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REACTIONS OF IODINE ACTIVATED BY RADIATIVE NEUTRON
CAPTURE AND ISOMERIC TRANSITION WITH GASEOUS
AND CONDENSED STATE POLYHALOMETHANES

A thesis by Norris J. Parks

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REACTIONS OF IODINE ACTIVATED BY RADIATIVE NEUTRON
CAPTURE AND ISOMERIC TRANSITION WITH GASEOUS AND
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University of Nebraska, 1969

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The organic yields of ^{130}I + $^{130}\text{I}^m$ activated by radiative neutron capture and those of ^{130}I activated by isomeric transition were found to decrease for the liquid systems studied in the order $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CFCl}_3 > \text{CCl}_4 \approx \text{CCl}_3\text{Br}$. The organic yields of (n, γ) activated $^{130}\text{I}^m$ + ^{130}I are consistently lower than the (IT) induced yields of ^{130}I . The products and their relative abundance were determined by radiogas chromatographic analysis. These determinations, together with other considerations, suggest the observed results may be primarily ascribed to variations in product stability which are related to variations in steric interactions among substituents of product molecules.

The reactions of (n, γ) activated ^{128}I with gaseous CH_3X , CH_2X_2 , CHX_3 , and CX_4 (X = F and/or Cl) were examined. The comparisons of total organic yields and indications that halogen replacement products are preferentially formed suggest that steric interaction between substitu-

ents of both reactant and product molecules is also an important factor controlling the extent of reaction in gaseous systems. The organic yields were found to decrease with increasing halogen substitution for the homologous halomethane series studied.

The similar yields of isomeric transition induced reactions of ^{130}I and the radiative neutron capture induced reactions of ^{128}I in liquid systems, and the finding that additives capable of efficient charge transfer reaction with the activated species in the gas phase effectively inhibit (n,γ) induced reaction of ^{128}I with the target system are indications that the reactive species are ions possessing excess kinetic and/or electronic energy.

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CONDENSED STATE POLYHALOMETHANES

by

Norris Jim Parks

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CHAPTER I
INTRODUCTION

Chapter I

Introduction

Nuclear transformations produce species that permit the study of high energy chemical interactions over a wide range of reactant energies that may be considerably greater than the minimum activation energies attained in thermal reactions. All nuclear activation yields product atoms which initially have high kinetic energy or electrical charge or both. Nuclear processes that have been successfully employed in studies of high energy chemical reactions are (p,n) , $(n,2n)$, (n,p) , (n,γ) , and (IT) . One of the most commonly employed nuclear activations is radiative neutron capture, (n,γ) , requiring a nuclear reactor, neutron generator, or other neutron source. The extensive use of this process is due to the relative availability of neutrons; the relative ease of using them under conditions where radiation damage and temperature effects are not serious; favorable cross sections for 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 Nuclear activation may yield a product nuclide in a metastable nuclear state. The decay of this state to the ground

state (isomeric transition) may result in a second activation as a consequence of internal conversion and associated Auger radiation processes. The nuclear activation methods employed in this research were the (n, γ) and (IT) transformations and subsequent discussion will refer to either or both of these processes.

Previous work discussed by several reviews¹⁻⁷, has posed several important questions. Predominant among these are: (1) The relative importance of kinetic energy and of charge in determining the chemical fate of the atoms studied; and (2) the effect of phase and target molecule properties on the mechanisms which lead to chemical stabilization. The criteria which must be met in the study of high energy reactions of this type are that the nuclear processes produce a radioactive nuclide and that the stable compounds which are formed by the product atoms do not undergo thermal exchange with each other or with environmental molecules.

Historical Background

Chemical effects of nuclear transformations were first demonstrated by Szilard and Chalmers⁸ in 1934 when they found that a portion of the ^{128}I produced in liquid ethyl iodide by radiative neutron capture splits off from the parent molecule and becomes stabilized in inorganic

form. They believed that the breaking of the C-I bond resulted from the physical process of momentum transfer from the neutron to the iodine atom. Shortly thereafter, Amaldi, Fermi, et al.⁹, found the bond breaking to result from the recoil energy imparted by the emission of gamma rays as the compound nucleus de-excites. Further investigation of the reactions of recoil halogens with several alkyl halides demonstrated that organic bonding of the activated atom may also occur.¹⁰

Since 1934 there have been over 300 papers published on the effects of nuclear transformations in organic systems, and therefore, a comprehensive discussion of all historically pertinent information will not be presented.

The various aspects of the chemical effects of nuclear transformations have been adequately summarized through 1967 by several reviewers. Willard^{1,2,11-13} has reviewed the literature concerning the reactions of activated halogen atoms. The kinetics and mechanism of nuclear recoil induced reactions of carbon and tritium are discussed by Wolfgang^{3,4}, Filatov⁶, and Wolf.¹⁴ Solid state reactions of nuclear activated isotopes have been examined by Campbell¹⁵, Walton¹⁶, Mueller¹⁷, Harbottle¹⁸, and Anderson.¹⁹ Other information includes a bibliography of

publications in hot atom chemistry* through 1962 by Suida²⁰ and the proceedings of two symposia on the chemical effects of nuclear transformations sponsored by the International Atomic Energy Agency.²¹

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

The first extensive attempt to explain the mechanism of hot atom reactions of halogens was made by Libby²² in 1947. He developed the "billiard-ball collision" hypothesis and later, in a co-authorship with Friedman, the "billiard-ball collision--epithermal collision" hypothesis.²³ He postulated that halogen atoms recoiling with a few hundred electron volts of energy in liquid or solid alkyl halides lose their energy by momentum transfer in elastic collisions with single atoms, and inelastic collisions with whole molecules when the energy of the recoil atom is re-

* The term "hot atom" will refer to all activated species possessing excess translational energy.

duced to the order of 10 e.v. by successive collisions. However, this hypothesis was oversimplified and could not give consistent correlation with the growing volume of experimental facts. In recent studies by Milman²⁴ and Mallison, et al.²⁵, a molecular model was found to be consistent with data obtained in particular cases, but in general the molecular models have difficulty in correlating existing data.

A more realistic and successful mechanistic theory of hot atom reactions in the condensed state was that of Willard¹² called the "random fragmentation", "brush heap", or "nest of radicals" hypothesis. Willard treated condensed state reactions in terms of kinetic energy dissipation and charge neutralization of the hot atom within a small volume element of the solution, which produced high concentrations of radicals, ions, and excited molecules in the region where the tagged atom deaccelerated to thermal energies. According to Willard, when a halogen atom in a liquid phase molecule acquires several hundred e.v. of recoil energy it accelerates rapidly and breaks its chemical bonds, but having traveled less than a molecular diameter it encounters a solvent molecule backed by and surrounded by a close packed and sometimes intertwined wall of other molecules. The result is that the energy is dissipated by breaking bonds in an indiscriminate

fashion in the vicinity of the hot atom. When the energy of the atom has been reduced below bond-breaking energies it is in, or adjacent to, a pocket of high local concentration of organic radicals and inorganic atoms. It may combine with one of these in a hot atom reaction before becoming thermalized, or enter into chemical combination by diffusion of the thermal atom if it escapes a hot atom reaction. Willard's approach was realistic but too qualitative and thus had limited quantitative applications.

One of the most significant studies was by Hornig, et al.²⁶, who found hot atom reactions to occur in the gaseous state between ^{128}I formed by radiative neutron capture of iodine in the presence of methane. This discovery led to more investigations in gaseous systems which until then had been assumed to produce no significant organic reactions of the hot atom. These investigations, especially using tritium, resulted in the development of a mathematical model by Estrup and Wolfgang^{27,28}, based partially on the mathematics of neutron cooling, to describe the kinetics of hot atom reactions in the gas phase. Miller, et al.²⁹ developed a mathematical model for recoil reactions in liquids, using the same concept, but a specific reaction mechanism, the cage model of Libby^{22,30}, to evaluate the kinetic expressions. These efforts met with little success probably because of the inadequacy

of the underlying mechanistic model. The Estrup and Wolfgang kinetic theory does not assume any model for the reaction itself. It is semi-empirical in nature and can provide a rigorous test of experimental data. The kinetic theory has been applied to reactions of hot tritium atoms with a number of hydrocarbons^{31,32} and with mixtures of hydrogen and methane.³³ It has also been used for analysis of the hot atom reaction of ^{18}F with CF_4 , by Wolfgang, et al.³⁴ Rack and Gordus were the first to show applicability of the kinetic model to hot atoms other than tritium by employing it to correlate reactions of ^{80}Br with CH_4 and ^{128}I with CH_4 .³⁵⁻³⁷ Their investigations provided definitive evidence regarding the ratio of kinetic energy dependent reactions to those of translationally thermalized but electronically excited ions.

Applications of the kinetic theory to liquid systems has been difficult due to a lack of suitable, non-reactive moderators. A recent effort was made by Milman to correlate data gathered in liquid organic halide systems³⁸ and hot bromine atom reactions in various organic liquids²⁵ with the Estrup-Wolfgang theory. Although the data support the theory, they may not represent true results from a single type of hot atom process.³⁹ Filatov, et al.⁴⁰ have also made kinetic analyses of certain recoil halogen reactions in liquid systems. This work incorporates some

assumptions of the mechanisms of reactions based largely on elastic collision models which seem to have limited applicability in the condensed systems.

Recently Geissler and Willard⁴¹ suggested another hypothesis as to the mechanism of hot atom reactions of halogens in liquid systems. This concept is commonly called the "Auger electron reaction" hypothesis. From their work with iodine and bromine, they noted that qualitatively similar products were formed by iodine or bromine atoms in a given solvent when activated by (n,γ) , (γ,n) , (d,p) , $(n,2n)$, or (IT) processes, and by irradiating with gamma rays. Since the activations result in varying amounts of kinetic energy imparted to the hot atom and nearly zero energy imparted in an isomeric transition, the fact that products are qualitatively similar and quantitatively the same in some cases indicates that the hot atoms may pass through a stage common to all activations. "If all the nuclear processes produce nuclei which pass through low-lying metastable levels which decay by internal conversion, the similarity of products could be explained in terms of the Auger radiation hypothesis."⁴¹ The energies of electrons emitted by ^{128}I would include the energy of the conversion electron, electrons with the energy of $L \rightarrow K$ transitions minus the L binding energy, i.e., about 20 kev., and in the case of highly charged

ions, additional electrons in the range of a few kev. down. Each of these electrons would excite and ionize molecules of the solution in the close proximity of the ^{128}I ion from which they came. Thus, a hot ion which has emitted several Auger electrons would be in the center of a highly localized concentration of species such as those found along the track of a Compton electron in a similar solution exposed to gamma radiation. The hot ion would rapidly neutralize by charge transfer with adjacent molecules if its ionization potential were higher than that of the solvent molecules. The probable fate of the atom thereafter would be combination with a radical which was formed from the activation of the surrounding solution by conversion and Auger electrons.

Geissler and Willard's hypothesis was given added support by the work of Thompson and Miller⁴² in their observations of the sequence of events following (n, γ) reactions in condensed phases. The initial recoil energy of the hot atom was due to gamma ray emission and was imparted to the recoil atom in less than 10^{-13} sec. after neutron capture. The high energy atom then followed a short and deviating path becoming stabilized chemically and/or thermalized only a few atomic diameters from the site of activation. The ejection of one or more conversion electrons, followed by loss of other electrons by

Auger radiation, occurred most frequently 10^{-12} to 10^{-5} sec after neutron capture. Thus charge buildup could occur long after the hot atom was brought to thermal energies and had the opportunity to become chemically stabilized.

If the Auger electron reaction hypothesis is valid, it implies that metastable nuclear states in hot atoms are sufficiently long-lived so that nuclear activation by internal conversion does not occur until after the atom has lost its recoil energy (as confirmed by Thompson and Miller⁴²) or that the length of the recoil path in the condensed phase is within the dimensions of the localized volume of high radical concentration produced by the electrons emitted in the nuclear activation process. Both possibilities are reasonable.

It should be noted that at least one mechanism other than that proposed by the "Auger electron reaction" hypothesis must contribute to the total organic yield observed in condensed iodine-scavenged systems.⁴¹ This is the displacement type of reaction, which has been observed in the gas phase, by which the recoil iodine atom or ion replaces a substituent from an organic molecule in a bimolecular process. With the exception of reactions of activated ^{128}I with CH_4 , the total organic yields of this type of process are only a few percent;^{37,43} however, it is not implausible that a change in phase may allow

considerable contribution by this type of reaction to the total yields observed in condensed systems.

Nuclear Activation

When nuclei are subjected to a high neutron flux, there is a probability that a certain proportion of them (depending on cross sections for neutron capture, magnitude of the flux, and time of irradiation) will capture a neutron and become activated with the energy equivalent of the neutron binding energy of the nuclei. The nuclear activation properties of the isotopes used in this are presented in Table I.

A compound nucleus, formed by thermal neutron absorption, is in an excited state. It is assumed from the compound nucleus model that the energy imparted by the incident particle is randomly distributed among all the nucleons in the compound nucleus such that none of the nucleons have enough energy to escape immediately. Considerations of nuclear theory indicate the compound nucleus has a lifetime of about 10^{-14} to 10^{-15} sec., and decays as a function of its energy, angular momentum, and parity, but not mode of formation.⁴⁴ The excess energy, equivalent to the neutron binding energy of the nuclei, can be dissipated by the emission of a combination of gamma radiation and conversion electrons. Conservation of momentum requires

Table I. Nuclear Activation Properties of Halogen Isotopes

Nuclear Activation Process	(n,γ) Thermal Neutron Cross Section (Barns)	Neutron Binding Energy of Product Nucleus (Mev) ^a	Halflife 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%

^aCalculated from nuclear masses⁴⁴ and disintegration energies.⁴⁶ For details, see reference 44.

^bThe internal conversion coefficients, i.e., the ratio of conversion electrons to gamma-rays emitted for ¹³⁰I^m isomeric transition processes is >>1.⁴⁷ Thus nearly all of the (IT) activated iodine is charged.

that the recoil energies of the nuclei resulting from gamma-emission will vary from zero to a maximum of $(537 B^2/M)$ ev for the emission of a single gamma ray. B is the neutron binding energy and M is the atomic mass of the activated atom. For example, when an ^{127}I nucleus absorbs a neutron, the binding energy, 6.8 mev,⁴⁴ if released in the form of a single gamma ray of 6.8 mev energy, would impart to the ^{128}I nucleus an energy of 182 ev. The other isotopes (^{130}I , $^{130}\text{I}^m$ and ^{38}Cl) whose chemical reactions are the subject of this thesis, have similar values. Since the release of all the neutron binding energy in a single γ -ray is unlikely, the average recoil energy is estimated to be ≈ 100 ev. Emission of more than one gamma ray results in an energy spectrum ranging from zero (due to momentum cancellation by emission in opposite directions) to the maximum kinetic energy. The probable distribution of the recoil energy transferred as a result of nuclear processes has been discussed.⁴⁵ Unfortunately, because of the complex structure of the gamma spectra, little information has been obtained regarding the neutron capture gamma-ray decay schemes of iodine isotopes used in this research. However, the energy equivalent to the neutron binding energy of the nuclei serves as a relative measure of the expected maximum gamma-emission energy following neutron capture.

Charge State and Electronic Excitation Energy

A recoil atom can acquire a positive charge and electronic excitation energy as a result of internal conversion of the neutron capture gammas and the emission of Auger electrons. Internal conversion is an electromagnetic interaction between the nucleus and the extra-nuclear electrons leading to nuclear de-excitation.⁴⁸ The lifetime of an excited nuclear state is on the order of 10^{-17} to 10^{-12} sec. However, the excited state may have a lifetime long enough to be measured; if the angular momenta (spin) of the excited state and the ground state are different.⁴⁹ The decay of long-lived metastable states is called isomeric transition. The emission of isomeric transition gammas or internal conversion electrons impart negligible recoil energy to the nuclide.

The iodine isotopes, ^{128}I , ^{130}I and $^{130}\text{I}^m$, used in this study have high internal conversion coefficients.^{47,50} The chemical reactivity of these species may be largely attributable to the production of a vacancy (hole) in the K-or L-shell as the result of conversion electron emission. The vacancy in the K-shell or L-shell is usually filled by an electron from an outer shell with the emission of a K or L X-ray respectively; however, the emission of an X-ray may be replaced by the ejection of an electron with a kinetic energy equal to the difference between the

X-ray energy and the binding energy of the electron. This latter process may continue with the successive emission of electrons (called "Auger" electrons after their discoverer) until the excess energy has been removed. This process may produce a high positive charge on the atom as shown schematically in Fig. 1. Carlson, Hunt and Krause⁵¹ have compiled extensive data on the charge build-up on an atom as a result of a sudden inner-shell vacancy such as that produced by conversion electron emission. They have devised a plot (Fig. 2) whereby the charge may be predicted as a function of shell level and Z number. Their studies indicate a charge of +8 or +9 for an unassociated iodine atom. Other studies by Carlson and White⁵² show that charge induced by Auger processes in the iodine atom are dependent on chemical composition, i.e., the most abundant charge of iodine initially combined as CH_3I was +5, and that combined as HI was +7. These results suggest iodine ions formed by $^{130}\text{I}^m$ decay may have a charge of +4 or less if initially combined as I_2 . Charge build-up on a combined iodine can produce recoil energies from coulombic repulsion as high as 25 ev.⁵² Factors controlling the behavior of an iodine activated by Auger processes are system state (gaseous or condensed), chemical combination at the time of charging, and, if unassociated due to bond rupture following

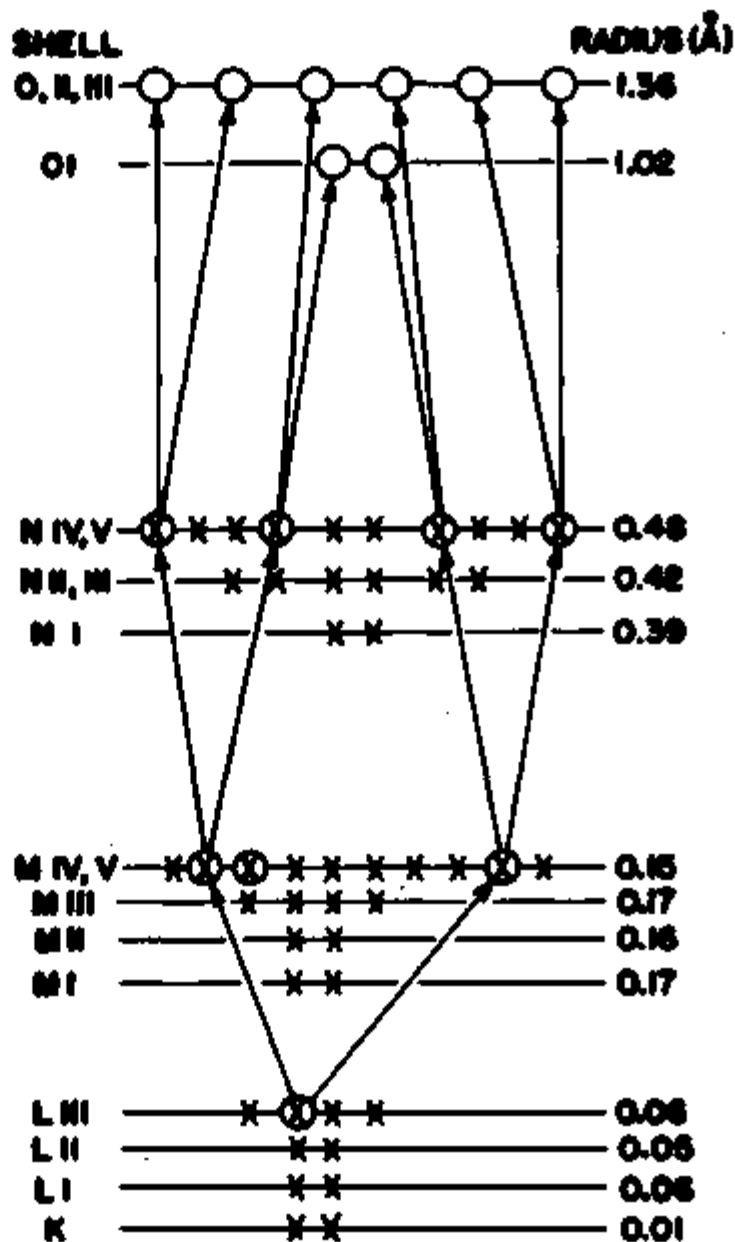


Figure 1. Typical vacancy cascade in I⁻ as the result of an initial L vacancy. The X's represent electrons; O's, vacancies; and x's, the cases where a vacancy has been formed and then filled by a subsequent Auger process.⁵²

