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THE UNIVERSITY OF NEBRASKA
DEPARTMENT OF CHEMISTRY

HALOGEN ATOM REACTIONS ACTIVATED BY RADIATIVE
NEUTRON CAPTURE AND $^{82}\text{Br}^m$ AND $^{130}\text{I}^m$ ISOMERIC TRANSITION

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THE UNIVERSITY OF NEBRASKA

Department of Chemistry

Progress Report No. 4

February, 1969 ~ February, 1970

HALOGEN ATOM REACTIONS ACTIVATED BY RADIATIVE
NEUTRON CAPTURE AND $^{82}\text{Br}^m$ and $^{130}\text{I}^m$ ISOMERIC TRANSITION

Edward P. Rack, Project Director

Supported by

The Department of Chemistry,

University Research Council,

and

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PREFACE

The following is a report of the work completed during the period February 15, 1969 to February 14, 1970. 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 Research Council. Most of the material for this report has been accepted, submitted, or will be submitted 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. FACILITIES

A. Triga Mark II Reactor

All neutron 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^{10} 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.g. $^{-1} \text{min}^{-1}$ using Fricke dosimetry. This was confirmed by studying the ^{131}I organic uptake in $\text{c-C}_6\text{H}_{12}$, due to radiation.

This past year the reactor operated routinely for at least four eight-hour days a week at 15.5 kilowatts. The radiochemistry group has used for the period from August 1, 1968 to July 31, 1969, 278.6 hours (integrated time in reactor) at 15.5 kilowatts power making 2,100 irradiations.

B. Radiochemistry Laboratory

All sample preparation and most of the 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, three separate vacuum lines for preparing gas, liquid and solid 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-Data

128-Channel analyzer with a 3" x 3" NaI crystal specially housed in a concrete, cadmium and lead cave.

Sometime in the spring of 1970 we expect to move into our new radiochemistry laboratory in the new Hamilton Chemistry Building, giving us about four times the working area we presently have. In the new building is a specially-built room to house a neutron generator.

For most of our ^{128}I and ^{38}Cl experiments, we used the radiochemistry facilities and radioassaying equipment of the Omaha VA Hospital. The use of their RIDL 400-channel analyzer with 3" x 3" NaI crystal was most helpful in many of our studies.

II. INSTRUMENTATION

(R. L. Ayres)

Radiogas Chromatograph

In our previous progress report (1) we described in detail our newly-constructed radiogas chromatograph which we have used for analysis of labeled organic halides. After one year of extensive usage, a critical evaluation of the instrument's performance suggests a number of improvements or modifications in the original design. On the basis of this evaluation a new chromatograph is being constructed in order to incorporate necessary modifications.

At the present time, the new radiogas chromatograph is not yet completely assembled and ready for use, therefore, a detailed description of the instrument will be presented in a future report. However, some of the improvements that are being incorporated in the new instrument are:

1. A more compact and accessible oven design with improved air flow.
2. Dual column operation with heated injection ports and provision for a pre-column.
3. Improved oven temperature control and automatic linear temperature programming.
4. More precise carrier gas flow control and readout.
5. Addition of a purge gas inlet ahead of the proportional counter to permit variable retention times of the compounds eluted from the column, thereby improving detector resolution.

In the operation of our present instrument we have encountered problems with false efficiencies and contamination or sticking with labeled halogen compounds

yielding signals in excess of 15,000 c/m, in our flow-through proportional counter.

In an effort to determine the cause of this contamination we deliberately contaminated the counter by introducing excessive amounts of labeled organic halides. The window insert was then dismantled and the individual components inspected for contamination. We found that the stainless steel window and window support surfaces and (to a greater extent) the exposed epoxy used to form and attach the window were contaminated. However, the degree of contamination of these surfaces was small in comparison to that observed during operation of the counter.

Examination of the design (1,2) of the window insert shows the existence of a small dead volume (~1 to 2 ml) between the entrance and/or exit gas ports and the window to insert seal. The trapping of a portion of the activity being detected in these dead volumes would account for the appearance of contamination when high specific activity compounds are passed through the counter.

The counter contamination was observed to decrease at a rate independent of the half-life of the isotope responsible. This observation would support the contention that the principle cause of the observed "sticking" in the counter results from the trapping of a portion of the compound in these dead volumes rather than actual contamination of the counter surfaces. This could also contribute to the false efficiencies observed by Wolf et. al. (2) in this type of counter.

