentration of excited species similar to those produced along the track of a Compton electron in a similar solution exposed to gamma irradiation.

The neutralization of the hot ion would occur rapidly if its ionization potential were higher than that of the solvent molecules. After neutralization the hot atom may combine with a radical produced by conversion and Auger electrons.

In support of the "Auger radiation" hypothesis, Thompson and Miller²⁹ observed that the initial recoil energy of a hot atom was imparted to the recoil atom in less than 10^{-13} seconds after neutron capture, while the ejection of one or more conversion electrons, followed by the loss of Auger electrons, occurred most frequently 10^{-12} to 10^{-5} seconds after neutron capture. Charge buildup could occur, then, in a time relatively long after the hot atom had reached thermal energies and had a chance to form a chemical bond.

In addition to the mechanism proposed by the "Auger radiation" hypothesis, the displacement type of reaction appears to contribute to the total organic yield observed in condensed systems. Such a mechanism has been observed in the gas phase and probably accounts for reactions in the condensed phase which are relatively unaffected by the presence of a scavenger.

Nuclear Activation

The isotopes used in this research and their nuclear activation properties are presented in Table I. The average thermal neutron flux to which the samples were subjected was 1.1×10^{11} neutrons/cm²-sec. The probability of neutron capture by a given nucleus is determined by the energy of the incident neutrons and the cross section for neutron absorption.

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 ⁸²Br) 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.

When a neutron is absorbed or captured a compound nucleus is formed which is in an excited quasi-stationary state. The energy imparted by the incident particle is assumed to be randomly distributed among all the nucleons in the compound nucleus so that not any of the nucleons has sufficient energy for immediate escape.³⁰ The compound nucleus, based on nuclear theory, has a lifetime of approximately 10^{-14} to 10^{-15} seconds, which depends on its energy, angular momentum and parity but is independent of its mode of formation.³¹

The instability of the compound nucleus has an energy equivalent to the neutron binding energy of the nucleus. The excess energy may be dissipated by the emission of gamma radiation and conversion electrons. The recoil energies of nuclei resulting from gamma emission will vary from zero to a maximum of $537 B^2/M \text{ ev}$ for the emission of a single gamma ray. B is the neutron binding energy and M is the atomic mass of the activated atom. To cite a specific case, the absorption of a thermal neutron by an ^{127}I nucleus, B is 6.8 Mev³¹, would impart an energy of 182 ev to the ^{128}I nucleus if all of the binding energy were released in the form of a single gamma ray of 6.8 mev energy. The other halogen nuclides used in this research have similar values. The probability of a single γ -ray being released is quite low, thus the recoil energy is estimated to have an average value of about 100 ev. Since momentum cancellation by emission in opposite directions occurs, the emission of more than one gamma ray results in an energy spectrum ranging from zero to a maximum kinetic energy. Although such spectra are discussed in the literature³⁰, little information regarding the neutron capture gamma-ray decay schemes of halogens used in this research is available. Nevertheless, one can take

the energy equivalent to the neutron binding energy of the nuclei as a representative measure of the expected maximum gamma-emission energy following neutron capture.

Charge State and Electronic Excitation Energy

An activated nuclide may not attain a ground state energy level after the initial high energy gamma emission, but rather move to a low-lying energy state or metastable nuclear state. Such a metastable state can change from one energy state to another as a result of internal conversion and gamma ray emission. The electromagnetic interaction between the nucleus and the extranuclear electrons, known as internal conversion, competes with photon emission as a means of nuclear de-excitation. An internal conversion coefficient, α , is the ratio of electrons to gamma rays. In general, an excited state is rather brief, usually of the order of 10^{-17} to 10^{-12} second, but if the angular momenta (spin) of the excited state and of the ground state are different, it may have a lifetime long enough to be measured.³⁶

Several of the halogen nuclides used in this study have rather high internal conversion coefficients, e.g. the $^{82}\text{Br}^m$ decay goes through 46 kev transition with $\alpha_K = 268^{(2)}$. The isomeric transition process often results in a chemical reaction as a result of a coulombic explosion caused by the production of a vacancy (hole) in the K- or L-shell of the nuclide. The vacancy is usually filled by an outer shell electron with the subsequent emission of a K or L x-ray; however, another electron may be ejected in place of the x-ray, with a kinetic energy equal to the difference

between the x-ray energy and the binding energy of the electron. This process may continue until the excess energy has been removed with a resulting highly charge positive species as depicted in Fig. 1. The successive emission of electrons following the initial internal conversion process is known as the "Auger" process and the electrons as "Auger" electrons after their discoverer.³⁷

Carlson, et al.³⁸, have compiled extensive data on the charge build-up on an atom as a result of a suddenly produced innershell vacancy as in the internal conversion process. From this a method was devised whereby the charge may be calculated as a function of shell level and atomic number. In another study, Carlson and White³⁹ produced Auger processes in methyl iodide iodine with x-rays and observed a distribution of charges ranging from +1 to +10 with +5 being the most abundant. The distribution of charge on recoiling atoms would most likely be similar. Using mass spectrometry, the recoil energies were found to vary from 2 to 25 ev. Due to conservation of momentum requirements, the larger halogen ions would be expected to possess smaller recoil energies than the smaller ones. Bromine was shown⁴⁰ to be highly charged, possibly as high as +13, with an average charge of +7. From the work of Kazanjian and Libby⁴¹, calculations were made for the various recoil energies associated with the spectrum of charges on a bromine atom following isomeric transition. If, for example, 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 distributed among the neighboring molecules and virtually explodes in response to the powerful

Figure 1. Typical vacancy cascade in I^- as the result of an initial L vacancy. The X's represent electrons; O's, vacancies; and ⊙'s, the cases where a vacancy has been formed and then filled by a subsequent Auger process. The mean radii for the shells are derived from relativistic SCF wavefunctions as determined for I^- by ref. 34, or calculated by ref. 35. See ref. 35 for detail.

coulombic repulsion. A number of recoiling fragments including free electrons and ions with varying velocities are produced as a result of isomeric transition processes.⁴² These fragments have high electron affinities and become neutralized rapidly by the environment either by free electrons or by electrons transferred from neutral species along their track.⁴¹ The hot species which produced the reactive fragments react with them or neutral molecules in the environment. Thus, the nuclide decaying by isomeric transition may react by virtue of charge, electronic excitation or recoil kinetic energy.

Although no precise data has been gathered, Wexler and Davies⁴³ have found that 50% or more of the ^{128}I atoms born by radiative neutron capture undergo internal conversion. Using bromine isotopes, they⁴³ reported a minimum of 12% of $^{80}\text{Br}^m$, 18% of ^{80}Br and 25% of ^{82}Br nuclides became positively charged due to internal conversion and accompanying Auger radiation.

In the sequence of events following radiative neutron capture, Thompson and Miller⁴⁴ observed that the initial recoil energy of a hot atom in the condensed phase was due to gamma emission which was imparted to the recoil atom in less than 10^{-13} second after neutron capture. The recoiling hot atom followed a short, deviating path and reached chemical and/or thermal stabilization only a few angstroms from the site of activation. The ejection of one or more conversion electrons, which was followed by Auger radiation, occurred most frequently 10^{-15} to 10^{-12} second after neutron capture. Thus, it appears that charge buildup occurs after the hot atom has been thermalized.

Final Chemical Stabilization

Following radiative neutron capture and possibly isomeric transition, the activated nuclides with high kinetic energy, positive charge and electronic excitation energy may undergo chemical reactions after losing most of their excess kinetic energy. Since chemical bond strengths are usually 2-3 ev. as compared to several hundred ev. kinetic energy for activated atoms, the atoms that pass through the hot reaction zone without reacting will react as thermal atoms. The positively charged recoil atoms will be quickly neutralized in condensed media provided the solvent has a lower ionization potential than the target atoms, e.g. the halogens. Two methods of probing hot atom halogen reactions in organic media are (1) the organic yield and (2) the labelled organic product distribution.

Organic Yield Concept

The organic yield is the percent or fraction of hot atoms produced by nuclear activation that are stabilized in organic combination. Organic yields are relatively easy to obtain and are therefore used widely as a research tool, particularly for hot atom reactions of the halogens, carbon and tritium.

Labeled Organic Product Distribution

As inferred in the organic yield concept, recoil atoms form inorganic

products as well as organic. In condensed media, the inorganic products are removed with an aqueous sulfite solution before radio gas chromatography determinations are made. The possibility of radiation damage during the neutron irradiation and rapid thermal exchange between the inorganic products and the organic products, especially in the presence of a halogen scavenger, may preclude the possibility of such an analysis unless eliminated.

Statement of Problem

Previous studies of nuclear activated halogen reactions have been mainly with alkyl halide and aliphatic hydrocarbon systems. Much of this work was hampered by a lack of knowledge concerning experimental parameters and metastable states, by the limited availability of carrier-free nuclides of interest, and by the lack of instrumentation capable of resolving multi-isotope system assays. With most of these problems taken care of, it has become possible to study multi-isotope systems in most of the hydrocarbons, especially those of relatively low molecular weight.

With the availability of organic yield and labeled organic product distribution probes in halogen hot atom chemistry, the possibility of investigating compounds of biological interest was considered. The iodothyronines, which are synthesized and used in the body, seemed to be a natural choice for an introductory study. Several studies have been reported in this area but essentially nothing in depth has been done in the area of hot atom reactions with the iodothyronines.

Due to the complexity of the iodothyronine molecules, only preliminary work was performed to ensure a solid foundation for such a project in the future. For a relatively comprehensive study, benzene and alkyl benzenes were probed with a number of halogen nuclides at 298° K and 77° K. Cyclopentane, a strained aliphatic ring system, was also studied for a broader picture of hot atom reactions with ring systems.

The primary goals of this research were to investigate the following:

- 1 (a) The reactions of $^{127}\text{I}_2$, $^{129}\text{I}_2$, and ICl activated by radiative neutron capture and isomeric transition in liquid and solid (77° K) cyclopentane; (b) the possibility of an isotope effect among the various isotopes of iodine activated by the two nuclear processes; (c) the labeled product distribution in comparison with cyclohexane.
- 2 (a) The reactions of $^{127}\text{I}_2$, $^{129}\text{I}_2$, Br_2 , IBr , and ICl activated by radiative neutron capture and isomeric transition in liquid and solid (77° K) benzene; (b) the possibility of an isotope effect among the various isotopes of bromine (and iodine) activated by the two nuclear processes; (c) the correlation between organic yield plateaus and the crystalline structure of the bromine-benzene system (77° K); (d) the labeled product distribution of the various halogen nuclides in benzene.
- 3 (a) The reactions of $^{127}\text{I}_2$ and ICl activated by radiative neutron capture in selected alkylbenzenes at 77° K and 298° K; (b) the role of a side chain on an aromatic

nucleus in organic yield and isotope effect studies; (c) the effect of the alkyl side chains in the labeled product distribution of selected alkylbenzenes.

CHAPTER II
EXPERIMENTAL

Chapter II

Experimental

Chemicals Used in the Research

All of the chemicals used in this investigation are listed with the name of manufacturer, grade, purity, and most probable impurities for the high purity reagents. Also, purification procedures are presented when employed.*

ICl	Matheson, pure, M.P. 25-27° C.
Br ₂	Mallinckrodt, Analytical Reagent; following distillation the center fraction was stored in a ground glass stoppered bottle placed in a desiccator with P ₂ O ₅ drying agent.
I ₂	Mallinckrodt, reagent grade; crystals were placed in a porcelain dish with equal volumes of CaO and KI and heated to sublime the I ₂ , which was collected on a cold glass surface and stored in a ground-glass stoppered bottle.
KI	Baker, reagent grade.
CaO	Baker, reagent grade.
CaCl ₂	Fisher, anhydrous technical grade.
H ₂ SO ₄	Baker and Adamson, reagent grade.
HNO ₃	Baker and Adamson, reagent grade.
H ₂ O ₂	Mallinckrodt, U.S.P. grade.

Na_2SO_3	Baker, reagent grade.
$(\text{NH}_4)_2\text{SO}_3$	Baker, reagent grade.
P_2O_5	Fisher, reagent grade.
Silica gel	Fisher, reagent grade.
NH_4OH	Baker and Adamson, reagent grade.
He	Matheson, 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 solvent with H_2O_2 catalyzed with HNO_3 , which was necessary for the rapid oxidation of $^{129}\text{I}^-$ to $^{129}\text{I}_2$. This solution was washed three times with triply-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.
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.
$\text{CH}_3\text{CHBrCH}_2\text{CH}_3$	Eastman, white label.
$\text{CH}_3(\text{CH}_2)_4\text{Br}$	Eastman, white label.
$n\text{-C}_5\text{H}_{11}\text{Br}$	Eastman, white label.
$n\text{-C}_6\text{H}_{13}\text{Br}$	Eastman, white label.
CH_3I	Eastman, white label.

CH_2I_2	Eastman, white label.
$\text{C}_2\text{H}_5\text{I}$	Eastman, white label.
$n\text{-C}_3\text{H}_7\text{I}$	Eastman, white label.
$1\text{-C}_3\text{H}_7\text{I}$	Eastman, white label.
$\text{CH}_2\text{ICH}_2\text{CH}_2\text{I}$	Eastman, white label.
$\text{CH}_3\text{CH}_2\text{CHICH}_2\text{CH}_3$	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 Biochem, white label.
$\text{CH}_2\text{I}(\text{CH}_2)_4\text{CH}_2\text{I}$	Baker, reagent grade.
$\text{C}_6\text{H}_5\text{I}$	Eastman, white label.
o-iodotoluene	Eastman, white label.
m-iodotoluene	Eastman, white label.
p-iodotoluene	Eastman, white label.
α -iodotoluene	Eastman, white label.
2(1odoethyl)benzene	Eastman, white label.
2-iodo-p-xylene	Eastman, white label.
2-iodo-m-xylene	Eastman, white label.
4-iodo-1,3-dimethylbenzene	Eastman, white label.
$\text{C}_6\text{H}_5\text{Br}$	Eastman, white label.
$n\text{-C}_6\text{H}_{14}$	Phillips, research grade, 99.95 mole % purity, GLC indicates methylcyclopentane as impurity.
cyclo- C_6H_{12}	Phillips, research grade, 99.98 mole % purity, probable impurity is 2,4-dimethyl pentane.
cyclo- C_5H_{10}	Phillips, research grade, 99.96 mole % purity, probable impurities are cyclopentane and 2,2-di- methylbutane.

C_6H_6	Phillips, research grade, 99.91 mole % purity, probable impurity is toluene.
$C_6H_5CH_3$	Phillips, research grade, 99.94 mole % purity, probable impurities are benzene and ethylbenzene.
$C_6H_5C_2H_5$	Phillips, research grade, 99.92 mole % purity, probable impurities are toluene and xylenes.
$o-C_6H_4(CH_3)_2$	Phillips, research grade, 99.97 mole % purity, probable impurities are m-xylene, methylethylbenzene and isopropylbenzene.
$m-C_6H_4(CH_3)_2$	Phillips, research grade, 99.95 mole % purity, probable impurity is p-xylene.
$p-C_6H_4(CH_3)_2$	Phillips, research grade, 99.95 mole % purity, probable impurities are m-xylene and ethylbenzene.
$C_6H_5CH(CH_3)_2$	Phillips, research grade, 99.92 mole % purity, probable impurity is o-xylene.
1,2,4-trimethylbenzene	Phillips, research grade, 99.57 mole % purity, probable impurities are 1,3,5-trimethylbenzene, methylethylbenzene, and 1,2,3-trimethylbenzene.
$n-C_6H_5(CH_2)_3CH_3$	Phillips, research grade, 99.98 mole % purity, probable impurities are n-butylcyclohexane and butylbenzene.
$sec-C_6H_5CH(CH_2)_2CH_3$	Phillips, research grade, 99.70 mole % purity, probable impurities are other alkylbenzenes.
sec-amylbenzene	Phillips, pure grade, 99.0 mole % purity (min), probable impurities are 3-phenylpentane and 2-phenyl-2-methylbutane.

- * The hydrocarbons were used as received or within thirty minutes after repurification. Benzene and several alkylbenzenes were repurified by stirring with concentrated H_2SO_4 at 23°C . for 48 hours. The H_2SO_4 was replaced if it turned yellow or discolored during the repurification treatment. The treated hydrocarbon was washed with aqueous NaHCO_3 , then triply-distilled water and dried over silica gel or anhydrous CaCl_2 . After a minimum of 12 hours of drying, the hydrocarbon was fractionally distilled through a 25-cm. bubble-cap column. Helium purging was used to remove trace gaseous impurities in most solid state studies. The impurities in the systems were detectable 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. Freshly purified hydrocarbons showed negligible organic retention with $^{131}\text{I}_2$ after several hours standing in the dark at room temperature.