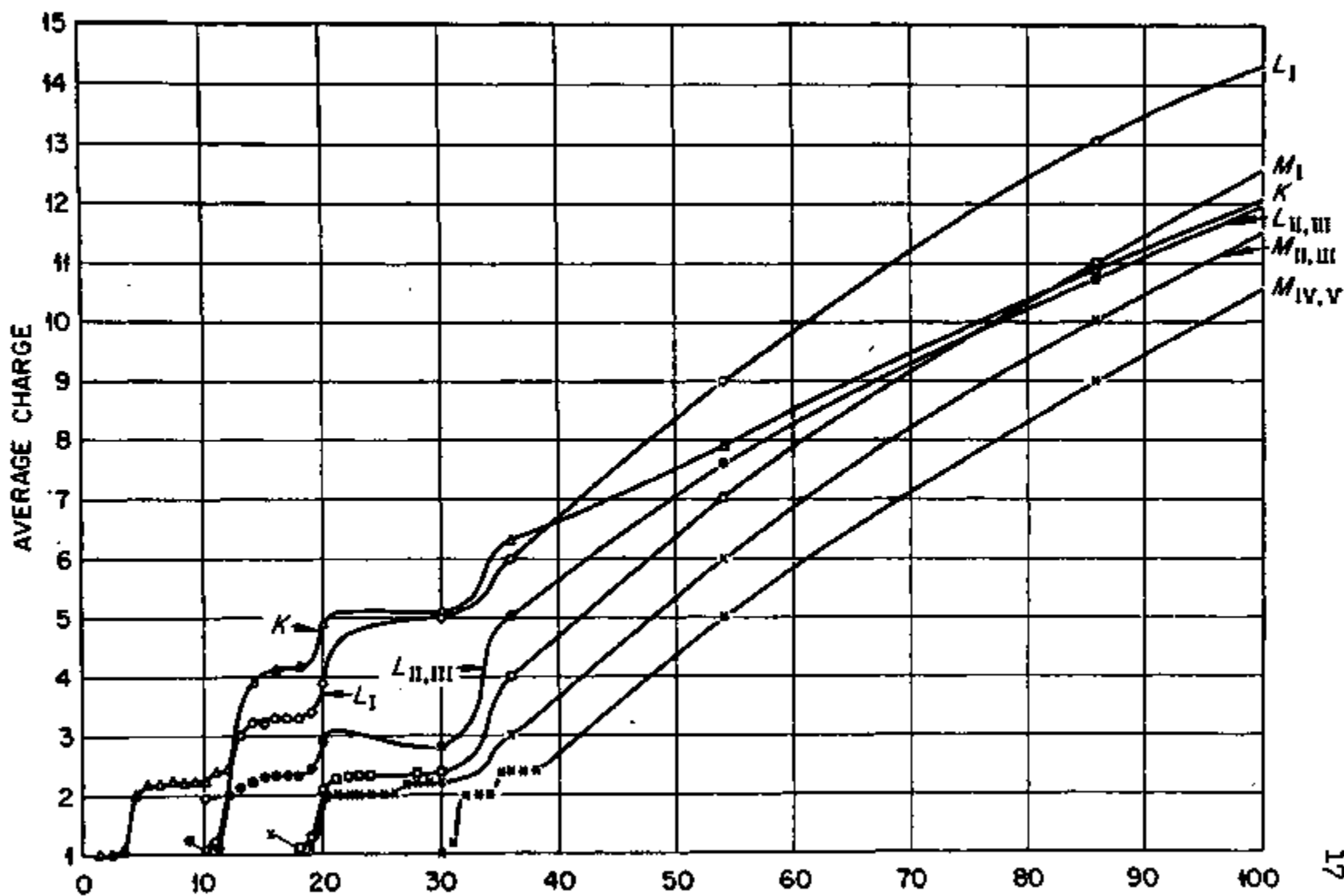


Figure 2. Estimated average charge as the result of a sudden vacancy in the K, L, and M shells as a function of the atomic number.⁵¹

emission of neutron capture gammas, its recoil energy at the time of charging. As a consequence of the electronic rearrangements following activation, excited iodine species formed in the gas phase were found to be $I(^3P_2, ^3P_1 \text{ and/or } ^3P_0)$ atoms or $I^+(^1D_2)$ ions.^{36,37}

Final Chemical Stabilization

After a nuclear activated atom is born with its high kinetic energy, positive charge, and electronic excitation energy it can undergo chemical reactions after losing most of its excess kinetic energy (chemical bond strengths are 2-6 ev., whereas activated atoms may have several hundred ev. kinetic energy). An atom that passes through the hot atom reaction zone without reacting will react as a thermal atom. Positively charged recoil atoms will be quickly neutralized in condensed media if the solvent has a lower ionization potential than the halogen. Two types of data which have proven valuable in recoil atom studies in organic media are (1) the organic yield and (2) the organic product distribution.

Organic Yield Concept

The organic yield is a measure of the percent or fraction of the hot atoms created by the nuclear activation process which become stabilized in organic combination.

The organic yield is used extensively as a research tool because of the ease with which it can be determined experimentally.

Organic Product Distribution

Recoil atoms, by nature of their activation, can react with organic molecules forming both inorganic and organic products. Because of the presence of a halogen scavenger in the reaction system, rapid thermal exchange between the inorganic products, and the inability to differentiate between inorganic halogen products formed by hot and thermal reactions, primary interest is in determining the labelled organic products.

Statement of Problem

Previous studies of nuclear activated iodine reactions have been with hydrocarbon systems,¹⁻⁷ and several of the previously discussed hypotheses are derived from these studies. Investigations of multi-isotope systems and of reactions of iodine isotopes other than ^{128}I ($T_{1/2} = 25$ min) have been hindered by the limited availability of carrier-free precursors of other suitable iodine isotopes and the lack of instrumentation capable of resolving the assay problems.

The availability of essentially carrier-free ^{129}I which produces ^{130}I ($T_{1/2} = 12.4$ hr) and the recently discussed isomer⁴⁷ $^{130}\text{I}^m$ ($T_{1/2} = 8.9$ min) following (n, γ) activation have made it possible to study the reactions of nuclear activated iodine in systems such as chloromethanes without interference from short-lived ^{38}Cl ($T_{1/2} = 37.3$ min). The development of efficient beta and gamma counters as well as high resolution gamma spectrometers has allowed the analysis of systems containing low activity levels of one or more nuclides.

My main objective in doing this research was to examine the following:

(1) The reactions of iodine activated by radiative neutron capture and isomeric transition in liquid polyhalomethanes, and dependence of reactivity on mode of

activation and target molecule substitution.

(2) The reactions of nuclear activated iodine with gaseous polyhalomethanes of the type CH_3X , CH_2X_2 , CHX_3 , and CX_4 ($\text{X} = \text{F}$ or Cl) in the absence of solvent effects present in liquid reaction systems.

(3) The effect of additives on the reactive iodine species and subsequent reactions it may undergo in gaseous systems.

(4) The relationship of reactions in these simple alkanes that have no carbon-carbon bonds, and in some cases, no carbon-hydrogen bonds, to those of the extensively studied hydrocarbon systems and mechanisms proposed for them.

CHAPTER II
EXPERIMENTAL

Chapter II
Experimental

Chemicals Used in the Research

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

I_2	Mallinckrodt, reagent grade I_2 crystals were placed in a porcelain dish with equal volumes of CaO and KI and heated to sublime the I_2 . The I_2 was collected on a cold glass surface placed above the dish and stored in a ground-glass stoppered bottle.
ICl	Matheson, pure, M.P. 25-27° C.
KI	Baker, reagent grade.
CaO	Baker, reagent grade.
$CaCl_2$	Fisher, anhydrous technical grade.
H_2SO_4	Baker and Adamson, reagent grade.
HNO_3	Baker and Adamson, reagent grade.
HCl	Baker and Adamson, reagent grade.
H_2O_2	Mallinckrodt, U. S. P. grade.
Na_2SO_3	Baker, reagent grade.

P_2O_5	Fisher, reagent grade.
Silica gel	Fisher, reagent grade.
Molecular Sieve	Analab, reagent grade.
Ammonia	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 phase with H_2O_2 catalyzed with HNO_3 which was necessary for the oxidation of the $^{129}I^-$ to $^{129}I_2$. This solution was washed three times with distilled water, and dried over silica gel or $CaCl_2$.
Iodine-131	Same as Iodine-129.
CH_3COCH_3	Fisher technical grade.
$CFCl_3$	Matheson, "Freon-11", purified by photobromination, extracted with aqueous sulfite solution, washed with distilled water, refluxed with 10% NaOH solution, washed with distilled water, dried over silica gel or $CaCl_2$, and distilled on a Vigreux column with the center cut being retained.

CCl_3Br

Eastman Kodak, yellow label, was freed from stabilizer by distillation, photobrominated, extracted with aqueous sulfite, washed and re-distilled in the absence of light within one hour before use, and the center cut taken for sample preparation.

 CCl_4

Baker and Adamson, reagent CCl_4 , purified by photobrominating, extracting with aqueous sulfite, washing with water, refluxing with 10% NaOH solution, washing with distilled water, drying over CaCl_2 , and fractionating twice in a Vigreux column taking the center cut.

 CHCl_3

Mallinckrodt, reagent CHCl_3 purified by washing several times with concentrated H_2SO_4 until colorless, washing with water, washing with dilute NaOH, washing with distilled ice water, drying over silica gel, stored in a light-proof container, and fractionally distilled in a Vigreux column shortly before use taking the center cut.

CH_2Cl_2	Matheson, reagent CH_2Cl_2 purified by washing several times with concentrated H_2SO_4 until colorless, washing with dilute NaOH , washing with distilled water, drying over CaCl_2 , and fractionating in a Vigreux column taking the center cut.
CH_3Cl	Matheson, 99.5 mole percent minimum purity.
CF_4	Matheson, 99.7 mole percent purity. 0.1% O_2 and 0.2% N_2 impurities.
CHF_3	Matheson "Genetron 23", 99.7 mole percent purity. 0.3% N_2 impurity.
CH_2F_2	du Pont research gas, 98 mole percent purity. 0.1% N_2 , 1.7% CHF_3 or CF_4 .
CH_3F	Matheson, 98 mole percent purity, 2% N_2 , CHF_3 or CF_4 .
CH_4	Phillips, 99.65 mole percent purity.
CH_3I	Eastman, white label, redistilled and stored over copper turnings.
HI	Matheson, 98 mole percent purity.
IF_5	Matheson, 98 mole percent purity. Degassed to remove volatile HF and CF_4 .
CF_3I	Pierce Chemical Company research gas. 0.1% CH_3I by radiogas-chromatography.

Sample Preparation; Liquid Samples

The reactions of ^{128}I and $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ activated by neutron capture and the $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I reactions were studied in liquid polyhalomethane-halogen mixtures. In particular, halogen concentration effects, the effect of solid phase irradiations, and time between irradiation and extraction were examined. All samples were prepared in 1-5 ml quartz ampoules. The ampoules were attached with a constricted neck to a quartz stem having a ground-glass joint for connection to a vacuum line. The stem and ampoule were cleaned by washing with concentrated HNO_3 , dilute aqueous NH_3 and a triple rinse with distilled H_2O . The rinsing was accomplished by alternately cooling the ampoule in liquid N_2 while introducing the wash solution, and then heating the ampoule to expel the liquid gaseous waste. The cleaning procedure removes any soluble contamination from the quartz surface. The ampoules were attached to the vacuum line and flamed to a red glow to volatilize any absorbed substances inside. After evacuating for several minutes, the ampoules were tested for leaks using a tesla coil.

Quartz, rather than pyrex, was used for several reasons. The neutron-induced activity in quartz was much less than in pyrex or other softer glasses. Sodium-24, which was produced in sodium-containing glasses could

be leached out in chemical extractions, described later, and affect the radioactive assaying. Quartz was also used because of its low coefficient of expansion which allowed it to undergo extreme and sudden temperature changes without breakage.

Generally triplicate, and at least duplicate samples were prepared for all experiments. The reaction mixtures were introduced into the ampoules as a liquid in all instances. The solutions were sufficiently cooled in all cases to prevent volatilization of the solvent or solute. The samples in the ampoules were degassed by the standard alternate freezing, evacuating and thawing procedure. All reaction systems were prepared in a dimmed room. The samples were wrapped in aluminum foil to eliminate light induced reactions, and stored under liquid N_2 to eliminate thermal exchange reactions. The ^{129}I and ^{131}I (for tracer studies) were obtained from Oak Ridge National Laboratory in aqueous $Na^{129}I$ or $Na^{131}I$ solution. The iodide salt was oxidized to iodine with H_2O_2 , catalyzed with a trace of HNO_3 , and extracted into the halomethanes. The solutions were washed at least three times with distilled water, and dried over silica gel or molecular sieves. Iodine concentrations were then determined photometrically with a Bausch and Lomb Spectronic 20.

Sample Preparation; Gaseous Samples

Quartz ampoules, varying in size from 7 to 10 ml, were washed with HNO_3 , rinsed with distilled H_2O , heated to dryness, and then sealed to quartz capillary tubing which could be connected to the vacuum line by means of a ground-glass (12-3) ball-socket joint. After sealing the quartz ampoule to the capillary tubing, the necks of the quartz ampoules were constricted by heating to facilitate easy sealing of samples after preparation of reaction systems. The ampoules were cleaned again, flamed, and evacuated as described for liquid systems. Evacuation of the ampoule was continued until no spark was observed between it and the Tesla coil.

Triplicate samples were prepared on the vacuum line. All samples contained 0.1 mm I_2 , except where noted, in order to serve as a radical scavenger in the system. The I_2 was metered into the ampoule at its vapor pressure at ambient temperature. In addition to I_2 , other iodine source molecules were introduced into the irradiation vessel at pressures determined from manometer readings. The target compound was then added to the reaction systems from tanks connected to the vacuum line by tygon tubing, these pressures also being determined from manometer readings. The actual individual compound pressure in the system was equal to the difference between the pres-

sure read on the manometer and the previous pressure existing in the reaction ampoule. The quartz ampoules were frozen in liquid N_2 and sealed off by heating at the thin-neck constriction. The ampoules were wrapped in aluminum foil and stored in N_2 in the dark until prepared for irradiation. The entire sample preparation was done in a dimmed room with indirect lighting sufficient to allow accurate manometer readings.

With additives having appreciable vapor pressures at liquid N_2 temperatures, a pressure correction might be considered necessary for the amount of gas between the constricted neck of the ampoule and the stopcock leading to the vacuum system. This correction was minimized to less than experimental error by using large (10 ml) reaction ampoules in comparison to the small volume of the capillary tubing between the constricted neck of the ampoule and the stopcock. Before sealing the ampoule, an internal vacuum was accomplished by warming the capillary tubing, which created a temperature difference between stem and ampoule, and shifted most of the gas in the capillary into the ampoule immediately before sealing. No pressure correction was incorporated in calculating the mole fraction of the reaction systems.

Neutron Irradiation

The thermal neutron irradiations were performed in the TRIGA Mark II "swimming pool" nuclear reactor at the U. S. Veteran's Administration Hospital at Omaha, Nebraska. An average flux of 1.1×10^{11} thermal neutrons $\text{cm}^{-2} \text{sec}^{-1}$ was present at an operating power of 15.5 kilowatts. Experiments designed to test for the occurrence of "fast" neutron induced reactions such as $^{19}\text{F}(n,2n)^{18}\text{F}$ and $^{127}\text{I}(n,2n)^{126}\text{I}$ were negative within the limits of detectability. Samples were placed either in the various ports of the "lazy susan" holder or the pneumatically operated "rabbit" facility. For irradiations of duplicate samples longer than two minutes, the various ports in the "lazy susan" sample holder were employed and the assembly was rotated to ensure that all samples received the same neutron flux and radiation dose. The radiation dose was approximately 3×10^{17} $\text{ev g}^{-1} \text{min}^{-1}$ as determined by using Fricke dosimetry,⁵³ and ^{131}I organic pickup in irradiated $\text{c-C}_6\text{H}_{12}$.³⁹ In most instances the organic yields were negligibly dependent upon the duration of irradiation.

The quartz samples containing the reaction systems were sealed in plastic bags to prevent radioactive gases from escaping if the ampoules were accidentally broken. The reactions systems were inserted into TRIGA tubes

or the "rabbits" which were specially designed for the TRIGA reactor. Neutron irradiation times varied from 1 sec to 60 min.

Samples to be irradiated in the solid-state were removed from liquid N_2 and irradiated for 2-30 sec. The average temperature rise in solid-state samples was determined under conditions as nearly identical as possible to irradiation conditions by sealing the probe in a quartz capillary extending into the sample contained in an evacuated ampoule. The results, shown in Fig. 3, indicate that maximum temperature reached by solid-state samples during the short irradiations employed in this study were insufficient to cause liquefaction. Remote handling equipment was employed whenever possible in order to minimize personal radiation hazards. Standard radiochemical techniques and practices were employed at all times.

Extraction of Organic and Inorganic Activities

The quartz ampoules containing the reaction systems were placed in specially designed separatory funnels. The reinforced separatory funnels contained aliquots of CCl_4 , halogen carrier and aqueous 0.5 M Na_2SO_3 such that the volumes of organic and inorganic phases were equal after the reaction system was added. The quartz

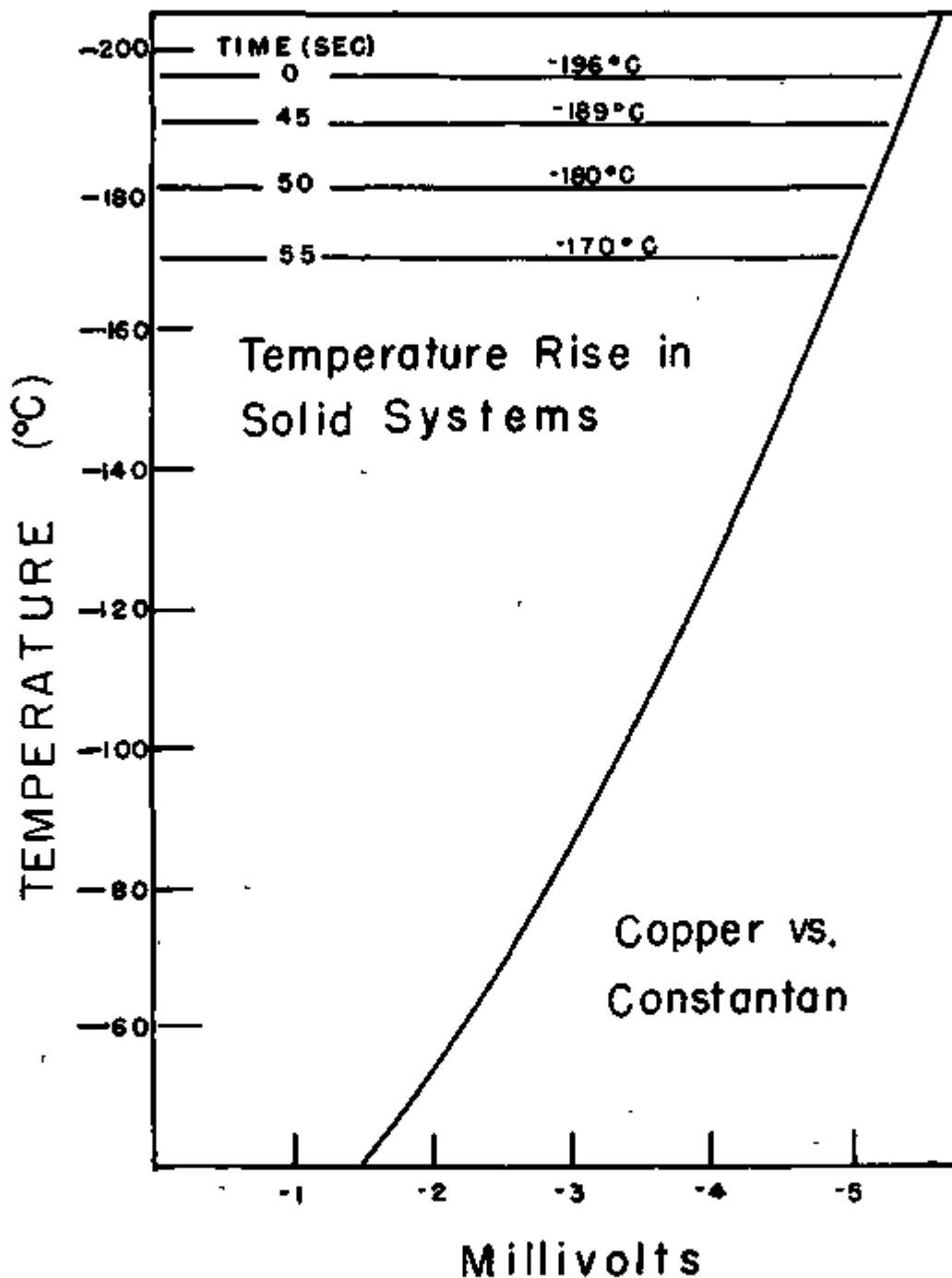


Figure 3. Average temperature rise of solid-state samples following removal from liquid N_2 . Data shown on calibration plot of the thermocouple employed.⁵⁷

ampoules were broken by vigorous shaking of the funnel. After mixing and equilibration, the CCl_4 phase contained the organically soluble labeled alkyl halides formed as a result of the nuclear induced reactions. The phases were separated within 10-30 sec after the interface appeared if isomeric transition induced reactions were occurring during the extraction process. The organic soluble portion was drained into an erlenmeyer flask which contained anhydrous CaCl_2 as a drying agent. The flask was stoppered and shaken before equal volumes of each phase were pipetted into separate labeled counting tubes.

Determination of Isomeric Transition

Induced Organic Yields

When ^{129}I is subjected to a thermal neutron flux, a large percentage of the activated nuclei are born in a metastable nuclear state.⁴⁷ As shown in Fig. 4, 67% of the ^{129}I atoms which absorb a neutron will result in $^{130}\text{I}^m$; whereas 33% are born as ground nuclear state ^{130}I . The $^{130}\text{I}^m$ decays to ^{130}I by isomeric transition and to ^{130}Xe by beta decay.