In an attempt to correct these difficulties a new window insert (see Figure 1) was designed. By eliminating the center support rod, which is unnecessary once the window insert is in place, the amount of surface exposed for possible contamination was reduced. In addition, a slightly better counting geometry was achieved.

The elimination of the center support rod also permitted an improved inlet and outlet design, which minimized or eliminated any dead volume in the detection volume of the counter thus eliminating the suspected major source of contamination.

Block Diagram of GC Radiation Detection System

Fig. 1.

A new 0.5 mil titanium window will be used in the new counter in order to completely eliminate all exposed stainless steel surfaces in the counting volume of the counter. This window is expected to be more inert to halides than stainless steel and, in addition, the smaller attenuation coefficient of this window material should result in an increase in detection sensitivity.

The use of high temperature silicon O-rings to seal the window to the inserts (tested and found to form a gas tight seal of the thin window material to the stainless steel surface) will eliminate the major portion of the epoxy surface on the inside of the window. This new window insert is presently being constructed by our machanist and will be installed in the new chromatograph. An evaluation of the performance of this design will be reported at a later date.

Since the earlier description of our present radiation detection system (1), new nuclear counting instrumentation has been added. The new electronics are NIM modules arranged as shown in the block diagram in Figure 2.

This instrumentation permits greater control over counter noise descrimination and analog data display. These modules, along with others, not shown in Figure 2, have greatly increased the versatility of our laboratory counting instrumentation.

Fig. 2. Flow-through proportional counter window assembly and insertion tool.

III. RADIOMETRIC ANALYSIS OF SERUM AND TISSUE PROTEINS

(Henry K. J. Hahn)

SUMMARY OF PROGRESS

A radiometric analysis of serum and tissue proteins utilizing Cu-64 ($t_{1/2} = 12.9h$) in the biuret reaction was developed. The advantages of the radiometric technique are (1) typical interferences, common to the usual biuret reaction, are eliminated, (2) preliminary adjustment by dilution is not required, and (3) a greater range of sensitivity - 0.04 mg to 18 mg of protein - is achieved.

INTRODUCTION

Recently Peters (3) in his survey of various standardization methods for total protein analysis in serum reported that some form of the biuret reaction, because of its simplicity and reliability, is employed by the majority of laboratories and that the biuret method of Corneli et.al. (4) is slightly favored over that of Weichselbaum (5).

Four possible sources of interference encountered with the biuret determination are turbidity, presence of bilirubin and certain free amino acids, and hemolysis. Turbidity can be readily eliminated by simple ether extractions (7) or subtraction of residual absorbance after the biuret color has been dispelled by cyanide (8). Except in the cases of abnormal sera, the interference by bilirubin and amino acids is negligible. Although it is best not to use hemolyzed serum, a correction can be made by independent determination of hemoglobin. Although sensitivity of the biuret reaction is not as good as that of the Lowry (9) phenol techniques, the phenol methods are not as reproducible as the biuret methods

because of color variations with different proteins and nonproportionality of color to concentration. Micro procedures (10-12) have not been found generally applicable to analysis because of precipitation and irregular interferences by free amino acids and salts.

In this paper we report a radiometric analysis of serum and tissue proteins utilizing Cu-64 ($t_{1/2} = 12.9\text{h}$) in the biuret reaction. The advantages of our technique are (1) typical interferences, common to the usual biuret reaction, are eliminated, (2) preliminary adjustment by dilution is not required, and (3) a greater range of sensitivity - 0.04 mg to 18 mg of protein - is achieved. Copper-64 is readily available commercially or from neutron irradiation of a copper salt.

EXPERIMENTAL

Apparatus. Vials of 0.02 M copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (Johnson, Matthey & CO., London) were irradiated for two hours in a Triga Mark I water cooled reactor at a flux of 1.1×10^{11} n/cm²/sec. The Cu-64 gamma activities resulting from the protein-complex were measured with an ORTEC single channel analyzer and 2" x 2" NaI crystal.