Sample Preparation

The reactions of ^{128}I , $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$, $^{80}\text{Br}^{\text{m}}$, $^{82}\text{Br}^{\text{m}}$, ^{82}Br and ^{38}Cl activated by radiative neutron capture and the isomeric transition reactions of $^{130}\text{I}^{\text{m}}$ and $^{82}\text{Br}^{\text{m}}$ were studied at 77° K and 298° K. The effects of halogen concentration, phase and phase change and solvent were investigated, as well as impurity levels and the time from midpoint of irradiation to extraction. All samples were prepared in 1-3 ml. quartz bulblets or ampoules. The ampoules were joined by means of a constricted neck to a quartz stem, which possessed a ground-glass joint for a tight fit on a vacuum line. After the ampoules were sealed onto the stems, they were thoroughly cleansed by alternately washing with concentrated HNO_3 , dilute aqueous NH_3 and triply-distilled water several times. The rinsing consisted of cooling the ampoules in liquid N_2 while introducing the wash solution and then heating to expel it. The ampoules were then attached to the vacuum line and flamed to a red glow to vaporize any absorbed residues. The evacuated ampoules were then tested with a tesla coil to reveal any leaks.

Although quartz is more expensive and difficult to work with it has a very low coefficient of expansion which minimizes sample loss during sealing and liquid nitrogen immersion. Also, pyrex contains sodium which has a high cross section for thermal neutrons and may leak out in chemical extractions, thus affecting the radioactive assaying.

Samples were prepared in triplicate in most cases for all experiments. All reaction solutions were introduced into the ampoules in the liquid phase by cooling with liquid nitrogen. In some cases it was necessary to keep the

solution cooled down to prevent any appreciable volatilization of the solvent or solute. All samples were degassed by alternately freezing, evacuating on the vacuum line and thawing. Generally, the samples were prepared and degassed in a dimmed room. The samples were wrapped in aluminum foil and stored under liquid nitrogen to essentially stop all thermal reactions. The ^{129}I and ^{131}I , which were received from Oak Ridge National Laboratory as aqueous sodium salts, were oxidized to I_2 with H_2O_2 , catalyzed with a trace of HNO_3 , and then extracted into the appropriate hydrocarbon. The hydrocarbon-iodine solutions were thoroughly washed and dried before using. The iodine concentrations were determined photometrically with a Bausch and Lomb Spectronic 20.

Neutron Irradiation

The thermal neutron irradiations were carried out 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 per square centimeter-second was produced at an operating power of 15.5 kilowatts. For the longer irradiations random ports in the "lazy susan" sample holder were used with the assembly rotated for uniformity of neutron flux and radiation dose. For short irradiations the "rabbit" facility as well as the ports of the "lazy susan" sample holder were used. The radiation dose was found to be approximately 3×10^{17} ev/g-min using Fricke dosimetry⁴⁵ and ^{131}I organic pickup in irradiated cyclo-hexane.⁴⁶

By and large, the duration of irradiation had negligible effect on the organic yields and only in systems containing a very dilute mole fraction

of the scavenger were corrections for radiation-induced reactions required.

The liquid samples were routinely sealed in plastic bags before irradiating to prevent radioactive gases from escaping should the ampoules be broken while being handled. The samples were inserted into TRIGA tubes or "rabbit" tubes which were specifically designed for use in TRIGA reactors. Organic yield samples were irradiated for 30 seconds or less while the chromatography samples were irradiated for times varying between 6 and 60 minutes.

Samples irradiated at 77° K were irradiated for thirty seconds or less. Parks⁴⁷ determined the average temperature rise for the experimental conditions in our work here and found that there was only a three degree rise in temperature after a 30 second removal from liquid nitrogen, five degrees after 45 seconds and 26 degrees after 55 seconds.

The samples were removed from the reactor with remote handling equipment and transferred to the hood in the "hot" room. They were either extracted immediately or stored in a lead pig or liquid nitrogen and analyzed later in the radiochemistry laboratory at the University of Nebraska. Standard radiochemical techniques and practices were followed throughout all procedures.

Extraction of Organic and Inorganic Activities

The quartz ampoules containing the irradiated samples were broken in specially designed separatory funnels. The separatory funnels were constructed of thick walled pyrex tubing with a breaker sealed in near the bottom and a heavy ground-glass stopper also designed for breaking the

ampoules. Before the hot sample was introduced, appropriate volumes of CCl_4 plus halogen carrier and aqueous $0.5\text{M Na}_2\text{SO}_3$ such that the volumes of the organic and inorganic phases were equal after the reaction systems were added. The quartz ampoules were broken by a vigorous vertical motion of the separatory funnel. After thoroughly shaking the reaction mixture with the extraction solvents and allowing the phases to equilibrate, the organic phase contained the organically bound halogen nuclides, formed as a result of the nuclear induced reactions. The inorganic phase contained halide ions coming from initially present halogen molecules and any halogen reacting with itself or forming hydrogen halides. The phases were separated within a reasonably short period of time (10-30 sec.) after the interface appeared, if isomeric transition induced reactions were occurring. The CCl_4 layer was drained into an Erlenmeyer flask containing anhydrous CaCl_2 as a drying agent. The drying flasks were stoppered with ground-glass stoppers, shaken and allowed to stand for several minutes before pipetting equal volumes of each phase into separate labeled counting tubes.

Determination of Isomeric Induced Organic Yields

When ^{129}I and ^{81}Br are subjected to thermal neutrons a large percentage of the activated nuclei are converted into a metastable nuclear state.³³⁻³⁵ As shown in Fig. 2(a), 67% of the ^{129}I nuclides which absorb a neutron will form $^{130}\text{I}^{\text{m}}$ nuclides, while 33% of the ^{130}I nuclides are born in the ground nuclear state. The $^{130}\text{I}^{\text{m}}$ decays to ^{130}I via isomeric transition and to

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

^{130}Xe by negation decay. A similar scheme, depicted in Fig. 2(b) is followed by ^{81}Br . Here, 91% of the ^{82}Br formed is in the metastable state, $^{82}\text{Br}^m$, which decays 99.8% by isomeric transition to ^{82}Br .

A freeze-thaw technique^{46,48-50} was developed for determining ^{82}Br isomeric transition induced organic yields independent of the radiative neutron capture organic yields. The technique consists of the neutron irradiation of a solid state sample containing halogen in an aliphatic hydrocarbon. In this case, the organic yields are normally below 1% at halogen concentrations where fractional crystallization or clumping occurs during the freezing process. Upon liquefying the sample after irradiation, the organic yields increase with the length of time that the isomeric transition reactions are allowed to have occurred. Merrigan⁴⁸ developed an expression to calculate the isomeric transition (IT) organic yields based on data obtained from the freeze-thaw technique. Equation (1) is the general expression applicable to the determination of bromine and iodine organic yields induced by isomeric transition reactions in liquid alkanes. Appendix I contains the derivation of equation (1) which is as follows:

$$\text{O.Y.}_{(\text{IT})} = [R^\infty - \alpha R^0 / \beta \exp(-\lambda t)] - [(1 - \exp(-\lambda t)) R^0 / \exp(-\lambda t)]. \quad (1)$$

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 $^{130}\text{I}^m$ systems, α and β are 0.39 and 0.61 respectively³³; for $^{82}\text{Br}^m$ systems, α and β are 0.09 and 0.91 respectively.⁵¹ R^∞ is the organic yield in the liquid state after immediate liquification of the sample, and $(\exp(-\lambda t))$ denotes the duration of time the sample was solid from the midpoint of irradiation to liquefaction until at least 99.9% of the metastable isomer had decayed to the ground

state. R^0 is the organic yield produced in the solid state ($n,\gamma + IT$). This technique is not valid, however, when the organic yield is not independent of the mode of activation in the solid state.

The (n,γ) organic yields can be obtained by irradiating the halogen in the hydrocarbon solvent and extracting immediately thereafter.

In benzene, the freeze-thaw technique was not applicable at all since the formation of charge-transfer complexes produces an ordered crystalline structure^{52,53} upon freezing. It appeared that the alkylbenzenes studied behaved similarly and therefore could not be treated in the same manner as the aliphatic hydrocarbons. There were, however, two other approaches which could be used to compare the radiative neutron capture and isomeric transition processes. One method was a variation of the technique employed by Wilkey and Willard³³ and the other involved immediate extraction of the sample versus extraction after 99.9% of the (IT) process had occurred.

The former method mentioned above consists of irradiating aliquots of the halogen (^{129}I as aqueous Na^{129}I or Br_2) and extracting into the appropriate hydrocarbon at different times after irradiation. After standing until all of the metastable nuclide (99.9%) decays, organic yields are determined for each sample. From these data the (IT) organic yields can be calculated. The (n,γ) organic yields can be obtained by irradiating the halogen in the hydrocarbon solvent and extracting immediately thereafter.

The latter method mentioned above is somewhat simpler and consists of an immediate extraction after irradiation of the sample and an extraction after 99.9% of the metastable isomer has decayed. The (IT) organic yield cannot be determined independent of the (n,γ) organic yield in this case,

rather the (n,γ) and the $(n,\gamma) + (IT)$ organic yields are determined.

Assaying Procedures

Three analyzers were used for the various radiohalogens used in this research. 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 was used at Avery Laboratory. At the Omaha V. A. Hospital, an RIDL 400 channel pulse height analyzer with a 4π 2" x 2" NaI (Tl) crystal was used for inter- and mixed halogens while an Ortec NIM single channel analyzer, also with a 4π 2" x 2" NaI (Tl) crystal, was used for ^{128}I and bromine samples. A description of the counting equipment and geometry and the unnecessary for corrections due to counting coincidence losses and density have been thoroughly discussed in earlier theses from this laboratory.^{45,46,54,55} The multichannel analyzer was used to examine the gamma-ray spectrum of a radioisotope for qualitative and quantitative determinations. The spectra for the various halogens as well as a number of other nuclides are available in the literature.⁵⁶

Both the Tracerlab and Ortec single channel analyzers were equipped with visual readouts, while the output of the multichannel analyzer was printed out by a typewriter or punched out on paper tape. The calculations required for the tapes where inter- and mixed halogen nuclides were involved were performed on the IBM 1620 computer which corrected for the background, radioactive decay and Compton scatter.

The timing of the various assays depended upon the decay characteristics of the several nuclides present in a given sample. Such procedures

for the various bromine nuclides have been discussed previously.⁴⁶ The timing procedures for ^{130}I and $^{130}\text{I}^m$ are similar but simpler. The simultaneous determinations of ^{128}I and ^{38}Cl from ICl -hydrocarbon systems were performed using spectrum stripping techniques.

Determination of Labeled Product Distributions

The labeled product distributions of cyclopentane, benzene and several alkylbenzenes were determined by means of radiogas chromatography. The schematic diagram of the instrument is depicted in Fig. 3 and its basic features have been described previously.^{46,57} Recent improvements⁵⁸ include a Gilmont Instruments, Inc. flowmeter, a Hewlett Packard D. C. power supply (Harrison 6202 B), Aerograph thermal conductivity cells, a four port backflush valve to facilitate elution of high boiling fractions, and a high efficiency window flow-counter similar to that discussed by Wolf, et. al.⁵⁹ An ND-110 128-channel analyzer (not shown) was connected to the rate meter with a signal-splitter in order to relay the signal from the counter to the memory of the analyzer as well as to the dual-pen recorder. The multi-channel analyzer was operated in the "Mossbauer mode" with a dwell-time of 10 seconds per channel. This produced a digital storage of the chromatograms up to 1280 seconds duration, and thus, a numerical integration of product peak areas. In cases where the 1280 seconds was not long enough to cover the entire chromatogram, a read-out between peaks was made and storage was begun again. A 8.1 m. pyrex spiral column with a 4-mm. I.D. was used throughout. The column was filled with 42-60 mesh Wilkens Instrumental firebrick coated with 40% of its weight of General Electric SF-81(5)

Figure 3. Schematic of the Radiogas Chromatograph

silicone oil when halogen-cyclopentane systems were run. For the aromatic-halogen systems, the column was packed with 15% GE-SE-30 on 60/70 ANAKROM ABS (max. temp. 300° C). Helium was used as the mobile phase in all chromatography runs.

Silicone oil was used as the stationary phase for the halogen-cyclopentane systems due to its non-selectivity and proven ability to separate alkyl halides. However, in the aromatic-halogen systems silicone oil proved to be too retentive for the high boiling fractions. The 15% GE-SE-30 proved to be the best stationary phase used in separating the aromatic halides, but appreciable tailing of the high boiling fraction peaks was not entirely eliminated. In general, both packings allowed the hydrocarbon halides to elute from the column in order of increasing boiling point and/or molecular weight. Compactness was also a factor in elution time in that tertiary compounds were eluted faster than the corresponding secondary compounds which were, in turn, eluted faster than the corresponding primary compounds.

The silicone oil-firebrick column was prepared by dissolving 40 g. of silicone oil in 250 ml. of CCl_4 and suspending 100 g. of firebrick in the solution. Using a mechanical stirrer, the mixture was vigorously agitated until most of the CCl_4 evaporated. The packing was kept warm until the CCl_4 was essentially all removed and then it was tightly packed in the spiral glass column. The same type of procedure was used to pack the other type column.

The chromatography samples, usually 2 ml. aliquots, were kept in liquid nitrogen after irradiation until extracted. After extraction with 1 ml. of the hydrocarbon solvent and 3 ml. of 0.5 M. Na_2SO_3 , the organic

phase was kept cool to prevent the loss of highly volatile components, e.g. methyl halides. The organic product distributions were initially determined in the absence of organic halide carriers to prevent any exchange between carriers and labeled products at the high temperatures in the chromatograph. Subsequent runs with carriers were used to identify the products. The flow rate was held constant but the background increased somewhat during a run. However, the activity before and after a peak could be used to calculate an average background correction. In the case of nuclides with short half-lives, corrections were made for decay rates also.

CHAPTER III

A STUDY OF THE VARIOUS NUCLEAR PROCESSES OF IODINE
($^{127}\text{I}_2$ AND $^{129}\text{I}_2$) AND IODINE MONOCHLORIDE IN CYCLOPENTANE

Chapter III

A Study of the Various Nuclear Processes of Iodine
($^{127}\text{I}_2$ and $^{129}\text{I}_2$) and Iodine Monochloride in Cyclopentane.

Previous studies of iodine-cyclopentane systems have been mainly radiolysis effects⁶¹⁻⁶⁵ using Co-60 as a source of gamma rays. Recently, Bryant⁵⁴ studied these systems using a TRIGA reactor as a gamma source and compared the effects with radiolysis induced by dissolved $^{131}\text{I}_2$. The results of these studies indicated mechanisms and product distributions similar to those found in studies of cyclohexane radiolysis. There was more ring fragmentation with cyclopentane due to the greater bond strain but the major product was still the parent cycloalkyl iodide, iodocyclopentane.

The mode of radical formation in the liquid phase is of paramount interest currently. The literature contains many articles discussing models to explain the relative roles of displacement and radical formation mechanisms. Geissler and Willard^{28,69} found that the R^{128}I products resulting from neutron irradiation were similar to the R^{131}I products from the gamma ray radiolysis of solutions of $\text{I}_2\text{-CH}_3\text{I-C}_5\text{H}_{12}$. They hypothesized that the fate of the ^{128}I atoms is usually determined by its reaction with radicals formed in its own solvent envelope by radiolysis by its own internal conversion and Auger electrons. This would explain why the ^{128}I product spectrum is much the same as that for radiolysis even at I_2 scavenger concentrations too high to permit interaction of

the ^{128}I with radicals produced by the gamma ray background radiation. Milman⁷⁰, however, rationalized the observed facts of liquid phase Szilard-Chalmers chemistry by a model which assumes that all (n,γ) recoil atoms react as neutral species and that the only collision important in determining their fate is the final reactive collision by which the atom becomes incorporated in a stable molecule or forms a free radical with which it subsequently combines.

In support of the autoradiation hypothesis, Wilkey and Willard³³ and Merrigan, et al.⁶⁷, found that the organic yields and product distributions of ^{130}I and ^{128}I activated by (IT) and (n,γ) processes, respectively, were similar to the yields and analogous product distributions of ^{82}Br activated by (IT) events in cyclohexane and other $\text{C}_5\text{-C}_9$ hydrocarbons. In a recent study⁶⁸ in this laboratory, it was found that although the spectrum of products formed by radioiodine and radiobromine were similar in the hexane isomers investigated, the relative yields of iodine and bromine products were somewhat different. This difference was assumed to be due to the difference in chemical nature between two different halogens and not the basic processes. It is interesting to note that the RI products resulting from neutron irradiation⁶⁸ do not correspond with those obtained by gamma ray radiolysis.