Rack and co-workers^{39,54-56} developed a freeze-thaw technique for determining ^{82}Br isomeric transition induced organic yields independent of the radiative neutron capture organic yields. Essentially the tech-

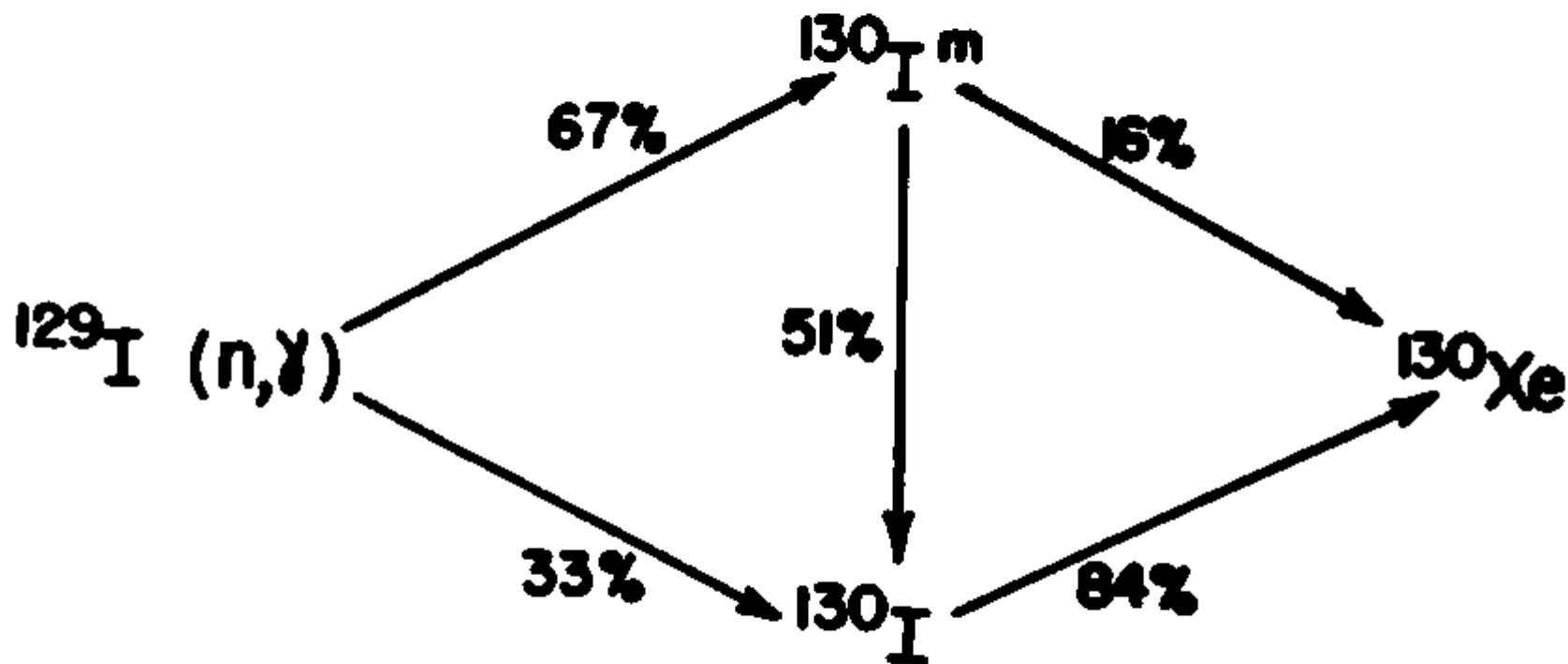


Figure 4. Radiative neutron capture and subsequent decaying routes of Iodine-129.

nique consists of the neutron irradiation of a solid sample containing halogen and an aliphatic compound. The solid-state organic yields were usually less than 1% at concentrations of halogen where fractional crystallization or clumping of the halogen occurs during the freezing process. However, when the sample is liquefied following the neutron irradiation, the organic yields increase with the duration of time that isomeric transition reactions have occurred. Merrigan⁵⁴ developed an expression to calculate the (IT) organic yields in bromine-systems based on information obtained with the freeze-thaw technique. This expression was developed specifically for the determination of $^{82}\text{Br}^m$ isomeric transition yields and was not adequate to describe $^{130}\text{I}^m$ isomeric transition yields because the solid-state yields were not always negligible in systems necessarily containing low concentrations of I_2 solute as a consequence of the limited solubility of iodine in the systems of interest, and the fraction ^{130}I born directly into the ground-state (39%) was not insignificant, whereas the fraction of ground-state ^{82}Br produced is less than 10%. The following general expression was developed to describe the isomeric transition organic yields in all systems where the freeze-thaw technique is applicable.

The observed organic yield may be described by equation (1):

$$O.Y._{obs} = \frac{\text{Org Act}_{IT}^{liq} + \text{Org Act}_{IT}^{sld} + \text{Org Act}_{n,Y}^{sld}}{\text{Total Activity}}$$

The organic yield due strictly to isomeric transition induced reactions in the liquid state is defined as the organic activity introduced into the liquid organic phase by (IT) reactions divided by only that fraction of total activity produced by the decay of the metastable isomer in the liquid state. This result is obtained by dividing Eq. 1 by the term, $\beta e^{-\lambda t}$, where β is the fraction of the total activity born by (IT)-activated processes decaying in the liquid state, λ is the decay constant of the metastable isomer, $^{130}\text{I}^m$, and t is the elapsed time from beginning of irradiation to thawing the sample.

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

Rearranging:

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

The solid-state organic activity induced by (IT)-activation is equal to $(1 - e^{-\lambda t}) \beta$ times the observed solid-state organic yield. The solid-state organic activity induced by (n,Y)-activation is equal to α times the observed solid-

state organic yield, where α is the fraction of the total activity produced directly by radiative neutron capture. By making the proper substitutions and rearranging, a general expression is obtained for systems where the freeze-thaw technique is applicable.

$$(4) \quad \text{O.Y.}_{\text{IT}}^{\text{liq}} = \frac{R^{\infty} - \alpha R^0}{\beta e^{-\lambda t}} - \frac{(1 - e^{-\lambda t}) R^0}{e^{-\lambda t}}$$

R^{∞} is the observed organic yield produced in the liquid state when a sample is thawed immediately after irradiation in the solid-state and after 99.9% of the metastable isomer, $^{130}\text{I}^{\text{m}}$, has decayed. R^0 is the organic yield produced in the solid-state neutron irradiation. A necessary condition is that the value of R^0 is not dependent upon time of extraction within experimental error. In systems involving $^{130}\text{I}^{\text{m}}$, the constants α and β are 0.39 and 0.61 respectively.⁴⁷ The ^{130}I liquid state organic yield due to isomeric transition at any time t after liquefaction can be determined by employing the following:

$$(5) \quad \text{O.Y.}_{\text{IT}}^{\text{liq}} = \frac{R^{\infty} - R^0}{\beta e^{-\lambda t}} - \frac{(1 - e^{-\lambda t}) R^0}{e^{-\lambda t}} - (e^{-\lambda t} \text{ liq}) R^0$$

The last term is negligible within experimental error if solid-state organic yields (R^0) are less than two percent, since it corrects only for the fraction solid-state organic activity induced by isomeric transition that cannot occur if the sample is liquefied. If essentially all the

metastable isomer is allowed to decay in the liquid state, the term vanishes, and the general expression for ^{130}I systems is equation 6.

$$(6) \quad \text{O.Y. } \frac{\text{liq}}{\text{IT}} = 1.71 R^\infty - .71 R^0$$

Assaying Procedures

The radioisotopes were assayed with either a tracerlab, Model SC-57, well scintillation detector with a two inch NaI(Tl) crystal in conjunction with a Tracerlab Spectromatic, Model SC-530, scaler-spectrometer, or a RIDL 400 channel pulse height analyzer with either a 2in x 2in well-type NaI(Tl) crystal, or two facing 2in x 2in NaI(Tl) crystals with near 4 pi geometry. A description of the counting equipment, the counting geometry and the lack of a need for corrections due to counting coincidence losses and density have been adequately discussed in previous theses from this laboratory.^{39,53,61,62} The multichannel analyzer was used primarily for ^{128}I and ^{38}Cl systems for quantitative determination of the isotopes being analyzed. Representative spectra of the various isotopes used in this research are available.⁶³

The readout of the Tracerlab instrument was recorded manually; whereas, the output of the multichannel analyzer was stored on paper tape or typed-out on paper. The

activities represented by the photopeaks of the nuclide of interest were computed and the organic yield values calculated using an IBM 1620 computer. Programs 1 and 2 listed in the appendix were modified for this purpose by R. L. Ayres of this laboratory. These programs incorporate corrections for radioactive decay, residual background, and compton scatter. The ^{130}I ($T_{1/2} = 12.4$ hr) activity was determined after allowing shorter lived species to completely decay.

Determination of Labeled Product Distributions

The labeled product distributions of the radioisotopes in the halomethanes were determined by radiogas chromatography. A schematic diagram of the radiogas chromatograph is depicted in Fig. 5. The basic features of the radiogas chromatograph have been described elsewhere.^{39,64} Recent improvements⁶⁵ include a Hewlett Packard D. C. power supply (Harrison 6202B), a Gilmont Instruments, Inc. flowmeter, Aerograph thermal conductivity cells, a four port backflush valve to facilitate elution of high boiling fractions which pass through the column slowly, and a high efficiency window flow-counter similar to that discussed by Wolf, et al.⁶⁶ Not shown in Fig. 3 is the ND-110 128-channel analyzer which was connected to the ratemeter with a signal-splitter so

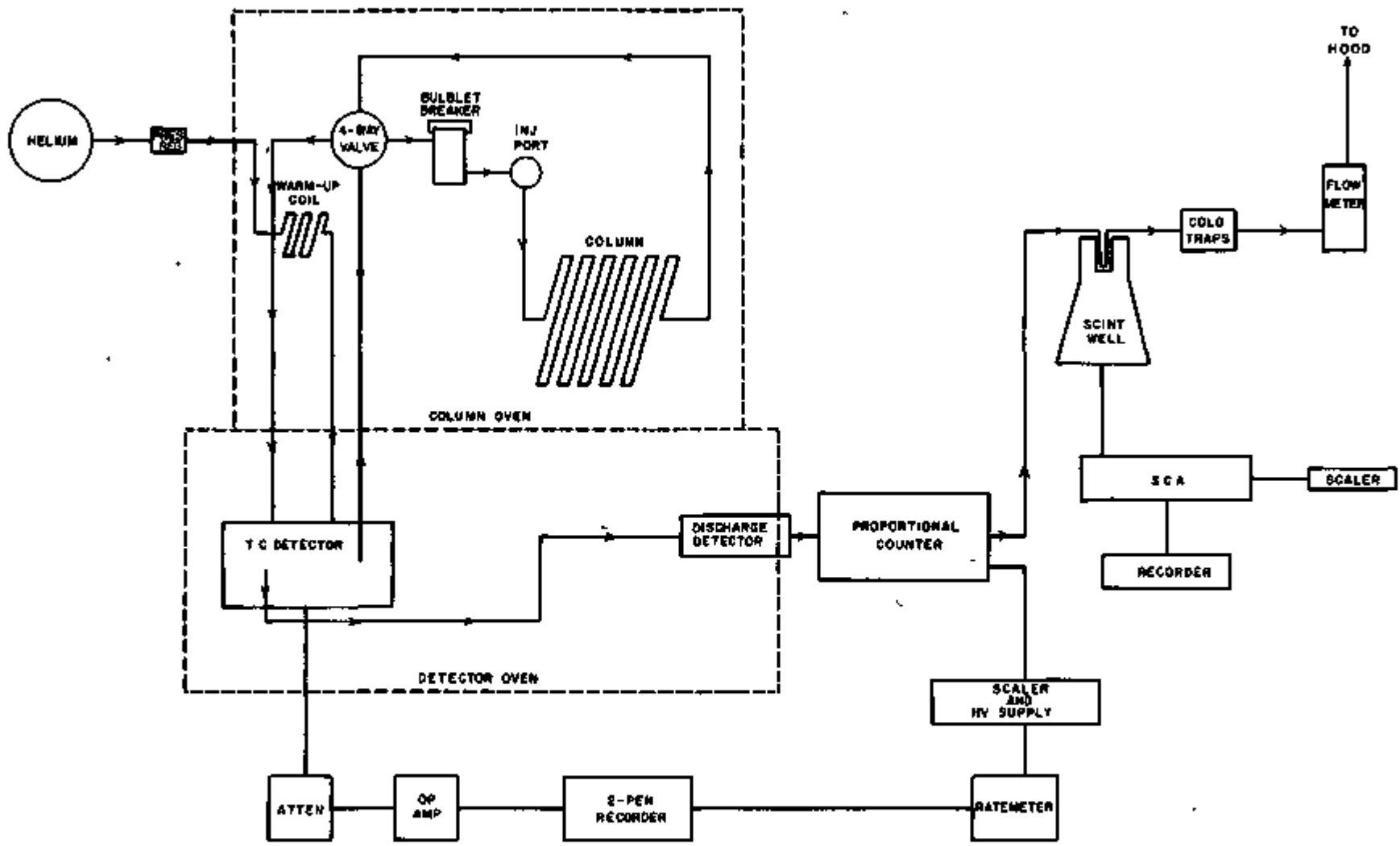


Figure 5. Schematic of the Radiogas Chromatograph

that the signal from the counter was relayed both to the dual-pen recorder and the memory of the analyzer. The multichannel analyzer was operated in the Mossbauer mode with a dwell-time per channel of 10 sec. This allowed digital storage of chromatograms up to 1280 sec duration and numerical integration of product peak areas. A 2.1 m spiral column, 4-mm i.d., filled with 42-60 mesh Wilkens Instrumental firebrick coated with 13% weight of DC-550 silicone oil, was used with He as the mobile phase.

Silicone oil was chosen as the stationary phase because of its general separating characteristics, rather than selective abilities, and for its ability to separate alkyl halides. Silicone oil is unselective to halomethanes and they were found to elute from the column in the order of increasing boiling point for all halomethanes used in this study.

Ground firebrick was prepared as the solid support for the liquid phase by dissolving 13 g of liquid silicone oil in 250 ml of methylene chloride, and suspending 100 g of firebrick in the solution. The methylene chloride was volatilized under vigorous mechanical stirring. The resultant firebrick coated with 13% of its weight of silicone oil was packed in the coiled glass column.

Liquid samples irradiated for radiogas chromatographic analysis were cooled to prevent evaporation of volatile

halides, and extracted with 1 ml of the hydrocarbon solvent being investigated and 3 ml of 0.5 M Na_2SO_3 . Quantitative organic product distributions were initially determined in the absence of organic iodide carriers to prevent any exchange between carriers and labeled products at the elevated temperatures of the chromatograph. Subsequent chromatograms employed carriers for product identification. Quartz ampoules containing gaseous samples were broken inside a gas-tight, on-line induction port. The sample gases were introduced directly into the carrier gas stream and passed through a potassium hexacyanoferrate (II) pre-column to prevent inorganic halogens from entering the analytical column.⁶⁷

CHAPTER III

SUBSTITUENT EFFECTS IN IODINE-130 REACTIONS
ACTIVATED BY (α, γ) AND (IT) WITH VARIOUS POLYHALOMETHANES

Chapter III

Previous studies of iodine reactions activated by nuclear transformations have been mainly with alkyl iodide and hydrocarbon systems.^{1,2,13,41,58} One striking feature of iodine reactions was that yields and product distributions of ^{130}I and ^{128}I activated by (IT) and (n, γ) processes, respectively, were similar to yields and analogous product distributions of ^{82}Br activated by (IT) events in cyclohexane and other $\text{C}_5\text{-C}_9$ hydrocarbons.^{47,59} The likeness between ^{130}I , ^{128}I and ^{82}Br yields and product distributions suggest that activated halogens may trace chemical processes which result from a similarity of environmental activation and/or decomposition.^{58,59}

The study of iodine reactions in various halogen substituted methanes is interesting because these mono-carbon compounds, containing, in some cases, no carbon-hydrogen bonds, present environments to the activated iodine that are highly dissimilar to hydrocarbons with respect to bond energies, molecular dimensions, and stability of potential products. In this research the effects of different substituents on the ^{129}I (n, γ) ^{130}I + ^{129}I (n, γ) $^{130}\text{I}^m$ and $^{130}\text{I}^m$ (IT) ^{130}I induced organic yields and the radioiodine organic product distributions at several iodine concentrations in various polyhalomethanes were determined.

The freeze-thaw technique for obtaining isomeric transition organic yields, extraction procedures and counting equipment have been described previously. This technique was used in all systems except CCl_3Br where the (IT) organic yields were determined in a manner similar to that employed by Willard, et al.^{47,60} The organic yields of ^{130}I induced by (IT) processes in CCl_3Br , and also CCl_4 , systems were determined by introducing $^{130}\text{I}^m$ and ^{130}I produced by neutron irradiation of ^{129}I into the solvent at various times following irradiation. The data are shown in Tables II and III. The values thus obtained were divided by the fraction (0.61) of the total activity born as $^{130}\text{I}^m$ to obtain the (IT) induced organic yields at various times. Since the maximum organic yield depends on the fraction of the $^{130}\text{I}^m$ that has not decayed when the irradiated iodine is introduced into the systems, the (IT) induced organic yield that would be observed if all the $^{130}\text{I}^m$ were allowed to decay in the system may be determined by preparing a plot of the corrected values and extrapolating to time zero (approximated by the midpoint of irradiation). The isomeric transition induced organic yields of ^{130}I in CCl_3Br and CCl_4 determined in this manner are shown in Fig. 6 and Fig. 7. Correction for pick-up of ^{130}I in systems where no $^{130}\text{I}^m$ was initially present was 0.1%. All samples for other isomeric transi-

Table II
 Percent ^{130}I Activity in Organic Combination Following
 Introduction of $^{130}\text{I}^{\text{m}}$ and ^{130}I at Varying Times After
 Midpoint of Irradiation into CCl_3Br

Mole Fraction I_2	Time	Percent Organic ^a (Observed)
3×10^{-4}	2	1.04
	2	1.09
	2	1.07
	5	0.85
	5	0.88
	5	0.84
	5	0.81
	8	0.67
	8	0.61
	8	0.75
	8	0.70
	12	0.50
	12	0.43
	12	0.40
	12	0.37

^aEstimated error is 0.1% as a result of thermal uptake of ^{130}I .

Table III
 Percent ^{130}I Activity in Organic Combination Following
 Introduction of $^{130}\text{I}^m$ and ^{130}I at Varying Times After
 Midpoint of Irradiation into CCl_4

Mole Fraction I_2	Time (min.)	Percent Organic ^a (Observed)
3×10^{-4}	2	1.02
	2	1.10
	2	1.10
	2	1.08
	5	0.91
	5	0.79
	5	0.86
	5	0.82
	8	0.60
	8	0.75
	8	0.67
	8	0.63
	12	0.41
	12	0.42
	12	0.44
	12	0.39

Table III(continued)

Mole Fraction I_2	Time (min.)	Percent Organic ^a (Observed)
9.5×10^{-4}	3	1.41
	3	1.40
	3	1.36
	6	1.08
	6	1.15
	6	1.14
	9	0.82
	9	0.87
	9	0.79

^aEstimated error is 0.1% as a result of thermal uptake of ^{130}I .

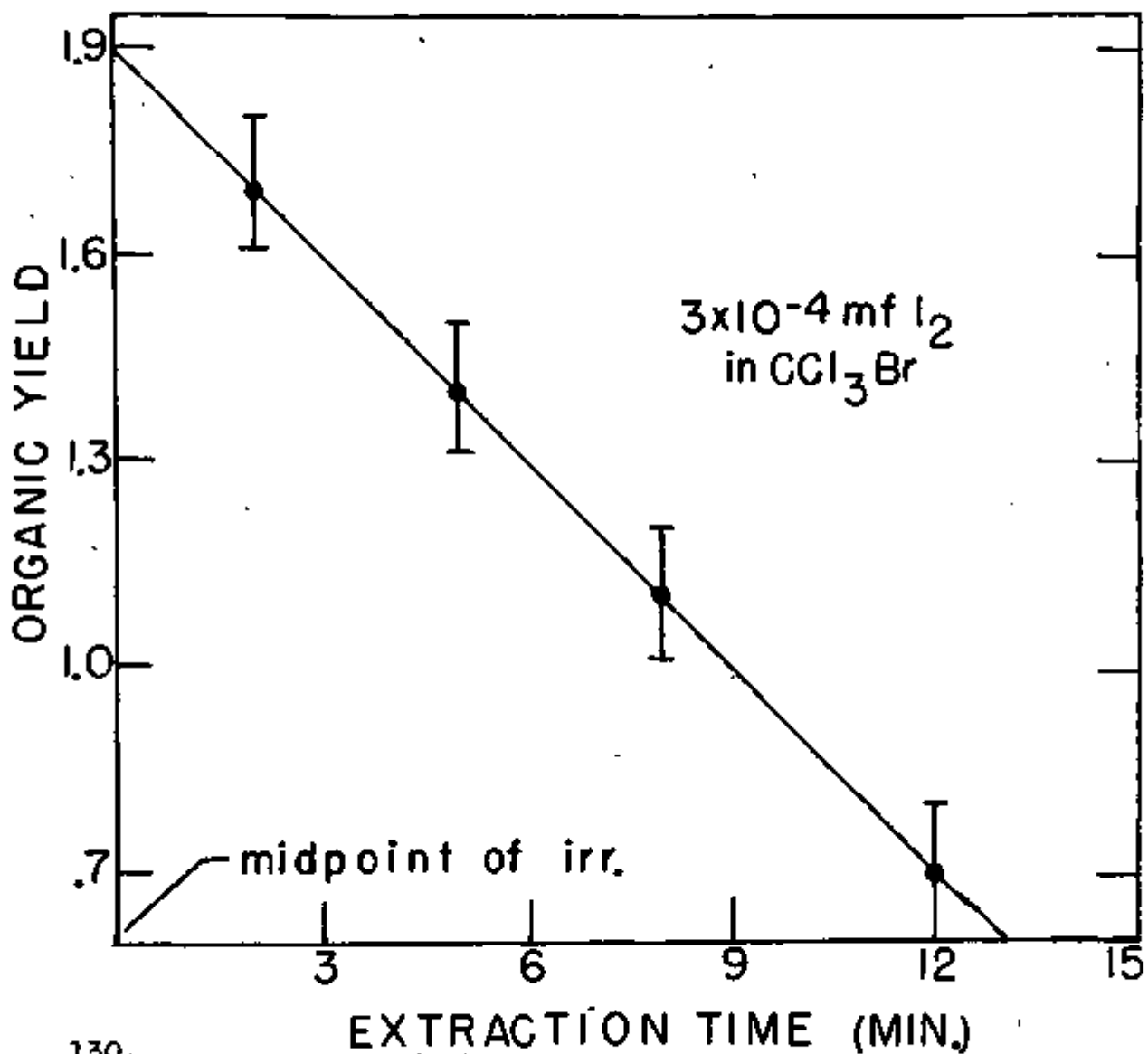


Figure 6. ¹³⁰I Organic Yield (IT) versus Time of Extraction in CCl₃Br.

