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NEUTRON CAPTURE AND $^{82}\text{Br}^{\text{m}}$ ISOMERIC TRANSITION, *5/66-2/67*

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HALOGEN ATOM REACTIONS ACTIVATED BY RADIATIVE
NEUTRON CAPTURE AND $^{82}\text{Br}^m$ ISOMERIC TRANSITION

Edward P. Rack, Project Director

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PREFACE

The following is a report of the work completed during the period May 15, 1966 to February 14, 1967. These studies were supported by the U.S. Atomic Energy Commission, Division of Research, Contract No. AT (11-1)-1617, The Department of Chemistry of the University of Nebraska, and the University of Nebraska Research Council. Most of the material for this report has been accepted for journal publication. Because of the U.S. Atomic Energy Commission's depository library system and the facilities of the Technical Information Service at Oak Ridge, it is possible to make available through a progress report the extensive original data only summarized in journal publications and results of unsuccessful experiments. It is hoped that this report will be of added value to workers in the field.

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I. INTRODUCTION

Since the discovery of the short-lived isomers $^{82}\text{Br}^{\text{m}} 1,2$ and $^{130}\text{I}^{\text{m}} 3$ it is now possible to do extensive studies of radiative neutron capture and isomeric transition activated reactions of bromine and iodine in organic media. Willard in a recent review⁴ stated that dominant among the questions to which answers are being sought are: (1) the relative importance of kinetic energy and of charge in determining the chemical fate of the atoms studied; (2) the effect of phase on the mechanisms which lead to chemical stabilization.

In our attempt to understand the mechanisms of halogen "hot atom" interactions, we studied the reactions of bromine and iodine in gaseous and condensed state hydrocarbon systems and the polychloromethanes. In all of these reactions systems the hot atom is not initially bound to the target molecule. The freeze-thaw technique⁵ was specially developed for these systems for determining organic retentions of the short-lived bromine and iodine isomers.

By employing rare gas and Br_2 additives, we have shown that 50% of the organically combined radio-bromine, resulting from the isomeric transition activated reaction of ^{82}Br with CH_4 , is formed via thermal processes involving bromine ions and 50% is formed via excess kinetic energy processes.

The ^{82}Br organic yields from $^{82}\text{Br}^{\text{m}}(\text{I.T.})$ ^{82}Br activations were found to be generally 1.7 to 1.8 times the yields of $^{80}\text{Br}^{\text{m}}$, $^{82}\text{Br}^{\text{m}}$, and ^{82}Br from the (n,γ) -induced reactions in all of the liquid isomers of hexane at Br_2 concentrations above 0.05 m.f. Scavenger curves and product distributions were found and evaluated with regard to several existing

hypotheses of the mechanisms of liquid state bromine reactions resulting from nuclear activation. A possible correlation was found between organic yields at given Br_2 concentrations and G-values for total organic radicals produced by X-rays in the hexanes. Support is given the Auger Electron reaction hypothesis for the reactions and systems studied.

By employing the freeze-thaw technique the (n, γ) and (I.T.) activated reactions of bromine were studied in various hydrocarbons ranging from pentane through undecane. The organic retention for the $^{80}\text{Br}^m$ activated by (n, γ) was found to be proportional to molecular weight. Variations within a series of isomers may be explained by the radiation chemistry G-value for total organic radical production. Since the organic retention of $^{80}\text{Br}^m$ appears to be proportional to G, it is concluded that Auger radiation and internal conversion are responsible for the organic retention. No correlation between the G-value, and the organic retention of the ^{82}Br activated by isomeric transition was found. However, the organic retention of ^{82}Br was a linear function, but not proportional to molecular weight. It is suggested that the (I.T.) reaction, although radical in nature is possibly influenced by additional processes.

In the study of the isomeric transition induced reactions of ^{130}I in cyclohexane by employing the freeze-thaw techniques, a $^{130}\text{I}^m$ half-life of 8.9 ± 0.3 min. was found. Similarities were found between ^{128}I organic retentions and ^{82}Br and ^{130}I organic retentions induced by isomeric transition.

By employing the freeze-thaw technique reactions of ^{130}I activated by the $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}$ and $^{130}\text{I}^m(\text{I.T.})^{130}\text{I}$ processes were studied in various polychloromethanes and cyclohexane in the range of 0.03 to 1.6 mole percent I_2 . The freeze-thaw equation for determining isomeric transition

induced organic retentions was modified for the above systems. In all systems studied, at low mole fraction I_2 , the (I.T.) organic yields were higher than the (n, γ) induced yields, but the organic yield separation disappeared at about 10^{-2} mole fraction I_2 . The data suggest this effect was produced by a difference in the nuclear activation of the two nuclear processes. The organic yields induced by both (I.T.) and (n, γ) decrease in the series CH_2Cl_2 , $CHCl_3$, CCl_4 at all mole fractions of I_2 studied. Interesting results were that iodine organic yields in CCl_4 were low: i.e., at 0.3×10^{-3} m.f. I_2 , O.Y. (I.T.) 2.5 ± 0.1 , O.Y. (n, γ) $= 4.3 \pm 0.6$; at 10^{-2} m.f. I_2 , O.Y. (I.T.) $= 2.4 \pm 0.2$, O.Y. (n, γ) $= 1.9 \pm 0.2$. Within experimental error, no difference in yields was observed between ^{128}I and ^{130}I (n, γ) activated reactions in the various systems. Product distributions were obtained by radiogas chromatography.

II. FACILITIES AND INSTRUMENTATION

Neutron Irradiation of Samples

All irradiations were made in the Triga Mark II "swimming pool" nuclear reactor at the Veteran's Administration Hospital at Omaha, Nebraska. A flux of 1×10^{17} thermal neutrons $\text{cm}^{-2} \text{sec}^{-1}$ was present at an operating power of 15.5 kilowatts. Various positions in the "lazy susan" sample holder were employed and the assembly was rotated to ensure that all samples received the same neutron flux and radiation dose. In very short irradiations the assembly was not rotated, but samples were all irradiated in the same position. The radiation dose was approximately 3×10^{17} e.v. $\text{g}^{-1} \text{min}^{-1}$ as determined by William Ellgren, of our laboratory using Fricke dosimetry. This was confirmed by studying the ^{131}I organic uptake in $\text{c-C}_6\text{H}_{12}$, due to radiation.

Quartz bubbles containing the reaction systems were packed in Kleenex tissues and sealed in plastic bags to prevent radioactive gases from escaping if the bubbles were accidentally broken. The bags containing the reaction system were inserted into Triga Tubes which were specially designed for the Triga reactor. Neutron irradiation times varied between one and 10,800 sec. In most reaction systems the organic yields were negligibly dependent upon the time of irradiation, i.e., to radiation-induced reactions. Only in systems with very little scavenger was it necessary to correct for such reactions

After taking a sample from the reactor it was immediately monitored for beta and gamma radiation, and opened. The ampoules were quickly taken out and submerged in liquid N_2 to freeze the sample. All handling was done with remote handling equipment and an 19 inch pair of tweezers to

minimize personal radiation hazards. Freezing of samples in liquid N_2 was done to halt changes in organic yields due to $^{82}Br^m$ (I.T.) ^{82}Br or $^{130}I^m$ (I.T.) ^{130}I reactions (except in instances where the effects of these reactions were being studied, in which case a definite timing procedure was employed). Samples, except those used for isomeric transition yields, were kept frozen for approximately two hours while enroute from Omaha to the radiochemistry laboratory at the University of Nebraska. Samples were extracted directly from the frozen state into a two phase liquid extraction system.

Radiochemistry Laboratory

All sample preparation and radioassaying were performed in a well-equipped, specially-designed radiochemistry laboratory. The hot laboratory contains two six-foot "Oak Ridge-Type" hoods, radioactive waste sink, radiation safety equipment, two separate vacuum lines for preparing gas and liquid state systems and the usual laboratory facilities. The counting room is equipped with a radiogas chromatograph, two single-channel analyzers with several 2" x 2" NaI crystals, four GM counting stations, four gas-flow counters, and a Nuclear-Date 128-Channel analyzer with a 3" x 3" NaI crystal specially housed in a concrete, cadmium and lead cave. Details for the radiogas chromatograph may be found elsewhere.^{5,23}

III. EFFECT OF MODERATORS ON THE ISOMERIC TRANSITION

INDUCED REACTION OF BROMINE - 82 WITH METHANE

Using rare gas and molecular moderators, Rack and Gordus⁵ suggested that reaction of (n,γ)-activated ⁸⁰Br with CH₄ to yield CH₃⁸⁰Br occurred mainly by virtue of the recoil kinetic energy of ⁸⁰Br. The reaction of fission-recoil bromine with CH₄⁷ appeared to proceed similarly. Spicer and Gordus⁸ suggested that the ⁸⁰Br yield induced by the ⁸⁰Br^m isomeric transition was lower than the (n,γ) induced ⁸⁰Br yield because of the smaller kinetic energy for the (I.T.) produced ⁸⁰Br.

Extensive research is now being conducted in isomeric transition chemistry. It is of fundamental importance to know the relative importance of charge and kinetic energy to (I.T.)-activated reactions.

The purpose of this work is to determine the role of excess kinetic energy and thermal processes in the ⁸²Br reaction in gaseous CH₄ activated by ⁸²Br^m isomeric transition, using rare gas moderators and bromine additive.

We employed the freeze-thaw technique developed in the study of ⁸²Br^m and ¹³⁰I^m (I.T.)-activated reactions in hydrocarbons,^{5,9,10} in determining the organic retentions. (See Chapters IV and VII). Recently a rigorous general expression was developed⁹ for freeze-thaw organic retentions. The ⁸²Br organic retention due to isomeric transition can be determined by employing the following:

$$^{82}\text{Br O.R. (I.T.)} = \frac{R^\infty - 0.09 R^0}{0.91 e^{-\lambda t}} - \frac{R^0(1 - e^{-\lambda t})}{e^{-\lambda t}}$$

where R^∞ is the organic retention reached in the gaseous system after all $^{82}\text{Br}^m$ has decayed, R° is the organic retention produced in the solid-state neutron irradiation, and $e^{-\lambda t}$ represents the fraction of $^{82}\text{Br}^m$ that decays in the gas phase. This expression, as compared to the one derived earlier,⁵ is necessary for systems having low R^∞ values and/or appreciable R° values, as in gaseous ^{82}Br systems. We obtained organic retentions due to the $^{82}\text{Br}^m$ (I.T.) ^{82}Br process in gaseous CH_4 within $\pm 0.5\%$ reproducibility using the above equation.

Ten ml. quartz bubblers filled with 15 mm. of Br_2 , CH_4 and additive, with a total gas pressure of one atmosphere, were irradiated at -78°C for 30 seconds. The Br_2 was frozen in the bubbler tip restricting contact with gaseous CH_4 during the neutron irradiation. Approximately 50 seconds after the beginning of irradiation the sample was gasified allowing the $^{82}\text{Br}^m$ to decay in the gas phase. Detailed experimental procedures and equipment used were described previously.^{5,11}

The percent of the ^{82}Br present as organic activity for the various systems are presented in Table I.

The effects of He, Kr, Xe, and Br_2 moderators on the reaction of CH_4 with ^{82}Br activated by the (I.T.) process (data of Table I) are depicted graphically in Fig. 1. By extrapolating the data for the systems where the mole fraction of moderator was less than 0.1, we found that at zero-mole-fraction-moderator the extent of ^{82}Br reaction was $7.4 \pm 0.5\%$, comparing well with the value, $6.8 \pm 0.8\%$, determined by Spicer and Gordus.⁸ The data appear to extrapolate, at zero-mole-fraction- CH_4 , to $3.7 \pm 0.5\%$ for the He, Kr, and Xe additives and to 0% for Br_2 . This would indicate that 7.4% minus 3.7% is formed via excess kinetic energy processes and that 3.7% of the organic ^{82}Br is formed via a process that does not require kinetic energy.

TABLE I

Percent ^{82}Br Stabilized in Organic Combination in a
Gaseous Mixture of Additive and Methane^a

	Pressure Additive (mm)	Pressure CH_4 (mm)	Mole Fraction Additive (b)	Percent ^{82}Br as Organic R° (c)	O.R. (IT) (d)
Br_2	6.5	684.5	0.010	2.00	7.15
	6.5	608.5	0.011	1.94	5.85
	13.5	606.0	0.022	1.45	5.43
	22.5	662.5	0.033	1.17	5.50
	21.0	586.0	0.034	1.16	4.34
	21.0	580.0	0.035	1.16	5.06
	28.5	654.5	0.042	1.06	4.00
	36.5	630.0	0.055	0.90	3.81
	50.0	620.0	0.075	0.71	3.80
	73.5	578.0	0.113	0.55	2.91
	108.0	580.0	0.156	0.45	3.42
	108.0	584.0	0.154	0.45	3.15
	143.0	567.0	0.201	0.40	2.89
	135.5	447.0	0.233	0.36	3.36
	135.0	445.0	0.234	0.36	2.82
	121.5	259.0	0.319	0.32	2.29
	125.0	177.0	0.415	0.26	1.65
	125.0	176.0	0.416	0.26	1.18
	83.0	52.0	0.615	0.18	0.62
	123.0	19.0	0.866	0.07	0.46

TABLE I (Con't.)