It was considered interesting to investigate the hot-atom reactions of ^{127}I , ^{129}I and ^{37}Cl (ICl) in cyclopentane and compare them with the various radiolysis studies of cyclopentane and hot-atom studies of cyclohexane, which has considerably less bond strain.

The freeze-thaw technique for obtaining isomeric transition organic yields, extraction procedures and counting equipment have been described

previously. Samples for isomeric transition time studies were irradiated in the solid state, usually between 77° and 90° K, and then thawed by immersing in warm water 10 seconds after the end of a 16 second irradiation. They were refrozen in liquid nitrogen after varying periods of time at room temperature in the dark. The freeze-thaw technique requires an essentially constant solid-state organic yield. These values were determined immediately and 90 minutes after irradiation. There were no differences within experimental limits as a result of the ^{130m}I (IT) ^{130}I processes in the solid state.

The samples irradiated for radiogas chromatography were kept in liquid nitrogen until extracted. During and after the extraction, the organic phase was kept cool to prevent the loss of volatile alkyl iodides.

Product identification where carriers were not available was made on the basis of relative position to labeled CH_3I and non-radioactive alkyl iodides of varying boiling points and molecular weights.

Radiative Neutron Capture Induced Reactions

The organic yields of the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ process at various concentrations of iodine in cyclopentane at 298° K are shown in Table II and depicted in Fig. 4. The ^{128}I organic yield extrapolates to $44 \pm 0.5\%$ at zero mole fraction (mf) iodine. The ^{128}I organic yield at 1×10^{-3} mf I_2 compares quite closely with the ^{130}I organic yield due to the ^{130m}I (IT) ^{130}I process (See Fig. 5). Previous studies^{33,67,68} have also shown that ^{128}I and ^{130}I (by IT) organic yields were similar for a given

TABLE II
EFFECT OF I_2 CONCENTRATION ON ^{128}I ORGANIC
YIELDS IN LIQUID CYCLOPENTANE

Mole Fraction I_2	Irrad. Time (sec.)	Organic Yield ^a %
1.0×10^{-5}	30	44.2
2.1×10^{-5}	30	44.1
5.3×10^{-5}	16	43.5
1.7×10^{-4}	16	43.0
9.1×10^{-4}	16	37.9
4.4×10^{-3}	10	28.8
9.2×10^{-3}	4	12.4

(a) Average of at least three determinations.

Figure 4. ^{128}I Organic Yields as a Function of $^{127}\text{I}_2$ Concentration in Liquid Cyclopentane.

Figure 5. ^{130}I Organic Yields as a Function of time the $^{130}\text{I}^m(\text{IT})^{130}\text{I}$ process occurred in liquid cyclopentane prior to freezing at 77°K (Irradiated liquid).

alkyl hydrocarbon. The ^{129}I (n, γ) $^{130}\text{I}^{\text{m}}$ and ^{129}I (n, γ) ^{130}I induced organic yields were determined by extrapolation of a plot of ^{130}I organic yields versus time liquid to zero time (Fig. 5). It was not possible to independently determine the radiative neutron capture organic yields of $^{130}\text{I}^{\text{m}}$ and ^{130}I , but an isotope effect between the two species would not be expected. The ^{130}I organic yield from the (n, γ) process is about 31%, which gives a ratio of slightly less than 1.2 when compared to the ^{128}I or ^{130}I (by IT) organic yields. Lambrecht and Rack⁶⁸ obtained ratios in the range of 1.2 to 1.4 for these same isotopes in C_5 - C_9 alkyl hydrocarbons. The fact that ^{128}I or ^{130}I (by IT) O. Y./ ^{130}I and $^{130}\text{I}^{\text{m}}$ (by n, γ) O. Y. ratio for cyclopentane was slightly less than 1.2 may indicate a somewhat reduced distinction between processes due to the enhanced bond strain in cyclopentane.

The scavenging action of iodine can be seen to be effective at concentrations above 1.7×10^{-4} and higher mf I_2 (Table II). Since the solubility of iodine in cyclopentane is a limiting factor⁶⁶, the "hot" and "cold" portions of the reaction cannot be separated in this system. A bromine-cyclopentane system was used in an attempt to separate the hot and cold reactions but the thermal reactivity was too great.

Isomeric Transition Induced Reactions

The isomeric transition organic yields were determined independent of the (n, γ) reactions by the freeze-thaw technique and along with them by freezing the samples at various times after liquid irradiation. The former values were found by irradiating samples at 77° K, thawing

immediately and refreezing at various times. The calculations for this technique are found in Appendix 1. The latter method involves liquid irradiations and freezing at various times to about ten half-lives of the metastable isotope, $^{130}_{\text{m}}\text{I}$. This allows for 99.9% of the metastable species to decay. If the (n,γ) reactions produced the same organic yields as the (IT) reactions, the ^{130}I organic yield versus time prior to freezing plot would give a straight line. The (IT) organic yields determined by the freeze-thaw technique are given in Table III and depicted in Fig. 5. The combined organic yields from both the (n,γ) and (IT) processes are given in Table IV and Fig. 6.

The pure (IT) organic yield extrapolates to a value of $35.8 \pm 0.4\%$ as shown in Table III, and the (IT) plus (n,γ) organic yield value is $35.6 \pm 0.5\%$ at 1×10^{-3} mf I_2 in cyclopentane at 298°K . Although approximately 66% of the radiative neutron capture events produce $^{130}_{\text{m}}\text{I}$, it is not expected that these two values would be as close together as calculated. Similar comparisons⁷¹ with other hydrocarbons yielded values for the (IT) organic yields within 1 or 2% of the $(n,\gamma) + (\text{IT})$ organic yields. Thus, it would appear that this close agreement in the I_2 -cyclopentane systems is coincidental, in part.

State of Aggregation of I_2 and ICl at 77°K

The use of organic yields as an indication of state of aggregation, complexing, and segregation during crystallization has been studied using Br_2 ⁵¹, I_2 ^{72,73} and ICl ⁷³ in various hydrocarbons. A constant

TABLE III
GROWTH OF ^{130}I ORGANIC YIELDS BY THE $^{130}\text{I}^m$ (IT) ^{130}I
PROCESS IN LIQUID CYCLOPENTANE. (1.0×10^{-3} mf I_2)

Time from Midpoint ^a Of Irradiation (min.)	Organic Yield ^{b,c}
2	10.5
4	14.3
6	16.4
8	18.8
10	24.3
12	27.0
14	28.0
16	29.5
18	30.7
25	33.7
40	35.1
60	35.6
90	35.8
R^0	2.8
R^∞	35.8

(a) All samples were irradiated by approximately 77° K for 16 sec. and thawed within 25 sec. from the midpoint of irradiation.

(b) Average of at least three determinations.

(c) Organic Yields were calculated from the Freeze-Thaw Equation:

$$\text{OY}_{\text{IT}} = (R^\infty - \alpha R^0) / \beta e^{-\lambda t} - [(1 - e^{-\lambda t}) R^0] / e^{-\lambda t}$$

$$\alpha = 0.39$$

$$\beta = 0.61$$

R^{∞} = OY of sample irradiated solid (77° K), liquefied immediately and extracted after 90 min.

R^0 = OY of sample irradiated solid (77° K) and kept at this temperature until extracted 90 min. later.

TABLE IV
 ^{130}I ORGANIC YIELDS AS A FUNCTION OF TIME THE
 $^{130}\text{I(IT)}^{130}\text{I}$ PROCESS OCCURRED IN LIQUID CYCLOPENTANE
 PRIOR TO FREEZING AT 77°K . (1.0×10^{-3} mf I_2)

Time from Midpoint ^a of Irradiation (Min.)	Organic Yield ^b
25 (sec)	31.1
1	31.1
2	31.2
5	31.6
10	32.1
15	32.8
20	33.5
25	34.1
35	34.6
45	35.3
60	35.4
75	35.5
90	35.6

(a) All samples were irradiated for 16 sec.

(b) Average of three or more determinations.

Figure 6. ^{130}I Organic Yields as Function of time the $^{130}\text{I}^m(\text{IT})^{130}\text{I}$ process occurred in liquid cyclopentane prior to freezing at 77°K .

organic yield over any degree of concentration range has been interpreted as a region of monomolecular dispersion or a uniform dispersion of halogen (or interhalogen) clusters with a relatively constant number of halogen molecules per cluster. In using ICl, Lambrecht⁷³ checked the effect of halogen differences in this type of study and found that the two produced organic yields which were relatively constant over the same concentration ranges. Because of the differences in bond strength, a similar study was performed with cyclopentane and I₂ and with cyclopentane and ICl.

Ayres⁵⁸ found that rigorous in-house repurification of alkanes with H₂SO₄, etc. discussed in Chapter II gave good, consistent solid state data at most iodine concentrations. It is particularly effective for the removal of olefinic impurities. At very low mole fractions of halogen, it was found that unless the hydrocarbons were purged with helium for at least 30 seconds, organic yield data contained a great deal of scatter, presumably due to trace amounts of CO₂ and O₂ not removed by the rigorous H₂SO₄ treatment. Such procedures were used in this study with cyclopentane.

In addition to the problems of repurification, radiolysis produced during the reactor irradiations forms products which react with ICl. The extent of these side reactions was determined in preliminary experiments by adding labeled ICl (¹²⁸I and ³⁸Cl) to the liquefied cyclopentane after solid state irradiation. Only a small correction was needed to correct for these reactions. It has been shown previously⁷⁴ that I₂ does not react with stable radiolysis products produced by reactor irradiations, nor does Br₂.

7

A more serious difficulty in this study arises from the differences in thermal neutron cross-section between ^{37}Cl and ^{127}I . There is a 100% natural abundance of ^{127}I and it has a 6.4 barn cross-section. On the other hand, ^{37}Cl constitutes only 24.5% of naturally occurring chlorine with a cross-section of 0.44 barns. The following scheme indicates the paths to the formation of ^{38}Cl :

Fig. 7. Radiative Neutron Capture of ^{37}Cl and Subsequent Decay Routes.

Fig. 7 indicates that the thermal neutron cross-section for the production of ^{38}Cl by (n,γ) is approximately 146 times greater than for ^{38}Cl by (IT) . The cross-section ratio for the formation of ^{128}I to ^{38}Cl is about 45 to 1, thus it is difficult to produce enough ^{38}Cl for good statistics while keeping the ^{128}I activity low enough for counting. At high concentrations of ICl the problem is not as serious since the samples can be counted when the ^{128}I activity has become tolerable for the electronics of the multichannel analyzer. However, at low mf ICl (10^{-4} mf and lower) the optimum time of irradiation does not produce very much ^{38}Cl activity. Even with longer periods of irradiation, the ^{38}Cl activity does not allow one to get good reproducible organic yields.

The solid phase organic yields of iodine in cyclopentane at various

mole fractions from 1×10^{-5} to 9.2×10^{-3} mf I_2 is given in Table V and Fig. 8. The organic yields appear to reach a maximum and level off at 2.1×10^{-5} mf I_2 and lower. In light of work done in other aliphatic solvents, this would probably be the region of monomolecular dispersion. Above 2.1×10^{-5} mf I_2 , the organic yield approaches zero as fractional crystallization becomes more pronounced. In approximately the same concentration range, the organic yields of ^{128}I and ^{38}Cl from ICl were determined in cyclopentane at $77^\circ K$. The yields are given in Table VI and Fig. 9. Here again, organic yield plateaus were found in the low mf ICl region but they did not start at the same concentration. The ^{128}I organic yields leveled off again at about 2×10^{-5} mf ICl as it did at 2.1×10^{-5} mf I_2 , but the ^{38}Cl organic yields leveled off sooner - at about 1×10^{-4} mf ICl .

Chien and Willard⁷⁵ found that in contrast to the effect of added halogen on the alkyl iodides and ethyl bromide in the liquid state, the organic yields of alkyl chlorides tested were not altered by the presence of a few mole % of added chloride. They concluded that the hot ^{38}Cl atoms or ions which escaped combination by "high energy" processes always reacted with carbon-hydrogen bonds to form hydrogen chloride. In the solid state, these same alkyl chlorides produced similar yields in some cases^{76,77} and higher yields in others. It was believed that the higher yields were related either to a higher density of radicals formed by the high energy atom in losing their energy to a solid medium or to a different relative yield of different types of radicals when the medium is solid. The ^{38}Cl solid state organic yields in cyclopentanes

TABLE V
EFFECT OF I_2 CONCENTRATION ON ^{128}I ORGANIC
YIELDS IN SOLID CYCLOPENTANE AT 77° K

Mole Fraction I_2	Irrad. Time (sec.)	Organic Yield ^a %
1.0×10^{-5}	30	53.8
2.1×10^{-5}	30	53.6
5.3×10^{-5}	16	32.8
1.7×10^{-4}	16	11.8
9.1×10^{-4}	16	4.2
4.4×10^{-3}	10	1.2
9.2×10^{-3}	4	0.4

(a) Average of at least three determinations

Figure 8. ^{128}I organic yield as a function of $^{127}I_2$ concentration in solid cyclopentane at 77° K

TABLE VI
 THE EFFECT OF ICl CONCENTRATION ON ^{128}I AND ^{38}Cl
 ORGANIC YIELDS IN CYCLOPENTANE AT 77°K

Mole Fraction ICl	Irradiation Time (sec.)	Organic Yield ^a	
		^{128}I	^{38}Cl
1.0×10^{-5}	30	60.6	51.1
2.5×10^{-5}	30	59.9	51.5
5.0×10^{-5}	30	51.1	49.8
1.0×10^{-4}	30	44.0	50.7
1.0×10^{-3}	16	22.3	20.1
1.0×10^{-2}	10	12.4	5.0

(a) Average of three or more determinations

Figure 9. Effect of ICl Concentration on ^{128}I and ^{38}Cl organic yields in cyclopentane at 77° K.

were also found to be significantly higher than the ^{38}Cl liquid organic yields, which were approximately 21% at all concentrations as found in a number of alkyl chlorides⁷⁵, heptane⁷⁵ and benzene.⁸⁰

It is, of course, not possible that both the ^{38}Cl organic yield plateau and the ^{128}I organic yield plateau begin with monomolecular dispersion of the ICl in solid state cyclopentane. Since the ^{38}Cl organic yield does not change appreciably above 1×10^{-4} mf ICl , it appears that the cluster size, $(\text{ICl})_x$, must remain essentially the same to infinite dilution. The drop in the ^{128}I organic yield from 1×10^{-4} mf to 2.5×10^{-5} mf ICl may indicate a concentration range in which some competitive reaction is operative. This process must then become inconsequential below 2.5×10^{-5} mf ICl , which is about the same point where the ^{128}I organic yield remains constant in the iodine-cyclopentane systems (77°K). Thus, on the basis of this study, it would appear that ^{38}Cl organic yields are a better indicator than ^{128}I organic yields (and probably ^{82}Br organic yields) of halogen cluster size in hydrocarbons and alkyl hydrocarbons.

Correlation of Organic Yields and Product Distributions

The ^{130}I product distributions from the ^{129}I (n, γ) ^{130}I and the ^{129}I (n, γ) $^{130}\text{I} + ^{130}\text{I}^m$ (IT) ^{130}I -process in liquid and solid state cyclopentane are presented in Table VII. Due to the activity required for meaningful chromatograms, concentrations below 5×10^{-4} mf I_2 were not feasible. Also, due to the length of time samples were irradiated

TABLE VII
PRODUCT DISTRIBUTION^(a) FROM THE $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}$ AND THE $^{129}\text{I}(\text{n},\gamma)^{130}\text{I} + ^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$
PROCESSES IN LIQUID ($\sim 25^\circ \text{C}$) AND SOLID ($\sim 77^\circ \text{K}$) CYCLOPENTANE

Process(es)	Mf $^{129}\text{I}_2$ $\times 10^3$	H_3CI to $\text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{I}$	Products ^(b) $\text{C}_3\text{H}_7\text{I} + \text{C}_4\text{H}_9\text{I}$	$\text{C}_5\text{H}_{11}\text{I}^{(c)}$	$\text{C}_5\text{H}_{11}\text{I}^{(d)}$	Other ^(e)	Total O. Y.
(n, γ)+(IT)	0.5	18.4	8.8	3.2	37.7	100	--	47.1 ^(g)
(n, γ)+(IT) ^(f)	0.5	22.9	11.5	6.4	38.4	100	--	35.3 ^(g)
(n, γ)	1.0	20.4	10.4	2.8	39.6	100	5.4	38.1 ^(h)
(n, γ)+(IT)	1.0	16.9	11.5	3.0	37.0	100	5.3	40.4 ^(h)
(n, γ)	3.3	15.2	8.1	2.2	32.6	100	7.1	30.8 ^(h)
(n, γ)+(IT)	3.3	15.0	9.6	2.5	33.0	100	8.6	31.6 ^(h)
(n, γ)	9.0	16.5	8.0	2.6	33.8	100	7.1	24.8 ⁽ⁱ⁾
(n, γ)+(IT)	9.0	17.8	7.9	2.5	34.0	100	7.3	25.3 ⁽ⁱ⁾

(a) Averages of at least two determinations; duplicate runs of a given sample were in good agreement.