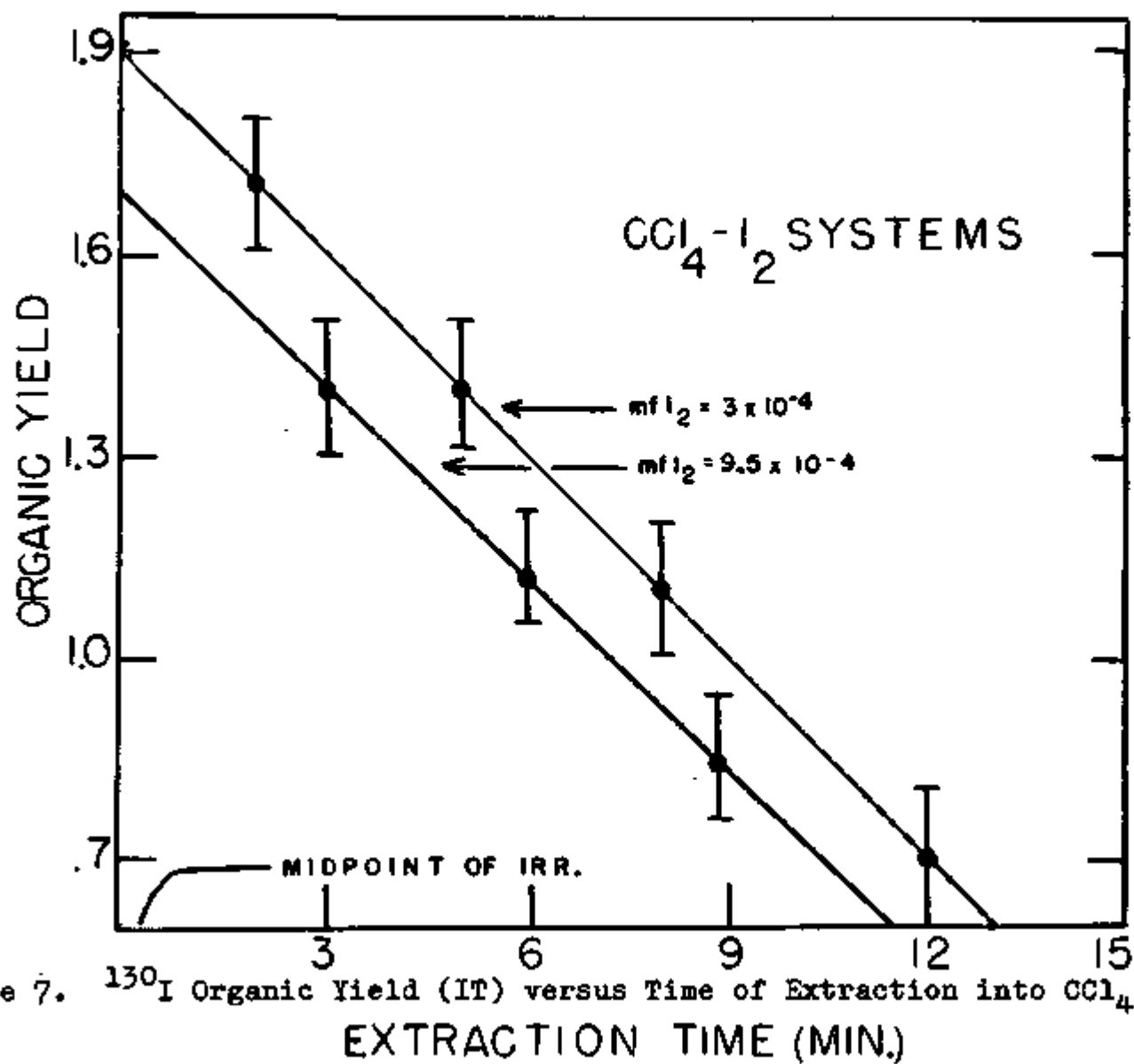


Figure 7. ^{130}I Organic Yield (IT) versus Time of Extraction into CCl_4 .

tion time studies were irradiated in the solid state ($77^{\circ} - 90^{\circ} \text{ K}$), and thawed by immersing in warm water 10 sec after the end of a 30 sec irradiation. They were resolidified in liquid nitrogen after varying periods of time at room temperature. A necessary condition for application of freezing techniques is an essentially constant solid-state organic yield. These values were determined immediately after irradiation and after 90 min for various mole fraction I_2 in the CH_2Cl_2 , CHCl_3 , CCl_4 , and CFCl_3 systems studied by this technique. The results shown in Tables IV, V, VI, and VII indicate that within experimental limits, there is no change in the observed yield as a result of $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ processes in the solid state.

The samples irradiated for radiogas chromatographic analysis were cooled to prevent evaporation of volatile compounds and extracted with aqueous sulfite, washed and dried to insure that only organic products were chromatographed.

Product identification where carriers were not available was made on the basis of relative position to labeled CCl_3I and non-radioactive halomethanes of varying boiling points and molecular weights.

Radiative Neutron Capture Induced Reactions

Determination of ^{130}I and $^{130}\text{I}^{\text{m}}$ organic yields acti-

Table IV
 Iodine-130 Yields in Solid CH_2Cl_2 for Immediate
 Post-Irradiation Extraction and After All
 Iodine-130m has Decayed (\approx 90 min)

Mole Fraction $\text{I}_2 \times 10^3$	Organic Yield*	
	Immed. Extractn.	After 90 min
0.3	1.9	2.4
	2.0	2.2
	2.1	2.1
	2.0	2.3
5.0	1.0	0.7
	0.8	0.7
	0.9	1.0
	1.5	0.5
10.0	0.6	0.5
	0.6	0.5
	0.5	0.4

* Irradiated 15 seconds

Table V

Iodine-130 Organic Yields in Solid CHCl_3 for Immediate
 Post-Irradiation Extraction and After All
 Iodine-130m has Decayed (\approx 90 min)

Mole Fraction $\text{I}_2 \times 10^3$	Organic Yield (Solid State)*	
	Immed. Extractn.	After 90 min
0.3	6.4	5.7
	6.7	5.6
	6.2	6.0
	6.0	5.8
8.0	5.4	5.1
	5.0	4.9
	4.7	4.9
12.0	3.8	3.8
	4.1	3.9
	3.2	3.5

*Irradiated 15 seconds

Table VI
 Iodine-130 Organic Yields in Solid CFCl_3 for Immediate
 Post-Irradiation Extraction and After all
 Iodine-130m has Decayed (\approx 90 min)

Mole Fraction $\text{I}_2 \times 10^3$	Organic Yield*	
	Immed. Extractn.	After 90 min
0.3	1.1	1.0
	1.0	0.6
	1.0	0.9
0.7	1.0	---
	0.9	---
2.0	0.6	0.6
	0.6	0.6
	0.6	0.5

*Irradiated 15 sec

Table VII

Iodine-130 Organic Yields in Solid CCl_4 for Immediate
 Post-Irradiation Extraction and After All
 Iodine-130m has Decayed (\approx 90 min)

Mole Fraction $\text{I}_2 \times 10^3$	Organic Yield*	
	Immed. Extractn.	After 90 min
0.3	4.6	4.3
	4.1	4.4
	4.0	4.1
9.5	2.5	2.5
	2.6	2.5
	2.1	2.3

* Irradiated 15 seconds

vated by $^{129}\text{I}(n,\gamma)^{130}\text{I}$ and $^{129}\text{I}(n,\gamma)^{130}\text{I}^{\text{m}}$ processes was accomplished by irradiating (15-30 sec) the liquid poly-halomethane systems, CH_2Cl_2 , CHCl_3 , CFCl_3 and CCl_4 , containing dissolved I_2 at various concentrations studied, with thermal neutrons and immediately freezing them in liquid nitrogen. It has been shown previously that changes (with time in the liquid state) in ^{82}Br and ^{130}I organic yields due to (IT) activated reactions in hydrocarbons could be halted by freezing the systems in liquid nitrogen.^{54,55,58} The existence of this effect in $\text{I}_2\text{-CH}_2\text{Cl}_2$, $\text{I}_2\text{-CHCl}_3$ and $\text{I}_2\text{-CFCl}_3$ systems is indicated by the data of Tables IV - VI where it is shown that negligible change in organic yield results from (IT) processes occurring in the solid-state. This effect is also demonstrated by the finding in (IT) time-studies that increases in the liquid state ^{130}I yield as a result of isomeric transition induced reactions are halted by re-solidification (see Fig. 8). If, after irradiation in the liquid state, these systems were not frozen immediately, increases were observed in the ^{130}I organic yields related to the duration of time $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ processes were allowed to occur in the liquid phase. Similar effects were reported for ^{82}Br and ^{130}I -hydrocarbon systems,^{55,58} where ^{82}Br and $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ induced yields were greater than those of (n, γ) activated ^{82}Br and $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$. Further evidence that changes in ^{130}I organic yields as a result of (IT)

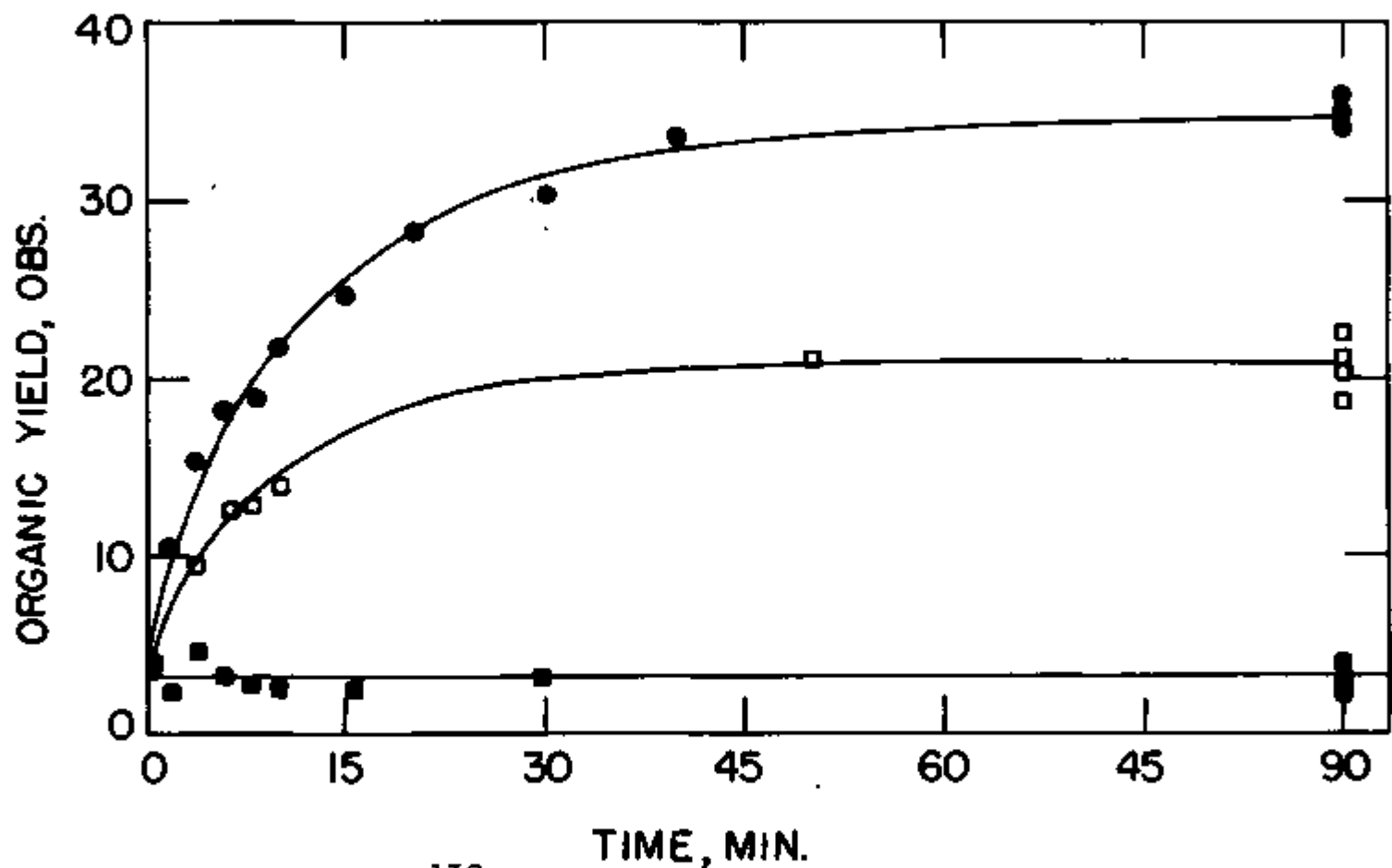


Figure 8. Growth of ¹³⁰I Organic Yields (observed) by (IT) Induced Reaction in Liquid Chloromethanes -- 0.0003 mf I₂.
Systems: CH₂Cl₂, ●; CHCl₃, ◻; CCl₄, ■.

processes occur only in the liquid state is presented in the next section. Presented in Table VIII are the organic yields of $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ activated by radiative neutron capture and ^{130}I activated by isomeric transition processes in various polyhalomethanes as a function of dissolved I_2 concentration.

Isomeric Transition Induced Reactions

The isomeric transition organic yields, determined by freeze-thaw technique (CH_2Cl_2 , CHCl_3 , CFCl_3 and CCl_4), and by the technique of Willard, *et al.* (CCl_4 and CCl_3Br), represent organic yields due entirely to isomeric transition. Characteristic growth of observed ^{130}I organic yields by (IT) is shown for CH_2Cl_2 and CHCl_3 (Table IX and Fig. 8) and is described by a 8.9 ± 0.3 min half-life, using the technique of Merrigan, *et al.*^{54,59} This technique is based on the postulate that if the observed increases in the ^{130}I organic yields were only a result of $^{130}\text{I}^{\text{m}}$ (IT) ^{130}I induced reactions, the rate of increase should be dependent only on $^{130}\text{I}^{\text{m}}$ decay, and hence related to its half-life. Then the growth of ^{130}I yields due to (IT) in the liquid state can be described by equation (7).

$$(7) \quad R^{\text{t}} - R_{\text{total}}^{\text{o}} = R^{\infty} - R_{\text{total}}^{\text{o}}(1 - e^{-\lambda t})$$

Table VIII
 Organic Yields Induced by $^{129}\text{I}(n,\gamma)^{130}\text{I}$, $^{129}\text{I}(n,\gamma)^{130}\text{I}^m$
 and $^{130}\text{I}^m(\text{IT})^{130}\text{I}$ in Liquid Polyhalomethanes

System	Mole Fraction $\text{I}_2 \times 10^3$	Organic Yield	
		$(n,\gamma)^a$	$(\text{IT})^b$
$\text{I}_2\text{-CH}_2\text{Cl}_2$	0.3	42.1	56.2
		46.4	52.8
		44.1	53.2
		44.4	52.4
$\text{I}_2\text{-CH}_2\text{Cl}_2$	5.0	37.1	47.5
		36.9	50.7
		36.2	47.9
		37.2	48.5
$\text{I}_2\text{-CH}_2\text{Cl}_2$	10.0	36.7	44.0
		36.0	43.5
		33.4	43.8
		35.2	42.8
$\text{I}_2\text{-CHCl}_3$	0.3	21.2	31.5
		22.5	30.6
		26.9	29.7
		23.5	28.8
$\text{I}_2\text{-CHCl}_3$	8.0	21.0	25.1
		22.1	24.6
		21.4	24.5
$\text{I}_2\text{-CHCl}_3$	12.0	19.3	21.8
		18.9	22.9
		19.5	---

Table VIII (continued)

System	Mole Fraction $I_2 \times 10^2$	Organic Yield	
		(n, γ) ^a	(IT) ^b
I_2 -CFCl ₃	0.3	11.4	15.8
		11.3	16.8
		11.2	16.2
I_2 -CFCl ₃	2.0	9.8	12.1
		9.0	13.0
		---	14.8
I_2 -CCl ₄	0.3	3.7	0.9
		4.3	1.6
		---	2.5
I_2 CCl ₄	9.0	1.7	---
		2.3	---
		1.8	---

^a Organic retentions of (n, γ) processes were determined by 30 sec irradiation in the liquid state and immediate freezing in liquid N₂ to quench any growth in organic phase activity by (IT) reactions.

^b Organic retentions of (IT) processes were determined by 30 sec irradiation in the solid state and immediate thawing to allow ¹³⁰I^m decay in the liquid state. The observed organic retentions were corrected by the equation 6, Chapter II.

Table IX
 Variation of ^{130}I Organic Yields with Duration of Time
 $^{130}\text{I}^m(\text{IT})^{130}\text{I}$ Processes Occurred in
 Liquid Chloromethanes^a

Time Liquid	R^t , Organic Yield ^b		
	CH_2Cl_2	CHCl_3	CCl_4
2	10.3	8.5	2.9
4	16.0	9.7	4.1
6	18.0	12.5	3.1
10	21.5	13.9	2.8
15	25.0	15.0	3.0
20	28.8	---	---
30	30.3	---	3.1
50	33.3	20.7	---
90	33.7	21.0	3.1

^a Mole fraction I_2 of 0.3×10^3 .

^b 30 sec neutron irradiation

Where: R^∞ is the maximum organic yield obtainable in a liquid system after $^{130}\text{I}^m$ has decayed to ^{130}I . R_{total}^0 is the organic yield produced in the solid state. Since the fraction of $^{130}\text{I}^m$ which would decay in the time, t , between the initial liquefaction and subsequent refreezing to halt further changes in the ^{130}I organic yields is $(1 - e^{-\lambda t})$, the organic yield, R^t , at any time, t , would be $(R^\infty - R_{\text{total}}^0)(1 - e^{-\lambda t})$. The decay constant, λ , is for $^{130}\text{I}^m$. Equation (7) may be rearranged⁵⁴ with the result that a plot of $\log \left[\frac{R^\infty - R^0}{R^\infty - R^t} \right]$ vs Δt will give a straight line with a slope of $(0.693)/(2.303 \cdot T_{1/2})$. The half-life may be determined to a first-approximation. However, only a fraction, β , of the total activated atoms are born in a metastable nuclear state which can give organic combination as a result of isomeric transition. If α and β are the fractions of the total activity resulting from (n, γ) and (IT) , respectively, and since the contribution to the organic yield as a result of (IT) is dependent on the fraction of $^{130}\text{I}^m$ decaying in the solid state

$$(8) \quad R_{\text{total}}^0 = \alpha R_{(n, \gamma)}^0 + \beta R_{(IT)}^0 (e^{-\lambda t})$$

Using the decay constant, as determined in the first approximation, and the corrected R^0 , an improved value of the half-life of $^{130}\text{I}^m$ may be determined. The data for CH_2Cl_2 , CHCl_3 (Table IX and Fig. 8) and CFCl_3 were

treated in this manner and the values obtained were described by a straight line as shown in Fig. 9. The value of the half-life obtained by this method is consistent with previously reported values of 9.2, 8.9, and 8.8 min.^{47,59,69} The "growth" of the liquid state isomeric transition induced organic yields as determined by equation (5), Chapter II are depicted in Fig. 10. All limiting (IT) yields reported (Table VIII) for systems examined by the freeze-thaw technique were calculated by equation (6) of Chapter II. Any changes in the observed yields of ^{130}I in CCl_4 with respect to time in the liquid state were of insufficient magnitude to be evaluated in terms of half-life correlation and are discussed separately in the next section.