	Pressure Additive (mm)	Pressure CH ₄ (mm)	Mole Fraction Additive (b)	Percent ⁸² Br As Organic R ^o (c)	O.R. (IT) (d)
He	101.5	687.0	0.139	4.15	7.69
	220.5	474.0	0.317	0.52	7.47
	323.0	3.8.0	0.504	2.80	6.87
	278.5	199.5	0.583	1.49	6.87
Kr	16.0	687.0	0.023	0.75	6.74
	25.0	690.5	0.035	0.74	5.89
	28.5	616.0	0.044	0.73	6.17
	38.0	681.5	0.053	0.73	7.10
	48.5	647.0	0.070	0.73	5.99
	54.0	670.5	0.075	0.72	5.57
	58.5	649.0	0.083	0.72	5.51
	86.0	627.5	0.122	0.71	5.54
	98.0	597.5	0.141	0.71	5.23
	104.0	557.0	0.157	0.70	5.28
	125.5	436.0	0.224	0.69	4.68
	212.5	469.5	0.312	0.66	4.12
	324.5	316.0	0.493	0.61	3.54
	455.5	204.5	0.690	0.57	3.68
Xe	17.5	669.5	0.026	1.90	7.39
	37.0	611.0	0.057	1.68	6.98
	71.0	553.0	0.122	1.50	5.75
	231.5	509.5	0.312	1.50	5.38
	231.5	500.5	0.316	1.50	5.13

Table I (Con't.)

Pressure Additive (mm)	Pressure CH ₄ (mm)	Mole Fraction Additive (b)	Percent ⁸² Br As Organic R° (c)	O.R. (IT) (d)
365.5	393.0	0.482	1.50	4.10
483.0	180.0	0.729	1.50	4.34
590.0	68.5	0.896	1.50	3.87
605.0	34.0	0.947	1.50	3.63
324.5 (e)	15.5	0.954	1.50	3.92

(a) All samples, except where noted, contained 15 mm. Br₂.

(b) Error $\pm$ 0.002.

(c) R° is the organic retention produced in the solid-state neutron irradiation. The values represent points from a plot of experimental data.

$$(d) \text{ } ^{82}\text{Br O.R. (IT)} = \frac{R^{\infty} - 0.09 R^{\circ}}{0.91 e^{-\lambda t}} - \frac{R^{\circ} (1 - e^{-\lambda t})}{e^{-\lambda t}}$$

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

(e) 7.5 mm. Br₂ scavenger present.

If the 3.7% of the ^{82}Br organic retention results from an excess kinetic energy (hot atom) process, the order of moderating efficiencies should increase in the order He, Xe, and Kr.* The data of Fig. 1 for He, Xe, and Kr are in accord with that expected for kinetic energy moderation.

In addition to moderating excess kinetic energy processes, Br_2 affects the thermal contribution of the organic ^{82}Br . The ionization potentials of Br and Br_2 are 11.84 and 10.55 eV, respectively. Br_2 additive behaved as expected of a kinetic energy moderator in the CH_4 system employing the (n, γ)-activated ^{80}Br .¹ Since there are plausible mechanisms by which Br_2 can scavenge $^{82m}\text{Br}^+$, we conclude that 50.0% of the ^{82}Br organic retention ($7.4 \pm 0.5\%$) results from Br ions via thermal (kinetic energy independent) processes.

If 3.7% ^{82}Br organic retention in CH_4 results from kinetic energy activation, the moderation by the rare gas additives should be described by the Estrup-Wolfgang kinetic theory.¹² From a plot (Fig. 2) of $-1/\ln(1-P)$ vs. $(1-f_{\text{CH}_4})/f_{\text{CH}_4}$,¹³ we experimentally determined $\infty_{\text{react.}}$ and the reactivity integral, $I_{(\text{Total})}$, in units of $\infty_{\text{moderator}}$ to be $0.9 \infty_{\text{Kr-Br}}$ and $0.06 \infty_{\text{Kr-Br}}$, respectively. P is the ^{82}Br organic retention and f_{CH_4} , the probability that the collision be with CH_4 , is a function of the mole fractions of the components and the cross-sections for the various possible collisions.

It is interesting to note that the reactivity integral for the ^{82}Br reaction activated by (IT) in CH_4 ($0.06 \infty_{\text{Kr-Br}}$) is comparable to that for the ^{80}Br reaction activated by (n, γ) process in CH_4 ($\sim 0.06 \infty_{\text{Kr-Br}}$).¹⁴ This is the first application of the Estrup-Wolfgang Kinetic theory to (IT)-activated reactions.

* For various calculations the following diameters were used:

He, 2.2; Kr, 4.3; Xe, 4.9; Br, 3.1; Br_2 , 6.1; CH_4 , 4.2 Å.

We do not know yet whether deviations from theory at higher mole-fraction additive in Fig. 2 are the result of our experimental error or real deviations from theory. However, small deviations in organic retentions would produce a large variation in the $-1/\ln(1-P)$ term.

Fig. 1. Effect of moderators on the reaction of gaseous CH_4 with ^{82}Br activated by the (IT) process. Moderators: helium, ○ ; xenon, □ ; krypton, ■ ; bromine, ● .

Fig. 2. Kinetic theory analysis of hot bromine - 82 reaction with methane.
Moderators: helium, ○ ; xenon, □ ; krypton, ■ .

IV. NATURE OF (n, γ) AND (I.T.)-ACTIVATED BROMINE REACTIONS IN LIQUID ISOMERS OF HEXANE

Several lengthy reviews of the state of hot atom chemistry have been published in the past year.^{15,(a)(b)(c)} It is evident that the mechanisms for condensed phase halogen systems are not as well established as those for the various gas phase systems. An experimental problem is that true hot atom reactions (as defined by Wolfgang^{15,(a)}) and reactions secondary to near thermalization of an energetic atom cannot be separated by present experimental techniques. In the case of ^{82}Br , postulations of its mechanism of reaction, and its relation to other bromine nuclides have been influenced by a previously unknown parameter; that of $^{82}\text{Br}^m$ isomeric transition reactions. The recently discovered $^{82}\text{Br}^m$ (6.1 min.)^{1,2} accounts for nearly 91% of total ^{82}Br in reaction systems and thus ^{82}Br data gathered in the past were produced by (mainly) isomeric transition rather than by radiative neutron capture.

Many hypotheses have been made regarding the mechanism and underlying causes of reactions of bromine activated by nuclear transformations in the liquid state. Milman¹⁶ has developed a working hypothesis from the Estrup-Wolfgang kinetic theory¹² which agreed very well with results of $^{79}\text{Br}(n,\gamma)^{80}\text{Br}$ -activated reactions in binary systems of Br_2 in cyclohexane and n-hexane. Kazanjian and Libby¹⁷ suggest that reactions of bromine activated by either (n, γ) or (I.T.) processes result from "combinations of the neutral bromine atom and the fragments it has created by energetic collisions." Still another hypothesis was made by Geissler and Willard¹⁸ that if (n, γ) processes are followed by internal conversion and Auger radiation (as was indicated by Thompson and Miller¹⁹), both (I.T.) and

(n, γ)-activated halogen reactions would be governed by localized radio-lysis occurring at the end of the recoil track.

Since the discovery of $^{82}\text{Br}^m$, bromine has evolved as an excellent laboratory for studying (I.T.) and (n, γ) activated reactions. Six nuclear reactions are available using naturally occurring Br_2 and a thermal neutron source. Comparisons can be made of (n, γ) versus (n, γ), (n, γ) versus (I.T.), and (I.T.) versus (I.T.)-induced reactions.

EXPERIMENTAL

Phillips research grade hexanes were used without further treatment. Bromine prepared from Mallinckrodt reagent grade $\text{K}_2\text{Cr}_2\text{O}_7$, KBr , and H_2SO_4 was used after three distillations over P_2O_5 , collecting middle fractions. Reaction mixtures were prepared immediately before introducing them into quartz ampoules. Sample preparations were made by vacuum line techniques employing four or more degassings in a dimmed room. Exposure to light was minimized, before, during, and after irradiation. The detailed experimental procedures and equipment used were described previously.^{5,11}

Samples were irradiated in the Omaha, Nebraska, V. A. Hospital TRIGA Reactor for 10 sec. in a thermal neutron flux of $10^{11} \text{ n.cm.}^{-2} \text{ sec.}^{-1}$. The accompanying gamma radiation dose rate¹¹ was $3 \times 10^{17} \text{ ev. g.}^{-1} \text{ min.}^{-1}$ as determined by Fricke dosimetry and by measuring the extent of radiation-induced I_2 reactions in cyclohexane. A value of 5.6 molecules RI produced per 100 ev. was used as the G factor. Radiation damage did not significantly influence the results in systems studied because of high scavenger concentrations and short irradiations.¹¹

Bromine-82 total organic yields produced by $^{82}\text{Br}^m(\text{I.T.})$ ^{82}Br processes in the liquid state were found by the method developed in reference.⁵ Insignificant reactions were induced in the solid state irradiations

because of phase separations in the freezing process.^{5,20,21} Samples were extracted directly from the frozen state into two-phase mixtures of CCl_4 plus Br_2 carrier and 0.5M aqueous Na_2SO_3 . Counting samples were assayed at proper times^{5,11} and after proper freezing and thawing procedures⁹ to arrive at $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$, and $^{82}\text{Br}^m(\text{I.T.})^{82}\text{Br}$ -induced organic yields. $^{79}\text{Br}(n,\gamma)^{80}\text{Br}$ and $^{80}\text{Br}^m(\text{I.T.})$ ^{80}Br reactions were not studied because of time and travel considerations.

Gas chromatographic analyses were made by methods similar to those of Evans, et. al.^{5,22} Firebrick coated with silicone oil was used as the stationary phase and helium as the carrier gas. The chromatograph was temperature programed to allow emergence of all radioactive products with little peak overlap in a minimum of time. Activities of peaks were obtained by summing the counts using a scaler, and by determining the area of each peak with a planimeter. Peak activities were corrected for background, gas flow rate, and radiobromine decay.²³

RESULTS AND DISCUSSION

Perhaps the most revealing tool in investigating hot atom reactions in the condensed state has been the addition, prior to neutron irradiation, of substances which react readily (scavenge) with thermalized halogen atoms. When one mole percent or less of elemental Br_2 was added to ethyl bromide²⁴ the organic yield was reduced 15 percent of its value for the pure liquid, but further increase in Br_2 concentration reduced the yield relatively little. That part of the organic yield which is relatively insensitive to added Br_2 has been commonly attributed to hot atom processes.^{39,40} The part which is sensitive has been ascribed to thermal processes, involving diffusion of recoil atoms to radicals which were formed in moderating the hot atom.

A plot of organic yield versus mole fraction of scavenger Br_2 is referred to as a "scavenger curve." Scavenger curves are illustrative of hot atom reactions in the region of high Br_2 concentration since radicals produced by a recoiling atom would react with Br_2 in the immediate area and the tagged bromine atom would have little chance of reacting thermally with one of these even if it escaped high energy reaction. Upon thermalization, the tagged atom would be scavenged by elemental Br_2 . At lower concentrations of Br_2 the chances of a tagged bromine atom reacting thermally with organic radicals produced in its slowing down process would increase and an abnormally high organic yield would result. The same considerations would hold true with respect to radicals produced by internal conversion of the energetic atom followed by Auger radiation. Hence, scavenger curves are illustrative of thermal plus hot atom reactions in the low mole fraction region and a proper extrapolation of hot atom organic yields has to be made from the high mole fraction region to zero mole fraction scavenger to separate hot atom and thermal contributions to the organic yield.

The shape of the hot atom region (usually above 0.1 m.f. Br_2) may indicate the type of mechanism involved in the hot atom reaction. As an example, if the reaction were between the highly energetic atom and a radical, the effect of adding Br_2 would be to dilute the organic radical concentration in the hot atom region. An increase in Br_2 concentration would be expected to reduce the organic yield because of increased probability that radicals produced in the high energy process would be formed from Br_2 and hence be inorganic. The resultant scavenger curve should be a nearly straight line in the hot atom region. On the other hand, if the reaction were a molecular type and depended upon the impact of a recoiling

atom with an organic molecule, the addition of Br_2 would not necessarily yield a straight line. The probability of a recoil atom impacting with an organic molecule would depend on the relative cross sections for hitting either Br_2 or organic molecules. Hence, addition of Br_2 may not merely dilute organic molecules, but present more inorganic area to the recoiling atom with which to interact (reducing the number of collisions with the organic reactant) and a non-linear curve may be obtained because of differences in area presented to a recoil atom by Br_2 and the organic solvent and differences in momentum transfer from the recoil atom to either Br_2 or solvent.