(b) The values are the percent of individual products relative to the major product, given as 100%.

(c) Pentyl iodides.

(d) Cyclopentyl iodide.

(e) Higher boiling fraction, possibly cyclopentyl diiodide.

(f) Only solid sample.

(g) 30 minute irradiation.

(h) 15 minute irradiation.

(i) 6 minute irradiation.

it was impossible to obtain pure (n, γ) yields, but since the differences between the two processes could not be detected with 6 minute irradiations, it is assumed that any differences must be relatively small. A comparison of the ^{130}I product distribution in liquid and solid state cyclopentane at 5×10^{-4} mf I_2 showed only minor differences, so further comparisons at higher concentrations of I_2 were not attempted.

Dauphin⁶² found that the radiolysis of cyclopentane at 20° C with ^{60}Co gamma rays produced about 65% iodocyclopentane, significant amounts of C_2 , C_3 and amyl iodides and 1,5-diiodopentanes.

The agreement in this study with that of Dauphin⁶² is good for the percent of iodo-cyclopentane found, but sizeable amounts of CH_3I , amyl iodides and possibly (cyclo) pentyl diiodides were also produced. Bryant⁵⁴ found iodocyclopentane as the major product when $^{131}\text{I}_2$ was used as an internal source of energy for the radiolysis of cyclopentane at room temperature. It would appear from these studies^{54,62} and the present one that the hot atom processes, (n, γ) and (IT), are relatively more effective in ring opening than gamma radiolysis. This was even more pronounced in a study of cyclohexane⁶⁸ under similar conditions, which is unexpected considering the greater stability in the C-C bonding. In the same study⁶⁸, it was found that the relative yield of pentyl iodide was relatively greater in the $^{127}\text{I}_2$ -n-pentane system, 50.6% of total, than hexyl iodide in the $^{127}\text{I}_2$ -n-hexane system, 40.1% of total. Thus it appears that molecular weight or size can also be a significant factor in such a comparison.

The similarity of product distribution from the (n, γ) and (IT) processes favored the autoradiation model proposed by Geissler and Willard⁶⁹,

as did the general similarity with radiolysis studies. The differences between the product distribution of hot iodine reactions in cyclohexane and cyclopentane were unexpected. Although increased chain length has been shown⁶⁸ to bring about increased organic yields, the increase in ring opening in going from cyclopentane to cyclohexane appeared to be out of proportion, especially since cyclopentane has a relatively large C-C bond strain compared to cyclohexane. Since radiolysis studies, mainly gamma ray radiolysis, show more ring opening in cyclopentane than cyclohexane, the reverse trend found with the (n, γ) and (IT) processes does not seem to support the autoradiation theory. More sensitive chromatography may be needed to resolve this seeming impasse.

CHAPTER IV

RADIATIVE NEUTRON CAPTURE AND ISOMERIC TRANSITION INDUCED
REACTIONS OF IODINE ($^{127}\text{I}_2$ AND $^{129}\text{I}_2$) AND BROMINE IN BENZENE

Chapter IV

Radiative Neutron Capture and Isomeric Transition Induced
Reactions of Iodine ($^{127}\text{I}_2$ and $^{129}\text{I}_2$) and Bromine in Benzene

Probably one of the most surprising results obtained by Macrae and Shaw⁸¹ in their study of (n,γ) induced reactions of iodine in benzene was the fact that there was no self-scavenging of the iodine. They concluded that no organic radicals were present in the diffusive stages of the reaction. Kontis and Katsanos⁸² determined the ^{130}I organic yields due to the (IT) induced reactions in liquid benzene and found only a small scavenging effect in the range of 0.014 to 0.475 M I_2 ($^{129}\text{I}_2 + ^{127}\text{I}_2$). They concluded that the mode of nuclear activation of iodine plays only a small role, if any, in the fate of the daughter iodine atom and that the organic yields observed are probably determined by the properties of one or more intermediate species, which in turn depend upon the nature of the halogen atom. Similar studies^{83,84} with bromine indicate only small amounts of self-scavenging in the same concentration range and beyond.

The purpose of this study was (1) to investigate other isotopes in liquid benzene; (2) to determine the neutron irradiation parameters in solid state halogen-benzene systems; (3) to determine and compare the bromine and iodine isotopic yields in solid state benzene; (4) to investigate the state of aggregation of I_2 and Br_2 in solid state benzene; and (5) to determine the product distribution in liquid and solid state

halogen-benzene systems.

Experimental Techniques

Three different techniques were attempted to determine the isomeric transition activated organic yields of ^{130}I in solid state benzene.

Method (1): ^{129}I was added to benzene, the solution was then 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): Aqueous Na^{129}I was irradiated to produce $(^{130}\text{I}^{\text{m}})^{-}$ which was oxidized to $\text{I}_2 (^{130}\text{I}^{\text{m}})$. The $\text{I}_2 (^{130}\text{I}^{\text{m}})$ solution was transferred immediately to the reaction vessel, containing a known amount of $^{127}\text{I}_2$ dissolved in benzene, and immersed under liquid nitrogen as soon as uniformity of mixture was achieved. The samples could not readily be dried or degassed. After essentially all of (99.9%) the $^{130}\text{I}^{\text{m}}$ had decayed within 90 minutes after irradiation, the solution was liquefied and extracted. A portion of each solution was removed before extraction to determine the iodine concentration. The time from the beginning of a 30 second neutron irradiation until the sample was frozen was maintained at 75 ± 5 seconds. Activities were corrected for decay of $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I induced reactions that occurred prior to mixing and for 39% of the total ^{130}I activity being formed by radiative neutron capture. The influence of dissolved gases, water, and possibly minute amounts of other contaminants here is not known. Method (3): Initially the samples are prepared as in Method 1. After irradiation in the solid state half of the samples at a given concentration are extracted

immediately and the other half after 90 minutes. This method merely indicates whether similar or different organic yields are produced by (IT) and (n, γ) processes.

Three different grades of benzene were used in this study. Phillips research grade benzene (99.94 quoted mole percent purity) was used when freshly opened and after a repurification which was described earlier. Baker and Adamson analytical reagent grade benzene was used only after the same repurification procedure and zone-refined benzene from the Applied Science Laboratory was used as received (5 g. vials with a 99.99 quoted mole percent purity). After repurification procedures, the benzene was purged with helium for 2-3 minutes.

The organic yields due to the ^{79}Br (n, γ) $^{80}\text{Br}^m$ and ^{81}Br (n, γ) ^{82}Br and $^{82}\text{Br}^m$ processes were gotten by extracting the samples immediately after neutron irradiation and counting twice; first, 4-5 hours after and again 45-60 hours after irradiation. The second count was due to ^{82}Br activity only since the half-lives of the other nuclides; $^{82}\text{Br}^m$ ($T_{1/2} = 6.1$ min.), ^{80}Br ($T_{1/2} = 18$ min.), and $^{80}\text{Br}^m$ ($T_{1/2} = 4.58$ hrs.), were short enough for all other activity to be essentially gone within 45 hours after irradiation. Thus the organic yields from the second counts gave the ^{82}Br organic yields with no corrections needed. By making $e^{-\lambda t}$ corrections for ^{82}Br activity present at the first count and subtracting this value from the total initial count, the $^{80}\text{Br}^m$ organic yields could be calculated. For the ^{82}Br organic yield due to the (IT) process, the samples were extracted one hour after irradiation and counted 45 to 60 hours later. The yields were then calculated using the following equation:

$$OY_{IT} = \frac{OY_{Obs} - 0.09 (OY_{n,\gamma})}{0.91} \quad (1)$$

The (n,γ) values used in these calculations were the experimentally determined $^{82}\text{Br} + ^{82}\text{Br}^m$ organic yields.

Determination of ^{130}I Organic Yields Activated by ^{129}I
 $(n,\gamma) \frac{^{130}\text{I}}{^{130}\text{I} + ^{129}\text{I}} + \frac{^{129}\text{I}}{^{130}\text{I} + ^{129}\text{I}} (n,\gamma) \frac{^{130}\text{I}^m}{^{130}\text{I}^m + ^{129}\text{I}^m}$ and $\frac{^{129}\text{I}}{^{130}\text{I} + ^{129}\text{I}} (n,\gamma) \frac{^{130}\text{I}}{^{130}\text{I} + ^{129}\text{I}}$
 $(n,\gamma) \frac{^{130}\text{I}^m}{^{130}\text{I}^m + ^{130}\text{I}^m} (IT) \frac{^{130}\text{I}}{^{130}\text{I}}$ Processes in Liquid Benzene

Benzene containing dissolved $^{129}\text{I}_2 + ^{127}\text{I}_2$ (1.7×10^{-3} mf) was irradiated with thermal neutrons and subsequently frozen in liquid nitrogen at various time intervals after removal from the reactor. Contrary to experiences with aliphatic hydrocarbons, the organic yields increased with the amount of time that the $^{130}\text{I}^m (IT) \frac{^{130}\text{I}}{^{130}\text{I}}$ process was allowed to occur in the solid phase (77° K). The results are summarized in Table VIII and Fig. 10. Apparently the phase separation characteristic of halogen-aliphatic hydrocarbon systems upon freezing did not hold here. Margolis and Bass⁸⁵ recently produced a glassy solid electron-donor-acceptor complex with iodine and benzene at 77° K. They calculated a ratio of benzene to iodine molecules in this complex to be approximately ten to one. This intermolecular attraction may have prevented any fractional crystallization except at high mole fractions of iodine, where it was

TABLE VIII
THE EFFECT OF PHASE CHANGE ON THE ORGANIC YIELDS OF ^{130}I ACTIVATED
BY RADIATIVE NEUTRON CAPTURE AND ISOMERIC TRANSITION

Part I. Duration of Time in Liquid Phase Prior to Freezing^a

Time After Midpoint of Irradiation that Samples were Frozen (Min)	Organic Yield of ^{130}I
0.3	38.0
	38.2
2	35.3
4	31.0
6	30.3
8	29.4
10	32.3
13	30.4
15	28.6
19	24.1
22	23.1
25	24.7
30	23.3
35	21.6
45	24.1
90	21.4

(a) Samples containing 1.7×10^{-3} mf $^{129}\text{I}_2$ (+ $^{127}\text{I}_2$) in liquid benzene were irradiated with thermal neutrons, frozen in liquid nitrogen at various times after the midpoint of irradiation and extracted 90 min after the midpoint of irradiation.

Figure 10. The effect of phase change on the organic yields of ^{130}I activated by radiative neutron capture and isomeric transition.

apparent that there was some separation during the freezing process with liquid nitrogen.

The ^{130}I organic yield produced by the combined $^{129}\text{I} (n,\gamma) ^{130}\text{I} + ^{130}\text{I}^m$ and $^{130}\text{I}^m (IT) ^{130}\text{I}$ processes was 21.4% (See Fig. 10). In an attempt to distinguish between the (n,γ) processes and the (IT) process, a number of samples at three different concentrations of I_2 were irradiated in the liquid phase with half of them extracted immediately and the other half after 90 minutes. The data shown in Table IX gave no indication of any significant difference and compared well with the data obtained in similar studies^{81,82} with the $^{127}\text{I}(n,\gamma) ^{128}\text{I}$ and $^{130}\text{I}^m (IT) ^{130}\text{I}$ processes.

The Determination of Neutron Irradiation Parameters in Solid State Halogen-Benzene Systems

The effect of most impurities raising the organic yields of halogens incorporated or dissolved in alkyl halides and of halogens in hydrocarbons has been known for a number of years. The usual types of criteria such as boiling point, freezing-point depression and optical measurements are not sensitive enough to detect impurities which affect hot atom reactions. A major difficulty in any repurification is introducing one type of impurity while removing another. Willard¹ has suggested three criteria that may indicate whether the necessary and sufficient purity requirements have been met for a given reaction. They are as follows: (1) identical results with reagents purified by different techniques; (2) different, but related, compounds which may contain different types and amounts of

TABLE IX

^{130}I AND $^{130\text{m}}\text{I}$ ORGANIC YIELDS BY (n,γ) COMPARED WITH ^{130}I ORGANIC
YIELDS BY (n,γ) AND (IT) PROCESSES IN LIQUID BENZENE

mf of $^{129}\text{I}_2(+^{127}\text{I}_2)$	Organic Yields Due to ^a		Organic Yields Due to ^b	
	$^{129}\text{I} (n,\gamma)$	$^{130}\text{I} +$ $^{129}\text{I} (n,\gamma) \text{ } ^{130\text{m}}\text{I}$	$^{129}\text{I} (n,\gamma)$	$^{130}\text{I} +$ $^{130\text{m}}\text{I} (\text{IT}) \text{ } ^{130}\text{I}$
1.6×10^{-4}	20.4		22.5	
	21.0		21.4	
	<u>20.7 $\pm$ 0.3</u>		<u>21.9 $\pm$ 0.6</u>	
4.4×10^{-3}	18.0		18.4	
	16.9		18.4	
	19.7		18.3	
	19.8		18.0	
	18.1		18.6	
	18.9		18.3	
	18.9		19.2	
	<u>18.6 $\pm$ 1.7</u>		<u>18.5 $\pm$.7</u>	
1.9×10^{-2}	19.2		19.9	
	17.4		18.9	
	<u>18.3 $\pm$ 1.9</u>		<u>19.4 $\pm$ 0.5</u>	

(a) Extracted within 25 sec. after midpoint of neutron irradiation.

(b) Extracted 90 min. after midpoint of neutron irradiation.

impurities before repurification should give identical results when brought to the same purity; (3) the product distribution should be independent of any impurity, whatsoever,

Preliminary experiments showed that the iodine and bromine organic yields increased with irradiation time but there was no significant difference during the first 30 seconds, and very little up to one minute. The time of extraction following neutron activation, the presence of air and the length of time the samples were at 77° K prior to neutron irradiation appeared to have little effect, especially in iodine studies. The effect of purification on bromine organic yields is shown in Table X. It is immediately apparent that the high purity, zone-refined benzene is necessary for reliable data in these systems. The fact that the gas-chromatographically repurified zone-refined (ASL) and Phillips research grade benzene gave organic yields within experimental error of the zone-refined benzene is strong support for the necessary and sufficient purity required in this study.

Little difference was found between the ^{130}I organic yields produced in the zone-refined and Phillips research grade benzene. This may have been due to the impurities introduced by the process of extracting the oxidized $^{129}\text{I}^-$ into the benzene. However, only little, if any, significant difference was found in the analogous $^{127}\text{I}_2$ -benzene systems either.

The Determination and Comparison of Bromine and Iodine Isotopic Yields in Solid State Benzene

In an attempt to separate the ^{130}I (n,γ) yields from the (IT)

TABLE X
ORGANIC YIELDS INDUCED BY $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br} + ^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$
AND $^{82}\text{Br}^m(\text{IT})^{82}$ PROCESSES AT VARIOUS MOLE FRACTIONS OF BROMINE IN BENZENE AT 77° K

mf of Br_2	Time Irradiated (Sec)	Grade of (a) Benzene	$^{80}\text{Br}^m(n,\gamma)^{(b)}$	$^{82}\text{Br}(n,\gamma)^{(c)}$	$^{82}\text{Br}(n,\gamma+\text{IT})^{(d)}$
10^{-1}	2	ASL (GC)	20.6	26.3	31.0
		Phillips (FO)	29.9	26.9	30.4
		Phillips (IH)	30.3	27.6	30.7
10^{-2}	4	ASL (GC)	20.6	28.5	32.7
		Phillips (FO)	(e)	(e)	(e)
		Phillips (IH)	30.2 (f)	29.8	34.1
10^{-3}	10	ASL (GC)	26.2	34.5	38.3
		Phillips (FO)	36.9	34.8	38.2
		Phillips (IH)	38.3	39.8	41.4
10^{-4}	30	ASL (GC)	30.1	38.6	41.8
		Phillips (FO)	(e)	(e)	(e)
		Phillips (IH)	48.2	53.4	(e)
10^{-5}	30	ASL (GC)	30.9	30.9	39.2
		Phillips (FO)	(e)	(e)	(e)
		Phillips (IH)	(e)	(e)	(e)

(a) (FO) Freshly Opened; (IH) In-house purification; ASL (GC) Applied Science Lab - purified by gas chromatography

(b) Each value represents the average of three or more samples

(c) Extracted within 25 sec. after midpoint of neutron irradiation

(d) Extracted 60 min. after midpoint of neutron irradiation

(e) Data not available or extremely sporadic

(f) Bromine-20 organic yield (corrected)

yields, which did not work, data was provided for an estimation of the pure (IT) organic yield in solid state benzene (See Fig. 10). A rough calculation* gives a value of approximately 50% for the ^{130}I isomeric transition organic yield at 1.7×10^{-3} mf $^{129}\text{I}_2$ ($+^{127}\text{I}_2$).