Nuclear Activated Reactions of ^{130}I with CCl_4 and CCl_3Br

The ^{130}I organic yield values in CCl_4 systems for varying times in the liquid state appeared to remain constant at ca 3.5% (Fig. 8). The corrected isomeric transition induced yields for these times are shown in Fig. 10. The negative initial values indicate that the probability of (IT) activated ^{130}I forming a stable organic compound in the liquid phase is less than that of (n, γ) activated $^{130}\text{I} + ^{130}\text{I}^m$ forming a stable organic compound during irradiation in the solid state. The limiting (IT) yield

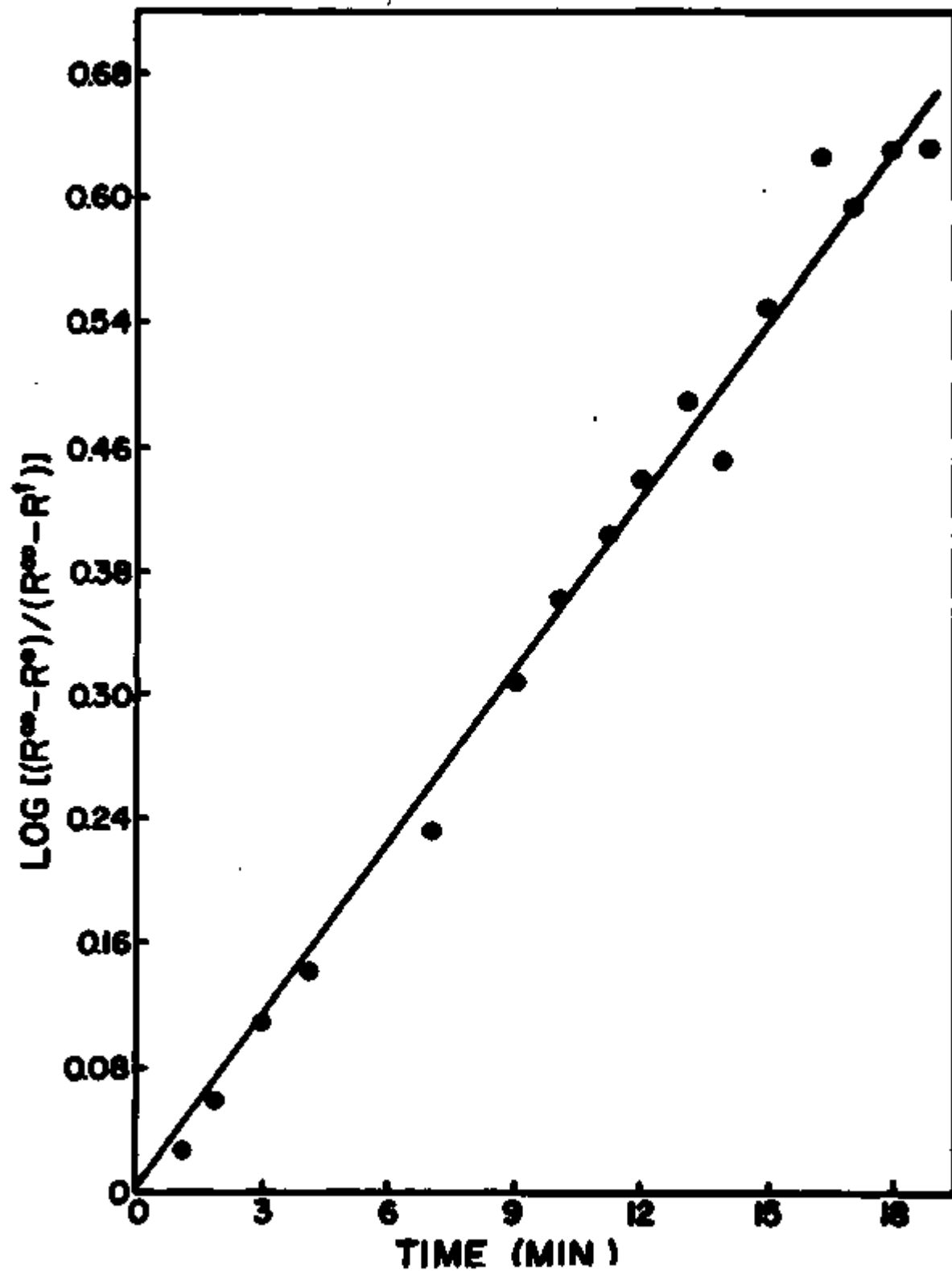


Figure 9. Determination of the Half-Life of $^{130}\text{I}^m$.

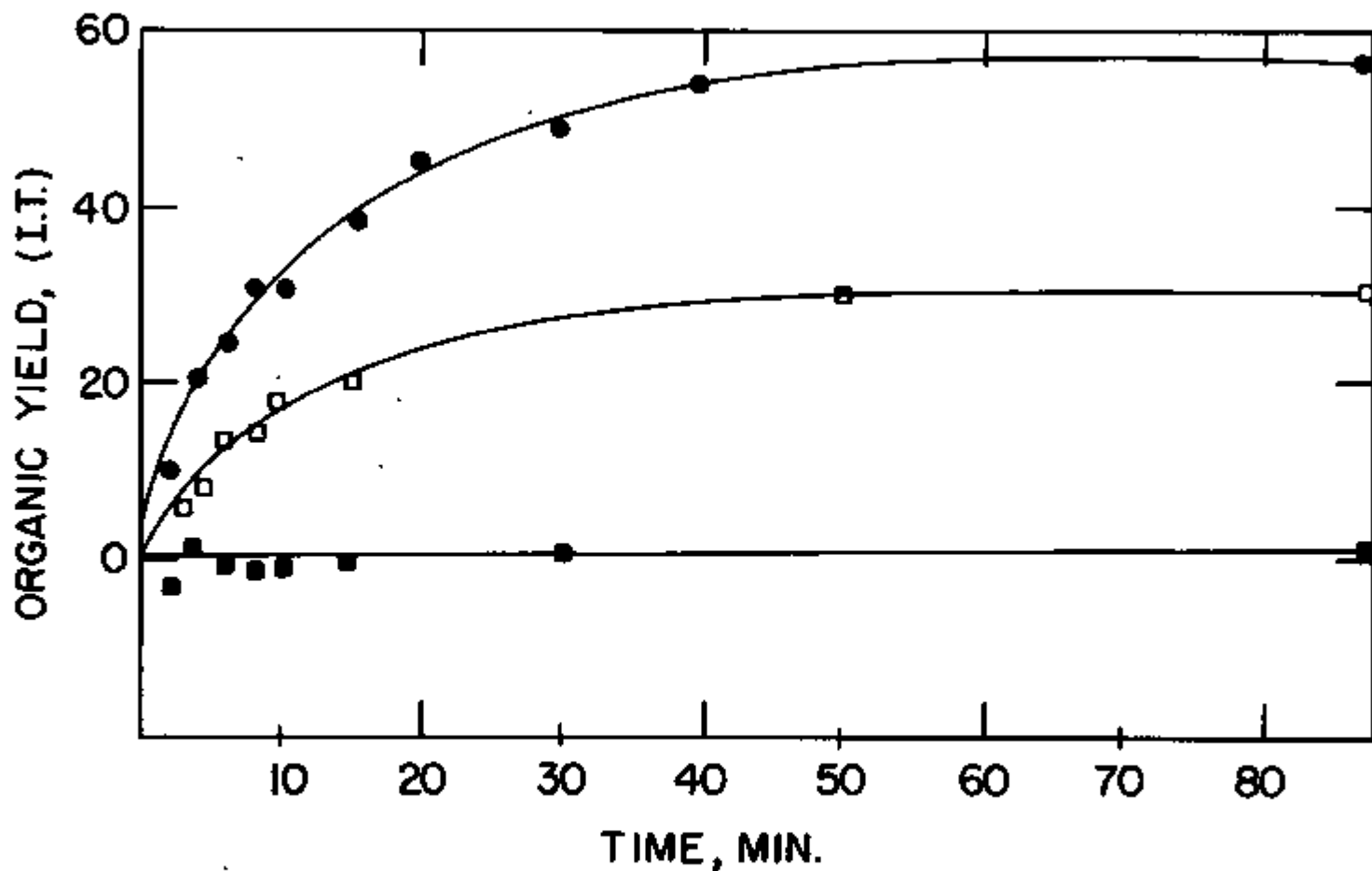


Figure.10. Growth of ^{130}I Organic Yields by the $^{131}\text{I}^{\text{m}}$ (IT) ^{130}I reaction in Liquid Chloromethanes -- 0.0003 mf I_2 .
Systems: CH_2Cl_2 , ●; CHCl_3 , □; CCl_4 , .

as calculated by equation (6) from the value observed after essentially complete decay of all $^{130}\text{I}^{\text{m}}$ is $1.8 \pm 2.0\%$. This is in substantial agreement with the value of 1.9% obtained by the extrapolation technique discussed previously. Additionally, isomeric transition induced organic yields of ^{130}I were compared in the solid and liquid phase at 0.3×10^{-3} mf I_2 by dissolving identical quantities of iodine containing $^{130}\text{I}^{\text{m}}$ in equal aliquots of CCl_4 exactly 30 sec after the beginning of a 20-sec irradiation and freezing (5-7 sec) one sample immediately in liquid N_2 . Repetitions of this experiment produced values for ^{130}I organic yields by (IT) processes that were the same ($1.8 \pm 0.1\%$) in both the solid and liquid phase. Since the freezing process would be expected to physically separate a portion of the I_2 from contact with CCl_4 or other halomethane molecules as a result of fractional crystallization,⁶⁸ it is apparent that the organic reaction probability of an activated ^{130}I exposed to the halomethane-iodine interface must be greater than that of an activated ^{130}I in solution in order for the solid and liquid state yields to have the same value. The (n, γ) activated $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ organic yields in liquid CCl_4 systems were the same whether determined immediately after irradiation (maximum delay was 30 sec) or frozen and extracted after all $^{130}\text{I}^{\text{m}}$ had decayed; this suggests either that activity born into organic or inorganic com-

ination remains predominantly as organic or inorganic activity after isomeric decay in the solid state, or that the overall extent of transfer from organic to inorganic activity and vice versa is equivalent and the net observed change in yield is negligible. The I_2-CCl_4 system is the first system ever observed where the organic yield of an (n, γ) activated halogen is greater than that of an (IT) activated halogen; whereas, for $I_2-CH_2Cl_2$, I_2-CHCl_3 , and I_2-CFCl_3 systems, $^{130}_{I^m}(IT)^{130}_I$ activated yields are greater than those of (n, γ) activated $^{130}_I + ^{130}_{I^m}$ by a factor of 1.15 to 1.30 (see Table X). The differences observed for CCl_4 systems as compared to others studied may be explained on the basis of two factors: (1) steric barriers to the reactive approach of the iodine ion to the carbon atom are greater for CCl_4 , and (2) the only target fragment found in combination with iodine is CCl_3 which may be sufficiently stable to diffuse away from the activated $^{130}_I$ before reacting with it in a liquid system, but not in a solid system. These factors are plausible reasons for (n, γ) yields greater than (IT) in liquid CCl_4 since the initial excess kinetic energy of the (n, γ) activated iodine species (a mean value of 100 ev is usually accepted) is larger than that accompanying (IT) processes (coulombic repulsion following Auger charging) and therefore steric factors are less effective in preventing reactive approach of (n, γ) activated $^{130}_I$. Additional

Table X
Iodine Organic Yields Induced by (n, γ) and (IT) Processes
in Various Liquid Polyhalomethanes

Solvent	Mole Fraction $I_2 \times 10^3$	Organic Yields ^a	
		^{130}I by (IT)	$^{130}I + ^{130}I^m$ by (n, γ) ^c
CH ₂ Cl ₂ ^a	0.3	53.9	44.3
	5.0	48.7	36.8
	10.0	43.5	35.3
CHCl ₃ ^a	0.3	30.4	23.6
	8.0	24.8	21.5
	12.0	23.3	19.2
CFCl ₃ ^a	0.3	16.3	11.3
	2.0	13.3	9.4
CCl ₄ ^b	0.3	1.9 ^d	3.5
	9.5	1.7	3.0 ^e
CCl ₃ Br ^b	0.3	1.9	---

^a Isomeric transition organic yields by freeze-thaw technique (15 sec irradiation).

^b Isomeric transition organic yields by post-irradiation introduction of $^{130}I^m$.

^c Sample frozen 7 sec after 15 sec irradiation.

^d Solid and liquid state.

^e Estimated from (n, γ) + (IT) determinations and separate (IT) determinations.

evidence of the importance of molecular and atomic dimensions is shown by the finding that for 0.3×10^{-3} mf Br_2 in CCl_4 , organic yields induced by $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$ and $^{82}\text{Br}^m$ (IT) ^{82}Br processes in the liquid state were 20-30 percent.⁵⁴ It was, therefore, interesting that $^{130}\text{I}^m$ (IT) ^{130}I and ^{129}I (n, γ) ^{130}I induced organic retentions would be low (less than 5%) at all mole fractions halogen studied, especially since the most probable product, CCl_3I , is a stable compound.⁷⁰ In $^{131}\text{I}_2\text{-CCl}_4$ radiation damage studies, we obtained yields of iodine in organic combinations as high as 17 percent at 3.0×10^{-4} mf I_2 for 30 min irradiation (see Fig. 11). This possibly suggests that in the CCl_4 system, the environment created by nuclear processes is less conducive to the formation of stable iodine products than that in systems exposed to external radiation as observed by iodine scavenging of radiation-produced radicals. The 1.9% organic yield of (IT) activated ^{130}I observed in $\text{I}_2\text{CCl}_3\text{Br}$ systems, where the hetero-substituent of the solvent molecule has greater atomic mass than chlorine and is less energetically bound to the carbon also supports the view that shielding from reactive approach and possibly the stability of target molecule fragments is dependent on the dimensions and number of the substituents. It was not possible to determine (n, γ) activated yields because of interference by the several bromine isotopes produced in reactor irradiations of CCl_3Br .

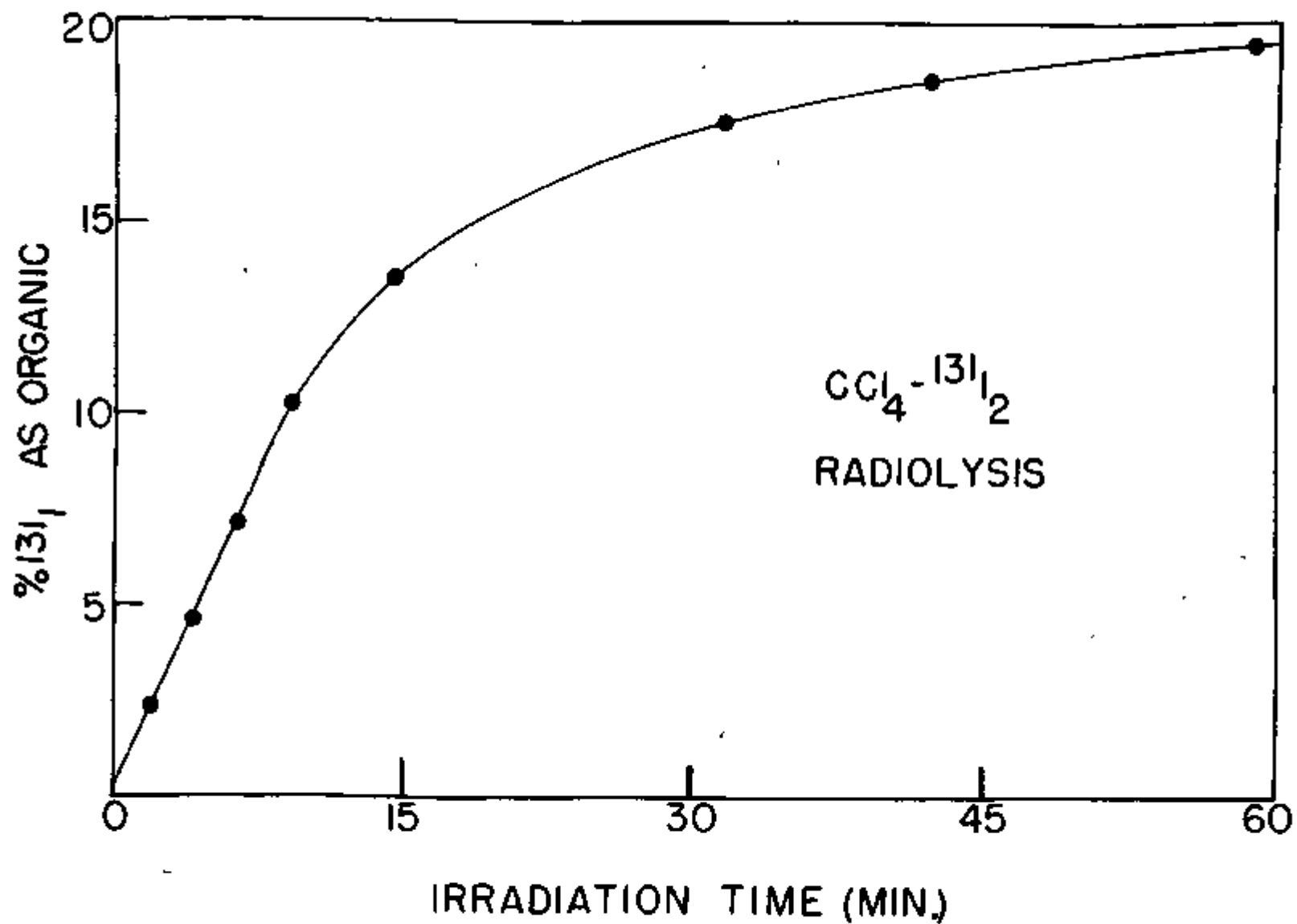


Figure 11. Radiation pickup of ¹³¹I in CCl₄ systems at 0.3 x 10⁻³ mf I₂.

Correlation of Organic Yields and
Product Distributions

Representative values of the ^{130}I radiative neutron capture and isomeric transition induced reactions with the systems studied are shown in Table X. The data show that the total organic yields decrease for the systems in the order $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CFCl}_3 > \text{CCl}_4 \approx \text{CCl}_3\text{Br}$. Table XI and Fig. 12 present the individual product yields for the $^{129}\text{I}(n,\gamma)^{130}\text{I} + ^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ induced reactions in several liquid polyhalomethanes. Product distributions and total organic yields were determined by irradiating liquid samples of $^{127}\text{I}_2 + ^{129}\text{I}_2$ in the systems shown with thermal neutrons for 1 min. At least 99.9% of the $^{130}\text{I}^{\text{m}}$ was allowed to decay in the liquid state in all systems. It is of interest to note that the total organic yield observed by irradiating a liquid sample and allowing all the isomeric transition events to occur in the liquid phase will result in an observed organic yield which is within a few percent of the isomeric transition organic yield. The effect of a 30 min irradiation was an increase in the organic yield in systems with no C-H bonds; however, the effect of duration of irradiation or of preparing the sample as described in a previous section (products formed by (IT) processes exclusively) did not appear to influence the relative product distributions.

Table XI
 Individual Product Organic Yields^a Resulting From $^{129}\text{I}(n,\gamma)^{130}\text{I}^{\text{m}}(\text{IT})$
 ^{130}I Processes in Liquid Polyhalomethanes

Systems	CH_2Cl_2	CHCl_3	CFCl_3	CCl_4	CCl_3Br
Mole Fraction $\text{I}_2 \times 10^4$	5.0	6.2	7.2	6.7	6.0
Product, O.Y. ^b	CH_2ClI , 37.8	CHCl_2I , 19.3	CFCl_2I , 3.5	CCl_3I , 3.5	$\text{CCl}_3\text{I}^{\text{c}}$, 0.5
	CHCl_2I , 15.0	CCl_3I , 5.0	CCl_3I , 1.0	---	CCl_2BrI 1.4 and other
	---	Other ^d 6.3	Other ^d 1.4	---	---
Total O.Y.	52.8	30.6	15.9	3.5	1.9

^a Yields from 1 min irradiation (except as indicated) in the liquid state and are resultant average of at least three runs

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

^c Products by $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ activations only.

^d Two later eluting peaks of approximately equal area; possible polymers.⁷¹

^e Broad peaks, possible decomposition at elution temperatures.