Figures 3 through 8 illustrate the scavenger curves obtained for the hot atom reactions of ^{82}Br from (I.T.); $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n, γ) in the liquid state, and all of these reactions in the solid state C_6 -alkanes. The general shape of these curves indicates that the mechanism of both (I.T.) and (n, γ)-activated reactions may be radical type as opposed to molecular type. The portions of the scavenger curves representative of hot atom reactions (above 0.1 m.f. Br_2) are linear for all activations and systems. The curves representing $^{82}\text{Br}^m$ (I.T.) ^{82}Br -activated reactions in the liquid state lie well above those for (n, γ)-activated reactions. When a combination of (n, γ) and (I.T.) reactions was allowed to occur, as in 30 min. neutron irradiations, the ^{82}Br scavenger curve lay between that due to (I.T.) and that due to (n, γ)-activated reactions. This is illustrated in Fig. 8 for the n-hexane system.

Recently⁵ we reported that isomeric transition of $^{82}\text{Br}^m$ caused much higher organic yields than those produced by radiative neutron capture processes of bromine. We have now determined that the ^{82}Br organic yields from $^{82}\text{Br}^m$ (I.T.) ^{82}Br activations is generally 1.7 to 1.8 times the yields of $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n, γ)-induced reactions in liquid CCl_4 ,

Fig. 3. —Organic yields of reactions of Br_2 with cyclohexane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n, γ), ^{82}Br from (I.T.) at -196°C ., ■ ; $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n, γ) at 25°C ., ▲ ; ^{82}Br from (I.T.) at 25°C ., ●.

Fig. 4. —Organic yields of reactions of Br_2 with 2,3-dimethylbutane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n,v), ^{82}Br from (I.T.) at -196°C , ■; $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n,v) at 25°C , ▲; ^{82}Br from (I.T.) at 25°C , ●.

Fig. 5. —Organic yields of reactions of Br_2 with 3-methylpentane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n,v), ^{82}Br from (I.T.) at $-196^\circ\text{C}.$, ■ ; $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n,v) at $25^\circ\text{C}.$, ▲ ; ^{82}Br from (I.T.) at $25^\circ\text{C}.$, ●.

Fig. 6. —Organic yields of reactions of Br_2 with 2-methylpentane.
 $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n,v), ^{82}Br from (I.T.) at -196°C .,
 ■ ; $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n,v) at 25°C ., ▲ ; ^{82}Br from
 (I.T.) at 25°C ., ● .

Fig. 7. —Organic yields of reactions of Br_2 with 2,2-dimethylbutane.
 $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n, γ), ^{82}Br from (I.T.) at -196°C ., $\blacksquare$;
 $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (n, γ) at 25°C ., $\blacktriangle$; ^{82}Br from (I.T.)
at 25°C ., $\bullet$.

Fig. 8. —Organic yields of reactions of Br_2 in n-hexane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$ and ^{82}Br from (n, γ), ^{82}Br from (I.T.) at -196°C . ■ ; $^{80}\text{Br}^m$, $^{82}\text{Br}^m$ and ^{82}Br from (n, γ) at 25°C ., ▲ ; ^{82}Br from (I.T.) at 25°C ., O ; ^{82}Br from (n, γ) plus (I.T.) in 30 min. Irr. at 25°C ., ● .

cyclohexane, and the isomers of hexane at Br_2 concentrations above 0.05 m.f. Furthermore, in a given system the (n, γ)-activated reactions all gave the same yields within experimental error. One would expect $^{82}\text{Br}^{\text{m}}$ (I.T.) ^{82}Br processes to contribute more and more to the ^{82}Br yields as irradiation of liquid samples continued, because of the decay of $^{82}\text{Br}^{\text{m}}$ born during the irradiation. Since this decay results in a higher organic yield than the (n, γ) processes, an increase in ^{82}Br yield should be found. This is exemplified for the $\text{c-C}_6\text{H}_{12}$ - 0.0021 m.f. Br_2 system in Fig. 9. The rate of ^{82}Br yield increase was greatest near the beginning of irradiation. After irradiation of about 30 min. increase in ^{82}Br yields was slight due to $^{82}\text{Br}^{\text{m}}$ being born and decaying in nearly equal amounts. When samples were left in the liquid state following irradiation a rather pronounced increase in yield occurred because of the decay of $^{82}\text{Br}^{\text{m}}$ born immediately before the end of irradiation. This increase ceased after about 30 min. When essentially all of the $^{82}\text{Br}^{\text{m}}$ (6 min.) had decayed.

As noted in reference 5, the changes in ^{82}Br organic yield due to (I.T.)-activated reactions could be halted by freezing the samples, essentially separating organic and inorganic phases. It was found experimentally⁵ that decay of organically combined $^{82}\text{Br}^{\text{m}}$ yielded primarily organically combined ^{82}Br after freezing, while the inorganically combined $^{82}\text{Br}^{\text{m}}$ produced inorganically combined ^{82}Br . Thus, by freezing samples immediately after taking them from the reactor and extrapolating a plot of organic yield versus time of irradiation to zero time, the $^{82}\text{Br}^{\text{m}}$ yield could be obtained. It would be expected that ^{82}Br born from the (n, γ) process (9% in abundance) would have the same yield as $^{82}\text{Br}^{\text{m}}$ and $^{80}\text{Br}^{\text{m}}$. The ^{82}Br yield induced by (I.T.) in the $\text{c-C}_6\text{H}_{12}$ --0.0021 m.f. Br_2 system was 51% as determined in a separate experiment. If the ^{82}Br

yield from (n,γ) activation were 30%, then the yield in a mixture of (n,γ) and (I.T.)-activated reactions after all $^{82}\text{Br}^m$ decayed should be $30\% \times 0.09 + 51\% \times 0.91 = 49\%$. This was found to be the case as shown. Fig. 9 is a very good illustration of (1) the fact that (n,γ) activations of $^{82}\text{Br}^m$, $^{80}\text{Br}^m$, and ^{82}Br give the same yields, (2) the growth of ^{82}Br yields due to $^{82}\text{Br}^m$ decay in and out of the reactor in liquid systems, (3) the role of $^{82}\text{Br}^m$ in producing isotope effects between ^{82}Br and the rest of the bromine nuclides.

Organic yields of $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br in the solid state, $^{80}\text{Br}^m$ and $^{82}\text{Br}^m$ in the liquid state, ^{82}Br and $^{80}\text{Br}^m$ after 30 min. neutron irradiations of liquid samples, and ^{82}Br produced by isomeric transition processes in the liquid state hexanes at various concentrations of Br_2 are presented in Table II. Normal hexane data were reported previously,⁵ but are given here for the sake of comparison. Since (n,γ)-activated reactions did not cause an isotope effect (as illustrated in Fig. 9), ^{82}Br yields resulting from radiative neutron capture in liquid systems may be represented by the same data as $^{82}\text{Br}^m$ and $^{80}\text{Br}^m$.

The ratio of ^{82}Br organic yields produced by (I.T.) to those of $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br following (n,γ) processes was approximately 1.7 at any given concentration of Br_2 above 0.05 m.f. in all liquids studied. Experimental results reported by Hornig and Willard⁴⁰ for $^{80}\text{Br}^m(\text{I.T.})$ ^{80}Br -activated reactions in CCl_4 were within experimental error of those of $^{82}\text{Br}^m(\text{I.T.})$ ^{82}Br -activated reactions found in this laboratory⁹ in CCl_4 . These results indicate that there are no isotope effects produced by the (n,γ) processes, possibly none by (I.T.) processes, but a definite and pronounced difference in organic yields produced by (n,γ) versus (I.T.) processes which were compared in these liquid systems.

Fig. 9. — Increase of ^{82}Br organic yield, 0, with irradiation time and time after irradiation in liquid $\text{c-C}_6\text{H}_{12}$ — 2.1×10^{-3} m.f. Br_2 . $^{80}\text{Br}^m$, ●.

TABLE II

Organic yields^(a) induced by $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$, and $^{82}\text{Br}^m(\text{I.T.})^{82}\text{Br}$ processes at various concentrations of Br_2 in solid and liquid C_6 -Alkanes.

m.f. Br_2 in $n\text{-C}_6\text{H}_{14}$	Solid ^(b)			Liquid (n, γ) ^(c)		Liquid 30 min. ^(d)		Liquid (I.T.) ^(e)
	$^{80}\text{Br}^m$	$^{82}\text{Br}^m$ and ^{82}Br		$^{80}\text{Br}^m$	$^{82}\text{Br}^m$	$^{80}\text{Br}^m$	^{82}Br	^{82}Br
0.0076	5.2	7.0		19.5	17.5	22.5	26.2	27.3
0.049	1.2	2.0		15.0	12.5	15.9	21.5	22.9
0.096	0.4	0.4		11.5	10.2	12.0	18.5	20.5
0.26	0.5	0.3		9.1	8.2	9.3	12.7	15.1
0.39	0.3	0.3		7.6	6.8	7.7	10.2	12.6
0.63	0.3	0.2		5.1	4.2	5.1	6.0	7.6
0.79	0.2	0.1		3.7	2.8	4.0	4.4	4.6
m.f. Br_2 in $c\text{-C}_6\text{H}_{12}$								
0.0007	—	—		30.0	30.9	31.1	50.1	53.7
0.0021	—	—		29.1	30.0	29.7	44.8	51.6
0.0035	—	—		28.0	28.9	28.6	42.3	42.2
0.0063	—	—		23.5	23.8	29.0	38.2	37.4
0.012	—	—		20.0	19.7	30.4	34.2	29.8
0.019	—	—		19.6	18.7	26.9	32.0	29.2
0.031	—	—		16.4	17.0	25.0	27.8	25.2
0.050	1.0	0.9		13.0	13.1	24.1	23.8	25.2

TABLE II (Con't.)

m.f. Br ₂ in <u>c-C₆H₁₂</u>	Solid ^(b)			Liquid (n, γ) ^(c)		Liquid 30 min. ^(d)		Liquid (I.T.) ^(e)
	⁸⁰ Br ^m	⁸² Br ^m	and ⁸² Br	⁸⁰ Br ^m	⁸² Br ^m	⁸⁰ Br ^m	⁸² Br	⁸² Br
0.069	—	—	—	11.2	11.1	15.0	21.8	24.1
0.14	—	—	—	10.5	10.6	11.7	18.8	19.0
0.26	0.3		0.4	9.2	9.7	10.3	14.8	15.9
0.45	0.3		0.3	7.1	7.0	7.8	11.5	11.8
0.60	0.2		0.3	5.6	5.9	7.0	8.5	8.8
0.73	0.1		0.1	4.2	3.9	6.2	6.4	6.6
m.f. Br ₂ in <u>CH₃CH₂CH(CH₃)CH₂CH₃</u>								
0.045	5.4		5.6	14.1	14.0	14.1	19.9	20.6
0.11	2.2		2.6	12.2	11.7	14.8	16.5	18.0
0.21	0.8		0.9	10.4	10.3	10.5	13.8	15.2
0.39	0.6		0.8	8.9	7.8	10.5	10.0	11.4
0.54	0.4		0.6	5.9	5.7	6.4	8.3	8.6
0.72	0.2		0.2	4.4	3.8	6.1	5.7	5.8
m.f. Br ₂ in <u>(CH₃)₂CHCH₂CH₂CH₃</u>								
0.036	3.6		3.9	14.5	14.8	14.5	21.5	22.9
0.074	2.3		1.8	11.8	12.2	12.0	18.8	20.2
0.22	0.7		0.6	10.1	10.1	9.9	14.8	15.4

TABLE II. (Con't.)

m.f. Br ₂ in <u>(CH₃)₂CHCH₂CH₂CH₃</u>	Solid ^(b)			Liquid (n, γ) ^(c)		Liquid 30 min. ^(d)		Liquid (I.T.) ^(e)
	⁸⁰ Br ^m	⁸² Br ^m	and ⁸² Br	⁸⁰ Br ^m	⁸² Br ^m	⁸⁰ Br ^m	⁸² Br	⁸² Br
0.39	0.5		0.8	7.3	7.1	7.3	12.0	13.2
0.58	0.3		0.4	5.9	5.3	6.4	8.8	9.1
0.79	0.2		0.2	3.9	2.1	4.8	4.8	4.9
m.f. Br ₂ in <u>(CH₃)₂CHCH(CH₃)₂</u>								
	⁸⁰ Br ^m	⁸² Br ^m		⁸⁰ Br ^m	⁸² Br ^m	⁸⁰ Br ^m	⁸² Br	⁸² Br
0.037	2.9		3.2	14.3	14.7	14.6	22.0	22.9
0.11	1.0		1.1	11.3	11.0	13.0	18.8	19.0
0.22	0.7		0.8	9.9	9.8	9.7	14.9	16.2
0.39	0.5		0.5	8.1	7.9	8.4	12.9	12.9
0.56	0.5		0.4	5.6	5.4	5.8	9.0	9.4
0.72	0.3		0.2	4.2	4.2	4.5	5.8	6.0
m.f. Br ₂ in <u>(CH₃)₃CCH₂CH₃</u>								
	⁸⁰ Br ^m	⁸² Br ^m		⁸⁰ Br ^m	⁸² Br ^m	⁸⁰ Br ^m	⁸² Br	⁸² Br
0.0003	—		—	18.9	18.5	27.8	35.5	—
0.049	1.9		1.7	14.5	14.3	17.0	23.8	26.0
0.12	0.9		0.8	13.2	13.3	13.4	20.1	22.6
0.25	0.7		0.6	11.4	11.3	11.5	16.7	18.1
0.39	0.6		0.5	9.0	9.2	9.1	13.4	14.2
0.60	0.2		0.2	6.1	6.3	6.1	8.6	9.8