Attempts were made to obtain (IT) organic yields by extracting neutron irradiated aqueous iodide ($^{129}\text{I}^-$) into a mixture of benzene, 10% aqueous H_2O_2 , and a trace of HNO_3 . Upon shaking, the iodide was oxidized and dissolved in the benzene as I_2 . The organic phase was drawn off, washed once and frozen (or not, depending on the study). The technique was first attempted with the liquid benzene- I_2 system, where the value is known to be approximately 19%⁸², in order to estimate the reliability of the technique. The results compared favorably with the liquid state data presented in Tables VIII and IX. The solid state (IT) organic yields by this technique, presented in Table XI, were considerably lower than these obtained by the other two methods. Considering the possibility of impurity effects in this method, it was not considered as reliable as

*The $^{129}\text{I} (n, \gamma) ^{130}\text{I} + ^{130m}\text{I}$ reaction stabilizes about 21% of the labeled atoms in organic combination and the remaining 79% as inorganic species. It is assumed that the 61% ^{130m}I nuclides are fixed proportionately in the two forms. This would mean that about 8% of the labeled nuclides (^{130}I only) would be present in organic combination and 31% in inorganic combination. Since the final ^{130}I organic yield is close to 38%, this represents an increase of 30% of the total activity in the organic phase; and in the inorganic (or aqueous) phase, the increase in organic yield is 31% (62%-31%).

TABLE XI
Organic Yields of ^{130}I Induced by the
 $^{130}\text{I}^m$ (IT) ^{130}I Processes in Benzene
298° K and 77° K^a

Organic Yields ^b at 298° K	Organic Yields ^c at 77° K
16.3	20.1
13.0	17.1

(a) 2×10^{-4} mf I_2

(b) The organic yield was corrected to account for 39% of ^{130}I born by (n, γ) process in the reactor and extracted into the aqueous phase. Also, the organic yield was corrected for the (IT) occurring before extraction into benzene.

(c) The same correction as above was made plus a correction for the yield (0.82%) produced prior to freezing.

the other two methods which were in much better agreement.

In a third method to determine the organic yield of the $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I process, samples were irradiated at 77-90° K in the rabbit facility and extracted at various times. The data are shown in Table XII. The organic yields obtained by immediate extraction were consistently lower, 6-11%, than those obtained by allowing the (IT) process to occur for 90 minutes at 77° K. Other studies in this laboratory⁷¹ have indicated that the ^{127}I (n, γ) ^{128}I and $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I gave similar yields which were consistently higher than the ^{130}I yields from (n, γ) processes in many aliphatic hydrocarbons. This trend was repeated in the I_2 -benzene systems. The similarity of the ^{127}I (n, γ) ^{128}I and $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I may indicate that the reactions are independent of the initial kinetic energy of the activated atom.

In the study⁵⁷ of the (n, γ) and (IT) activated reactions of bromine in liquid C^6 -alkanes and CCl_4 , it was found that the (IT) yields were about 1.7 times greater than the (n, γ) yields. Lambrecht⁷¹ found a ratio of 1.2 to 1.4 for the ^{130}I organic yields by (IT) over those by (n, γ) in C_5 - C_9 liquid alkanes. Perhaps a prime consideration in the similarity of reactions is the amount of internal conversion undergone by the various nuclides. Wexler⁴³ has determined that a minimum of 50% of the ^{128}I atoms are born with a positive charge. According to the autoradiation hypothesis, the ^{128}I nuclei may be sufficiently long lived that internal conversion does not occur until it has lost its recoil kinetic energy. The similarity of (n, γ) activated ^{128}I and ^{130}I activated by isomeric transition suggests a high percentage of ^{128}I atoms born by radiative neutron capture undergo

TABLE XII

Organic Yields Induced by ^{129}I (n, γ) ^{130}I , ^{129}I (n, γ) $^{130}\text{I}^{\text{m}}$,
 ^{127}I (n, γ) ^{128}I , and $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I Processes at Various
 Mole Fractions of Iodine in Benzene at 77° K

mf of I_2 $\times 10^3$	(n, γ) ^{128}I	(n, γ) $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$	(n, γ) + (IT) ^{130}I
0.10	63.5 ^a		
0.16		49.3 52.9 48.3 48.5 51.5 <hr/> 50.4 $\pm$ 2.5	60.1 62.4 61.4 <hr/> 61.3 $\pm$ 1.2
0.56		48.4 47.2 49.6 <hr/> 48.4 $\pm$ 1.2	55.6 54.2 53.8 <hr/> 54.8 $\pm$ 1.0
0.82		51.8 49.9 49.6 <hr/> 50.3 $\pm$ 1.5	
1.1	51.7 53.7 <hr/> 53.7 $\pm$ 1		60.8 60.0 <hr/> 60.4 $\pm$ 0.4
1.7	57.5		56.1 55.1 <hr/> 55.6 $\pm$ 0.5
3.7		47.9 47.4 45.2 <hr/> 46.8 $\pm$ 1.6	

TABLE XII (Continued)

mf of I_2 $\times 10^3$	(n_D)	(n_D)	$(n_D) + (IT)$
	^{128}I	$^{130}I + ^{130}I^m$	^{130}I
5.2	49.5		
6.0		38.8	49.0
7.5	49.8	41.7	52.2
	50.0	44.8	51.8
		42.8	54.1
	49.9 $\pm$ 0.1	42.8	54.1
		44.2	53.9
		43.5	52.0
		45.7	56.3
		43.6 $\pm$ 2.1 ^b	53.5 $\pm$ 2.8 ^b
10.0	46.2		
14.0	39.8	34.4	
		28.7	
		31.0	
		31.4 $\pm$ 3	
19.0	31.7	20.6	
		28.4	
		24.6 $\pm$ 4	
29.0		19.6	
		17.3	
		17.4	
		18.3 $\pm$ 1.3	
32.0	20.9		
84.0	11.2		

(a) Phillips research grade benzene was used without further purification.

(b) Benzene- I_2 solution was saturated with helium for CO_2 removal.

internal conversion, since it is known that the decay of $^{130}\text{I}^m$ is highly converted.³³

The lower organic combination of (n, γ) activated $^{130}\text{I} + ^{130}\text{I}^m$ may be due to accompanying internal conversion occurring before the recoil energy has been dissipated, thus carrying the hot species away from the center of a pocket of radiolytically produced species (ions, radicals, etc). Present evidence however, makes it seem more likely that the lower reactivity is due to a lower percent of ^{130}I and $^{130}\text{I}^m$ nuclides being born in low-lying metastable states.⁸⁶

The results of the ^{130}I organic yields as a function of time that the $^{130}\text{I}^m$ (IT) ^{130}I process was allowed to occur in solid state benzene before extraction are shown in Table XIII and Fig. 11. For uniformity all samples were frozen 45 seconds from the midpoint of irradiation and all contained 6.0×10^{-3} mf $^{129}\text{I}_2$ (+ $^{127}\text{I}_2$). After $e^{-\lambda t}$ corrections were made, it was found that here again a value of approximately 50% was found for the ^{130}I solid state organic yield by (IT).

Although there was generally good correlation between the ^{128}I and ^{130}I (by IT) organic yields in solid state benzene, the necessity of extracting the oxidized $^{129}\text{I}_2$ into benzene did not allow for the purity desired in this study. Bromine, on the other hand, can be readily purified and added directly to benzene. It contains approximately equal amounts of ^{79}Br and ^{81}Br with six nuclear reactions available so comparisons can be made between (n, γ), (n, γ) and (IT) and (IT) activated reactions. It is also miscible at all concentrations.

Preliminary studies indicated that the bromine-benzene system is more sensitive to impurities than is the iodine-benzene system. In order

TABLE XIII

The Effect of Phase Change on the Organic Yields
of ^{130}I Activated by (n,γ) and (IT)

Part II. Duration of Time in Solid Phase After
Freezing^a

Time After Midpoint of Irradiation Samples were Extracted (min.)	Organic Yield of ^{130}I
1	17.9
5	20.2
8	26.5
10	25.0
15	28.3
25	32.5
30	34.3
55	37.8

- (a) Samples containing 6×10^{-3} mf $^{129}\text{I}_2$ ($+^{127}\text{I}_2$) in liquid benzene were irradiated with thermal neutrons, frozen in liquid nitrogen 45 sec. after the midpoint of irradiation and extracted at various times after the midpoint of irradiation.

Figure 11. Organic Yields of ^{130}I as a function of time that the $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ processes were allowed to occur in solid benzene (77°K) when frozen 45 sec. from the midpoint of irradiation.

to obtain the best results more care was taken in every step during sample preparation and zone-refined benzene (99.99 mole % purity) was used for most of the studies. No liquid state work was done in view of the results from the liquid state iodine-benzene study.

Referring again to Table X, it was noted that although the $^{80}\text{Br}^m$ organic yields by (n, γ) processes fluctuated considerably with the grade of benzene used, this was not the case with the ^{82}Br organic yields activated by (n, γ) and (IT). Also, the isotope effect noted between $^{82}\text{Br} + ^{82}\text{Br}^m$ by (n, γ) and ^{82}Br by (IT) does not change to any extent in this range of benzene purity and mf of Br_2 . The isotope effect between the ^{79}Br (n, γ) $^{80}\text{Br}^m$ and ^{81}Br (n, γ) $^{82}\text{Br} + ^{82}\text{Br}^m$ processes is completely covered up by the impurities present in all grades of benzene except the very pure. This effect appears to offer a good criterion for benzene purity.

The solid state organic yields obtained from the various nuclear processes of bromine are presented in Tables XIV-XVI. This study as well as others^{87,88} indicate that there are exceptions to the general evidence for independence of yield on method of activation. In a number of cases the organic yields for isomeric transition have been observed to be higher than that for the (n, γ) process, while the distribution of organic products for the two is identical.⁸⁹ It seems quite plausible that the higher organic yields result from a higher availability of radicals from the recoil track of the more energetic atoms or from the highly localized charge of the isomeric transition.

The yields observed for the reactions of $^{80}\text{Br}^m$, ^{80}Br and ^{82}Br produced by (n, γ) processes in $\text{C}_6\text{H}_5\text{Br}$ and in C_6H_6 vapor, both scavenged with

TABLE XIV

ORGANIC YIELDS OF THE $^{79}\text{Br}(n,\gamma)^{80}\text{Br}$, $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$,
 $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$ AND $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ PROCESSES IN FRESHLY
 OPENED PHILLIPS RESEARCH GRADE BENZENE AT 77°K

mf of Br_2	Time Irrad. (sec)	$\text{Br}-80m(n,\gamma)$	Organic Yield: $\text{Br}-82(n,\gamma)$	$\text{Br}-82(n,\gamma + \text{IT})$
10^{-5}	30	25.7		
		39.6		
		41.1		
		<u>106.4</u>		
10^{-4}	30	<u>35.5</u>		
		37.8		
		39.5		
		46.4		
10^{-3}	10	<u>123.7</u>		
		<u>41.2</u>		
		35.7	35.3	
		44.1	42.7	
10^{-2}	10	43.8	48.6	
		29.8	28.7	
		36.3	34.3	
		29.7	29.2	
		36.3		36.1
		38.7	218.8	39.3
		29.4		31.1
		<u>322.8</u>		<u>106.5</u>
		<u>35.9</u>	<u>36.4</u>	<u>35.5</u>
		28.6	28.0	
10^{-1}	10	37.0	23.9	
		38.3	33.6	
		37.9		38.5
		37.3		41.5
		30.6		31.2

TABLE XIV (Continued)

mf of Br ₂	Time Irrad.	Br-80m(n,γ)	Organic Yield: Br-82(n,γ)	Br-82(n,γ + IT)
		37.6	33.4	
		36.2	35.3	
		38.1	34.4	
		38.9	34.5	
		38.0	—	40.6
		39.3		41.0
		39.9	234.1	41.3
		39.1		41.1
		—		—
		516.8		275.2
		<u>36.9</u>	<u>33.4</u>	<u>39.3</u>
10 ⁻¹	2	29.9	27.2	
		30.3		32.0
		30.1	27.2	
		29.4	27.1	
		30.0	26.4	
		29.0	—	30.0
		29.4	107.8	30.5
		30.8		30.6
		—		—
		238.9		123.1
		<u>29.9</u>	<u>27.0</u>	<u>31.0</u>
7x10 ⁻¹	2	36.1	20.7	
		21.1	15.7	
		25.4	21.4	
		25.1		24.6
		25.5		25.2
		26.3		25.7
		—		—
		158.5		
		<u>26.4</u>		
		Br-80 (n,γ)		
		21.4	18.7	
		24.0	23.3	
		22.4	21.0	
		21.7	—	23.0
		22.0	120.8	23.1
		22.6		22.9
		—		—
		134.1		144.5
		<u>22.3</u>	<u>20.1</u>	<u>24.1</u>

TABLE XV
 ORGANIC YIELDS OF THE $^{79}\text{Br}(n,\gamma)^{80}\text{Br}$, $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$,
 $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$ and $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ PROCESSES
 IN REPURIFIED PHILLIPS RESEARCH GRADE BENZENE AT 77°K

mf of Br_2	Time Irrad. (sec)	$\text{Br-80}(n,\gamma)$	$\text{Br-80m}(n,\gamma)$	$\text{Br-82}(n,\gamma)$	$\text{Br-82}(n,\gamma + \text{IT})$
10^{-4}	30	48.1		47.7	51.9
		47.6		48.1	54.0
		50.4		48.8	54.3
		<u>48.7</u>		<u>48.2</u>	<u>53.4</u>
10^{-3}	10		37.6	34.4	
			39.0		41.0
		36.7		35.3	
		43.1		42.7	
		43.8		48.6	
		38.3		38.2	
		41.7		39.7	
		41.5		40.0	
		37.6			41.6
		40.3			39.8
		41.8			43.3
10^{-2}	4	<u>40.5</u>	<u>38.3</u>	<u>39.8</u>	<u>41.4</u>
		30.3		29.0	
		33.3		28.8	
		32.2		31.6	
		31.6			33.6
		33.0			34.5
		32.0			34.2
		<u>32.1</u>		<u>29.8</u>	<u>34.1</u>
		32.5	35.8	30.8	
		30.1	35.7	30.9	
		35.3	33.7	30.9	
5×10^{-3}	4		23.9		40.8
			21.9		39.4
		<u>32.5</u>	<u>30.3</u>	<u>30.9</u>	<u>40.1</u>

TABLE XV (Continued)

mf of Br ₂	Time Irrad. (sec)	Br-80(n,γ)	Br-80m(n,γ)	Br-82(n,γ)	Br-82(n,γ+IT)
10 ⁻¹	2		30.6	27.7	
			30.0	26.9	
			29.2	26.0	
			32.7	29.8	33.5
			29.4	31.4	31.8
			32.0	29.9	32.6
			30.0	26.2	30.2
			29.4	28.8	30.1
			30.0	27.5	29.8
		26.9	30.0	27.2	30.0
		28.9	30.3	27.1	30.5
		30.0		26.4	30.6
		30.7		27.2	32.0
		30.1		26.8	30.8
				27.4	30.0
				27.7	30.4
				26.3	29.7
				26.8	30.0
		<u>29.3</u>	<u>30.3</u>	<u>27.6</u>	<u>30.7</u>
7x.0 ⁻¹			16.8	21.7	
			19.4	18.9	
			21.3	19.0	
			22.4	15.7	22.5
			22.2	16.0	22.2
			22.3	20.2	22.8
			25.6		23.2
					22.5
					24.5
			<u>22.1</u>	<u>18.8</u>	<u>22.9</u>

TABLE XVI
ORGANIC YIELDS OF THE $^{79}\text{Br}(n,\gamma)^{80}\text{Br}$, $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$,
 $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$ AND $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ PROCESSES IN ZONE-
REFINED BENZENE ^a AT 77° K

mf of Br_2	Time Irrad. (sec)	Br-80m (n,γ)	Br-82 (n,γ)	Br-82 (n,γ+IT)	Br-82 ^b (IT)
10^{-1}	2	19.7	25.7		
		20.4	27.2		
		21.1	26.1		
		20.4		29.8	
		21.0		31.7	
		21.3		31.5	
		<u>20.6</u>	<u>26.3</u>	<u>31.0</u>	31.5
10^{-2}	4	20.8	29.1		
		21.6	28.0		
		21.1	28.4		
		20.2		31.8	
		20.3		33.4	
		19.6		33.0	
		<u>20.6</u>	<u>28.5</u>	<u>32.7</u>	33.0
10^{-3}	10	27.6	37.0		
		23.4	31.9		
		28.1	34.8		
		25.2		37.5	
		29.3		41.9	
		23.9		35.7	
		<u>26.2</u>	<u>34.5</u>	<u>38.3</u>	38.7
10^{-4}	30	27.7	38.5		
		37.7	38.3		
		28.6	39.1		
		28.1		40.0	
		31.7		44.3	
		28.0		41.2	
		<u>30.3</u>	<u>38.6</u>	<u>41.8</u>	42.1