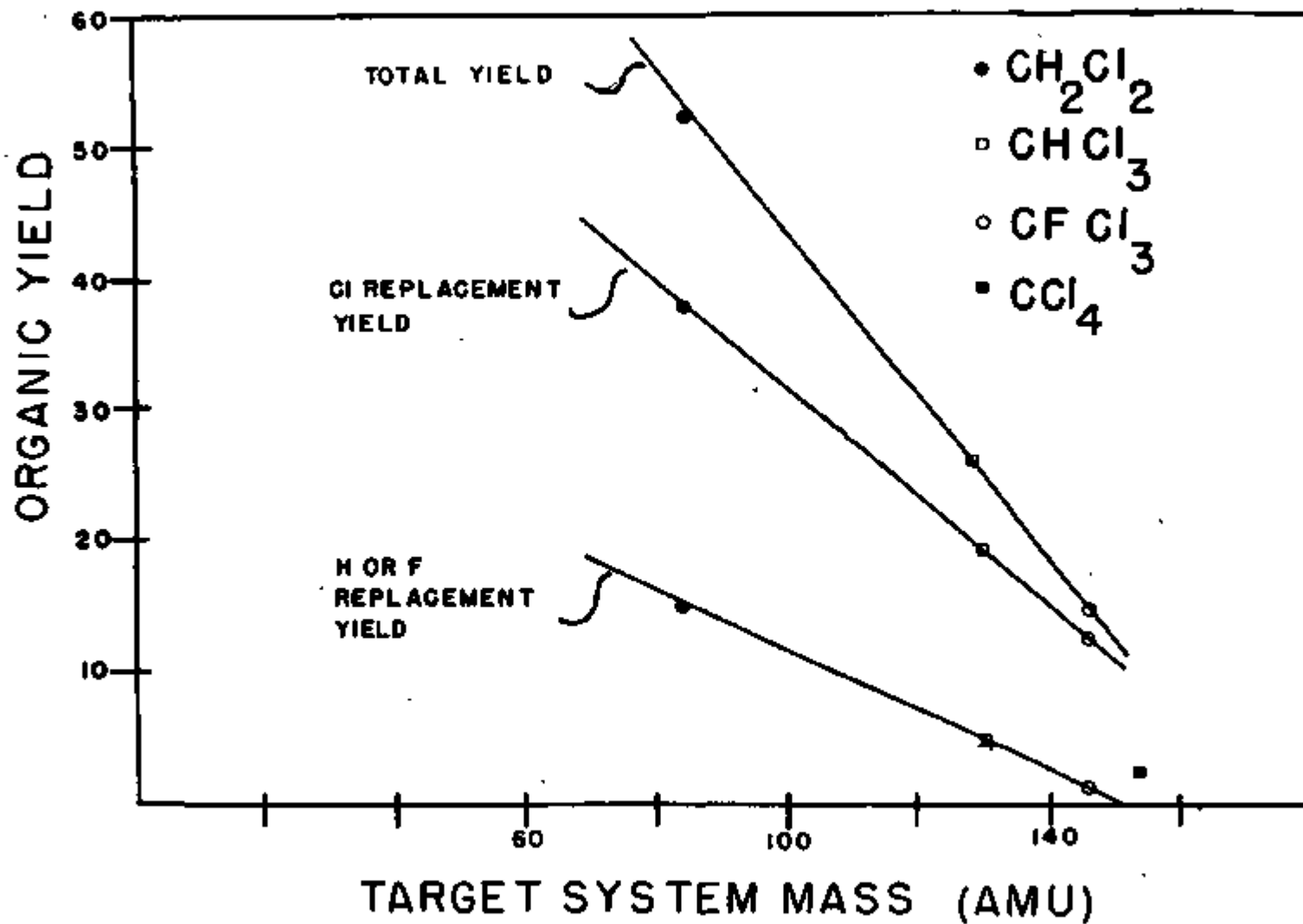


Figure 12. Total ¹³⁰I organic yields and individual product yields for liquid halomethane systems.

The trends found are that activated ^{130}I is preferentially stabilized in organic combination with the target molecule fragment of least mass in the various systems shown. This corresponds to the Cl-replacement yield in Fig. 12, and may indicate that lower rotational inertia of lighter fragments results in a higher probability of forming a stable organic iodide. For H and Cl substituted methanes, the ratios of Cl and H replacement products are approximately inversely proportional to the masses of the target molecule fragments combining to form a stable organic product. For CFCl_3 systems, the ratios of the observed target molecule fragments are close to unity; however, the ratio of Cl replacement to F replacement is 13:1, and indicates that the nature of the substituents has a substantial effect on the reaction patterns of activated iodine with halomethanes. The only product definitely identified in $\text{I}_2\text{CCl}_3\text{Br}$ systems was CCl_3I because of decomposition of chloro-, bromo-, iodo-substituted products.

Extensive comparison of the total reactivity and product distributions of (n, γ) activated ^{128}I and $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ in hydrocarbon systems⁵⁸ and comparison of available ^{128}I data in halomethanes⁷² with ^{130}I data obtained in this study indicate that the nature of the activated species is very nearly the same in all cases, but that the total production of organic iodide by (n, γ) activated

$^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ is less than that produced by (n,γ) activated ^{128}I or (IT) activated ^{130}I which are identical within experimental limits and must be so because of equally charged fractions since only a fortuitous combination of their unequal initial kinetic energies and differing charged fractions would produce the similarities observed. It is well established that at least 50% of the (n,γ) activated ^{128}I is charged,⁵⁰ and since it can be assumed that approximately 100% of the (IT) activated ^{130}I is positively charged as a result of internal conversion and Auger processes,^{41,47} the similarity of total organic yields and product distributions suggest that ^{128}I may also be approximately 100% charged following activation by (n,γ) processes. Comparison of the dissimilar gamma emission spectra⁴⁷ of ^{130}I to that⁶³ of ^{128}I do not suggest that the same fraction of charged iodine species would be formed as a result of internal conversion processes following $^{127}\text{I}(n,\gamma)^{128}\text{I}$ and $^{129}\text{I}(n,\gamma)^{130}\text{I}$, $^{130}\text{I}^{\text{m}}$ events. Therefore, the lower organic reactivity of (n,γ) activated $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ may be primarily attributable to a fractional yield of charged species that is less than that formed by (n,γ) activated ^{128}I or (IT) activated ^{130}I which the experimental evidence has shown to be completely analogous.

The first ionization potentials (assuming gas phase

values) of the polyhalomethanes studied are higher than that of iodine atoms (polyhalomethane >11.0 vs iodine atom 10.44); consequently, a positively charged ^{130}I ion, which has emitted several Auger electrons and is situated in a "radical pocket" created by those electrons, may undergo ion-radical and ion-molecule reactions with the solvent and charge transfer reactions. The result of ion-radical and ion-molecule reactions can be positively charged species of obvious lesser stability than comparable neutral species. Furthermore, if these charged species represent molecular arrangements of atoms that are inherently unstable even in the uncharged state, the probability of their survival may be very low. This type of mechanism may partially account for apparent lower survival of CCl_3I produced by nuclear activation than by iodine scavenging of radiation-produced radicals.

The differences in replacement product yields for the iodine reactions with the various polyhalomethanes may be the result of decreasing stability with increasing steric interactions among substituents.

CHAPTER IV
REACTIONS INDUCED BY (n, γ) ACTIVATIONS OF ^{128}I IN
HOMOLOGOUS HALOMETHANE GASES

Chapter IV

The $^{127}\text{I}(n,\gamma)^{128}\text{I}$ reaction produces ^{128}I species with kinetic energies as high as 182 ev and a positive charge for at least 50% of the atoms.⁵⁰ In addition, at least 25% of the iodine ions formed in this manner are in one of several possible excited states.³⁷

The study of reactions of ^{128}I with gaseous alkane and alkyl halide systems^{26,36,37,73-75} has also indicated the existence of a multiplicity of ionic and electronically excited iodine species. Cross and Wolfgang⁷⁶ studied reactions of (γ,n) activated ^{126}I with CH_3I and obtained results (4%) higher than those reported for (n,γ) activated reactions of ^{128}I with CH_3I (1%).^{36,37} If iodine nuclei formed by (γ,n) reaction are not excited to metastable levels which may de-excite by the emission of low-energy gamma rays and cause re-ionization of the recoil atom after it has undergone collisional de-excitation, the high kinetic energy (10-100 Kev) imparted by neutron emission should allow the recoiling species to reach electronic equilibrium before its energy decreases sufficiently for chemical combination to occur.⁷ The lower organic yield values obtained for (n,γ) activated reactions of iodine with CH_3I suggest that if organic products (primarily CH_3I) are formed as a result of reaction with excited or ionized species, their survival probability is lower than those

formed by reaction with ground state or neutral species. However, it has been definitively shown that (n, γ) induced reactions of ^{128}I with CH_4 , whose major product is also CH_3I , produce an organic yield of at least 36% as a result of reaction with excited and/or charged ^{128}I ,³⁷ indicating that the nature of the environment and properties of the reagent or target system are also primary factors controlling the stabilization of the labeled iodine-128 as an organic product.

In an attempt to determine the role of activated-atom and molecular parameters, we have studied the reactions of (n, γ) activated ^{128}I species with CH_3X , CH_2X_2 , CHX_3 , CX_4 (X=F and Cl) and mixed halogen CFCl_3 and CF_3I systems. These systems allow the variation of target molecule parameters such as ionization potential, mass, steric factors and capability of forming a stable product with the attacking atom.

Determination of ^{128}I Limiting Organic Yields

Contained in Table XII, are the percent ^{128}I found as organic for various mixtures of molecular additive, polyhalomethane and 0.1 mm I_2 .

In order to interpret properly the relative effects of the additives on the ^{128}I + polyhalomethane reaction, the data must be corrected as follows:

Table XII
 PERCENT ^{128}I STABILIZED IN ORGANIC COMBINATION FOR
 VARIOUS GASEOUS SYSTEMS

System	Total ^a Pressure	Additive	Additive Pressure b	M.F. Additive	Percent ^c ^{128}I as Organic
$\text{CH}_3\text{F}^{\text{d}}$	696	CH_3I	12	0.018	7.4
	669		29	0.043	6.4
	671		45	0.067	7.0
	600		90	0.130	5.9
	211		3	0.014	6.3
	196		10	0.054	5.5
	214		14	0.064	6.1
	200	19	0.095	4.9	
	685	CF_3I	42	0.059	4.7
	690		22	0.032	5.1
$\text{CH}_2\text{F}_2^{\text{d}}$	692	CH_3I	12	0.017	3.4
	680		30	0.044	3.4
	203		6	0.030	2.1
	199		11	0.052	2.2
	198		22	0.111	2.1
CHF_3^{d}	716	CH_3I	6	0.008	2.6
	667		15	0.022	2.3
	683		28	0.040	3.3
	653		66	0.101	2.2
	202		6	0.030	2.0
	196		11	0.056	1.4
	221		18	0.081	1.4
	216		23	0.106	1.9

Table XII (continued)

System	Total ^a Pressure	Additive	Additive Pressure b	M.F. Additive	Percent ^c I ₂₈ as Organic
CF ₄ ^d	687	CH ₃ I	7	0.008	1.7
	685		29	0.040	1.7
	685		97	0.131	1.8
	197		11	0.056	1.5
	197		20	0.108	1.7
	197		6	0.031	1.6
CH ₃ Cl	714	CH ₃ I	6	0.008	5.1
	718		17	0.024	5.1
	626		23	0.037	4.7
	700		52	0.074	4.4
	649		59	0.090	4.1
	645		82	0.127	3.7
	210		3	0.014	4.3
	204		16	0.085	3.2
	201		25	0.124	2.5
CH ₂ Cl ₂	194	CH ₃ I	12	0.056	1.8
	194		21	0.108	2.1
	193		29	0.130	1.8
CHCl ₃	102	CH ₃ I	8	0.078	1.5
	103		23	0.240	2.6
CFCl ₃	207	CH ₃ I	4	0.020	1.1
	193		14	0.070	1.7
	192		19	0.099	1.8

^a Calculated assuming additive pressures.

^b All samples contained 0.1 mm I₂.

^c An uncertainty of ± 0.5% is associated with this data. Generally triplicate samples.

^d Private communication, D. W. Oates.

(1) As a result of cancellation of gamma-ray momenta in (n, γ) cascade-gamma emission, a small fraction of the activated ^{128}I will receive a net gamma-recoil which is less than that required for the ^{128}I to rupture from its parent molecule. The percent failure to bond-rupture has been reported as 1.1% and 0.1% for CH_3I and CF_3I respectively.³⁶

(2) Nuclear-activated ^{128}I reacts with the CH_3I and CF_3I additives to form labeled organic iodides. The organic yield values (corrected for failure to bond-rupture) for pure CH_3I and CF_3I systems scavenged with 0.1 - 0.2 mm of I_2 are 0.2% and 0.1%. On the basis of this data, the corrections for ^{128}I reactions with additive are 0.2% for CH_3I and 0.1% for CF_3I at the additive pressures employed.

(3) As a result of the 3×10^{17} $\text{ev g}^{-1} \text{min}^{-1}$ gamma-radiation flux associated with the neutron irradiations, any radiative-induced reactions will result in the transfer of some inorganic ^{128}I to organically bound ^{128}I . Determination of radiation induced pick-up of ^{128}I was made by obtaining organic yields for increasing irradiation times and extrapolating to zero irradiation time. For the conditions employed, the radiation induced pick-up was circa 0.1%.

The data, corrected for the effects described, were

plotted and extrapolated to zero mole fraction additive. The limiting organic yields are shown in Table XIII.

Organic Yields and Product Distributions as an
Indication of System Parameters

The information presented in Table XIII indicates that the effect of increasing both the size and number of halogen substituents on the methane target molecule is a decrease in the organic yield for the series studied. All the reactions were studied at total system pressures of 200 mm and 700 mm Hg except as indicated. The presence of a small but consistent pressure effect, wherever comparisons were made, suggests the formation of excited products that have a higher survival probability in higher pressure systems where collisional de-excitation is more favorable.

The relationship of the organic yields to mass and substituent effects is depicted for the two homologous series and associated compounds³⁶ in Fig. 13. The general flow of arrows shown in Fig. 13 is in the direction of decreasing organic yields, increasing target molecule mass, and also in the direction of increasing mass of possible target molecule fragments that may combine with the activated iodine. However, the direct comparison of

Table XIII
 LIMITING ^{128}I ORGANIC YIELDS^a IN VARIOUS
 POLYHALOMETHANES^d

Pressure = 700 mm				Pressure = 200 mm			
CH_3F	6.2	CH_3Cl	4.3	CH_3F	5.4	CH_3Cl	3.6
CH_2F_2	2.5	CH_2Cl_2	b	CH_2F_2	1.2	CH_2Cl_2	0.7
CHF_3	1.6	CHCl_3	b	CHF_3	1.0	CHCl_3	0.2 ^c
CF_4	0.5	CFCl_3	0.1	CF_4	0.3	CFCl_3	0.1

^a Uncertainty in extrapolated values of $\pm 0.5\%$.

^b Ambient temperature vapor pressure < 700 mm.

^c System pressure = 100 mm.

^d Fluorocarbons, private communication, D. W. Oates.

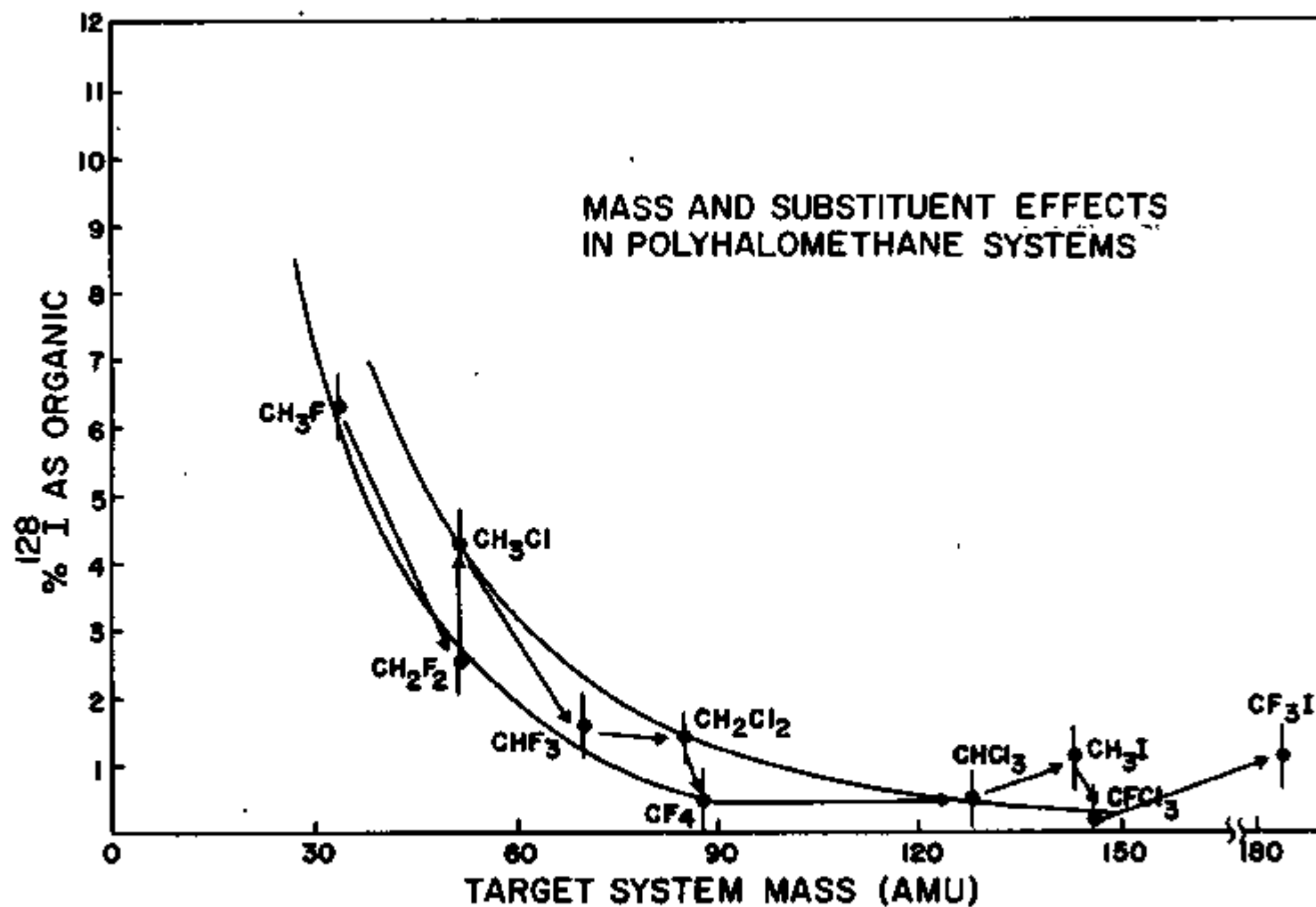


Figure 13. Organic yield versus target system mass for ¹²⁸I + polyhalomethane reaction systems. Correlations are described in text.

the two series and related compounds has shown that in addition to mass effects, the steric effects of various substituents are important factors controlling total organic reactivity, i.e., in areas where vertical or near-vertical arrows are shown will be found compounds of similar mass and differing organic reactivity as a consequence of unequal number of substituents presenting steric barriers to reaction; conversely, in areas of horizontal or near-horizontal arrows will be found compounds of equal organic reactivity and unequal mass and again this may be ascribed to an unequal number of substituents presenting steric barriers to reaction.

Although a combination of low activity and interference from ^{38}Cl activity did not allow product determinations in gaseous chloromethane systems, a consideration of trends in total reactivity suggests they would not be considerably different from those found for liquid systems. Single replacement products were found to comprise the major fraction of organic activity in fluoromethane systems and the ratios of these products are shown in Table XIV. The dominant trend observed in these systems as well as the liquid systems is that although the total organic yield decreases with increasing halogen substitution, halogens are preferentially replaced by the activated ^{128}I . Wolfgang⁷ has recently reported similar observations for photonuclear

Table XIV
 RATIOS OF ^{128}I AS ORGANIC IODIDES IN DIFFERENT
 ADDITIVE POLYFLUOROMETHANE SYSTEMS AT 700 mm PRESSURE

System	Mole Fraction Additive	Product Ratio a, b		Organic Yield (Corrected)
$\text{CH}_3\text{F}-\text{CF}_3\text{I}$	0.010	CH_3I 1.00	CH_2FI 0.68	6.0
$\text{CH}_2\text{F}_2-\text{CH}_3\text{I}$	0.020	CH_2FI 1.00	CHF_2I 0.90	3.4
$\text{CHF}_3-\text{CH}_3\text{I}$	0.020	CHF_2I 1.00	CF_3I 0.85	1.5
$\text{CF}_4-\text{CH}_3\text{I}$	0.020	CF_3I 1.00	Other 0.10	0.5

^a Average of three or more determinations.

^b Estimated variation \pm 0.10.

induced reactions of ^{18}F and ^{39}Cl which have sufficiently high initial kinetic energies that they are expected to enter the range of chemical energies as neutral species. He has postulated that for these neutral recoiling species the results obtained may be ascribed to a "translational inertial" factor. This hypothesis states that for replacement reaction to occur, the translationally hot halogen must strike in the vicinity of the central carbon atom, tending to stop the motion of both the C atom and the incident hot halogen. The ligand halogen and hydrogen atoms will tend to continue in the direction of their original motion. From conservation-of-momentum calculations it can be seen that this will greatly strain and weaken the carbon-halogen bond but there will be little effect on the carbon-hydrogen bond, and thus it is plausible that a halogen substituent will be preferentially detached. Although evidence presented in Chapter III and Chapter V of this thesis strongly suggest that nuclear activated ^{128}I reacts primarily as an ion, this replacement mechanism followed by charge transfer neutralization of the product ion is a reasonable explanation of the observed processes.

It is known that 25% of the ^{128}I formed by (n, γ) activation is I^+ ($^1\text{D}_2$) ions which have a potential energy of 12.16 ev.³⁷ It is evident that charge alone is not responsible for the reactivity of the activated species

since all the chloromethanes studied have ionization potentials less than 12.00 ev, and therefore charge transfer interactions might be expected with chloromethanes but not fluoromethanes which have ionization potentials greater than 12.50 ev. However, the reactivities observed appear to be related primarily to steric obstruction of reactive approach of the activated iodine by the halogen substituents rather than directly related to target molecule properties such as mass or ionization potential. The relationship of charge and excess kinetic energy to the reactivity of (n, γ) activated ^{128}I is discussed further in Chapter V.