Reagents. Alkaline tartrate reagent was prepared by mixing equal volumes of 0.886 M sodium potassium tartrate and 3.12 M sodium hydroxide. Alkaline copper tartrate was prepared by mixing 2 ml of radioactive 0.02 M copper sulfate and 8 ml of alkaline tartrate. Chelex 100, Bio-rad, analytical grade chelating resin, 200-400 mesh, sodium form, was suspended in deionized water at the concentration of 500 mg/ml. Albumin Bovine Fraction V (Nutritional Biochemical Corporation) was used as a protein standard. The precise protein concentration was determined by Kjeldahl analysis using the factor 6.25. It was then diluted to the desired concentration with deionized water.

Procedures. One milliliter of alkaline copper tartrate (Cu-64) was added to a test tube containing the protein sample. The total volume was adjusted to 5 ml

with water and mixed thoroughly. The solution was allowed to stand for 10 minutes at room temperature. Two milliliters of chelex 100 were added and shaken for 20 to 30 seconds and then centrifuged for 2 minutes at moderate speed. A 5 ml aliquot of supernatant was transferred into another test tube containing 2 ml of chelex 100. It was then shaken for 20 to 30 seconds and again centrifuged for 2 minutes. A five milliliter aliquot of the supernatant was then counted for one to two minutes. In the case of serum, 1 ml was diluted to 10 ml with water; and 1 ml of the diluted sample was analyzed. Liver samples weighing 50 to 100 mg were homogenized in 8 ml of 1.0 M sodium hydroxide with a Virtis homogenizer for less than one minute. The homogenates were then transferred into a volumetric flask and diluted with water to 50 ml. One drop of normal octyl alcohol was added to prevent foaming. Four ml of the diluted homogenates were used for the analysis. The blanks (initially deionized water) and standards were prepared in the same manner as the samples. In the tissue protein analysis, 0.0256 g of sodium hydroxide was added to the blank and protein standards to make them the same concentration as the samples.

Protein concentrations of the samples were calculated simply by comparing the counts per minute of the standard protein solution to the counts per minute of the unknown sample.

RESULTS

The results of the described radiometric procedure on the analysis of known concentrations of proteins are presented in Table I. The lowest concentration (0.04 mg) tested gave approximately 1100 counts per 1.5 minutes after the subtraction of the activity of the blank (700 counts/1.5 minutes). This is still more than twice the counts of the blank. The highest relative standard deviation obtained was 3% and was consistently less than 1% for the higher concentrations

of the protein tested. Figure 3 demonstrates the linearity between Cu-64 activity and concentration of protein for the radiometric method. Although the concentrations less than 1 mg protein are not shown in the figure, it can be seen from Table I that the concentrations below 1 mg are also linear with respect to Cu-64 activity.

Table II summarizes the results of analysis of various samples. The method of Cornell et.al. (4) was employed in the serum analysis for comparison with our method and it was found to yield slightly higher values (7.05g% as compared to 6.82g% for the radiometric method). Moni-Trol I was analyzed for comparison with the manufacturer's analysis. A value of 6.75g% was obtained with our method whereas 6.70g% was given by the manufacturer. The results obtained on rat liver analysis by our radiometric method are about 2.6% lower than the Kjeldahl analysis. This difference may simply be due to the inherent differences of the two methods.

DISCUSSION

The radiometric method described has been found to be superior to the previous biuret methods in that the effects of interferences are minimized, the sensitivity is increased, and the linear range of determination of protein concentration (Fig. 3) is extended. In addition, tissue protein can also be analyzed. These improvements make the radiometric method more versatile and useful for the analysis of total protein.

The reason the biuret reaction is seldom applied in tissue analysis is that high alkalinity must be employed in homogenating the tissues. In order to obtain a clear solution after homogenation, one can only use small samples of tissue. This in turn creates the need for a more sensitive method of analysis.

Out of 21 amino acids tested for interference, proline, threonine, serine, glycine and cystine interfered slightly but still much less than in the usual

TABLE I.

ANALYSIS OF SOLUTION OF KNOWN CONCENTRATIONS OF PROTEINS

mg Protein N = 5	Counts/1.5 min.	St. Dev.	Rel. Std. Dev. %
0.04	1,152	28	2.43
0.22	5,998	184	3.07
0.44	12,138	345	2.84
0.64	17,780	297	1.67
0.87	23,336	391	1.61
0.98	26,648	444	1.67
1.96	51,526	352	0.68
3.93	104,740	288	0.27
5.89	160,822	1,598	0.99
7.85	214,429	1,747	0.81
9.82	266,852	2,269	0.85
11.78	320,584	1,954	0.61
13.75	372,563	2,293	0.62
15.71	432,732	3,079	0.73

Fig. 3. Radiometric analysis of solutions of known protein concentrations.

spectrophotometric method. If large numbers of samples are analyzed in a given period of time, it is necessary to make decay corrections for Cu-64 ($t_{1/2} = 12.9\text{h}$) or count the protein standard periodically in between the samples.