TABLE XVI (Continued)

mf of Br ₂	Time Irrad. (sec)	Br-80m (n,γ)	Br-82 (n,γ)	Br-82 (n,γ+IT)	Br-82 ^b (IT)
10 ⁻⁵	30	26.0	38.1		
		17.9	38.9		
		31.7	37.6		
		37.3		38.9	
		29.6		41.5	
		32.6		37.2	
		<u>29.2</u>	<u>38.2</u>	<u>39.2</u>	39.5
10 ⁻⁶ ^c	30	29.9	37.6	40.2	40.6

(a) 99.99 quoted Mole Percent Purity

$$(b) \text{ OY}_{IT} = \frac{\text{OY}_{Obs} - 0.09 (\text{OY}_{n,\gamma})}{0.91}$$

(c) Average of 3 samples

Br_2 , are indistinguishable.⁹⁰ This is strange in light of the finding⁴³ that these three nuclear species are charged at birth to the extent of a minimum of 18, 12 and 25% respectively (above). The indication is that either ions are not required for the gas-phase reactions or that the values for the fraction of atoms charged by each process are incorrect. Since the correlation is qualitatively correct in the present study it would appear that there is at least some validity in the differences found by Wexler and Davies.⁴³

In some cases the organic yields in this study could be compared with values from other laboratories. Iyer and Willard⁵¹ reported an organic yield of 25% for the $^{80}\text{Br}^m$ (IT) ^{80}Br reaction at 5×10^{-3} mf Br_2 in solid state benzene (77° K). Our value obtained with repurified Phillips research grade benzene was 32.5%, which indicates an impurity effect raising the yield about 7.5%. Milman, et al., reported a 24% organic yield for the $^{80}\text{Br}^m$ reaction in the range of 0.1 to 0.5 mf Br_2 in the same system. In this instance our value was about 3% lower, 20.6%, using the zone-refined benzene. Another study⁹² reported the ^{82}Br organic yield by (IT) to be $113.1 \pm 15.6\%$ but no information on purity of benzene was given. The method involved irradiating molecular bromine, adding it to benzene and freezing to dry ice temperature for 60 minutes before extraction. Our value for the same mole fraction of bromine was between 31.5 and 33%. It does not appear that any valid comparison can be made in this case.

An Investigation of the State of Aggregation of ICl,
I₂ and Br₂ in Solid State Benzene at 77° K

It was mentioned earlier that Margolis and Bass⁸⁵ established that benzene and iodine produce a donor-acceptor complex at 77° K. Under this experimental condition, a 10 to 1 ratio of benzene to iodine was present in the complex. This particular complex apparently cannot be achieved by freezing down a solution of iodine in benzene since the solubility is not that great and visible separation can be seen at concentrations near saturation. Hassel and Stromme⁵² established that the structure of the solid state (-40 to -50° C) solution of bromine and benzene formed a 1:1 complex. It was considered interesting to investigate these complexes with the organic yield probe and compare the effect of the various nuclides.

The organic yield due to the ¹²⁷I(n,γ)¹²⁸I at various mole fractions of I₂ in benzene at 77° K are given in Table XII and Fig. 12. It would appear that fractional crystallization began to appear at about 10⁻³ mf I₂. In order to corroborate this conclusion, organic yields were obtained from the ICl-benzene system at 77° K. Fig. 13 and Table XVII show that a similar, though somewhat lower, ¹²⁸I organic yield curve was produced, but the ³⁸Cl curve was a straight line. It is not likely that the ³⁸Cl organic yields would remain constant at higher concentrations of ICl if clustering occurred to any extent. The only logical conclusion appears to be that the ¹²⁸I organic yield dropped even though no fractional crystallization occurred. At least two structures are possible here: (1) a random distribution of ICl molecules throughout the benzene at all concentrations or (2) a mixture of some donor-acceptor

Figure 12. Organic Yields of ^{128}I activated by radiative neutron capture in solid benzene at 77°K .

TABLE XVII

ORGANIC YIELDS OF THE $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$, $^{127}\text{I}(n,\gamma)^{128}\text{I}$,
 $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$ AND THE $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ PROCESSES IN
 ZONE REFINED ^a BENZENE AT 77°K

mf of Halogen or Interhalogen	Time of Irrad. (sec)	Br-80m (n,γ)	Br-82&Br-82m (n,γ)	Br-82 (IT) ^b	I-128 (n,γ)	Cl-38 (n,γ)
10^{-1}Br_2	2	20.6	26.3	31.5		
$\text{I}_2 + \text{Br}_2$ ^c		10.3	14.8	15.2	— d	
IBr		15.1	20.6	21.3	11.8	
ICl					16.8 ^e	20.9
I_2					— d	
10^{-2}Br_2	2	20.6	28.5	33.0		
$\text{I}_2 + \text{Br}_2$ ^c		11.0	15.0	18.6	28.8	
IBr		15.6	21.1	22.0	33.6	
ICl					29.3	21.5
I_2					34.1	
10^{-3}Br_2	5	26.2	34.5	38.3		
$\text{I}_2 + \text{Br}_2$ ^c		24.4	35.1	35.2	50.2	
IBr		25.8	33.4	33.8	50.4	
ICl					43.4	22.1
I_2					50.7	
10^{-4}Br_2	10	30.3	38.6	41.8		
$\text{I}_2 + \text{Br}_2$ ^c		31.7	41.5	50.5	51.2	
IBr		32.0	40.8	42.1 ^f	50.8	
ICl					45.7	21.8
I_2					52.7	

TABLE XVII (Continued)

mf of Halogen or Interhalogen	Time of Irrad. (sec)	Br-80m (n, γ)	Br-82&Br-82m (n, γ)	Br-82 (IT) ^b	I-128 (n, γ)	Cl-38 (n, γ)
10^{-5} Br ₂	20	29.2	38.9	39.2		
I ₂ + Br ₂ ^c		32.3	42.2	51.2	48.9	
IBr		33.2	41.6	51.3	49.7	
ICl					46.1	20.8
I ₂					51.7	

(a) 99.99 quoted mole percent purity

(b) $O.Y._{IT} = (O.Y._{obs} - 0.09(O.Y._{n,\gamma})) / 0.91$. The (n, γ) value used in this calculation are the experimentally determined $^{82}\text{Br} + ^{82}\text{Br}^m$ organic yields, the $O.Y._{Obs}$ are the organic yields determined after the sample was maintained in the polycrystalline state at 77°K for 1 hour after neutron irradiation allowing 99.9% of the metastable isomer to decay to ground state.

(c) Equimolar ratio with the sum of the two concentrations being equal to the above stated value.

(d) Values are missing due to limited solubility.

(e) Concentration was approximately 5×10^{-2} mf.

(f) Later data using a single-channel analyzer is presented here.

Figure 13. Organic yields induced by $^{127}\text{I}(n,\gamma)^{128}\text{I}$ and $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$ processes in zone-refined benzene at 77° K.

complex and solvent containing a monomolecular dispersion of ICl molecules.

The organic yields due to the ^{79}Br (n,γ) $^{80}\text{Br}^m$, ^{81}Br (n,γ) ^{82}Br + $^{82}\text{Br}^m$ and $^{82}\text{Br}^m$ (IT) ^{82}Br in solid state benzene are presented in Table XVIII and Fig. 14. Although the processes produced different organic yields, the shape of the curves on the organic yield vs. mf Br_2 plot are essentially the same. The bromine organic yield curves closely resembled those of ^{128}I in the concentration range from 1×10^{-5} to 5×10^{-2} mf halogen. The plateau region which began to drop off around 10^{-4} mf halogen may well represent a monomolecular dispersion as indicated earlier. A second plateau region occurred in the region from 5×10^{-2} to 5×10^{-1} mf Br_2 (beyond the solubility limit of I_2). Milman, et al.⁹¹, suggested that the constancy of the organic yield from 0.1 to 0.5 mf Br_2 indicates that the fate of the $^{80}\text{Br}^m$ atom is settled in an environment of constant composition, namely the 1:1 bromine-benzene complex. Their study showed a eutectic mixture at 0.23 mf Br_2 . They concluded that in the region between 0.23 and 0.50 mf Br_2 , the mixture consisted of pure complex and eutectic, and below 0.23 mf Br_2 , pure benzene and eutectic. The eutectic itself is a mixture of pure benzene and the bromine-benzene complex. Milman's model of the solid state bromine-benzene mixture can be extended to concentrations of Br_2 below 5×10^{-2} mf by assuming a transition from the eutectic-pure benzene mixture to a monomolecular dispersion.

The drop in the ^{129}I organic yield curve above 10^{-4} mf I_2 may, by analogy, be due to the formation of a mixture of a complex and the monomolecular dispersion. When the iodine or bromine atoms are close enough,

TABLE XVIII
 ORGANIC YIELDS^a OF THE $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$, $^{127}\text{I}(n,\gamma)^{128}\text{I}$,
 $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$ AND THE $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ PROCESSES IN
 ZONE REFINED BENZENE AT ROOM TEMPERATURE

mf of Halogen or Interhalogen	Time of Irrad. (sec)	Br-80M (n, γ)	Br-82&Br-82M (n, γ)	Br-82 (IT)	I-128 (n, γ)	Cl-38 (n, γ)
10^{-2} Br ₂	2	17.1	25.0	33.0		
I ₂ + Br ₂		9.8	15.6	15.6	19.8	
IBr		9.3	16.1	16.5	19.6	
ICl					23.3	19.7
I ₂					21.3	
10^{-3} Br ₂	5	20.0	28.4	33.8		
I ₂ + Br ₂		13.4	20.8	21.3	25.8	
IBr		13.8	20.4	21.9	23.2	
ICl					27.8	21.0
I ₂					22.5	
10^{-4} Br ₂	10	19.8	28.7	33.9		
I ₂ + Br ₂		17.6	24.4	25.1	29.5	
IBr		19.0	25.0	25.8	27.9	
ICl					28.1	20.7
I ₂					22.6	

(a) Averages of two or more determinations.

as in a complex, it is quite possible that appreciable self-scavenging may occur. It is unfortunate that iodine is not more soluble in benzene so that this model could be verified, or not, by the occurrence of a second organic yield plateau around 0.1 mf. I_2 .

The Product Distribution in Liquid and Solid State Halogen-Benzene Systems

In a study⁹³ of the product distribution due to the (n,γ) processes of iodine in liquid iodobenzene and bromine in liquid bromobenzene or benzene containing 3 mole % Br_2 relatively few products were found compared to aliphatic systems. Only iodobenzene was formed in iodobenzene; while in the bromine-benzene and bromine-bromobenzene systems, six products containing radiobromine were obtained. Over 85% of the labeled products was bromobenzene and the other products were the three isomeric dibromobenzenes, benzyl bromide and a small amount of an unidentified product.

It was also found in the above study⁹³ that the product distribution from the $^{80}Br^m$ (IT) ^{80}Br process was the same as from the (n,γ) process.

In light of the differences in yield between the various nuclear processes of iodine and bromine in liquid and solid state benzene, it was considered of interest to investigate the product distributions in both phases at high and low scavenger concentration. Due to limiting experimental conditions and the results of a previous study⁹³, no attempt was made to compare product distributions between (n,γ) and (IT) activated reactions.

Irradiations of solid state chromatography samples were performed by returning the samples to a liquid nitrogen dewar at regular intervals

so that the sample temperature did not rise more than about 30 degrees.⁴⁷ Liquid samples were kept in liquid nitrogen after reactions were finished.

Samples of benzene containing $^{127}\text{I}_2$ and $^{129}\text{I}_2$ ($+^{127}\text{I}_2$) were irradiated in the rabbit facility for fifteen minutes, both in the liquid phase and the solid phase (as described above). Iodine concentrations varied from 5×10^{-4} to 5×10^{-2} mf. Radiogas chromatography indicated relative yields of 1-4% $\text{C}_2\text{-C}_4$ alkyl iodides with more being present in liquid phase samples. Irradiations of benzene- $^{131}\text{I}_2$ samples showed comparable yields in this region of the chromatogram indicating that these lower molecular weight iodides were probably due to radiation damage. The only other product was iodobenzene. Attempts to detect diiodobenzene or iodobiphenyl were in vain.

The lack of a self-scavenging effect in the liquid I_2 -benzene system indicates the absence of thermal reactions.⁸¹ In the solid phase, however, the drop in the ^{128}I O.Y.s with increasing ICl concentration while the ^{38}Cl O.Y. remain constant indicates that there may be iodine self-scavenging here. Self-scavenging of the iodine would suggest thermal as well as hot reactions in the solid state, which apparently produce the same product, iodobenzene.

Macrae and Shaw⁸¹ found that the ^{128}I yield in liquid benzene was approximately half as great at 75°C as at 15°C and theorized that the reactions governing organic combination have small activation energies. This, along with no iodine self-scavenging was explained by assuming that the capture event causes the dissociation of some of the neighboring molecules of benzene into hydrogen atoms and phenyl radicals which can combine with the active atom or undergo the following reaction:

They reasoned that if the above reaction required a small activation energy, a small increase in temperature would reduce the concentration of phenyl radicals available at any time, and lead to a decrease in organic yield. If all the phenyl radicals generated in the hot zone reacted to form hydrogen atoms before diffusive recombination occurred, no self-scavenging would be observed since the ensuing recombination reactions would not involve any organic radicals, and thus not contribute to the organic yield.

The conclusions drawn by Chien and Willard⁷⁵ concerning hot ^{38}Cl atoms discussed earlier and by Macrae and Shaw⁸¹ as discussed above, appear to explain the data obtained in this study. At liquid nitrogen temperature, reaction 2, shown above, may not be significant and thus the phenyl radicals produced by the various nuclear processes would be available for reaction with thermalized, labeled iodine nuclides. Iodine self-scavenging could be a possibility at higher mole fractions if phenyl radicals were available long enough for reactions with I_2 . The tagged chlorine atoms, on the other hand, which escape combination by other "high energy" processes, always react with carbon-hydrogen bonds to form HCl .⁷⁵ Thus, the presence of phenyl radicals would increase the ^{128}I O.Y.s but would not influence the ^{38}Cl O.Y.s. Fractional crystallization would be indicated by a drop in ^{38}Cl O. Y. but apparently not by a drop in ^{128}I O.Y.s in systems where halogen complexes are formed. In aliphatic solvents either iodine or chlorine may produce organic yield curves which reflect the concentration at which fractional crystallization occurs.

Samples of bromine dissolved in benzene ranging from 5×10^{-4} to

3×10^{-1} mf Br_2 were irradiated in a manner analogous to the iodine benzene system. Only ^{82}Br products were investigated and no attempt was made to investigate the (n, γ) and (IT) processes separately for reasons discussed earlier. Liquid samples were stored in liquid nitrogen after the $^{82}\text{Br}^m$ (IT) ^{82}Br reactions were finished, which was 60 min.

All samples, liquid and solid, showed a small percentage of $\text{C}_2\text{-C}_4$ alkyl bromides which again appeared to be produced by radiation damage. The major product was bromobenzene at all concentrations with varying amounts of the dibromobenzene isomers. The other two products reported in another study⁹³ were not detected, possibly due to their low activity or sticking in the column. Backflushing produced no other products either.

The amount of dibromobenzene produced in the liquid phase was generally small except at high concentrations of bromine, 0.1 mf and above (See Table XIX). In the solid phase the yield of dibromobenzene remained fairly constant and relatively higher than that formed in the liquid phase except at 0.3 mf Br_2 . Apparently, in the liquid phase another reaction, not leading to dibromobenzene, is competing with the one that does and when the concentration of scavenger is high enough, the former reaction is no longer important. The fact that the relative yield of dibromobenzene in the solid phase does not increase seems to rule out a simple probability relationship. Other than this observation, it does not seem possible to draw any meaningful conclusion from this data.

TABLE XEX

Product Distribution^a Resulting from the $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$
and $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ Processes in Liquid and Solid (77° K) Benzene

Mole Fraction Br_2	$\text{C}_2\text{-C}_4$ R-Br Liquid & Solid	Products ^b		$\text{C}_6\text{H}_4\text{Br}_2$ Liquid	$\text{C}_6\text{H}_4\text{Br}_2$ Solid
		$\text{C}_6\text{H}_5\text{Br}$ Liquid	Solid		
5×10^{-4}	2.4	100	100	3.8	28.9
5×10^{-3}	2.1	100	100	4.2	31.0
5×10^{-2}	1.9	100	100	12.5	28.7
1×10^{-1}	1.8	100	100	18.7	27.1
3×10^{-1}	1.6	100	100	23.9	24.5

(a) Averages of two or more determinations.