CHAPTER V
GAS-PHASE REACTIONS OF EXCITED ^{128}I IONS WITH CH_3F

Chapter V

Gas-Phase Reactions of Excited ^{128}I Ions with CH_3F

The reactive iodine species in reactions of (n, γ)-activated ^{128}I with CH_4 have been shown to be atoms or ions possessing excess kinetic energy and translationally thermalized but electronically excited I^+ ($^1\text{D}_2$) ions, or I^+ ions in $^3\text{P}_2$, $^3\text{P}_1$, and/or $^3\text{P}_0$ states.³⁷

The above reaction is apparently unique in that 54% of the ^{128}I activity is stabilized as an organic product; whereas, (n, γ)-activated ^{128}I reactions with similar molecules result in much lower organic yields, i.e., C_2H_6 (2%), C_3H_8 (3%), and CH_3I (1%).^{36,74}

The reactions of ^{128}I , formed by (n, γ) activation, with fluoromethane were investigated in an attempt to determine the relative importance of ionization potential, mass, steric shielding, and polarity, to the interaction of attacking species with substituted methane systems. The ^{128}I limiting organic yield in CH_3F is sufficiently large ($6.3 \pm 0.5\%$) that the effects of molecular additives can be readily observed.

Environmental modification was accomplished by introducing varying amounts of gaseous additives into the iodine-fluoromethane reaction systems. The data of Table XV, represent the observed organic yields in the various fluoromethane-additive systems.

Table XV
 PERCENT ^{128}I STABILIZED IN ORGANIC COMBINATION FOR
 VARIOUS FLUOROMETHANE-ADDITIVE SYSTEMS

System	Total ^a Pressure	Additive	Additive Pressure b	M.F. Additive	Percent ^c ^{128}I as Organic
CH_3F	696	$\text{CH}_3\text{I}^{\text{d}}$	12	0.018	7.4
	669		29	0.043	6.4
	671		45	0.067	7.0
	600		90	0.130	5.9
	680		ICl	4	0.006
	700	9		0.013	3.4
	700	15		0.025	.2
	685	32		0.047	>.1
	667	CF_3I		105	0.160
	685		42	0.059	4.7
690	22		0.032	5.1	
	680	IF_5	10	0.015	6.4
	665		16	0.024	6.2
	670		21	0.032	6.4

^a Calculated assuming additive pressures.

^b All samples contained 0.1 mm I_2 .

^c An uncertainty of $\pm 0.5\%$ is associated with this data.
 Triplicate samples.

^d Private communication, D. W. Oates

CH₃I, CF₃I, IF₅, AND ICl Additives

The CF₃I and CH₃I additive systems were corrected for the 0.1% and 1.1% (respectively) failure to bond-rupture of the source molecules as discussed in Chapter IV, and the values obtained were plotted as shown in Fig. 14. Within the limits of experimental variation, the failure to bond-rupture for ICl and IF₅ is probably $\leq 0.5\%$, since corrections for these systems did not appear to be necessary. As obtained from Fig. 14, the ¹²⁸I limiting organic yield at zero mole-fraction additive is $6.3 \pm 0.5\%$. Data for ³⁸Cl organic yields (omitted from Fig. 14 for purposes of clarity) in ICl-CH₃F systems are shown in Table XVI.

Table XVI
COMPARISON OF (n,γ) ACTIVATED ³⁸Cl AND ¹²⁸I ORGANIC
IN CH₃F-ICl^a GASEOUS MIXTURES

ICl Mole Fraction	% ³⁸ Cl as Organic ^b	% ¹²⁸ I as Organic
0.006	11.4	5.4
0.025	3.9	0.2
0.047	3.8	0.1

^a 0.1 - 0.2 mm I₂ also present.

^b Maximum uncertainty is $\pm 1.0\%$.

The comparison of ³⁸Cl and ¹²⁸I organic yields in multi-isotope systems indicates higher yields for ³⁸Cl reactions with CH₃F. This is not unexpected from consid-

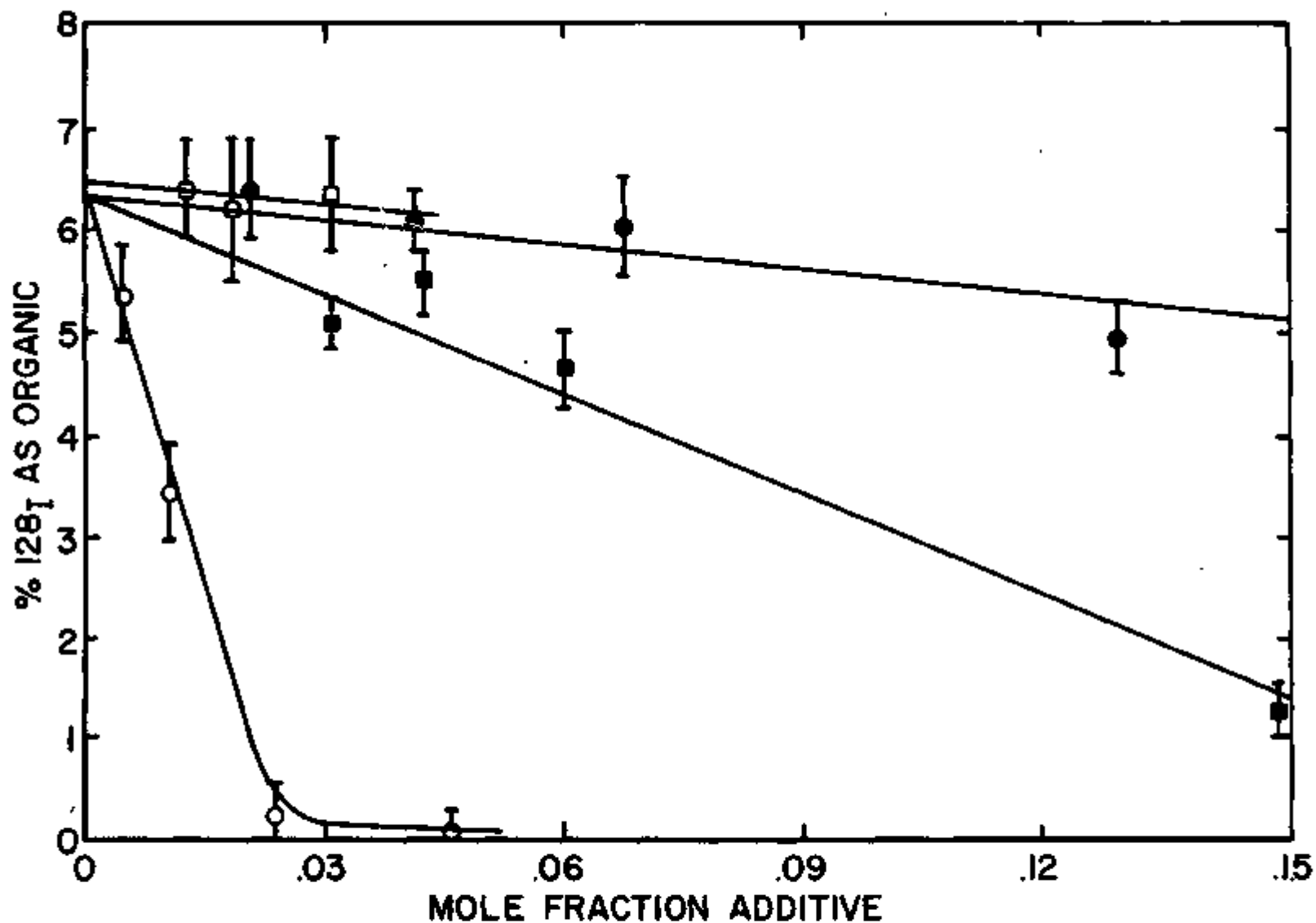


Figure 14. Effect of additives on the reaction of ^{128}I with gaseous CH_3F at ≈ 700 mm pressure. ICl and IF_5 terminated at limiting vapor pressure. Additives: IF_5 , \blacksquare ; CH_3I , \bullet ; CF_3I , \circ ; ICl , \triangle .

eration of differences such as charge state of the recoiling species and atomic dimensions which, as previously discussed, are important factors controlling stabilization as an organic product. The divergence of additives curves in Fig. 14 is much greater than would be expected from differences in their ability to moderate kinetic-energy dependent reactions and must result from the varying efficiency of the several additives to deactivate charged and/or excited iodine species.

Presented in Table XVII are the ratios of single replacement products which constitute the major fraction of organic activity. Products resulting from double replacement varies for different systems and could not be compared directly. Significant trends shown are that increasing additive concentration causes a decrease in hydrogen-replacement relative to halogen replacement and the magnitude of the decrease is proportional to the effectiveness of the additive in inhibiting the formation of stable organic products incorporating ^{128}I .

The finding that the additives employed inhibit the $\text{I} + \text{CH}_3\text{F}$ reaction producing organic iodides in the order $\text{ICl} > \text{CF}_3\text{I} > \text{CH}_3\text{I} \approx \text{IF}_5$ suggests the possibility that comparatively long-range resonance interaction⁸⁶ as well as collisional de-excitation are important processes in deactivating the attacking iodine because the effects observed in the ICl and CF_3I additive systems are considerably

Table XVII
 DISTRIBUTIONS OF ^{128}I AS ORGANIC IODIDES IN DIFFERENT
 ADDITIVE CH_3F SYSTEMS AT 700 mm PRESSURE

System	Mole Fraction Additive	Product Ratio ^a		Organic Yield ^b
		CH_3I	CH_2FI	
$\text{CH}_3\text{F-IP}_5$	0.010	1.00	0.71	6.3
$\text{CH}_3\text{F-CF}_3\text{I}$	0.010	1.00	0.68	6.0
$\text{CH}_3\text{F-CF}_3\text{I}$	0.157	1.00	0.25	1.5
$\text{CH}_3\text{F-ICl}$	0.006	1.00	0.65	5.6
$\text{CH}_3\text{F-ICl}$	0.032	1.00	0.14	0.2

^a Average of three or more determinations.

^b Experimental deviation, $\pm 0.5\%$.

larger than would be possible to attribute to kinetic energy moderation for the mole fractions additive present.⁷⁸

Gurnee and Magee⁷⁹ have calculated the relative probabilities of charge transfer reactions as a function of the relative velocities of the species involved and their energies. Their results indicate that the charge-transfer cross-section increases as the energy defect approaches zero. The ionization potentials of CF_3I and ICl are lower than the ionization potential of I^+ ions by only 0.054 eV,⁸⁰ and the first excited level of ICl is 0.07 eV^{80,82} lower in potential energy than $\text{I}^+(\text{}^1\text{D}_2)$ ions; therefore, near-resonant charge transfer neutralization of $\text{I}^+(\text{}^1\text{D}_2)$ ions by ICl and of I^+ ions by ICl and CF_3I may be possible.⁷⁹ CH_3I and IF_5 apparently do not interact with activated ^{128}I in the same manner as the previously discussed additives, because the ionization potentials of these molecules (9.54 and 13.5 respectively) are considerably different from that of any activated iodine species. At high additive concentrations, CH_3I would be expected to neutralize eventually any iodine ions present due to its lower ionization potential, but at low concentrations, apparently both CH_3I and IF_5 primarily undergo short-range⁸⁶ charge-transfer reactions that can occur only with an accompanying transfer of translational energy because of the magnitude of the energy differences.⁷⁸

The efficiency of additives such as ICl in decreasing the organic yield by processes involving the removal of charge and excitation from the activated species are strong evidence that reaction of neutral atoms by reaction pathways involving only excess kinetic energy are negligible. Similar results are predicted according to calculations by Filatov⁸¹ indicating that a $\text{CH}_3^{128}\text{I}$ molecule formed by replacement of a substituent atom by an ^{128}I atom will have too much energy to be stabilized in the gas phase.

The relative increase in halogen replacement product as a function of increasing mole fraction additive suggests a primary role for charge and/or excitation in reactions involving hydrogen-replacement since the probability that a recoiling ion will be neutralized is increased at higher additive concentrations. This effect was only observed for additives capable of charge and/or excitation removal from the activated ^{128}I and suggests that if reaction of atoms possessing excess kinetic energy with target molecules does occur to a small extent, the probability of replacing the heavier halogen substituent rather than a hydrogen is considerably enhanced as shown in Table XVII. Wolfgang and co-workers^{83,84} have recently reported that reactions of neutral, ground state, recoiling F and Cl atoms with halomethanes preferentially yield halogen replace-

ment products as a result of "steric" and "inertial" factors associated with the target molecule, which were discussed in Chapter IV.

CH₃F-CH₄ Systems

Previous work^{36,37} has shown that by introducing varying amounts of gaseous molecules into the iodine-methane reaction systems, it is possible to determine the manner in which these additives affect the ¹²⁸I + CH₄ reaction and determine indirectly the manner in which ¹²⁸I interacts with the additives. Shown in Table XVIII. are the experimentally observed organic yields and the calculated extents of reaction due to excess kinetic energy processes and reactions of I⁺(¹D₂) ions as discussed below. The calculations are described in Appendix I.

It was found that after subtracting contributions to the over-all organic yield resulting from iodine reaction with additive, the addition of CH₃F to methane reaction systems reduced the yield of organic ¹²⁸I to 11%, as shown in Fig. 15. Evaluation of this data in a manner analogous to that of Rack and Gordus³⁶ indicates that in addition to an 18% decrease in the iodine organic yield from 54% to 36% by inhibiting kinetic energy dependent reaction, the yield is further decreased another 25% by

Table XVIII
 EFFECT OF CH₃F ON ¹²⁸I + CH₄ REACTIONS BY EXCESS
 KINETIC ENERGY AND ION-MOLECULE PROCESSES^a

Mole Fraction CH ₃ F	Organic Yield Observed	Organic Yield KE Dependt.	Organic Yield (I ⁺ (¹ D ₂)+CH ₄) ^c
0.000	57.6	18.4	28.2
0.000	52.5	18.4	23.1
0.000	58.1	18.4	28.7
0.206	41.9	12.2	17.4
0.206	48.0	12.2	23.5
0.425	37.8	8.1	16.1
0.425	37.7	8.1	15.9
0.425	40.6	8.1	18.9
0.674	28.8	4.0	9.7
0.674	33.3	4.0	14.1
0.674	30.5	4.0	11.4
0.794	25.2	2.4	7.0
0.794	27.5	2.4	9.2
0.794	27.1	2.4	8.8

^a Calculated as in Appendix I.

^b Calculated from average experimental values.

^c In collaboration with D. W. Oates.

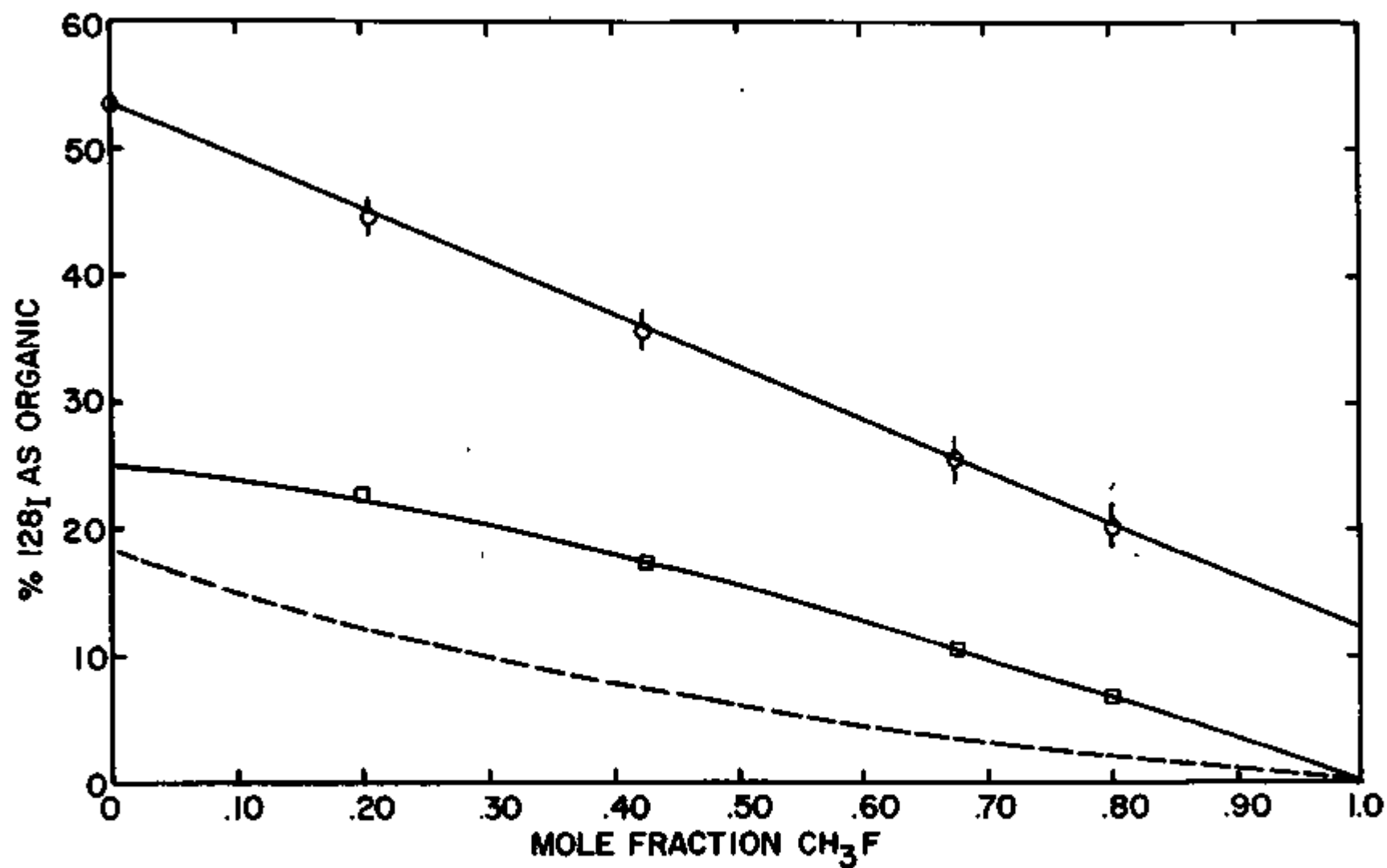


Figure 15. Effect of CH_3F additive on reaction of ^{128}I with CH_4 . CH_3F , \circ ; $\text{I}^+(\text{}^1\text{D}_2) + \text{CH}_4$, \square ; ---, see text.

possible hydrogen abstraction reaction of $I^+(^1D_2)$ ions with CH_3F . The lower solid curve and dashed curve represent the inhibition of $I^+(^1D_2) + CH_4$ and kinetic energy dependent reactions respectively; the sum of corresponding points on these curves plus the 11% organic yield not affected by CH_3F additive are equal to the experimentally determined values depicted by the upper curve. Bonding and structural differences of the additive molecule may be predominant reasons for this since the ionization potentials of CH_4 and CH_3F , 12.99 ev and 12.80 ev, are both greater than $I^+(^1D_2)$, 12.16 ev.

The significantly lower iodine organic yields with CH_3F compared to CH_4 are at least partially caused by the greater probability of hydrogen abstraction in the former system. Differences in ionization potential cannot account for the effect observed; therefore changes in target molecule mass, steric shielding, and polarity as a consequence of F for H substitution, must account either singly or in combination for the lower probability of ^{128}I reacting to form organic products with CH_3F . However, the results of polyhalomethane studies discussed in Chapter IV show that steric factors may be more important than mass effects since molecules of near identical mass were found to have dissimilar reactivities that may be reasonably attributed to variations in steric obstruction to reactive approach of the attacking species.

The determination that the reactive ^{128}I is charged and/or excited approximately 100% of the time indicates that both endothermic and exothermic non-thermal reactions with the systems studied may be initiated by ^{128}I ions possessing excess kinetic energy. Wolf⁶⁵ has recently reported calculations for charge transfer cross-sections of endothermic and exothermic reactions showing that cross-sections for endothermic reactions are zero for low relative kinetic energies of the reactants, and go through a maximum, as relative kinetic energies increase, that is somewhat less than the maximum cross-section for exothermic reactions occurring at low energies (<1 ev), but nearly equivalent to the cross-section for exothermic processes in the 10-100 ev range since the exothermic cross-sections decrease with increasing relative kinetic energies. If the reactive species are iodine ions possessing excess kinetic energy, a similarity of cross-section for both endothermic and exothermic reactions may explain the general similarity of organic yields for the fluoro- and chloro-methane gaseous reactions which were independent of ionization potentials and related primarily to steric effects.