TABLE II (Con't.)

m.f. Br ₂ in (CH ₃) ₃ CCH ₂ CH ₃	Solid ^(b)			Liquid (n,Y) ^(c)		Liquid 30 min. ^(d)		Liquid (I.T.) ^(e)
	⁸⁰ Br ^m	⁸² Br ^m and ⁸² Br		⁸⁰ Br ^m	⁸² Br ^m	⁸⁰ Br ^m	⁸² Br	⁸² Br
0.72	0.2	0.1		4.8	4.4	5.1	5.8	6.3
0.91	0.1	0.1		1.9	1.3	2.3	2.8	2.7

- (a) Maximum experimental error was ± 0.5 .
- (b) Samples were irradiated in the reactor for 10 sec. at -196°C and kept frozen until $^{82}\text{Br}^{\text{m}}$ had decayed.
- (c) $^{82}\text{Br}^{\text{m}}$ organic yields in liquid systems were found by extrapolating a plot of ^{82}Br organic yield vs. irradiation time to zero irradiation time. Samples were frozen within 20 sec. after irradiation of various periods of time to prevent further changes in observed ^{82}Br organic yields due to $^{82}\text{Br}^{\text{m}}$ (I.T.) ^{82}Br activations.
- (d) Samples were irradiated in the reactor for 30 min. at 25°C and frozen within 20 sec. after irradiation.
- (e) ^{82}Br organic yields induced by $^{82}\text{Br}^{\text{m}}$ (I.T.) ^{82}Br processes were found by irradiating the samples for 10 sec. at -196°C , thawing exactly 35 sec. after the beginning of irradiation, allowing the $^{82}\text{Br}^{\text{m}}$ to decay in the liquid systems at room temperature and multiplying the observed ^{82}Br organic yield minus the solid state ^{82}Br yield by 1.17. See reference 5.

At very low concentrations of Br_2 , organic yields increased greatly with decreasing Br_2 concentrations due to diffusion-controlled thermal reactions of radioactive bromine with unscavenged organic radicals formed by the deactivation of high energy bromine. At mole fractions of Br_2 greater than 0.1, yields decreased linearly with increasing Br_2 concentration. The linear portions (extrapolated to zero m.f. Br_2) of scavenger curves for all of the isomers of hexane are delineated in Fig. 10. The (n,Y)-activated curves for $^{80}\text{Br}^m$ and $^{82}\text{Br}^m$ lie below those reported by Milman for the ^{80}Br curves in cyclohexane and n-hexane.¹⁶ Isomeric transition-induced ^{82}Br scavenger curves lie much higher.

No inert substances have been found which are conveniently miscible with most organic liquids and could thus act as moderators in evaluating liquid state results of nuclear transformations in light of the Extrup-Wolfgang kinetic theory.¹² Hence, it is difficult to distinguish between direct "hot reactions"¹⁷ and two-step sequences of fragmentation and radical recombination occurring within a solvent cage.²⁵ An unsuccessful attempt was made to correlate our data with the working hypothesis developed by Milman,¹⁶ using the same values of parameters used by Milman in describing the reactions of ^{80}Br in cyclohexane and n-hexane.

Qualitative and quantitative results of gas chromatographic analyses²³ are presented in Table III. It is obvious that polymeric substances and polybromides contributed more to the total organic yield of ^{82}Br as the concentration of Br_2 was increased. This was probably due to proximity of Br_2 in the reaction zone. The variety of compounds formed is indicative of the energy associated with the chemical effects of nuclear transformations. A definite structural effect existed in regard to certain products. Methyl bromide was not produced in cyclohexane, but

Fig. 10.—Comparison of hot atom scavenger curves in liquid state hexanes.

TABLE III

Per Cent of Products in Chromatographic Spectra* of ^{82}Br Tagged Organic Compounds Following Five Minute Neutron Irradiation and Subsequent Decay of $^{82}\text{Br}^m$ in the Liquid State as a Function of Br_2 Concentration

<u>n-C₆H₁₄</u>					
<u>m.f. Br₂</u>	<u>polymers, polybromides</u>	<u>n-hexyl bromide</u>	<u>sec-hexyl bromide</u>	low boiling bromides, methyl, ethyl, methylene, propyl, butyl, pentyl	<u>Total Organic Yield, %</u>
0.05	43.9	14.2	18.4	23.5	22.0
0.09	42.2	20.1	26.6	11.1	19.7
0.39	52.3	11.6	25.3	10.8	12.1
0.39	53.1	10.2	24.1	12.6	12.1
0.63	54.8	13.0	20.1	12.1	7.3
0.63	58.2	12.7	19.8	9.3	7.3
0.79	59.2	13.1	21.8	5.9	4.4
0.79	63.1	14.0	18.2	4.7	4.4
<u>c-C₆H₁₂</u>					<u>Total Organic Yield, %</u>
<u>m.f. Br₂</u>	<u>polymers, polybromides</u>	<u>sec.and normal- hexyl bromide</u>	<u>c-hexyl bromide</u>		
0.07	24.8	29.5	45.6		23.2
0.07	21.2	34.3	44.5		23.2
0.25	38.6	38.3	23.1		14.8
0.25	44.6	34.3	21.1		14.8
0.60	48.6	44.2	7.2		7.7
0.60	51.2	41.7	7.1		7.7
0.73	70.7	27.7	1.6		5.4
0.73	71.9	24.6	3.5		5.4

TABLE III (Con't.)

<u>(CH₃)₃CCH₂CH₃</u>						
m.f. Br ₂	polymers poly- bromides	hexyl bromides	t-butyl and pentyl bromides	ethyl bromide	methyl bromide	Total Organic Yield; %
0.12	11.3	36.1	20.4	13.9	18.3	21.7
0.12	15.8	24.5	34.5	10.8	14.4	21.7
0.39	34.4	32.5	11.1	9.8	12.2	13.6
0.39	37.3	26.1	10.8	12.1	13.7	13.6
0.72	54.4	24.1	12.3	4.7	4.5	6.0
0.72	59.3	18.5	11.7	4.5	6.0	6.0
0.91	52.8	22.8	13.9	4.9	5.6	2.6
0.91	58.1	18.4	11.2	5.3	7.0	2.6

<u>(CH₃)₂CHCH₂CH₂CH₃</u>								
m.f. Br ₂	poly- mers, poly- brom.	hexyl brom.	n-pentyl brom.	sec- pen. brom.	iso and n-pro- pyl brom.	ethyl brom.	methyl brom.	Total Organic Yield, %
0.14	25.1	38.1	5.1	13.2	6.1	5.2	7.2	17.3
0.14	21.6	37.2	4.6	16.1	8.2	5.5	6.8	17.3
0.39	32.6	41.8	2.2	8.5	4.4	3.8	6.7	12.7
0.39	36.1	39.2	4.1	7.6	3.7	4.0	5.3	12.7
0.79	56.2	26.7	1.0	5.6	3.2	4.1	4.2	4.7
0.79	57.8	25.1	1.4	5.2	3.7	3.6	4.2	4.7
0.91	62.4	23.2	1.3	3.1	3.9	3.3	2.8	2.5
0.91	65.7	21.0	1.1	2.9	3.8	3.0	2.5	2.5

TABLE III (Con't.)

<u>m.f. Br₂</u>	<u>polymers polybrom.</u>	<u>hexyl brom.</u>	<u>pentyl brom.</u>	<u>sec.-butyl bromide</u>	<u>ethyl brom.</u>	<u>methyl bromide</u>	<u>Total Organic Yield, %</u>
0.10	9.6	22.9	6.9	27.9	23.4	9.3	17.3
0.10	8.2	26.3	8.1	26.4	21.9	9.1	17.3
0.39	18.7	27.3	5.8	21.6	18.6	8.0	10.9
0.39	17.1	26.3	6.8	23.2	17.2	9.4	10.9
0.71	27.6	23.4	4.2	21.2	15.0	8.6	5.6
0.86	35.3	17.9	4.5	23.7	11.4	7.2	2.9
0.86	32.7	18.5	6.2	23.5	12.1	7.0	2.9

<u>m.f. Br₂</u>	<u>polymers poly- bromides</u>	<u>hexyl bromides</u>	<u>sec-pentyl bromide</u>	<u>iso-propyl bromide</u>	<u>methyl bromide</u>	<u>Total Organic Yield, %</u>
0.11	5.2	28.1	22.1	18.1	26.5	18.2
0.11	4.7	27.2	20.6	21.3	26.2	18.2
0.39	9.4	38.4	15.6	17.7	18.9	13.6
0.39	8.2	41.2	16.3	16.5	17.8	13.6
0.71	40.6	28.5	24.3	2.9	3.7	6.0
0.71	48.4	20.8	25.6	2.8	2.4	6.0
0.91	69.8	11.1	11.1	4.7	2.9	2.6
0.91	61.2	14.2	16.5	5.1	3.0	2.6

* See reference 23 for spectra.

became more abundant (at a given Br_2 concentration) as branching of the molecules increased. It was particularly abundant in 2,2-dimethylbutane. Isopropyl bromide was produced in great quantities in 2,3-dimethylbutane, while t-butyl bromide was produced in large quantities in 2,2-dimethylbutane. This indicates that carbon to carbon bond breakages were most likely to yield radioactive products when a highly branched site existed.

Decay characteristics of bromine nuclides made it difficult to obtain product distributions of (n, γ)-activated reactions independently of (I.T.) influences. To obtain $^{80}\text{Br}^m$ product distributions one must account for the product peaks being "contaminated" by ^{80}Br products produced by the isomeric transition of $^{80}\text{Br}^m$ to ^{80}Br . Thus, radiopeaks in a chromatogram may not be representative of $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$ -induced products formed in the reaction systems, but may represent the products of $^{80}\text{Br}^m(\text{I.T.})^{80}\text{Br}$ -activations in the reaction system and the chromatograph itself. Elemental bromine should also be removed before injection of the organic products to prevent exchange of tagged bromine at the relatively high temperature of the chromatograph.

Bromine-82 product distributions resulting from isomeric transition processes were obtained by irradiating samples in the solid state (less than 1% organic yield) and melting them immediately to study the products of $^{82}\text{Br}^m(\text{I.T.})^{82}\text{Br}$ reactions in the liquid state. Identical samples were irradiated in the liquid state and allowed to sit until all $^{82}\text{Br}^m$ decayed, giving a mixture of 91%(I.T.) and 9% (n, γ)-induced products. No additional peaks were observed due to (n, γ) activations and product distributions were identical to completely (I.T.)-induced products. This gives evidence that both (I.T.) and (n, γ) reactions result in the same product distributions and thus, that the mechanisms of reaction by both processes may be

similar. The same type of evidence has been found in other organo-halide systems.^{6,14,16}

Kazanjian and Libby¹⁷ have suggested that reactions of bromine activated by (n,γ) and (I.T.) processes are a result of "hot atoms" produced by recoil and molecular explosions, respectively. By this hypothesis an (I.T.)-activated atom would react in the same type of an environment as an (n,γ)-activated atom at the end of its track. Thus, the total organic yield should be the same for both reactions. As pointed out previously, $^{82}\text{Br}^m(\text{I.T.})^{82}\text{Br}$ processes produced at least 1.7 times the yields that $^{79}\text{Br}(\text{n},\gamma)^{80}\text{Br}^m$ and $^{81}\text{Br}(\text{n},\gamma)^{82}\text{Br}^m$ activations caused. This was a general characteristic in all liquid hexanes containing more than 0.05 m.f. Br_2 , as well as in CCl_4 .⁵ It can only be concluded that this hypothesis is not valid in the cases studied. It seems highly improbable that a bromine atom activated by (I.T.) would transfer charge in only one direction when situated in a close-packed matrix such as the liquid system. Thus, it is hard to imagine how an atom activated in this way could possess enough energy to act exactly as an (n,γ)-activated atom especially if the reactions were "hot atom" in nature.