(b) The values are the percentage of individual products relative to the major product given the value of 100%.

CHAPTER V

RADIATIVE NEUTRON CAPTURE AND ISOMERIC
TRANSITION INDUCED REACTIONS OF SELECTED HALOGENS
AND INTERHALOGENS IN LIQUID AND SOLID BENZENE

CHAPTER V

Radiative Neutron Capture and Isomeric
Transition Induced Reactions of Selected Halogens
and Interhalogens in Liquid and Solid Benzene

In an attempt to shed more light on the problems discussed earlier, two interhalogens (IBr and ICl) and a mixed system of I_2 and Br_2 were studied along the same lines as iodine and bromine in liquid and solid benzene. Preliminary studies indicated that thermal and exchange reactions could be kept at low enough levels with the procedures used for aliphatic solvents that no problems determining organic yields and radiogas chromatograms were indicated.

The organic yields of mixed systems of halogens were determined by means of spectrum stripping using computer programs developed by Omaha V. A. Hospital research personnel for this purpose. When the ICl organic yield data were run with a different computer program prepared by Ayres⁹⁴ in this laboratory the results were almost identical. Only the ^{82}Br organic products from the nuclear processes in the IBr- and ($I_2 + Br_2$)-benzene systems were analyzed by radiogas chromatography. All products in the ICl-benzene systems were analyzed.

Figure 14. Organic yields induced by $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br} + ^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$ and $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$ processes in zone-refined benzene at 77° K.

A Comparison of Organic Yields, Isotope Effects
and Scavenging Ability of I_2 , IBr, $Br_2 + I_2$ and
ICl in Liquid and Solid Benzene

The organic yields observed for the ^{37}Cl (n, γ) ^{38}Cl , ^{127}I (n, γ) ^{128}I , ^{79}Br (n, γ) $^{80}Br^m$, ^{81}Br (n, γ) $^{82}Br^m + ^{81}Br$ (n, γ) ^{82}Br and $^{82}Br^m$ (IT) ^{82}Br processes as a function of ICl, I_2 , Br_2 , IBr and $I_2 + Br_2$ concentration in solid state benzene at 77° K are given in Table XVII and Figs. 13 and 14. The data for the iodine-benzene and bromine have been reported previously but are repeated here for comparison.

The isotope effect ($^{80}Br^m$ O.Y. vs. ^{82}Br O.Y.) and the general position of the organic yield plateaus found in the bromine-benzene system were also found in the IBr- and ($I_2 + Br_2$)-benzene systems for the ^{79}Br (n, γ) $^{80}Br^m$, ^{81}Br (n, γ) $^{82}Br + ^{81}Br$ (n, γ) $^{82}Br^m$ and the $^{82}Br^m$ (IT) ^{82}Br processes. In the region of mono-molecular dispersion, generally less than 10^{-4} mf halogen, the various nuclear processes yielded approximately equal organic yields in each system. The notable exception was the lower (ca 10%) organic yield produced by the $^{82}Br^m$ (IT) ^{82}Br process in the bromine-benzene systems in the 10^{-4} - 10^{-5} mf Br_2 region compared to the other two systems (See Table XVIII).

In an attempt to resolve this difference, ^{82}Br organic yields in the IBr- and ($I_2 + Br_2$)-benzene systems were analyzed with a single channel analyzer after all other nuclides were dead. The values were in the region of 42%. The corresponding values at higher mole fractions of IBr and $I_2 + Br_2$ showed a good correlation, however. As a further check, several samples at 10^{-4} mf IBr were rerun at a higher irradiation time

(30 sec.) and just after the multichannel was calibrated for these nuclides. The data were very close to that obtained from the single-channel analysis. This data was presented in Table XVII in parentheses.

In light of improved data it appeared that the three systems containing bromine produced the same organic yields in the region of monomolecular dispersion, within experimental error, for each of the processes investigated. At the higher concentrations of halogen, 10^{-2} - 10^{-1} mf, the presence of iodine apparently reduced the organic yields of all three processes observed, I_2 being the more effective. At 10^{-3} mf halogen, the effect that iodine had on bromine organic yields at higher concentrations was effectively gone. The scavenging effect of bromine appeared to operate in the same halogen concentration range as iodine and iodine monobromide, indicating a similarity in structure but a difference in reactivity among the species, I_2 , Br_2 and IBr .

The scavenging effect of ICl , IBr and Br_2 on ^{128}I organic yields showed a similar trend over the concentration ranges studied, but ICl appeared to be somewhat more effective than the other two. The fact that ^{128}I O.Y.s were somewhat lower than 50% in the 10^{-4} - 10^{-5} mf ICl region was somewhat puzzling. Perhaps it was an experimental artifact.

The data showed that ICl was the most effective scavenger in ^{127}I (n, γ) ^{128}I reactions and I_2 or the combination of I_2 and Br_2 was the most effective scavenger in the nuclear reactions observed for bromine. Since the ^{38}Cl O.Y.'s were unaffected by the presence of relatively large amounts of ICl , it seemed quite evident that only the hot reactions produced organic combination.

The isotope effects persisted in the presence of several different scavengers even though the organic yields were significantly reduced.

This would tend to indicate a difference inherent in the reactive species and not the type of process, e.g. hot versus thermal reactions.

The organic yields due to the ^{37}Cl (n, γ) ^{38}Cl , ^{127}I (n, γ) ^{128}I , ^{79}Br (n, γ) $^{80}\text{Br}^m$, ^{81}Br (n, γ) $^{82}\text{Br}^m$ + ^{81}Br (n, γ) ^{82}Br and $^{82}\text{Br}^m$ (IT) ^{82}Br processes as a function of ICl , I_2 , Br_2 , IBr and $\text{I}_2 + \text{Br}_2$ in benzene at room temperature are presented in Table XVIII and Fig. 15. Several similarities between these systems and the same systems at 77° K were apparent; namely, (1) no scavenging effect in the ^{37}Cl (n, γ) ^{38}Cl process; (2) the isotope effects among the nuclear processes of bromine, and; (3) significantly higher scavenging in the bromine systems when iodine was also present. The one difference, which was mentioned earlier⁸¹, was the constant ^{128}I organic yields over the concentration range studied in the I_2 -benzene systems.

The fact that the ^{38}Cl organic yields were not affected by the change in phase agrees with previous results^{76,77} in several aliphatic systems containing chlorine. This is perhaps a reasonable result and indicates that the hot reaction(s) is independent of temperature and phase. However, several investigators^{75,78,79} have found the organic yield to increase considerably in the solid phase.

Chien and Willard⁷⁵ showed that the stable products of the ^{37}Cl (n, γ) ^{38}Cl reaction in liquid hydrocarbon-containing organic chlorides are all produced by "high energy processes". It would appear then that an increase in yield in going to the solid phase would be due to either a higher density of radicals formed by the high energy atom or to a different relative yield of different types of radicals when the medium is solid. Since the ^{38}Cl organic yield remains unchanged in going from liquid to solid benzene, one would expect a comparable product distribution.

Figure 15. Organic yields induced by various nuclear processes in liquid benzene as a function of halogen or interhalogen concentration.

It is interesting to note that in the presence of I_2 and IBr the apparent isotope effect between the $^{82}Br^m$ (IT) ^{82}Br and ^{81}Br (n,γ) ^{82}Br + ^{81}Br (n,γ) $^{82}Br^m$ processes disappeared, whereas the $^{80}Br^m$ O. Y.s by (n,γ) remained significantly lower than the O.Y.s produced by the other two nuclear processes. Also of special note was the increase in 128 O.Y.s with decreased mf of halogen in all systems except the I_2 -benzene system. Essentially analogous trends occurred in the case of bromine organic yields. Thus, there was apparently little or no self-scavenging in the liquid state systems containing one halogen but it was noticeable in mixed halogen systems. Although the ^{38}Cl O.Y.s were not affected by the ^{127}I (n,γ) ^{128}I process, the ^{128}I O.Y.s were enhanced by the ^{37}Cl (n,γ) ^{38}Cl process as well as by the various nuclear processes of bromine. The various bromine organic yields were depressed by the ^{127}I (n,γ) ^{128}I process by approximately the same extent in the IBr -benzene and $(I_2 + Br_2)$ -benzene systems.

The species, I_2 and IBr , appeared to be about equal in scavenging ability for the various nuclear reactions of bromine; both being much more effective than Br_2 , which hardly had any effect at all. The presence of iodine depressed the organic yields of the various bromine nuclides, but the presence of bromine and chlorine tended to raise the ^{128}I organic yields, especially at lower mf's of halogen. The higher ^{128}I O.Y.s may have been due to enhanced radical formation which readily reacted with thermalized ^{128}I as well as scavenger molecules containing iodine.

From these results, it seemed that no self-scavenging occurred in systems containing one halogen in liquid benzene for presumably different reasons. In the Cl_2 -benzene system no scavenging occurred presumably

because all thermalized ^{38}Cl atoms formed HCl .~ In the I_2 -benzene system, and possibly the Br_2 -benzene system, there appeared⁸¹ to be more favored (at room temperature) competitive reactions which prevented any significant amount of the thermalized species from reacting with excited organic moieties. Since a previous study⁹³ showed that the number of detectable species increased in going from iodo- to bromo- to chlorobenzene, it seems reasonable that the ^{128}I O.Y.s increase when either chlorine or bromine nuclear reactions occur along with the ^{127}I (n, γ) ^{128}I process. Perhaps bromine organic yields would also increase in mixed systems containing chlorine, unless the scavenging ability of Br_2 were particularly poor. The conclusion one may draw here, admittedly limited in scope, is that the organic yields of a given halogen are dependent upon the nuclear reaction, i.e. what excited species it produces, the reactions among the various species produced and the scavenging ability of the cold and hot species of halogen present.

Product Distribution of Radioiodine +
Radiochlorine and Radiobromine

The results of a previous study⁹³ of nuclear reactions of halogen in aromatic systems established the following: (1) Halogen atoms activated by nuclear processes in aromatic systems produced fewer products than in aliphatic systems. (2) Iodobenzene by (n, γ) produced only one readily detectable organic iodide containing ^{128}I . Bromobenzene produced six labeled products and chlorobenzene, thirteen. (3) The organic product distribution of radiobromine by (n, γ) in solutions of 3 mole % Br_2 in

C_6H_5F , C_6H_5Cl or C_6H_5Br was essentially the same as by (IT). (4) For solutions of 3 mole % Br_2 in C_6H_5Br , C_6H_5Cl and C_6H_5F , the O.Y.s from the ^{81}Br (n, γ) ^{82}Br process were about 34, 34 and 22% respectively, while the yields of C_6H_5Br were about 22, 16 and 3%.

For the sake of simplicity, only ^{82}Br labeled organic products were investigated in the IBr - and $(I_2 + Br_2)$ -benzene systems at 5×10^{-3} mf I_2 . The only readily measureable products besides bromobenzene were the dibromobenzene isomers. In the two systems containing iodine and the Br_2 -benzene systems, the ^{82}Br labeled dibromobenzenes produced between 3-4% of the activity compared to the ^{82}Br -containing bromobenzene which was assigned a value of 100%. In the solid state, the dibromobenzene yields were higher, around 31%, but there were no differences between systems. The scavenging by the IBr and I_2 species appeared to be non-selective. Iodine-131 or -129 could have been used in an attempt to analyze the iodine labeled products, but impurities introduced in the process of oxidizing the ions and dissolving the I_2 into benzene tend to produce major variations in yield.⁹³

The product distribution due to the ^{127}I (n, γ) ^{128}I and ^{37}Cl (n, γ) ^{38}Cl processes in the ICl -benzene system was analyzed at 5×10^{-2} and 5×10^{-4} mf ICl in both solid (77° K) and liquid systems and compared to analogous I_2 -benzene systems. In all systems containing ICl a measureable fraction of the iodine activity showed up in compounds eluted in advance of iodobenzene whereas essentially none showed up in the I_2 -benzene systems. Apparently, one effect of the nuclear processes of chlorine was the production of fragments (ions, radicals, excited species or some form capable of reacting with iodine) which reacted with the labeled iodine.

Here, a much better system for study would be ^{129}ICl - or ^{131}ICl -benzene since this would allow one to analyze the iodine activity after all of the ^{38}Cl activity was gone.

CHAPTER VI

RADIATIVE NEUTRON CAPTURE REACTION OF IODINE AND IODINE MONOCHLORIDE IN SELECTED ALKYL BENZENES

CHAPTER VI

Radiative Neutron Capture Reaction of Iodine and
Iodine Monochloride in Selected Alkylbenzenes

In a study⁹⁵ of the reactions of benzene, toluene, para- and ortho-xylene and mesitylene with ^{80}Br as a result of isomeric transition, it was found that both KOH hydrolyzable and nonhydrolyzable organic bromides were formed. The total organic yield produced in benzene was lower than in the alkylbenzenes, but the percent of nonhydrolyzable organic bromide was higher in benzene. Increased bromoacetic acid concentration or temperature increased the hydrolyzable organic yield in all systems but neither had any significant effect on the nonhydrolyzable yields. It appeared as though the hydrolyzable fraction was due to thermal reactions and the nonhydrolyzable due to hot reactions.

In a recent study⁹⁶ on the effects of γ -irradiation on n-alkylbenzenes, it was found that the $G(\text{H}_2)$ values in systems at 77° K increased with alkyl chain length while the $G(\text{R})$ values at 93° K did not increase regularly. Ethylbenzene had a lower $G(\text{R})$ value than toluene and propylbenzene had a larger $G(\text{R})$ value than either butylbenzene or amylbenzene. Also, of general note, in liquid n-alkylbenzenes and at 77° K, energy transfer from an excited alkyl group to the phenyl group was about 13 times as fast ($P_1 \sim k_i$) as deactivation and dissociation together.

In order to investigate thyroxine and related compounds with hot atom chemistry probes, preliminary studies of alkylbenzenes was considered important in exploring the relationship of the alkyl side chains to aromatic

nuclei. The study was carried out with $^{127}\text{I}_2$, $^{129}\text{I}_2$ and ICl in liquid and solid state alkylbenzenes through arylbenzenes.

Phillips research grade toluene; ethylbenzene; cumene; n-butylbenzene; sec-butylbenzene; tert-butylbenzene; sec-arylbenzene; ortho-, meta- and para-xylene; and 1,2,4-trimethylbenzene were investigated using the above mentioned halogens. Comparative organic yields, scavenging and isotope effects and product distributions were carried out and the results were compared to similar benzene systems.

Organic Yield Scavenger Studies at 25° C

Presented in Table XX are the ^{128}I organic yields of the 11 alkylbenzenes and benzene at I_2 mole fractions from 10^{-5} to $>10^{-2}$ and the ^{130}I organic yields due to (n, γ) and (n, γ) + (IT) processes in the same hydrocarbons at 10^{-3} mf $^{129}\text{I}_2$ (+ $^{127}\text{I}_2$).