If analyses of samples containing less than 2 ml total protein are made, it is better to use the combination of 1 ml 0.02 M copper sulfate (Cu-64) and 9 ml of alkaline tartrate reagent, adding chelating resin only once. Otherwise, two separate additions are necessary to completely remove free cupric ions. This is very important in obtaining consistent reproducibility. The chelex-100 effectively removes all the free cupric ions so that the blanks are colorless. The samples also appear colorless in the lower concentration ranges of proteins, even though copper-protein is present. When additional sodium hydroxide is added to the reaction mixture, the intensity of the color is increased. Reinvestigation indicated that this is caused by the slight solubility of $\text{Cu}(\text{OH})_2$ in excess base and not to the increasing yield of copper-protein complex.

The reaction time is not critical after 10 min. of reaction but it does vary the yield from 90 to 96% in the first 10 minutes. Maximum reaction occurred at 50 min. but the difference between 10 min. and 50 min. is very slight. This difference is eliminated by having the samples and standard react for the same period of time.

Neutron activation analysis for copper concentration (13) on tissue and serum, showed residual protein correction to be insignificant.

Other metal affinities for the protein were tested with this procedure. We found that cobalt-60 ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) gave a similar reaction as copper but was linear only up to 7.65 mg total proteins. In this case the NaOH concentration was doubled. Zinc-65 ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) did not give any reaction with the proteins tested.

TABLE II.
ANALYSIS OF ACTUAL SAMPLES

Type of Samples N = 5	g%	Std. Dev.	Rel. Std. Dev. %
Serum	6.82	0.18	2.64
Liver	18.78	0.52	2.77
Liver ^a	19.28	1.00	5.19
Moni-Trol I	6.75	0.12	1.78
Moni-Trol I ^b	6.70	0.20	2.99

a Kjeldahl method

b Lot No. LTD-102 C,D

IV. RADIATIVE NEUTRON CAPTURE AND ISOMERIC TRANSITION ACTIVATED
REACTIONS OF HALOGENS AND INTERHALOGENS IN LIQUID (25°)
AND SOLID (77°K) BENZENE

(E. J. Kemnitz)

SUMMARY OF PROGRESS

In a previous study (1), the effects of bromine concentration and benzene purity were investigated for the $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$, and $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ processes in benzene at 77°K. As in the earlier study with the $^{129}\text{I}_2$ -benzene system at 77°K, an isotope effect was found. Also, in addition to the organic yield plateau established by Milman et.al. (16) in the 0.1 to 0.5 mf Br_2 region in the bromine-benzene system at 77°K, a somewhat higher O.Y. plateau was found in the 5×10^{-4} to 10^{-6} mf Br_2 region.

In order to gain more insight into the observed isotope effects and organic yield plateaus, mixed halogens and interhalogens were used in comparative study in both liquid and solid (77°K) benzene systems.

Finally, radiogas chromatography was attempted in all systems investigated with less than satisfactory reproducibility achieved. With improved instrumentation, plans are being made to extract meaningful chromatograms from these systems.

INTRODUCTION

Several studies (16,19-21) indicated a relationship between organic yields induced by nuclear transformations and the state of aggregation (or dispersion) of a solute and its tendency toward complexing. The constancy of organic yields over a considerable range in concentration appears to indicate either a preferred

cluster size, $(X_2)_n$, where X_2 represents some halogen or interhalogen, or a similar number of halogen or interhalogen molecules at sites in polycrystalline organic matrices.

Although there is some evidence of solid state organic yields being independent of isotope and mode of activation in aliphatic hydrocarbons (16,17,18), this does not appear to be true in benzene (16). In order to probe this system further, a study of mixed halogens ($I_2 + Br_2$, IBr , and ICl) in benzene was initiated and a comparison made with the systems containing I_2 and Br_2 . These same systems were also studied in the liquid state in order to compare isotopes, mode of activation, and scavenging effects.