Geissler and Willard's¹⁸ Auger radiation hypothesis would also predict similar products and product distributions induced by (I.T.) and (n,γ) processes, but for entirely different reasons than postulated by Kazanjian and Libby. They postulate that if (n,γ) reactions are followed by internal conversion of a low-lying metastable nuclear state (as was indicated by Thompson and Miller¹⁹); the products of this activation will be the same as those of (I.T.)-activated reactions because of similar localized radiation chemistry caused by Auger and I. C. electrons. The electrons emitted in the vicinity of the activated atoms would cause radical formation by radiation processes and the radiobromine would react with them.

The products would be the same in (n, γ) and (I.T.)-activated reactions but the organic yields could be different due to differences in localized radical concentrations resulting from differing energies of nuclear transformation. Thus, their hypothesis closely agrees with the results we obtained.

If the Auger electron reaction hypothesis is valid, in a general sense the total yield of organic products should be proportional to the G-value for organic radical production. Reactions should be similar to those along the track of a Compton electron in an identical solution exposed to X-rays with the added effect of a high dose rate in the area of nuclear transformation. The higher the G-value, the higher should be the organic yield. If Auger radiation were the only process contributing to the organic yield, a plot of yield versus G-value for organic radical production should extrapolate to zero at zero G. However, if the reactions were only partially due to Auger effects, the plot would extrapolate at zero G to an organic yield attributable to other processes. By plotting the (extrapolated) zero m.f. Br₂ organic yields of ⁸²Br produced by (I.T.) and ⁸⁰Br^m and ⁸²Br^m produced by (n, γ) processes versus G-value for total organic radicals produced in the hexanes, a reasonable correlation was found (Fig. 11). The (I.T.) induced yields do not appear, however, to extrapolate to zero at zero G. The G-values were established by Hardwick.²⁸ Errors involved in Hardwick's determinations as well as our own may account for the deviation from linearity in the case of 2,3-dimethylbutane for both (I.T.) and (n, γ) processes. However, a general linear correlation between yields produced by (I.T.) and especially (n, γ) reactions, and G-value for total organic radical production seems justified. Neohexane definitely lies well above the rest of the isomers in both G-value and organic yields. Fig. 10 also illustrates the higher yields in neohexane.

Fig. 11. —Correlation of radiation G-values and hot atom yields.

Because the organic yield depends somewhat on a competition between processes which yield inorganic combination and those which yield organic, the types of organic radicals produced and caging abilities of the system may have an influence on organic yields. This could cause deviations from a linear correlation between organic yield and G-value for organic radical production. However, if a general correlation is found over a large number of systems the Auger electron reaction hypothesis may be given added impetus and it may be shown that there is a direct link between chemical effects of nuclear transformations and radiation chemistry.

V. THE INFLUENCE OF MOLECULAR PARAMETERS ON THE

$^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$ AND THE $^{82}\text{Br}^m$ (I.T.) ^{82}Br

PROCESSES IN LIQUID HYDROCARBONS.

The Auger electron reaction hypothesis¹⁸ has given impetus to the study of halogen reactions activated by isomeric transistion and radiative neutron capture processes in various organic solvents. According to the hypothesis the (n,γ) and (I.T.) processes should give similar products due to combination of hot atoms with radicals formed by localized radiation induced by the conversion and Auger electrons emitted by the atom itself. Since the (n,γ) and (I.T.) activated reactions of bromine atoms in CCl_4 and n-hexane⁵ produced the same products, support was given to the Auger hypothesis.

Merrigan et. al.²⁷ (Chapter IV) found similar products, but observed a difference in the organic retention of $^{80}\text{Br}^m$ by (n,γ) activation and ^{82}Br by (I.T.) activation to be universal for the isomers of hexane. Employing a correlation relating radiation G-value for radical production with organic retention, the authors found that the organic retention for the (n,γ) yields appeared to be proportional to the G-value. This suggested that only radical processes were contributing to the yield. However, the yields from the (I.T.) process were not proportional to the G-value, and in all instances the (I.T.) organic retention was greater than the (n,γ) retention. The differences between the two processes were ascribed either to other processes, in addition to Auger radiation and/or differences in localized radical contributions resulting from differing energies of the nuclear transformations.

Recently this laboratory¹⁰ has shown that the organic retentions of ^{82}Br and ^{130}I induced by the (I.T.) processes, and ^{128}I organic retention, induced by the (n, γ) processes, in cyclohexane are similar; whereas the organic retention of $^{82}\text{Br}^m$ induced by the (n, γ) process is different. We suggested that processes additional to Auger radiation reactions may occur in iodine and (I.T.) activated ^{82}Br , or possibly that internal conversion of (n, γ) activated bromine occurs before the recoil energy has been dissipated. Thus, the atom could be carried away from the center of the pocket of fragments caused by radiolytic effects.

Nicholas et. al.²⁸ (Chapter III) employing moderators on the (I.T.) induced reaction of ^{82}Br with methane suggested that 50% of the ^{82}Br organic retention results from bromine ions via kinetic energy independent processes and 50% via excess kinetic energy activation.

The purpose of this work is to explore the (n, γ) and (I.T.) activated reactions of bromine with the various hydrocarbons from pentane through undecane in an attempt to determine whether the (I.T.) and (n, γ) activated bromine reactions are similar or somewhat different as implied by recent results.

EXPERIMENTAL

A total of 375 one-ml. samples in quartz bubbles were individually degassed five times and irradiated for 10 seconds at a flux of 1.1×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ at the Omaha V. A. Hospital TRIGA reactor. Exposure to light was minimized, before, during, and after irradiation. The freeze-thaw technique and the extraction and counting procedures used have been described previously.^{5,11} All hydrocarbons used were Phillips research grade, and the bromine was redistilled Mallinckrodt analytical reagent.

RESULTS AND DISCUSSION

Organic yields of $^{80}\text{Br}^m$ induced by the (n, γ) process and of ^{82}Br induced by (I.T.) in the various hydrocarbons at various concentrations of Br_2 are presented in Table IV. Figures 12 through 25 illustrate the scavenger curves obtained for the (I.T.) and (n, γ) activated bromine in the various systems studied.

Table V presents a summary of the data obtained in this investigation. A comparison of the $^{80}\text{Br}^m$ organic retentions induced by the (n, γ) reaction shows that the organic retention of the normal hydrocarbon increases proportionally with increasing molecular weight. This is shown in Fig. 26. For the (n, γ) process there appears to be a structural influence within any series of isomers ranging from pentane through nonane. The organic retention follows the general order for molecular structure: normal $\approx$ cyclic $<$ single secondary group $\approx$ two secondary groups $<$ branched methyl alkane $<$ tertiary.

Hardwick²⁶ confirmed Dewhurst's²⁹ observation that the extent of organic radical formation (the radiation G-value for total radical formation) from C-C bond scission is clearly related to chemical structure. It appears that the greater the branching of the chain hydrocarbon, the greater the number of organic radicals formed by C-C bond scission. The opposite trend for the G-value was observed for substituted cyclic compounds. Apparently we may conclude that variations in the (n, γ) activated $^{80}\text{Br}^m$ organic retentions for a given series of isomers of similar molecular weight are clearly a function of the G-value, the total number of radicals formed. This was suggested previously²⁷ for the hexane isomers. We observed that the $^{80}\text{Br}^m$ organic retention is also proportional

TABLE IV

Organic Retentions Induced by $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$
 $^{82}\text{Br}^m(\text{I.T.})^{82}\text{Br}$ Processes at Various Concentrations of Br_2 in
Solid and Liquid Saturated Hydrocarbons.

m.f. Br ₂	Solid ^b Br ^{80m} Br ^{82m} Br ⁸²		Liquid (n,γ) ^c Br ^{80m}	Liquid (I.T.) ^d Br ⁸²
<u>n-C₅H₁₀</u> (e)				
0.050	2.4	2.9	11.1	22.2
0.095	0.8	0.8	9.5	20.5
0.174	0.8	0.7	7.7	18.6
0.297	0.6	0.5	4.9	15.0
0.613	0.5	0.4	4.1	7.5
0.725	0.2	0.2	2.5	6.2
<u>(H₃C)₂CHCH₂CH₃</u> (f)				
0.108	1.3	1.4	9.9	19.0
0.194	0.6	0.7	7.4	----
0.617	0.8	0.7	3.5	7.3
0.784	0.3	0.2	2.0	4.1
<u>n-C₇H₁₆</u>				
0.0135	7.0	6.3	18.4	----
0.063	1.0	1.1	15.7	25.2
0.118	0.9	0.9	13.2	20.9
0.215	0.3	0.5	11.9	17.8
0.392	1.3	0.4	9.2	13.1

TABLE IV (Con't.)

m.f. Br ₂	Solid ^b			Liquid (n, γ) ^c Br ^{80m}	Liquid (I.T.) ^d Br ⁸²
	Br ^{80m}	Br ^{82m}	Br ⁸²		
0.606	0.4		0.4	6.8	7.6
0.800	0.2		0.2	4.2	4.9
<u>(H₃C)₂CHCH₂CH(CH₃)₂</u>					
0.064	2.6		2.1	17.7	25.6
0.120	1.4		1.6	14.4	19.7
0.214	---		---	14.0	16.6
0.343	0.2		0.3	10.6	11.9
0.618	0.9		0.6	6.8	7.8
0.803	0.1		0.1	4.0	5.0
<u>H₃C-cyclo-C₆H₁₂</u>					
0.054	3.1		3.4	25.8	32.1
0.103	2.5		2.4	16.3	20.9
0.216	1.7		1.5	13.9	17.6
0.364	0.7		0.7	11.3	13.7
0.496	1.0		0.9	9.0	10.6
0.774	1.2		0.5	4.2	5.9
<u>n-C₈H₁₈</u>					
0.069				19.1	25.2
0.129	1.6		1.4	14.8	20.2
0.229	0.7		0.6	12.4	18.1
0.426	1.3		1.7	11.1	13.9
0.639	0.4		0.3	7.1	8.0
0.817	0.6		0.6	4.8	4.9

TABLE IV (Con't.)

m.f. Br ₂	Solid ^b			Liquid (n, γ) ^c Br ^{80m}	Liquid (I.T.) ^d Br ⁸²
	Br ^{80m}	Br ^{82m}	Br ⁸²		
<u>(H₃C)₃CCH₂CH(CH₃)₂</u>					
0.0021	16.6		18.5	30.4	46.0
0.0106	13.8		15.1	22.3	42.8
0.0219	8.7		9.1	23.4	38.7
0.131	0.9		0.9	15.1	22.9
0.232	0.4		0.4	12.8	19.1
0.668	0.9		0.8	----	8.1
0.833	0.3		0.3	3.9	4.8
<u>(H₃C)₂CHCH(CH₃)CH(CH₃)₂</u> (g)					
0.128	5.7		4.8	15.5	26.8
0.267	1.9		1.9	12.0	16.3
0.636	1.1		1.0	8.3	10.3
0.763	1.2		1.1	2.0	6.2
<u>cis-1,2-(CH₃)₂-cyclo-C₆H₁₂</u>					
0.061	0.4		3.0	19.7	26.4
0.114	2.1		2.2	17.0	22.0
0.205	1.6		1.6	13.4	17.0
0.244	1.1		1.1	12.1	16.7
0.564	0.7		1.2	7.8	8.9

TABLE IV (Con't.)

m.f. Br ₂	Solid ^b Br ^{80m} Br ^{82m} Br ⁸²		Liquid _{80m} (n,γ) ^c Br ^{80m}	Liquid (I.T.) ^d Br ⁸²
<u>trans-1,2-(CH₃)₂-cyclo-C₆H₁₂</u> (h)				
0.062	5.6	5.4	15.2	23.2
0.117	5.0	4.6	14.2	----
0.209	1.8	1.8	11.4	17.2
0.415	1.1	1.1	9.3	13.2
0.702	1.3	1.1	4.9	7.2
0.850	1.1	1.1	2.4	4.9
<u>n-C₉H₂₀</u>				
0.140	3.1	3.5	17.5	21.8
0.246	0.8	0.8	14.5	17.0
0.551	0.6	0.6	9.7	11.2
0.767	0.9	0.7	5.0	6.6
<u>(H₃C)₃^c-(CH₂)₂CH(CH₃)₂</u>				
0.144	8.7	9.0	24.4	23.0
0.294	4.4	4.6	18.6	18.0
0.556	2.0	1.7	11.9	11.9
0.723	1.3	1.0	7.9	6.3
<u>n-C₁₀H₂₂</u>				
0.151	3.3	3.4	----	24.0
0.263	0.9	0.8	13.4	20.5
0.572	0.2	0.6	9.6	10.9
0.789	0.4	0.3	2.9	6.1

TABLE IV (Con't.)

m.f. Br ₂	Solid ^b Br ^{80m} Br ^{82m} Br ⁸²			Liquid (n,γ) ^c Br ^{80m}	Liquid (I.T.) ^d Br ⁸²
<u>n-C₁₁H₂₄</u>					
0.126	1.1		1.2	18.9	26.7
0.225	0.8		0.8	16.4	22.5
0.548	0.4		0.4	11.2	12.9
0.778	0.3		0.5	7.2	8.5

^a Maximum experimental error was ± 0.5 .