Unlike benzene, a significant drop in organic yield occurred with increased iodine concentration in each of the alkylbenzenes. It should be noted that due to the differences in iodine solubility, the comparison of ^{128}I organic yields in saturated solutions may not be very meaningful except to indicate that further scavenging beyond 10^{-2} mf I_2 occurs. The greatest drop in organic yields in the 10^{-5} to 10^{-2} mf I_2 range occurred in the systems of I_2 in ethylbenzene, cumene, tert-butylbenzene and sec-arylbenzene. It was noted that in these four systems, a considerable portion of the organic iodides decomposed, forming free iodine in quantities large enough to produce color in the organic phases some hours after extraction. Although attempts to identify the unstable compound(s) were

TABLE XX

ORGANIC YIELDS INDUCED BY $^{127}\text{I}(\text{n},\gamma)$, ^{128}I , $^{129}\text{I}(\text{n},\gamma)$, ^{130}I , $^{129}\text{I}(\text{n},\gamma)^{130\text{m}}\text{I}$,
 AND $^{130\text{m}}\text{I}(\text{IT})^{130}\text{I}$ REACTIONS AT VARIOUS MOLE FRACTIONS OF
 IODINE IN ALKYL BENZENES AT ROOM TEMPERATURE

Isotope	mf of I_2 1.0 x	Organic Yield ^a				
		Benzene	Toluene	Ethyl Benzene	Cumene	t-butyl Benzene
$^{128}\text{I}(\text{n},\gamma)$	10^{-5}	19.4	29.5	36.2	35.1	34.3
	10^{-4}	18.5	25.8	28.6	26.1	29.8
	10^{-3}	17.4	23.8	24.4	24.2	27.0
	10^{-2}	16.9	21.1	16.4	19.3	23.5
	Sat'd	16.4	19.1	15.3	18.8	17.5
$^{130}\text{I}(\text{n},\gamma)$	10^{-3}	18.6	24.7	25.2	24.9	27.3
$^{130}\text{I}(\text{n},\gamma+\text{IT})$	10^{-3}	18.5	24.6	24.5	25.0	27.4
	mf of I_2					
		m-butyl Benzene	O-xylene	M-xylene	P-xylene	S-butyl Benzene
$^{128}\text{I}(\text{n},\gamma)$	10^{-5}	37.9	39.1	33.9	38.1	33.4
	10^{-4}	32.5	32.7	31.5	34.1	28.5
	10^{-3}	29.5	31.1	28.7	29.8	27.8
	10^{-2}	25.6	28.6	26.4	26.9	22.0
	Sat'd	16.9	22.5	21.1	14.4	18.1

TABLE XX (Continued)

Isotope	mf of I ₂	m-butyl Benzene	O-xylene	M-xylene	P-xylene	S-butyl Benzene
¹³⁰ I(n,γ)		28.7	31.8	28.7	29.1	27.3
¹³⁰ I(n,γ+IT)		27.3	34.8	27.6	32.0	26.5
	mf of I ₂	Pseudo Cumene	Sec-amyl Benzene	---	---	---
¹²⁸ I(n,γ)	10 ⁻⁵	42.8	49.9			
	10 ⁻⁴	40.5	49.7			
	10 ⁻³	35.4	46.3			
	10 ⁻²	31.3	31.8			
	Sat'd	17.1	---			
¹³⁰ I(n,γ)	10 ⁻³	35.6	---			
¹³⁰ I(n,γ+IT)	10 ⁻³	35.6	---			

(a) Results of at least three determinations

unsuccessful, compounds such as benzyl iodide and 1-iodo-1-phenylethane were indicated.

Another trend which was not surprising was the increase in iodine organic yields both with an increase in alkyl chain length and with an increase in the number of methyl groups on the ring. However, when the eleven alkylbenzenes were very highly scavenged with I_2 , the ^{128}I O.Y.s were all about the same as in the I_2 -benzene system, which perhaps indicated that reactions involving the alkyl side chains involved thermal reactions.

In an attempt to look for isotope effects in these I_2 -alkylbenzene systems, the ^{129}I (n, γ) $^{130}I + ^{130m}I$ and the ^{129}I (n, γ) $^{130}I + ^{130m}I$ (IT) ^{130}I processes carried out at 10^{-3} mf $^{129}I_2$ (+ $^{127}I_2$). Within experimental error the ^{130}I O.Y.s from these process were the same as the ^{128}I O.Y.s from the ^{127}I (n, γ) ^{128}I process.

Although the aromatic nucleus plays a big role⁹⁶ in energy transfer from an excited alkyl group in gamma radiolysis, a rather sizeable portion of the organic yield from the ^{127}I (n, γ) ^{128}I process involves the side chain(s) directly or indirectly. Product distribution was attempted but no satisfactory column for the higher boiling iodide could be found; however, sizeable quantities of low molecular weight alkyl iodide, C_1 - C_3 , were identified.

Organic Yield Studies of I_2 - and ICl -Alkylbenzene Systems at 77° K and Product Distribution

Benzene and iodine have been shown⁸⁵ to form a solid electron-donor-

acceptor complex at 77° K. This model would explain the relatively high and constant ^{128}I (and ^{130}I) organic yields in this system in the range of 10^{-6} to 10^{-3} mf. I_2 . Since organic yields induced by nuclear transformations have been shown^{51,73} to give information concerning the state of aggregation and tendency toward complexing, I_2 - and ICl -Alkylbenzene systems at 77° K were studied to obtain this and possibly other information about these systems.

The ^{128}I and ^{38}Cl organic yields produced by the ^{127}I (n, γ) ^{128}I and ^{37}Cl (n, γ) ^{38}Cl processes in the I_2 - and ICl -Alkylbenzene systems are shown in Table XXI. The O.Y. plateau found in the I_2 -benzene system showed up in the same region, 10^{-3} mf I_2 (and ICl) less, in the I_2 - and ICl -alkylbenzene systems studied. The ^{38}Cl organic yields were around 20% in each of the alkylbenzenes studied regardless of the mole fraction of ICl present. Apparently the rather sharp drop in the ^{128}I organic yields at 10^{-2} mf ICl in the alkylbenzene solvents was not due to any gross clustering but rather the formation of a complex where effective competitive reactions reduced the ^{128}I yields.

The product distribution from the ^{127}I (n, γ) ^{128}I process in several I_2 -alkylbenzene systems is presented in Table XXII. The major product in each case was methyl iodide, except in the case of the I_2 -ethylbenzene system, which produced essentially equal quantities of methyl and ethyl iodide as the major products. It was somewhat unexpected that no iodo-benzene was detected in any of the systems studied since the product distribution indicated that relatively large quantities of alkyl groups were formed during the ^{127}I (n, γ) ^{128}I process. The column did not produce in separation of iodinated parent molecule isomers so the structure of the

TABLE XXI
EFFECT OF ICl CONCENTRATION ON ^{128}I AND ^{38}Cl ORGANIC YIELDS IN VARIOUS
ALKYLBENZENES AND CYCLOPROPANE AT 77° K

mf ICl	Organic Solvent	^{128}I Organic Yield ^a	^{38}Cl Organic Yield ^a
10^{-2}	Benzene	29.3	21.5
	Toluene	23.6	20.2
	Ethylbenzene	24.0	20.1
	Cumene	22.6	19.4
	Pseudocumene	22.5	19.6
	n-Butylbenzene	21.8	18.8
	Cyclopentane	12.4	14.3
10^{-3}	Benzene	43.4	22.3
	Toluene	38.8	20.6
	Ethylbenzene	28.6	21.1
	Cumene	38.4	18.8
	Pseudocumene	38.4	20.1
	n-Butylbenzene	29.6	19.4
	Cyclopentane	38.0	14.1
10^{-4}	Benzene	45.7	21.8
	Toluene	40.2	21.1
	Ethylbenzene	38.6	20.6
	Cumene	41.3	19.4
	Pseudocumene	41.3	20.2
	n-Butylbenzene	37.8	18.8
	Cyclopentane	44.0	14.2
10^{-5}	Toluene	39.9	
	Ethylbenzene	38.4	
	Cumene	42.1	
	Pseudocumene	42.3	

TABLE XXI (Continued)

mf ICl	Organic Solvent	^{128}I Organic Yield ^a	^{38}Cl Organic Yield ^a
10^{-5}	n-Butylbenzene	38.2	
	Cyclopropane	59.6	

(a) All samples were irradiated for ten seconds.

TABLE XXII
 PRODUCT DISTRIBUTION FROM THE $^{127}\text{I}(n,\gamma)^{128}\text{I}$ PROCESS IN SOLID STATE
 ALKYL BENZENES AT $77^\circ\text{K}^{(a)}$

Solvent	CH_3I	$\text{C}_2\text{H}_5\text{I}$	$\text{C}_3\text{H}_7\text{I}$	Products			
				$\text{C}_7\text{H}_7\text{I}$	$\text{C}_8\text{H}_9\text{I}$	$\text{C}_9\text{H}_{11}\text{I}$	$\text{C}_{10}\text{H}_{13}\text{I}$
Toluene	100.0			16.8			
Ethylbenzene	100.0	100.0			38.8		
Cumene	100.0	22.3	69.0			11.2	
t-Butylbenzene	100.0						11.0

(a) 10^{-3} mf I_2 present in all samples-Irradiation time was 6 minutes.

higher boiling iodide was not elucidated. The spontaneous production of free iodine occurred in the organic phases of the extracted ethylbenzene-, cumene- and tert-butylbenzene-I₂ systems as it did in the liquid phase systems. Attempts were made to determine the amount of free iodine released, with less than satisfactory results.

Of particular interest was the decreased ¹²⁸I O.Y.s in the ICl-alkylbenzene and ICl-benzene systems at 10⁻⁴-10⁻³ mf halogen compared to the analogous systems containing I₂ at 77° K since the reverse was true in I₂- and ICl-benzene systems at room temperature. In the liquid phase systems of ICl and benzene, it was concluded that the increase in organic yield over that in the I₂-benzene systems was due to thermal reactions between thermalized ¹²⁸I atoms or ions and radicals (or some other excited species) produced by the ³⁷Cl (n,γ) ³⁸Cl process. The most logical explanation for the reduced ¹²⁸I organic yields in solid state ICl-aromatic systems compared with analogous I₂- aromatic systems is a difference in the structure of the complexes believed to be formed in these systems. Should this prove to be the case, this would be another piece of evidence pointing to the usefulness of organic yields in elucidating structure, particularly where other means are limited by lower limits of concentration.

INTEGRATING SUMMARY

INTEGRATING SUMMARY

Cyclopentane, benzene and selected alkylbenzenes were probed both in the liquid and solid phases with nuclear processes induced by the neutron activation of one or more of the following species: $^{127}\text{I}_2$, $^{129}\text{I}_2$, Br_2 , ICl and IBr . Of particular interest in each of the systems were the following: (1) isotope effects due to (n,γ) and (IT) processes; (2) individual and comparative scavenging effects in the liquid phase systems of the various halogens and interhalogens; (3) crystalline structure at 77°K , and; (4) product distributions of organic halides.

As in previous studies of the ^{127}I (n,γ) ^{128}I , ^{129}I (n,γ) ^{130}I and $^{130}\text{I}^m$ (IT) ^{130}I processes in aliphatic hydrocarbons, the ^{128}I and ^{130}I (by IT) organic yields in cyclopentane were essentially the same and in the range of 1.2 to 1.4 times higher than the ^{130}I (by n,γ) organic yields. Of further similarity was the product distribution which was seemingly independent of the nuclear process and phase. The major organic product was found to be iodocyclopentane although in the iodine-cyclohexane system the major product was reported to be the hexyl iodides. In comparing the ^{128}I and ^{38}Cl organic yields in the solid state I_2 - and ICl -cyclopentane systems, it was found that although the ^{128}I O.Y. plateaus cover about the same concentration range (2×10^{-5} and lower mf of I_2 and ICl) the ^{38}Cl O.Y. plateau starts somewhat lower, approximately 10^{-4} mf ICl , thus indicating that the ^{38}Cl organic yields are probably a better guide to fractional crystallization.

All of the nuclear processes used in this study were used in the study of benzene in order to thoroughly probe this aromatic system found in thyroxine and related compounds. The study of the alkylbenzenes was made

to further lay the groundwork for future study of certain amino acids and hormones containing one or more aromatic nuclei.

It was found that essentially no scavenging effect occurred in liquid I_2 - and Br_2 -benzene systems, and ^{38}Cl organic yields were not affected by either ICl concentration or phase effects in benzene. In liquid benzene systems containing two halogens both bromine and iodine showed a significant scavenging effect ($^{80}Br^m$, $^{82}Br + ^{82}Br^m$, ^{128}I and ^{82}Br organic yields). The nuclear processes of both chlorine and bromine tended to increase the ^{128}I organic yields in liquid benzene while the ^{127}I (n,γ) ^{128}I process generally lowered the bromine isotope organic yields and had no effect on the ^{38}Cl O.Y.s. In liquid I_2 -alkylbenzene systems, a self-scavenging effect was quite evident in all of them. The ^{128}I organic yields were generally higher at 10^{-5} mf I_2 than in the I_2 -benzene system but became approximately equal in saturated solutions.

The product distribution studies along with the comparative organic yield studies in the liquid systems indicated that the number of different products produced by the nuclear processes of the halogens increases as one goes from iodine to bromine to chlorine, whereas relative "scavenging" ability is in the reverse order. The increased ^{128}I O.Y.s in mixed systems is apparently due to thermal reactions of ^{128}I species with excited species produced by either bromine or chlorine nuclear processes. The decreased bromine isotope organic yields appear to be caused by the enhanced scavenging of excited species by I_2 and ^{38}Cl O.Y.s are constant since there are no thermal reactions of ^{38}Cl atoms (or ions).

In solid state systems of benzene and the various halogens and inter-halogens, isotope effects occurred between ^{129}I (n,γ) $^{130}I + ^{130}I^m$ and

^{129}I (n, γ) ^{130}I + $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I processes and the various nuclear processes of bromine studied. There was also an appreciable difference in the ^{79}Br (n, γ) $^{80}\text{Br}^{\text{m}}$ and ^{81}Br (n, γ) ^{82}Br processes in liquid benzene. Since the presence of extremely small quantities of impurities were found to cover up or indicate isotope effects when the reverse was found at higher purity levels, only the isotope effect studies in the Br_2 -benzene systems were regarded with a high degree of confidence. The alkylbenzenes could not be purified well enough for such a study nor were such purities available commercially as was benzene.

Organic yield studies of Br_2 in benzene at 77°K produced two O.Y. plateaus, the various isotopes producing different but parallel curves. The lower curves between 5×10^{-1} and 5×10^{-2} mf Br_2 have been interpreted to indicate a region of uniform 1:1 complex to a mixture of complex plus pure solvent. The upper curves were interpreted here to be a monomolecular dispersion of Br_2 in benzene. Due to limitations in solubility, 5×10^{-2} mf I_2 in benzene was probably not reached in the solid state. Although ^{128}I organic yields in both the I_2 - and ICl -benzene systems indicated a monomolecular dispersion at 10^{-4} and lower mf I_2 and ICl , the ^{38}Cl O.Y.s remained at about 21% throughout the concentration range studied. Thus, although the ^{128}I O.Y.s dropped rapidly at higher concentrations of I_2 and ICl , apparently no significant clustering occurred. Iodine O.Y.s are seemingly a misleading guide to structure in aromatic systems at the present.

^{128}I and ^{38}Cl organic yields in solid state I_2 - and ICl -alkylbenzene systems resemble those in the analogous benzene systems, indicating complex formation with a probable difference between the ICl and I_2 systems since

the ^{128}I O.Y.s from ICl are consistently lower than those from I_2 except at 10^{-2} mf halogen. Product distribution of the I_2 -alkylbenzene systems indicate that alkyl side chains are quite vulnerable to attack by hot atom processes. Methyl iodide was the major product by far in several alkylbenzenes studied except in the case of ethylbenzene where ethyl iodide essentially equalled the methyl iodide formed. Also a large amount of an unstable organic iodide was formed in the I_2 -ethylbenzene, I_2 -cumene and I_2 -tert-butylbenzene systems.

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APPENDIX

APPENDIX

General Expression for Obtaining
Isomeric Transition Organic Yields

By using the "freeze-thaw" technique as a basis, Merrigan^{46,49} derived an expression for obtaining isomeric transition induced organic yields. A more general expression was later derived by Merrigan and Parks (See eq. 4).

In a system for which it is applicable, the observed organic yield, OY, for a freeze-thaw type experiment may be obtained as follows:

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

The organic yield (R^∞) due strictly to isomeric transition (IT) 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 the total activity produced by the decay of the metastable nuclide in the liquid state. This value is obtained by dividing Eq. 1 by the term, $\beta e^{-\lambda t}$, where β is the fraction of the total activity (TA) produced by (IT) in the liquid state, and $e^{-\lambda t}$ describes the duration of time the sample was solid from the midpoint of irradiation to liquefaction.

$$\frac{OY_{Obs}}{\beta e^{-\lambda t}} = \frac{\text{Org. Act.}_{(IT)}^{(liquid)}}{\beta e^{-\lambda t} (TA)} + \frac{\text{Org. Act.}_{(IT)}^{(solid)}}{\beta e^{-\lambda t} (TA)} + \frac{\text{Org. Act.}_{(n,\gamma)}^{(solid)}}{\beta e^{-\lambda t} (TA)} \quad (2)$$

upon rearranging,

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

The organic activity induced by the (IT)-activation in the solid state is $(1-e^{-\lambda t})\beta$ times the observed solid state organic yield. The organic activity induced by the (n, γ)-activation in the solid state is α times the observed solid state organic yield, R^0 , where α is the fraction of the total activity produced by radiative neutron capture. In the case of $^{82}\text{Br}^m$ systems, α and β are 0.09 and 0.91, respectively⁵¹; and in the $^{130}\text{I}^m$ systems, α and β are 0.39 and 0.61, respectively.³³ By making the appropriate substitutions and rearranging, a general expression (Eq. 4) is obtained for aliphatic systems where the freeze-thaw technique is applicable.

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

It is necessary that R^∞ is not dependent upon the time of extraction within experimental error. As an example, the general expression for ^{130}I systems is as follows:

$$O.Y._{(IT)}^{(liquid)} = 1.71R^\infty - 0.71R^0 \quad (5)$$

PUBLICATIONS

Publications

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