EXPERIMENTAL

Several hundred samples of zone refined benzene (99.99 quoted mole percent purity by G-C analysis from Applied Science Laboratories) containing varying amounts: Br_2 , $I_2 + Br_2$, IBr , ICl and I_2 were irradiated in quartz bulblets. Matheson, Coleman, and Bell ICl ; Mallinkrodt Br_2 ; K and K IBr ; and Mallinkrodt iodine, which was sublined from a mixture of reagent grade I_2 , KI and CaO , were used. Sample preparation, neutron irradiation facilities, extraction and counting procedures employed have been described earlier (1,15). The mixed radio halogens were assayed with a 3 x 3 inch $NaI(Tl)$ crystal and a RIDL 400 channel pulse height analyzer. Spectrum stripping techniques were used to determine the ^{38}Cl and ^{128}I activities for ICl (1) and the $^{80}Br^m$ and ^{128}I for IBr and $I_2 + Br_2$ activities.

The radiogas chromatograph has been described previously (1). Two-ml samples of zone refined benzene with varying amounts of bromine (5×10^{-4} to 0.3 mf Br_2) and 5×10^{-3} mf IBr were irradiated for periods of 6 to 30 minutes depending upon the concentration. The solid state samples were frozen in mineral oil and refrozen periodically to maintain a temperature near 77°K throughout the period of

irradiation. When the $^{82}\text{Br}^m$ activity became negligible (approximately one hour after irradiation) all samples, wrapped in aluminum foil, were kept under liquid nitrogen until extracted. When the $^{80}\text{Br}^m$ activity became negligible (approximately 46 hours after irradiation), the frozen samples were broken under 5 ml of aqueous sodium sulfite solution and extracted. After drying in silica gel 0.2 ml was injected into the radiogas chromatograph.

RESULTS AND DISCUSSION

The organic yields observed for the $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$, $^{127}\text{I}(n,\gamma)^{128}\text{I}$, $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br} + ^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$, and $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ processes as a function of ICl , I_2 , Br_2 , $\text{I}_2 + \text{Br}_2$, and IBr concentration, in polycrystalline benzene at 77°K , are given in Table III and Figure 3. The data for the iodine-benzene and the bromine-benzene systems have been reported previously (1,15), but are presented again for comparison purposes.

The isotope effects and the general position of the organic yield plateaus found in the bromine-benzene system are also found in the $(\text{I}_2 + \text{Br}_2)$ -benzene and the IBr -benzene systems for the $^{79}\text{Br}(n,\gamma)^{80}\text{Br}^m$, $^{81}\text{Br}(n,\gamma)^{82}\text{Br} + ^{81}\text{Br}(n,\gamma)^{82}\text{Br}^m$, and the $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ processes. In the region of monomolecular dispersion, generally less than 10^{-4} mf halogen or interhalogen, the various nuclear processes yield approximately equal organic yields in each system. The notable exception is the somewhat lower organic yield produced by the $^{82}\text{Br}^m(\text{IT})^{82}\text{Br}$ process in the bromine-benzene system compared to the other two systems (See Figure 3c). This may, however, be an experimental artifact since it is inconsistent with the results obtained not only in this work but in others (10-21). It can be seen in Figure 3d that the I-128 organic yields in the region of monomolecular dispersion are essentially equal within experimental error for these three systems. The ICl -benzene system yields a somewhat lower organic yield curve in this region.

TABLE III

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

mf of Halogen or Interhalogen	Time of Irrad. (sec)	Br-80m (n, γ)	Br-82&Br-82m (n, γ)	Br-82 (IT) (b)	I-128 (n, γ)	Cl-38 (n, γ)
10^{-1} Br ₂	2	20.6	26.3	31.5		
I ₂ + Br ₂ (c)		10.3	14.8	15.2	—(d)	
IBr		15.1	20.6	21.3	11.8	
ICl					16.8	20.9
I ₂					—(d)	
10^{-2} Br ₂	2	20.6	28.5	33.0		
I ₂ + Br ₂ (c)		11.0	15.0	15.6	16.4	
IBr		15.6	21.1	22.0	33.6	
ICl					29.3	21.5
I ₂					46.2	
10^{-3} Br ₂	5	26.2	34.5	38.3		
I ₂ + Br ₂ (c)		24.4	35.1	35.2	50.2	
IBr		25.8	33.4	33.8	50.4	
ICl					43.4	22.1
I ₂					50.7	
10^{-4} Br ₂	10	30.3	38.6	41.8		
I ₂ + Br ₂ (c)		31.7	41.5	50.5	51.2	
IBr		32.0	40.8	50.0	50.8	
ICl					45.7	21.8
I ₂					52.7	