^b Samples were irradiated in the reactor for 10 seconds at 77°K in a flux of 1.1×10^{11} neutrons cm.⁻² sec.⁻¹ and kept frozen until ⁸²Br^m had decayed.

^c Samples were irradiated for 10 sec. at 298°K in flux of 1.1×10^{11} neutrons cm.⁻² sec.⁻¹ and frozen within 20 sec. after irradiation to prevent further changes in observed ⁸²Br organic retention due to ⁸²m(I.T.)⁸²Br activations.

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

^e The ⁸⁰Br^m organic retention was corrected for a thermal contribution of 2.2, which was obtained by extrapolating the experimental ⁸⁰Br^m data to the intercept corresponding to the organic retention at the mole fraction of bromine equal to one.

^f A thermal contribution of 3.0 was corrected as in e. above.

^g A thermal contribution of 3.0 was corrected as in e. above.

^h A thermal contribution of 2.2 was corrected as in e. above.

Figure 12—Organic retentions of reactions of Br_2 with n-Pentane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■ ; $^{80}\text{Br}^m$ from (N, γ) at 298° K., O ; ^{82}Br from (I.T.) at 298° K., ●

Figure 13—Organic retentions of reactions of Br_2 with isopentane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■ ; $^{80}\text{Br}^m$ from (N, γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ●

Figure 14—Organic retentions of reactions of Br_2 with n-Heptane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■ ; $^{80}\text{Br}^m$ from (N, γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ● .

Figure 15—Organic retentions of reactions of Br₂ with 2,4-dimethyl pentane. ⁸⁰Br^m, ⁸²Br^m, and ⁸²Br from (N,γ), ⁸²Br from (I.T.) at 77° K., ■ ; ⁸⁰Br^m from (N,γ) at 298° K., ○ ; ⁸²Br from (I.T.) at 298° K., ● .

Figure 16—Organic retentions of reactions of Br_2 with Methyl cyclohexane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■ ; $^{80}\text{Br}^m$ from (N, γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ● .

Figure 17—Organic retentions of reactions of Br_2 with n-octane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ) , ^{82}Br from (I.T.) at 77° K., ■ ; $^{80}\text{Br}^m$ from (N, γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ● .

Figure 18—Organic retentions of reactions of Br₂ with 2,2,4-trimethyl pentane. ⁸⁰Br^m, ⁸²Br^m, and ⁸²Br from (N,γ), ⁸²Br from (I.T.) at 77° K., ■ ; ⁸⁰Br from (N,γ) at 298° K., ○ ; ⁸²Br from (I.T.) at 298° K., ●

Figure 19—Organic retentions of reactions of Br_2 with 2,3,4-trimethyl pentane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ◻ ; $^{80}\text{Br}^m$ from (N, γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ● .

Figure 20—Organic retentions of reactions of Br₂ with Cis-1,2-dimethyl cyclohexane. ⁸⁰Br^m, ⁸²Br^m, and ⁸²Br from (N,γ), ⁸²Br from (I.T.) at 77° K., ■ ; ⁸⁰Br^m from (N,γ) at 298° K., ○ ; ⁸²Br from (I.T.) at 298° K., ●

Figure 21—Organic retentions of reactions of Br_2 with trans-1,2-dimethyl cyclohexane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■ ; $^{80}\text{Br}^m$ from (N, γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ● .

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

Figure 23—Organic retentions of reactions of Br_2 with 2,2,5-trimethyl hexane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■ ; $^{80}\text{Br}^m$ from (N, γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ●

Figure 24—Organic retentions of reactions of Br₂ with n-decane. ⁸⁰Br^m, ⁸²Br^m, and ⁸²Br from (N,γ), ⁸²Br from (I.T.) at 77° K., ■ ; ⁸⁰Br^m from (N,γ) at 298° K., ○ ; ⁸²Br from (I.T.) at 298° K., ● .

Figure 25—Organic retentions of reactions of Br_2 with n-undecane. $^{80}\text{Br}^m$, $^{82}\text{Br}^m$, and ^{82}Br from (N, γ), ^{82}Br from (I.T.) at 77° K., ■ ; $^{80}\text{Br}^m$ from (N, γ) at 298° K., ○ ; ^{82}Br from (I.T.) at 298° K., ●

Table V

Comparison of the Organic Retentions of ^{79}Br (n, γ) $^{80}\text{Br}^m$
and $^{82}\text{Br}^m$ (I.T.) ^{82}Br Processes in Liquid Hydrocarbons.

Hydrocarbon	Organic ⁽¹⁾ Retention ^{79}Br (n, γ) $^{80}\text{Br}^m$		Organic ⁽²⁾ Retention $^{82}\text{Br}^m$ (I.T.) ^{82}Br		Molecular Weight ⁽³⁾	G-value ⁽⁴⁾ (total, organic radicals)
	Obs.	Calc. ⁵				
<u>C₅ Isomers</u>						
n-pentane ⁶	10.0	10.0	21.6	72.15	8.7	
isopentane ⁶	10.6	9.4	20.3	72.15	7.9	
<u>C₆ Isomers⁷</u>						
n-hexane	11.6	11.6	20.8	86.18	7.8	
cyclohexane	12.0	11.5	21.5	84.16	7.7	
2-methyl pentane	12.8	12.8	22.0	86.18	8.5	
3-methyl pentane	13.0	13.0	20.0	86.18	8.7	
2,3-dimethyl butane	12.6	13.7	24.0	86.18	9.2	
2,2-dimethyl butane	14.7	14.3	21.0	86.18	9.5	
<u>C₇ Isomers</u>						
n-heptane	15.7	15.7	21.0	100.21	9.1	
2,4-dimethyl pentane	17.3	16.3	20.5	100.21	9.3	
methyl cyclohexane	17.8	17.8	21.6	98.18	6.9	
<u>C₈ Isomers</u>						
n-octane	17.4	17.4	22.0	114.23	8.3	
2,3,4-trimethyl pentane ⁶	18.2	16.8	28.0	114.23	8.1	
2,2,4-trimethyl pentane	17.6	18.5	25.2	114.23	8.9	
cis-1,2-dimethyl cyclohexane	17.5	17.0	22.0	112.22	6.7	
trans-1,2-dimethyl cyclohexane ⁶	15.6	17.0	22.0	112.22	6.7	

Table V (Con't.)

<u>C₉ Isomers</u>				
n-nonane	20.0	24.3	128.26	9.4
2,2,5-trimethyl hexane	28.0	28.0	128.26	8.9
n-decane	20.8	28.0	142.29	8.9
n-undecane	22.5	30.5	156.31	---

1. The organic retentions given are the extrapolated zero-mole fraction bromine organic retentions, which we obtained by extrapolating the linear portion of the scavenger curve for the bromine reactions in the hydrocarbon. In all instances the scavenger curve was linear for both the (n,Y) and (I.T.) processes at concentrations greater than 0.1 m.f. bromine. Maximum experimental error was $\pm 0.5\%$.
2. The corrected (I.T.) organic retention was obtained by the new relationship (9,10).

(14) N. J. Parks, J. A. Merrigan and E. P. Rack, (to be published).

$$^{82}\text{Br} \text{ O.R. (I.T.)} = \frac{R^\infty - 0.09 R_0}{0.91 e^{-\lambda t}} - \frac{R_0(1 - e^{-\lambda t})}{e^{-\lambda t}}$$

where O.R. is the organic retention, R^∞ is the maximum organic retention after all $^{82}\text{Br}^m$ has decayed, R_0 is the organic retention produced in the irradiation of the sample for 10 seconds at 77°K, exactly 35 seconds after irradiation the sample was liquified and $e^{-\lambda t}$ describes the fraction of $^{82}\text{Br}^m$ that decays in the liquid phase. This expression is comparable to the one derived earlier (2), but is necessary for systems having either low R^∞ values and/or appreciable R_0 values.

3. Handbook of Chemistry and Physics, 46th ed., Chemical Rubber Publishing Company, Cleveland, Ohio. (1965-6).
4. G-values of total radical production were determined by Hardwick.²⁶
5. See text for discussion.
6. Data corrected for thermal reactions of bromine with the hydrocarbon.
7. See reference (27) for original data on the hexane isomers.

to the G-value for the octane isomers, and it appears within experimental error that the other isomers follow the trend in proportionality.

For any given chain series of hydrocarbon isomers, assuming no structural dependence (other than that incorporated with the G-value) on the yield, the organic retention should be proportional to the G-value for organic radical production. The calculated values, as obtained by the extrapolation of the organic retention of the normal hydrocarbon to zero G-value are presented in Table V for the $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$ process. The correlation between the experimental and calculated values of the organic retentions follow this prediction.

The data and G-values suggest that the substituted cyclic hydrocarbons are different from the chain hydrocarbons. Although the organic retention for substituted cyclohexanes is greater than for cyclohexane, only the organic retention of cis-1,2-dimethyl cyclohexane is approximated by the G-value extrapolation of the chain hydrocarbon organic retentions. Evidently the substituted cyclic compounds are influenced by different parameters than chain hydrocarbons, as the substituted cyclohexanes are proportional to G, if extrapolated through the methyl substituted parent. It is our contention that the $^{80}\text{Br}^m(n,\gamma)$ induced organic retentions in hydrocarbons are the result of Auger radiation and internal conversion.

There is no correlation of the G-value with the ^{82}Br organic retention induced by isomeric transistion. The (I.T.) yields appear to be approximately the same ($\pm 2\%$) for 15 of the 20 hydrocarbons studied. The deviations may occur due to the influence of parameters not experienced by shorter and less branched chains. Likewise, the ^{82}Br (I.T.) organic retention, although a linear function, is not proportional to the molecular weight. (See Fig. 26).

Figure 26—Organic retentions of $^{80}\text{Br}^m$ from (N,γ), ○ ; and ^{82}Br from (I.T.), ● at 298° K., as a function of molecular weight.

Aditya and Willard³⁰ studied the reactions of $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$ and $^{80}\text{Br}^m$ (I.T.) ^{82}Br reactions in hydrocarbons, and found that the organic retentions of both the (n, γ) and (I.T.) processes increased with increasing chain length. They concluded that both reactions may proceed by the same mechanism. Our data does not support this conclusion. However, Aditya and Willard³⁰ were working in the thermal region (low mole fraction bromine) and we were interested in the hot atom region with mole fraction of bromine greater than 0.1.

Libby,³¹ in an excellent review of isomeric transistion chemistry, proposes, after evaluating the existing data for isomeric transistion reactions, that the (I.T.) yield is entirely due to radical processes. He further proposes that the differences in the organic retentions of (n, γ) and (I.T.) is due to the fact that the processes are different. We support the contention that the two processes are somewhat different. We believe that if radical processes are responsible for the (n, γ) yield, as our analysis implies, they should contribute to the (I.T.) yields. In all of the compounds studied, we observed the organic retention to be a linear decreasing function with mole fraction of bromine greater than 0.1. In all instances, but for 2,2,5-trimethylhexane, the organic retention of the isomeric transistion reaction was greater than the (n, γ) retention. However, the isotope separation decreases gradually from n-pentane through n-undecane.

The differences in organic retention for the (n, γ) and (I.T.) processes have often been ascribed to the fact that nearly 91% of the ^{82}Br atoms are born as a result of isomeric transistion.^{1,2} The (I.T.) processes are accompanied by internal conversion and Auger electron emission resulting in build up of charge on the atom.³²

If the organic retention for isomeric transistion reactions was strictly radical in nature, it should be expected that the organic retention of the ^{82}Br activated by (I.T.) would parallel the changes in organic retention as observed for the (n, γ) reaction with increasing molecular weight. We suggest that while the $^{80}\text{Br}^{\text{m}}$ organic retention may be the result of Auger radiation and internal conversion, the (I.T.) reaction may be due in part to other processes, i.e. ion-molecule, excited molecule, etc., that are occuring in addition to Auger radiation and internal conversion. Additional evidence from radiation chemistry and ion-molecule chemistry will undoubtly be of value in deducing the mechanism of isomeric transistion reactions.

VI. ISOMERIC TRANSITION INDUCED REACTIONS

of ^{130}I in CYCLOHEXANE

Discovery of the $^{130}\text{I}^{\text{m}}$ (I.T.) ^{130}I nuclear reaction (T 1/2 9.2 min.)³ has made it possible to compare isomeric transition-induced reactions with reactions effected by other nuclear transformations in the iodine system. The processes; (n,2n), (d,p), (γ ,n), and (n, γ) were reported to produce the same organic yields and product distributions in several liquid alkyl halides.^{39,34} However, in the cyclohexane- I_2 system, where iodine is not contained in the target molecule, the (n,2n) reaction was reported to cause higher organic yields than the (n, γ) reaction.³⁵ This was attributed to a higher recoil energy in the former case. Since in the liquid state, (I.T.)-activated ^{130}I may acquire electrons for neutralization somewhat symmetrically from its surroundings, it would be expected to have less kinetic energy than (n, γ)-activated ^{128}I . Thus, if the chemical reactions were predominately due to kinetic energy dissipation, an isotope effect might be expected. None was found in the n-hexane- I_2 system¹ within $\pm 5\%$.