REFERENCES

REFERENCES

1. J. E. Willard, Ann. Rev. Nucl. Sci., 3, 193 (1953).
2. J. E. Willard, Symposium on Chemical Effects Associated with Nuclear Reactions and Radioactive Transformations, Vol. 1, p. 221, IAEA, Vienna (1965).
3. R. Wolfgang in "Progress in Reaction Kinetics", Vol. 3, G. Porter, ed., Pergamon Press, Oxford, 1965, p. 99-169.
4. R. Wolfgang, Ann. Rev. Phys. Chem., 16, 15 (1965).
5. I. G. Campbell, Advan. Inorg. Chem. Radiochem., 5, 135 (1963).
6. E. S. Filatov, Russ. Chem. Rev., 34, 680 (1965).
7. A. G. Maddock and R. Wolfgang, Nuclear Chemistry, Vol. 2, L. Yaffe, ed., Academic Press, New York, 1968, p. 185-249.
8. L. Szilard and T. A. Chalmers, Nature, 134, 462 (1934).
9. E. Amaldi, E. Fermi, B. Pontecorvo, F. Rasetti, and E. Segre, Proc. Roy. Soc. (London), A 149, 522 (1935).
10. E. Glueckauf and J. Fay, J. Chem. Soc., 390 (1936).
11. J. E. Willard, Ann. Rev. Phys. Chem., 6, 141 (1955).
12. J. E. Willard, Nucleonics, 19, No. 10, 61 (1961).
13. J. E. Willard, Proceedings of the 1960 Prague Symposium on Chemical Effects of Nuclear Transformations, Vol. 1, p. 215, IAEA, Vienna (1961).

14. A. P. Wolf in "Advances in Physical Organic Chemistry", Vol. 2, V. Gold, ed., Academic Press, New York, 1964, p. 202-277.
15. I. G. Campbell, Nukleonika, 3, 43 (1958); AEC-tr-4112 (translation).
16. G. N. Walton, Radiochim. Acta, 2, 201 (1964).
17. H. Muller, Angewandte Chemie, (English Edition) 6, 133 (1967).
18. G. Harbottle, Ann. Rev. Nucl. Sci., 16, 89 (1966).
19. T. Anderson, "Experimental Investigations of Chemical Effects Associated with Nuclear Transformations in Some Inorganic Solids", Aarhus University, Denmark, 1968.
20. A. Suida, Information Center of the Polish Atomic Energy Commission, Report No. 6 (1963).
21. Proceedings of Symposia on the Chemical Effects of Nuclear Transformations held in Prague, October, 1960, and published in two volumes; and Chemical Effects Associated with Nuclear Reactions and Radioactive Transformations held in Vienna, December, 1964, and published in two volumes by the International Atomic Energy Commission (IAEA).
22. W. F. Libby, J. Am. Chem. Soc., 69, 2523 (1947).
23. L. Friedman, and W. F. Libby, J. Chem. Phys., 17, 647 (1949).

24. M. Milman, Radiochim. Acta, 2, 180 (1964).
25. J. H. Mallison, G. E. Miller and P. F. D. Shaw, Phys., 20, 1556 (1952).
26. J. F. Hornig, G. Levey and J. E. Willard, J. Chem. Phys., 20, 1556 (1952).
27. P. J. Estrup and R. Wolfgang, J. Am. Chem. Soc., 82, 2661, 2665 (1960).
28. R. Wolfgang, J. Chem. Phys., 39, 2983 (1963).
29. J. M. Miller, J. W. Gryder, and R. W. Dodson, J. Chem. Phys., 18, 579 (1950).
30. W. F. Libby, J. Am. Chem. Soc., 62, 1930 (1940).
31. A. H. Rosenberg and R. Wolfgang, J. Chem. Phys., 41, 2159 (1964).
32. D. S. Urch and M. J. Welch, Symp. Chem. Effects Assoc. Nuclear Reactions, IAEA, Vienna, 1964.
33. L. Spicer and R. Wolfgang, J. Am. Chem. Soc., 90, 2426 (1968).
34. N. Colebourne, J. F. J. Todd and R. Wolfgang, Symp. Chem. Effects Assoc. Nuclear Reactions, IAEA, Vienna, 1964.
35. E. P. Rack and A. A. Gordus, J. Phys. Chem., 65, 944 (1961).
36. E. P. Rack and A. A. Gordus, J. Chem. Phys., 36, 287 (1962).
37. E. P. Rack and A. A. Gordus, J. Chem. Phys., 34, 1855 (1961).

38. M. Milman, Radiochim. Acta, 1, 15, (1962).
39. J. A. Merrigan, Ph.D. Thesis, The University of Nebraska, 1966.
40. E. Filatov, An. N. Nesmeyanov and Yu. B. Chepyzhev, Radiochemistry, 6, 595 (1964); Moscow University Newsletter, Ser. II, Chemistry, 4, 13 (1964).
41. Geissler, P. R. and J. E. Willard, J. Phys. Chem., 67, 1675 (1963).
42. J. L. Thompson and W. W. Miller, J. Chem. Phys., 38, 2477 (1963).
43. G. Levey and J. E. Willard, J. Chem. Phys., 25, 904 (1956).
44. G. Friedlander, J. Kennedy, J. Miller, "Nuclear and Radiochemistry", 2nd Ed., John Wiley & Sons Inc., New York, 1964.
45. See for example: C. Hsiung, H. Hsiung and A. A. Gordus, J. Chem. Phys., 34, 535 (1961).; H. C. Schweinler, Ref. 15, Vol. 1, p. 63.; J. W. Cobble and G. E. Boyd, J. Amer. Chem. Soc., 74, 1282 (1952).
46. D. T. Goldman, "Chart of the Nuclides", 8th Ed., General Electric Company, New York, 1965.
47. D. D. Wilkey and J. E. Willard, J. Chem. Phys., 44, 970 (1966).
48. B. G. Harvey, "Introduction to Nuclear Physics and Chemistry", Prentice-Hall, Inc., New Jersey, 1962, p. 116.

49. L. R. B. Elton, "Introductory Nuclear Theory", 2nd Ed., Sir Isaac Pitman & Sons, Ltd., London, 1965, p. 16.
50. S. Wexler and H. Davis, J. Chem. Phys., 20, 1588 (1952).
51. T. A. Carlson, W. E. Hunt., M. O. Krause, Phys. Rev., 151, 41 (1966).
52. T. A. Carlson and R.M. White, J. Chem. Phys., 44, 4510 (1966).
53. W. K. Ellgren, Jr., M. S. Thesis, The University of Nebraska, 1965.
54. J. A. Merrigan, W. K. Ellgren, Jr., and E. P. Rack, J. Chem. Phys., 44, 174 (1966).
55. J. A. Merrigan, J. B. Nicholas and E. P. Rack, Radiochim. Acta., 6, 94 (1966).
56. J. A. Merrigan and E. P. Rack, J. Phys. Chem., 69, 3795 (1965).
57. "Thermocouple Calibration Tables and Alloy Data", Omega Engineering, Inc., Bull. CT-2.
58. R. M. Lambrecht and E.P. Rack, J. Chem. Phys., 48, 3735 (1968).
59. J. A. Merrigan, J. B. Nicholas, R. M. Lambrecht, N. J. Parks, and E. P. Rack, J. Phys. Chem., 70, 2417 (1966).
60. R. M. Iyer and J. E. Willard, J. Am. Chem. Soc., 87, 2494 (1965).

61. F. J. Bryant, M. S. Thesis, The University of Nebraska, 1966.
62. J. B. Nicholas, M. S. Thesis, The University of Nebraska, 1967.
63. O. U. Anders, "Gamma Ray Spectra of Neutron Activated Elements", 3rd Ed., Dow Chemical Company, Midland, Michigan, 1964.
64. J. A. Merrigan, J. B. Nicholas, and E. P. Rack, J. Chem. Ed., 43, 543 (1966).
65. R. L. Ayres, Private Communication, This Laboratory, 1968.
66. M. Welch, R. Withnell, and A. P. Wolf, Anal. Chem., 39, 275 (1967).
67. W. E. Harris, Can. J. Chem., 39, 121 (1961).
68. R. L. Ayres, E. J. Kemnitz, R. M. Lambrecht, and E. P. Rack, Radiochim. Acta (In Press).
69. Oak Ridge National Laboratory, Report No. 3994, 1966, p. 1-26.
70. B. J. Pullman and B. O. West, J. Inorg. and Nucl. Chem., 19, 262 (1961).
71. T. H. Chen, K. Y. Wong, and F. J. Johnston, J. Phys. Chem., 64, 1023 (1960).
72. AA. Gordus and E. P. Rack, Private Communication (1966).
73. G. Levy and J. E. Willard, J. Chem. Phys., 25, 904 (1957).

74. A. A. Gordus and J. E. Willard, J. Am. Chem. Soc., 79, 4609 (1957).
75. G. S. Lawrence and L. Stranks, Radioisotopes in Phys. Sci. and Industry, Vol. III, IAEA, Vienna (1962) 483.
76. R. J. Cross and R. L. Wolfgang, Radiochim. Acta, 2, 112 (1964).
77. C. E. Moore, Natl. Bur. Standards Circ. No. 467, 108 (1958).
78. E. Lindholm, Ion Molecule Reactions in the Gas Phase (American Chemical Society, Washington, D. C., 1966) p.8.
79. E. F. Gurnee and J. L. Magee, J. Chem. Phys., 26, 1237 (1957).
80. R. W. Kiser, "Tables of ionization potentials", Office of Technical Services, Department of Commerce Washington, D. C., U. S. Atomic Energy Commission Rept. TID-6142 (1960).
81. E. S. Filatov, Uspekhi Khim., 31, 752 (1962) / Russ. Chem. Rev., 383 (1962) /.
82. G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Co., Princetown, New Jersey, 1950).
83. L. Spicer, J. F. J. Todd, R. Wolfgang, J. Am. Chem. Soc., 90, 2425 (1968).

84. L. Spicer and R. Wolfgang, J. Am. Chem. Soc., 90, 2426 (1968).
85. F. A. Wolf, J. Chem. Phys., 44, 1619 (1965).
86. "Long-Range" interactions imply no transfer of translational energy, conversely, if a large transfer of translational energy takes place, then the charge exchange process probably takes place at small distances.⁷⁸

APPENDICES

Appendix I

Determination of Kinetic Energy Moderation and
Inhibition Effects of CH₃F on ¹²⁸I + CH₄ Reactions

The necessary calculations to describe kinetic energy moderation and inhibition of reaction by chemical interaction of an additive are as follows.

In order to correct for unequal collision cross sections between the "hot atom" and CH₄ or the moderator, a function f is used instead of the mole fraction of CH₄ or CH₃F. The quantity, f , was calculated from the expression:

$$f_{\text{CH}_4} = \frac{X_{\text{CH}_4} S_{\text{CH}_4}^2}{X_{\text{CH}_4} S_{\text{CH}_4}^2 + X_{\text{CH}_3\text{F}} S_{\text{CH}_3\text{F}}^2}, \text{ and}$$

$$f_{\text{CH}_3\text{F}} = 1 - f_{\text{CH}_4};$$

where X denotes the mole fraction and S^2 denotes the cross section for an ¹²⁸I collision with either CH₄ or CH₃F.

S^2 is equal to the sum of the two diameters (collision partners) divided by 2, the quantity squared.

The quantity α^* is the average logarithmic energy loss per collision in the system:

$$\alpha^* = f_{\text{CH}_4} \alpha_{\text{CH}_4} + f_{\text{CH}_3\text{F}} \alpha_{\text{CH}_3\text{F}}$$

$$\alpha_{\text{CH}_4} \text{ or } \alpha_{\text{CH}_3\text{F}} = 1 - \frac{(M_j - m)^2}{2M_j m} \ln \frac{M_j + m}{M_j - m}$$

where m is the mass of the hot atom and M_j is the mass of the molecule struck -- either CH_4 or CH_3F .

The moderation equation derived by the Estrup-Wolfgang model³ for a system composed of a single reactant can be written as:

$$\frac{\alpha^*}{f_{\text{CH}_4}} \text{ Organic Yield (K.E.)} = 1 - \frac{f_{\text{CH}_4}}{\alpha^*} \times K$$

where the constants, I and K , are 0.06 and 0.0004.³⁷

Since the various non-experimental parameters are known from previous studies,^{36,37} the organic yield (kinetic energy dependent) can be calculated for the various mole-fractions additive employed. Reaction with additive: The correction is determined by multiplying the maximum extent of reaction in the pure additive system times the mole-fraction additive present, and subtracting the value obtained from the observed organic yield. Reactions not effected by additive: This value is determined from the extrapolated value at unit mole-fraction additive after corrections for reaction with the additive have been applied.

This value was 11%. Inhibition of $I^+(^1D_2)$ ion reaction:
This value is determined by subtracting the kinetic energy
moderation values and the above corrections from the experi-
mentally observed organic yields.

Appendix II* +

Program 1.

C Program number 1
C
C
C This program integrates the peak of interest and then
C subtracts the background value (which is obtained from the
C first tape total) and then proceeds to compute the organic
C yields using these values.
C
C Compile using special subroutines so that paper tape may
C be read using the rcd routine and the presence of a record
C mark may be ascertained using the rtc routine
C
C Sense switch 1 on calls for channels on tape to be punched
C out
C
C sense switch 2 on calls for the partial relisting of headings,
C starting with (scavenger) and ending with (mole fraction).
C
C sense switch 3 off provides for a pause after each tape total
C
C To relist headings turn sense switch 2 on after the execu-
C tion of the pause provided by sense switch 3)
C
C Branch to (4911068) to enter bkg if other than the value on
C the first tape total. If this is used also branch to loca-
C tion (4910998) to enter the proper deck number in order to
C have the following tape total properly labeled.
C This will allow the order of org vs aq to be changed. (i.e. if
C 0001 is entered the sum of the following tape will be labeled
C bkg, or if 0002 is entered the following sum will be labeled
C org, or if 0003 is entered the following sum will be labeled
C aq.
C
C Branch to (4909570) to have stored channel numbers punched
C on cards
C
C Branch to (4908456) to enter data group. (5 digits)
C
C branch to (4910998) to enter deck number. (4 digits)
C
C Header cards should contain the following-
C first card - (1) no. of channels to be read(4 digits) (2)

Program 1 (continued)

```

C   the decay constant (a blank or + sign, a digit, a decimal
C   pt., and then 4 digits) (3) the no. of minutes the background
C   is to be divided by (a blank, 3 digits, and a decimal pt.)
C   Second card- number of totals to be taken from each tape.
C   (4 digits)
C   Third and following cards- channel numbers to be intergrated
C   over (two 4 digit fields)
C
C
C   All branch statements providing for the entrance of data
C   calls for the data to be entered on the typewriter.
C
C
C   Dimension X(400), NA(15), NB(15), A(10), B(8)
C   DX = CDS(5.)
215  DX = .3003 + 0.0
C   DX = UMI(2991.)
C   DX = FAS(29728101.)
13   Read 13, itest, decay, tbkg
C   Format (14,F7.4, F5.0)
C   Decay = ((1.0)/(decay))
C   KD = 1
1    Read 5, NN
C   DO 10 1=1, NN
10   Read 11, NA(1), NB(1)
11   Format(214)
C   DO 500 1=1,400
500  X(1)=0.0
22   Type 33
33   Format (//6H date-, 10X,12H background-, 10X,9Hcounter-,10X,
C   19H voltage-,//37H irradiation facility-Omaha VA Triga,11X,
C   217H flux- 1.1*10**11,/)
400  Type 420
420  Format (//10H channels-, 6X,4H to-,6X,13H calibration-,//)
36   Type 55
55   Format(11H scavenger-,15X,10H additive-, 15X,8H amount-,10X,/,
C   17H phase-,15X,15H counting time-,10X,//14H purification-,25X)
66   Type 77
77   Format(iH target-, 15X,8H amount-, 10X,//8H source-,15X,18H
C   amount-,//12H extraction-,//10H comments-,//15H mole fraction-,
C   230X, 9H isotope-,//)
102  1 = 1
C
C   Tape read-in block

```


Program 1 (continued)

```

199 DO 212 1 = 1, itest
200 DX = PAS (11151101.)
    DX = RCD (51.)
    DX = CMP (11151101.)
    IF (DX) 191, 190, 191
191 Print 192
192 Format (25HCHAN missed, restart tape)
    Go to 300
190 DX = RTC(501)
    If(DX) 204, 201, 204
202 Control 102
    Control 108
    Type 240, 1, KD
240 Format (4HCHAN, 14,5H tape, 14,3H is)
    Accept 241, DZ
241 Format (F5.0)
    DX = PAS (12052020.)
    Go to 212
201 If (1 -1) 202, 200, 202
204 DX = RTC(504.)
    If (DX) 220, 203, 220
203 ICK = GET(50330.) + 1.
    If (I -ICK) 210, 210, 210
C Channel number from tape could be checked
210 DX = RCD(51.)
    DX = RTC(506.)
    If (DX) 202, 211, 202
211 DZ = GET(50550.)
    Go to 212
220 DX = RTC(507.)
    If (DX) 230, 221, 230
221 DX = CMP(28150601.)
    If (DX) 222, 211, 222
222 DZ = GET(50660.)
    Go to 212
230 DX = CMP(28150901.)
    If (DX) 202,231, 202
231 ICK = GET(50330.) +1.
    If (1 -ICK) 232,232,232
232 DZ = GET(50850)
212 X(1) = DZ
C
C
    If (sense switch 1) 703, 335

```

Program 1 (continued)

```

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

```

Program 2

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

Program 2 (continued)

```

Dimension X(400), NA(15), NB(15), A(10), B(8)
DX = CDS(5.)
215 LX = .3003 + 0.0
DX = FAS (29728101.)
head 13, itest, u, F, decay
13 Format (14,2F5.0,F7.4)
Decay=((1.0)/(decay))
KD = 1
1 read 5, NN
DO 10 I=1, NN
10 Read 11, NA(I),NB(I)
11 Format(214)
Do 500 I=1,400
500 A(I)=0.0
22 Type 33
33 Format (//6H date-, 10X,12H background-, 10X,9H counter-,
10X, 19H voltage-, //37H irradiation facility - Omaha Vn
TRIGA, 11X, 217H flux- 1.1*10**11,/)
400 Type 420
420 Format (//0H channels)
55 Format(11H scavenger-, 15X,10H additive-, 15X,8H amount-,
//,17H phase-,15X,15H,counting time-,10X//14H purification-,
25X)
66 Type 77
77 Format(8H target-,15X,8H amount-,10X,//8H source-,15X,18H
amount-,//12H extraction-,//10H comments-,//15H mole fraction-,
23CX,9H isotope-,//)
102 I = 1
C
C Tape read-in block
199 Do 212 I = 1, itest
200 DX = FAS (11151101.)
DX = RCD (51.)
DX = CLP (11151101.)
IF (uX) 191,190,191
191 Print 192
192 Format (25HCHANNEL missed, restart tape) go to 300
190 DX = RTC(501.)
If (DX) 204,201,204
202 Control 102
Control 108
Type 240,1,AD
240 Format (4HCHANNEL, 14,5H tape,14,3H IS)
accept 241,9Z

```

Program 2 (continued)

```

241 Format (F5.0)
    DX = PAs (12052020.)
    Go to 212
201 If (1 - 1) 202, 200, 202
204 LX = RTC(504.)
    If (DX) 220, 203, 220
203 ICK = GET(50330.) + 1.
    If (1 - ICK) 210, 210, 210
C Channel number from tape could be checked
210 DX = RCD (51.)
    DX = RTC(506.)
    If DX 202, 211, 202
211 DZ = GET(50550.)
    Go to 212
220 DX = RTC(507.)
    If (DX) 230, 221, 230
221 DX = CMP(28150601.)
    If (DX) 222, 211, 222
222 DZ = GET(50660.)
    Go to 212
230 DX = CIP(28150901.)
    If (1 - ICK) 232, 232, 232
232 DZ = GET(50850.)
212 X(1) = DZ
C
C
    If(sense switch 1) 700, 335
700 DO 701 I=1, itest, 10
701 Print 702, X(1), X(1+1), X(1+2), X(1+3), X(1+4), X(1+5), X(1+6),
    IX(1+7), X(1+8), X(1+9)
702 Format (10F7.0)
    Pause
335 Continue
    DO 88 I=1, MN
    NLOW = NA(1)
    B=0.0
    DO 40 J=NLOW, NHI
40 B=B+X(J)
    Go to 345
88 Continue
345 Go to (7,8,9,12,14,17), KD
7 A=B
    KD=2
    Go to 88
8 org=B
    KD=3
    Go to 88

```

Program 2 (continued)

```

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

```

* Tape read-in block and special subroutines prepared by
F. J. Kerrigan, U. S. V. A. H., Omaha, Nebraska.

+ Adaptation by R. L. Ayres, University of Nebraska, 1968.

PAPERS AND PUBLICATIONS

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Publications:

1. "Isomeric Transition Induced Reactions of Iodine-130 in Cyclohexane", with J. A. Merrigan, J.B. Nicholas, R. M. Lambrecht and E. P. Rack, J. Phys. Chem., 70, 2417 (1966).
2. "Substituent Effects of Iodine-130 Reactions Activated by (n, γ) and (IT) with Various Polyhalomethanes", with E. P. Rack, Radiochim. Acta., 10, 26 (1968).
3. "Gas-Phase Reaction of Excited ^{128}I Ions with CH_3F ", with D. W. Oates, R. L. Ayres and E. P. Rack (submitted to J. Phys. Chem.).

Papers Presented:

1. "Radiative Neutron Capture and Isomeric Transition Induced Reactions of Iodine with Chloromethanes", with R. M. Lambrecht, J. B. Nicholas, E. P. Rack and A. A. Gordus. Division of Nuclear Chemistry and Technology, American Chemical Society, Miami Beach, Florida. April 9-14, 1967.
2. "Reactions of Iodine-128 Induced by Radiative Neutron Capture in Homologous Systems", with D. W. Oates, R. L. Ayres and E. P. Rack. Division

of Nuclear Chemistry and Technology, American
Chemical Society, Minneapolis, Minnesota. April
13-18, 1969.