Using the freeze-thaw technique developed in the study of $^{82}\text{Br}^{\text{m}}$ (I.T.) ^{82}Br reactions,⁵ we obtained the organic yields due to $^{130}\text{I}^{\text{m}}$ (I.T.) ^{130}I processes in liquid cyclohexane within $\pm 0.8\%$. Detailed experimental procedures and equipment used were described previously.^{5,11} Neutron irradiations were performed at a flux of 10^{11} n. cm.⁻² sec.⁻¹ in the Triga Reactor at the Omaha, Nebraska, V. A. Hospital. One ml. samples of cyclohexane- I_2 ¹²⁹ were frozen by immersing in liquid nitrogen, resulting in opaque crystalline solids. These were irradiated for 30 sec. in the frozen state. They were thawed 20 sec. after irradiation to allow $^{130}\text{I}^{\text{m}}$ to decay in the liquid system. Cyclohexane- I_2 ¹²⁷ systems were irradiated

in the liquid state for 10 sec. to obtain ^{128}I data from (n, γ) activation. Radiation damage was negligible.¹¹

The organic yield of ^{130}I following neutron irradiation and decay of $^{130}\text{I}^{\text{m}}$ in the solid state was 2.8% in the 7.8×10^{-3} m.f. I_2^{129} system. This low yield was attributed to a phase separation between iodine and the cyclohexane (clumping) upon freezing, similar to that found in Br_2 containing systems.^{5,20,21} When an identical sample was melted 20 sec. after irradiation and the $^{130}\text{I}^{\text{m}}$ allowed to decay in the liquid system, the yield was 21.7%. Since ^{130}I formed by radiative neutron capture accounts for 0.39 of the total ^{130}I after decay of the isomer,³ and organic reactions occurring during a solid state irradiation were not negligible, corrections were made for its presence in the 21.7%. By employing the expression for determining freeze-thaw organic retentions, (See Chapter VII) the organic yield due to (I.T.) was found to be 35.3%.

By resolidifying samples containing $^{130}\text{I}^{\text{m}}$, the high rate of increase in organic yield due to (I.T.) could be halted by the clumping of $^{129}\text{I}^{130}\text{I}^{\text{m}}$. Thus, growth in ^{130}I yield due to (I.T.) in the liquid state could be described by the equation;⁵ $R^t - R^0 = R^\infty - R^0 (1 - e^{-\lambda t})$. Where R^∞ is the yield due to (I.T.) after all $^{130}\text{I}^{\text{m}}$ had decayed, R^t is the yield due to (I.T.) at any time t , R^0 is the yield contribution of (n, γ) and the part of the (I.T.) processes occurring in the solid state, and λ is the decay constant for $^{130}\text{I}^{\text{m}}$. A plot of ^{130}I organic yield due to (I.T.) in liquid cyclohexane — 7.8×10^{-3} m.f. I_2^{129} versus time after irradiation is presented in Fig. 27. By analyzing this data a $^{130}\text{I}^{\text{m}}$ half-life of 8.9 ± 0.3 min. was found.

Fig. 27. - Growth of ^{130}I organic yields by isomeric transition in liquid $\text{c-C}_6\text{H}_{12}$ — 0.0078 m.f. I_2 following neutron irradiation of the solid system.

Organic yields of ^{130}I due to $^{130}\text{I}^{\text{m}}(\text{I.T.})^{130}\text{I}$ processes were the same within experimental error as those of ^{128}I produced by the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ process. These values are compared with those due to $^{82}\text{Br}^{\text{m}}(\text{I.T.})^{82}\text{Br}$ and $^{79}\text{Br}(\text{n},\gamma)^{80}\text{Br}^{\text{m}}$ in Table VI.

TABLE VI
Organic Yields of (I.T.)-Produced ^{130}I and ^{82}Br and (n, γ)-Produced ^{128}I and $^{80}\text{Br}^{\text{m}}$ in Cyclohexane at Room Temperature.

<u>m.f. Halogen</u>	<u>^{130}I</u>	<u>^{128}I</u>	<u>^{82}Br</u>	<u>$^{80}\text{Br}^{\text{m}}$</u>
7.8×10^{-3}	35.3	36.1	35.3	22.5
5.2×10^{-3}	39.6	40.5	39.2	25.4

It may be seen that $^{130}\text{I}^{\text{m}}(\text{I.T.})^{130}\text{I}$, $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ and $^{82}\text{Br}^{\text{m}}(\text{I.T.})^{82}\text{Br}$ processes produce essentially the same organic yield, while the $^{79}\text{Br}(\text{n},\gamma)^{80}\text{Br}^{\text{m}}$ process results in a lower yield. The similarity between ^{130}I and ^{128}I yields may indicate a similarity of reaction mechanisms independent of the initial kinetic energy of the activated atom. Their likeness to ^{82}Br yields would suggest that activated atoms may be tracing chemical processes which result from a similarity of environmental activation and/or decomposition. These similarities were also found between ^{130}I , ^{128}I , and ^{80}Br formed by (I.T.), (n, γ), and (I.T.) processes, respectively, in n-hexane by D. D. Wilkey and J. E. Willard.³³ The Auger electron reaction hypothesis¹⁸ may explain these phenomena. The fact that radiative neutron capture-induced yields of bromine were lower than (I.T.)-produced yields of ^{82}Br was found universal for the liquid C_6 -alkanes.²⁷ This may indicate that processes additional to Auger radiation-induced reactions occur in iodine and (I.T.)-activated ^{82}Br , or possibly that internal

conversion of (n, γ)-activated bromine occurs before the recoil energy has been dissipated, thus it would be carried away from the center of the pocket of fragments caused by radiolytic effects. The freeze-thaw technique,⁵ which lends itself to a high degree of precision has become a very valuable tool in the study of isomeric transition-induced reactions. It may also be used in efforts to isolate metastable nuclear states and determine their half-lives. It is conceivable that short half-life isomers of other nuclides studied in "hot atom" chemistry may exist and contribute significantly to data interpretation. Presently, studies are underway to determine if there are previously undiscovered isomers of halogens which may have affected the history of this field.

VII. REACTIONS OF IODINE ACTIVATED BY THE (I.T.)
AND (n, γ) PROCESSES TRANSITION IN CHLOROMETHANES.

Introduction

Since the discovery of the short-lived isomer of Iodine-130,³ it is now possible to compare the (n, γ) and (I.T.) activated reactions for iodine in various organic systems.

In preliminary experiments, Merrigan et. al.¹⁰ report that at 7.8×10^{-3} and 5.2×10^{-3} m.f. halogen in the liquid cyclohexane system, the organic retentions produced by $^{130}\text{I}^{\text{m}}$ (I.T.) ^{130}I , ^{127}I (n, γ) ^{128}I , and $^{82}\text{Br}^{\text{m}}$ (I.T.) ^{82}Br processes are similar while the ^{79}Br (n, γ) $^{80}\text{Br}^{\text{m}}$ process results in a lower retention. The authors indicate that the similarity between ^{130}I and ^{128}I organic retentions may indicate a similarity of reaction mechanisms independent of the initial kinetic energy of the activated atom. Their likeness to ^{82}Br retentions would suggest that activated atoms may be tracing chemical processes which result from a similarity of environmental activation and/or decomposition. The authors further suggest that processes additional to Auger radiation reactions may occur in iodine and (I.T.) activated ^{82}Br , or possibly that internal conversion of (n, γ) activated bromine occurs before the recoil energy has been dissipated. Thus, the atom could be carried away from the center of the pocket of fragments caused by radiolytic effects.

The purpose of this paper is to extend the study of (n, γ) and (I.T.) activated iodine reactions into low mole fraction I_2 -cyclohexane and the highly dissimilar chloromethane systems; observing whether the similarities for the cyclohexane system persist at different conditions and in additional systems.

Experimental

One ml. $^{127}\text{I}_2$ -polychloromethane samples which were encapsulated in quartz bubbles and degassed several times were irradiated in the Ford Nuclear Reactor at the University of Michigan for approximately 2-3 second duration at a reactor level of 1 megawatt (flux = 2×10^{-12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$). Some samples were irradiated at reactor power levels of 0.01, 0.1, 0.5, and 2.0 megawatts for durations which resulted in approximately the same integrated neutron dose. Organic retentions of ^{128}I were determined by gamma-ray spectrometry employing a 100-channel analyzer and a 3" x 3" sodium-iodide crystal. Organic retentions of ^{128}I from (n, γ) processes were used primarily as a comparison for organic retentions of ^{130}I from (n, γ) processes determined by the freeze-thaw technique. Organic retentions of ^{130}I determined by the latter method were the same or slightly lower than the former indicating zero-contribution to (n, γ) yields by (I.T.) reactions in the ^{130}I , $^{130}\text{I}^m$ systems.

One ml. samples of the $^{129}\text{I}_2$ -cyclohexane and $^{129}\text{I}_2$ -polychloromethane systems were placed in quartz bubbles, degassed at least three times, and irradiated in the Omaha, Nebraska, V. A. Hospital TRIGA reactor for 30 seconds at a thermal neutron flux of 1.1×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. The freeze-thaw technique and the extraction and counting procedures have been described previously.^{5,11} In ^{129}I , ^{130}I samples, the absence of any other radio chemical species was determined with a Nuclear-Data 128 channel Analyzer and 3" x 3" sodium iodide crystal. The radiogas chromatograph used to determine preliminary product distributions has been described previously.^{5,36}

All cyclohexane samples were prepared from Phillips Research grade cyclohexane. Mallinckrodt reagent CHCl_3 and Matheson CH_2Cl_2 was purified by washing several times with concentrated H_2SO_4 until colorless, washing with distilled water, washing with dilute NaOH , washing with distilled water, drying with CaCl_2 , and fractionating in a Vigreux column shortly before use. Baker and Adamson reagent CCl_4 , was purified by photo brominating, extracting with aqueous sulfite, washing with distilled water, refluxing with NaOH solution, washing with distilled water, drying with CaCl_2 , and fractionating in a Vigreux column shortly before use. The center fraction of all distilled materials was taken for sample preparation.

The ^{129}I used in these studies was obtained from Oak Ridge National Laboratories in aqueous NaI solution ($\text{pH} = 8$). The iodine was extracted into the organic phase with H_2O_2 catalyzed by a small amount of HNO_3 which was necessary for the oxidation of the $^{129}\text{I}^-$ to $^{129}\text{I}_2$. This solution was washed three times with distilled water and dried over silica gel. Concentration of samples containing the extracted $^{129}\text{I}_2$ was then determined photometrically with a Bausch and Lomb Spectronic 20.

Results and Discussions

The organic retention of ^{130}I in cyclohexane following neutron irradiation and decay of $^{130}\text{I}^{\text{m}}$ in the solid state was 14.7% in the $0.3 \times 10^{-3} \text{ }^{129}\text{I}_2$ system. This yield, higher than previously observed in I_2 -cyclohexane systems, suggested a possible growth in the solid state due to isomeric transition induced reactions. A series of identical samples containing $^{129}\text{I}_2$ in cyclohexane was prepared at $0.25 \times 10^{-3} \text{ m.f. } ^{129}\text{I}_2$ and irradiated for 30 seconds at -196°C . The samples were liquified and extracted immediately at times varying from 55 sec. to 90 min. The results, shown in Table VII, indicate that keeping the sample solid

Table VII. Organic Retentions Observed in the
I₂-Cyclohexane Solid-State System at Various
Times at 0.00025 m.f. I₂^a

Time of extraction from mid point of irradiation in sec.	Percent Organic Retention
55	25.81
365	22.28
555	23.36
995	20.32
1045	19.48
1595	25.51
5400	<u>17.94</u>
Avg. 22.10 ± 2.44	

(a) Because of various factors encountered in
solidification, the reproducibility increases
as mole fraction I₂ increases.

prevents any growth of ^{130}I into the solid state by (I.T.) induced reactions. This is important to the following general derivation of the equation to describe organic retentions in the liquid state induced by isomeric transition reactions when using the freeze-thaw technique.⁵

The observed organic retention may be described as follows:

$$\text{O.R.}_{\text{obs.}} = \frac{\text{Org.Act.}_{\text{I.T.}}^{\text{Liq.}} + \text{Org.Act.}_{\text{I.T.}}^{\text{Sld.}} + \text{Org.Act.}_{\text{n,Y}}^{\text{Sld.}}}{\text{Total Activity}}$$

The organic retention due to isomeric transition induced reactions in the liquid state is defined as the organic activity introduced into the liquid organic phase by (I.T.) 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 upon dividing the above equation by $\beta e^{-\lambda t}$ where β is the fraction of the total activity born by (I.T.) processes decaying in the liquid state.

i.e.

$$\text{O.R.}_{\text{I.T.}}^{\text{Liq.}} = \frac{\text{Org.Act.}_{\text{I.T.}}^{\text{Liq.}}}{\beta e^{-\lambda t} \text{Total Act.}} = \frac{\text{O.R.}_{\text{obs.}}}{\beta e^{-\lambda t}} - \frac{\text{Org.Act.}_{\text{I.T.}}^{\text{Sld.}} + \text{Org.Act.}_{\text{n,Y}}^{\text{Sld.}}}{\beta e^{-\lambda t} \text{Total Activity}}$$

The solid state organic activity induced by (I.T.) activation is equal to $(1 - e^{-\lambda t}) \beta$ times the observed solid-state organic retention, and induced by (n,Y) activation is equal to α times the observed solid-state organic retention where α is the fraction of the total activity produced directly by radiative neutron capture. By making the proper substitutions and rearranging, the following general expression is obtained for systems where the freeze-thaw technique¹⁰ is applicable.

$$\text{O.R.}_{\text{I.T.}}^{\text{Liq.}} = \frac{R^{\infty} - \alpha R^0}{\beta e^{-\lambda t}} - \frac{(1 - e^{-\lambda t}) R^0}{e^{-\lambda t}}$$

R^∞ is the organic retention produced in the liquid state when a sample is thawed immediately after irradiation at -196°C , and R^0 is the organic retention produced in an identical sample which is kept solid until all the metastable isomer has decayed. In systems involving $^{130}\text{I}^m$, the constants α and β are 0.39 and 0.61 respectively.³ This equation produces results similar to previous equations⁵ when R^0 's are low. Using the equation described above to obtain (I.T.) induced organic retentions, I_2 -cyclohexane studies were extended into the low mole fraction halogen region to determine whether the similarities in the I_2 -cyclohexane and Br_2 -cyclohexane systems reported by Merrigan, et.al., would still be present. As indicated in Table VII^{IX}, the similarities noted at 5.2×10^{-3} and 7.8×10^{-3} m.f. halogen persist for the (I.T.) process at low m.f. halogen; however, a separation of (n, γ) and (I.T.) iodine organic retentions appeared.

Organic retentions of ^{130}I by (n, γ) and (I.T.) induced reactions at various mole fractions of iodine in chloromethanes are presented in Table VII^{IX}. The same separation of (n, γ) and (I.T.) iodine organic retentions that appeared in the cyclohexane system is found in the methylene chloride and chloroform systems. Growth of ^{130}I activity into CH_2Cl_2 , CHCl_3 and CCl_4 curves are described by a 8.9 ± 0.3 min. half-life using the technique of Merrigan et.al.,¹⁰ as depicted in Fig. 28. By describing the correct half-life, the growth curves indicate that the (I.T.) organic retentions were not influenced by thermal photochemical, or radiation induced reactions. At 0.3×10^{-3} m.f. Br_2 in CCl_4 , organic retentions induced by $^{81}\text{Br}(\text{n},\gamma)$ $^{82}\text{Br}^m$ and $^{82}\text{Br}^m(\text{I.T.})$ ^{82}Br processes were 24.0 and 34.0 percent respectively;³ it was, therefore, unexpected that $^{130}\text{I}^m(\text{I.T.})$ ^{130}I and $^{129}\text{I}(\text{n},\gamma)$ ^{130}I induced organic retentions would be low (less than 5%) at all mole fractions halogen studied in view of the

TABLE VIII. Organic Retentions^a of (I.T.) Produced ¹³⁰I and ⁸²Br, and (n,γ) Produced ¹²⁸I and ⁸²Br^m in Cyclohexane

m.f. Halogen times 10 ³	$\frac{(n,\gamma)^b}{^{128}\text{I and } ^{130}\text{I}}$	$\frac{(n,\gamma)^b}{^{82}\text{Br}^m}$	$\frac{(I.T.)^c}{^{130}\text{I}}$	$\frac{(I.T.)^c}{^{82}\text{Br}}$
0.30	45.0	----	54.6	----
0.70	----	30.9	----	53.7
2.10	----	29.7	----	51.6
5.20	40.5	24.5	39.6	39.2
7.80	36.1	21.7	35.3	35.3

(a) Maximum experimental error was ± 1.0%

(b) Organic retentions determined by irradiating samples in the liquid state and freezing in liquid N₂ to prevent (I.T.) contributions.

(c) Sample irradiated in the solid state and thawed immediately to allow ⁸²Br^m and ¹³⁰I^m decay in the liquid state.

TABLE IX. Organic Retentions Induced by $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}$, $^{129}\text{I}(\text{n},\gamma)^{130\text{m}}\text{I}$,
and $^{130\text{m}}\text{I}(\text{I.T.})^{130}\text{I}$ in Various Liquid Chloromethanes.

m.f. I_2 in CH_2Cl_2	Org. Retentions (n, γ) ^a (I.T.) ^b		m.f. I_2 in CHCl_3	Org. Retentions (n, γ) ^a (I.T.) ^b		m.f. I_2 in CCl_4	Org. Retentions (n, γ) ^a (I.T.) ^b	
0.0003	46.4	56.3	0.00026	21.2	27.8	0.00034	4.9	2.6
	48.3	56.9		22.5	34.9		<u>3.7</u>	<u>2.4</u>
	47.1	57.3		<u>26.9</u>	<u>30.6</u>		4.3	2.5
	<u>45.8</u>	<u>56.5</u>		23.5	31.1	Avg.	<u>+0.6</u>	<u>+0.1</u>
	46.9	56.8	Avg.	<u>+2.3</u>	<u>+2.5</u>	0.00944	1.7	
Avg.	<u>+1.2</u>	<u>+0.5</u>	0.0120	19.3	21.8		2.3	2.6
				20.8	18.6		<u>1.8</u>	<u>2.2</u>
0.0157	30.3			<u>18.9</u>	<u>22.9</u>		1.9	2.4
	29.5	30.9		19.5	21.1		<u>+0.2</u>	<u>+0.2</u>
	28.0	35.2	Avg.	<u>+0.7</u>	<u>+1.7</u>			
	<u>32.9</u>	<u>24.7</u>						
Avg.	30.2	30.3						
	<u>+1.4</u>	<u>+3.5</u>						

- (a) Organic retentions of (n, γ) processes were determined by 30 sec. irradiation in the liquid state and immediate freezing in liquid N_2 to quench any growth in organic phase activity by (I.T.) reactions.
- (b) Organic retentions of (I.T.) processes were determined by 30 sec. irradiation in the solid state and immediate thawing to allow $^{130\text{m}}\text{I}$ decay in the liquid state. The observed organic retentions were corrected by the equation in the text.

results in the cyclohexane system. The dissimilarities between $\text{Br}_2\text{-CCl}_4$ and $\text{I}_2\text{-CCl}_4$ systems suggests differences in molecular parameters since the most probable product, CCl_3I , is a known compound, and it has been shown in $^{131}\text{I-CCl}_4$ radiation damage studies that retentions of iodine in organic combination as high as 25% can be obtained at a m.f. I_2 of 0.2×10^{-3} for 90 minute irradiation at 1.1×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ flux.³⁷ Preliminary product analysis by radiogas chromatography indicates that in both the CH_2Cl_2 and CHCl_3 systems, similar products are formed by both (I.T.) and (n, γ) activation as shown in Table IX^X. Major products obtained in the CH_2Cl_2 system were $\text{CH}_2\text{Cl}^{130}\text{I}$ and $\text{CHCl}_2^{130}\text{I}$. Primary product of the CHCl_3 system was $\text{CCl}_3^{130}\text{I}$. Some $\text{CHCl}^{130}\text{I}_2$ and other products were found in both systems, but accounted for a greater percentage of total activity in the (n, γ) systems than the (I.T.) systems.

The results of the chromatography studies indicate that the order of organic retentions from Table VIII^{IX} and Fig. 28, CH_2Cl_2 CHCl_3 CCl_4 , is not directly dependent on the decreasing number of hydrogens in the series, which would account for the low CCl_4 yield.

In addition to the low retentions obtained in CCl_4 systems, a most surprising result was the isotope separation for ^{130}I by (n, γ) and (I.T.) processes at low m.f. I_2 in cyclohexane and chloromethanes. Since this effect persists in these two dissimilar systems, it must be a nuclear activation effect independent of molecular parameters of solvent molecules.

Lambrecht and Rack³⁸ suggest that bromine (I.T.) and (n, γ) reactions may be somewhat different. This thermal isotope separation may be additional evidence to support differences between the two nuclear activating processes.

Table X. Percent^a of Total Organic Activity
Represented by Various Products^b in Chloroform
and Methylene Chloride at 0.002 Mole Fraction
Iodine

System	CH ₂ ClI	CHCl ₂ I	CCl ₃ I	^c CHCl ₂ I and other
I ₂ -CH ₂ Cl ₂ (I.T.)	57.95	29.58	---	12.45
I ₂ -CH ₂ Cl ₂ (n,Y)	42.58	33.06	---	24.34
I ₂ -CHCl ₃ (I.T.)	---	18.17	72.08	9.73
I ₂ -CHCl ₃ (n,Y)	---	11.20	51.26	37.60

-
- (a) Relative percentages determined by planimetry of all products appearing in the radiogas chromatograph
- (b) Product assignments made on the basis of boiling pt. and molecular weight data.
- (c) CHClI₂ underwent some decomposition at elution temperatures.

Fig. 28. - Growth of ^{130}I Organic Retentions by Isomeric Transition in Liquid Chloromethanes at 0.0003 m.f. I_2 Following Neutron Irradiation of the Solid Systems. Systems: ●, $\text{CH}_2\text{Cl}_2\text{-I}_2$; □, $\text{CHCl}_3\text{-I}_2$; and ■, $\text{CCl}_4\text{-I}_2$

VIII. PERSONNEL, PUBLICATIONS, TALKS, and MEETINGS

A. Personnel Listing

1. Project Director

E. P. Rack

2. Graduate Students

F. J. Bryant*

R. M. Lambrecht

E. Kemnitz⁺

J. A. Merrigan**

J. B. Nicholas

N. J. Parks

3. Manuscript typing and Progress Report preparations

(Mrs.) P. A. Nicholas***

* terminated, received M.S. in June, 1966

** terminated, received Ph.D. in June, 1966

*** main part of funds from the University of Nebraska work study program

⁺ National Science Fellow, 1966-1967

B. Publications

1. "Isomeric Transition Induced Reactions of Iodine-130 in Cyclohexane" by J. A. Merrigan, J. B. Nicholas, R. M. Lambrecht, N. J. Parks and E. P. Rack, J. Phys. Chem., 70, 2417 (1966).
2. "A Radiochemical Experiment in Gas Chromatography" by J. A. Merrigan, J. B. Nicholas, and E. P. Rack, J. Chem. Ed., 43, 543 (1966).
3. "Nature of (n, γ) and (I.T.)-Activated Bromine Reactions in Liquid Isomers of Hexane^e" by J. A. Merrigan, J. B. Nicholas and E. P. Rack, Radiochim. Acta., 6, 94 (1966).
4. "Effect of Moderators on the Isomeric Transition Induced Reaction of Bromine-82 with Methane" by J. B. Nicholas, J. A. Merrigan and E. P. Rack, J. Chem. Phys. (in press) 1967.
5. "The Influence of Molecular Parameters on the $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$ and $^{82}\text{Br}^m(\text{I.T.})^{82}\text{Br}$ Processes in Liquid Hydrocarbons" by R. M. Lambrecht and E. P. Rack, Radiochim. Acta, submitted for publication.
6. "Radiative Neutron Capture and Isomeric Transition Induced Reactions of Iodine with Liquid Chloromethanes" by N. J. Parks, R. M. Lambrecht, J. B. Nicholas, E. P. Rack and A. A. Gordus, Radiochimica Acta, submitted for publication.

C. Talks

1. J. A. Merrigan (with E. P. Rack), "Reactions Produced by $^{82}\text{Br}^m$ (I.T.) ^{82}Br , $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$, and $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$ Processes in Condensed C_6 Alkanes," Hot Atom Chemistry Symposium, April 1, 2, 1966, Purdue University.

2. J. B. Nicholas (with E. P. Rack), "Effect of Moderators on the Isomeric Transition Induced Reaction of Bromine-82 with Methane," Division of Nuclear Chemistry and Technology, American Chemical Society, Miami Beach, Florida, April 9-14, 1967
3. R. M. Lambrecht (with E. P. Rack) "Influence of Molecular Parameters on the Reactions Activated by the $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$ and $^{82}\text{Br}^m(\text{I.T.})^{82}\text{Br}$ Processes in Liquid Hydrocarbons," Division of Nuclear Chemistry and Technology, American Chemical Society, Miami Beach, Florida, April 9-14, 1967.
4. N. J. Parks (with E. P. Rack), "Radiative Neutron Capture and Isomeric Transition Induced Reactions of Iodine with Chloromethanes," Division of Nuclear Chemistry and Technology, American Chemical Society, Miami Beach, Florida, April 9-14, 1967.

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