TABLE III (continued)

mf of Halogen or Interhalogen	Time of Irrad. (sec)	Br-80m (n,γ)	Br-82 ^m Br-82m (n,γ)	Br-82 (IT) ^(b)	I-128 (n,γ)	Cl-38 (n,γ)
10^{-5} Br ₂	20	29.2	30.9	39.2		
I ₂ + Br ₂ ^(c)		32.3	42.2	51.2	48.9	
IBr		33.2	41.6	51.3	49.7	
ICl					46.1	20.8
I ₂					51.7	

(a) 99.99 quoted mole percent purity

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

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

Fig. 3a-e. Organic yields induced by various nuclear processes in benzene at 77°K as a function of halogen or interhalogen concentration.

In the region, 10^{-2} to 10^{-4} mf halogen, organic yield plateaus indicate similar $(X_2)_n$ cluster sizes in each of the systems. For a given nuclear process, the organic yield plateau is highest in the bromine-benzene system, lower in the IBr-benzene system, and lowest in the $(I_2 + Br_2)$ -benzene system (See Figures 3a., 3b., and 3c.). It is not evident whether this difference is due to a difference in $(X_2)_n$ cluster sizes, scavenging ability of the halogens, or combination of factors.

The scavenging ability of these halogens was compared in a study of identical systems in the liquid state. It can be seen from Figures 4b., 4c., and 4d. (See Table IV) that the scavenging effect is essentially the same for the nuclear processes $\{^{79}Br(n,\gamma)^{80}Br^m, ^{81}Br(n,\gamma)^{82}Br + ^{81}Br(n,\gamma)^{82}Br^m, \text{ and } ^{82}Br^m(IT)^{82}Br\}$ in the $(I_2 + Br_2)$ -benzene and IBr-benzene systems, while it is significantly less in the bromine-benzene system. The scavenging effect of the various halogens $(I_2 + Br_2, I_2, IBr, \text{ and } ICl)$ on the $^{127}I(n,\gamma)^{128}I$ process in the systems containing benzene and each of these halogen combinations is shown in Figure 4a. (See Table IV). As yet, no work (15,23,24) has indicated a scavenging effect of I_2 on the $^{127}I(n,\gamma)^{128}I$ process, but $I_2 + Br_2, IBr, \text{ and } ICl$ all seem to exhibit a significant amount.

The ^{128}I organic yields in polycrystalline benzene (77°K) are depicted in Figure 3d. for the same four systems mentioned above. In the region of monomolecular dispersion, generally less than 5×10^{-3} mf halogen, each system has an organic yield plateau near 50% except the ICl-benzene system, which is at 41%. It is difficult to determine whether a second O.Y. plateau at a higher mf of halogen would show up since there is a solubility limitation in each system. Experimentally it is difficult to prepare reproducible samples at concentrations higher than 10^{-2} mf halogen ($I_2, I_2 + Br_2, ICl, IBr$). I-128 organic yields in the iodine-biphenyl and iodine-naphthalene systems are given in Table III and

Fig. 4. Organic yields induced by various nuclear processes in liquid benzene as a function of halogen or interhalogen concentration.

depicted in Figure 3d. The comparatively low organic yields in these systems suggests the absence of complex formation under our experimental conditions. At 10^{-2} mf iodine it appears that there is essentially a complete separation of iodine clumps and hydrocarbon.

The $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$ process is somewhat unique in this study since its interaction with benzene does not seem to be affected by either concentration of halogen or phase (See Figure 3e.). It would seem that the Cl-38 organic yield in polycrystalline benzene (77°K) would decrease in the higher mf ICl region if $(\text{ICl})_n$ clusters of any size were formed. We are presently investigating this anomaly.

Although no quantitative data could be obtained from radiogas chromatography, some general information was gained.

1. No polymeric product was found at any mf Br_2 .
2. The amount of dibromobenzene detected from the solid phase reaction was much higher (~10x) when compared to the amount of monobromobenzene formed than from the liquid phase reaction.
3. Two and four carbon monobromides appeared at 0.3 mf Br_2 to a small extent (less than 5% when compared to the monobromobenzene as 100%).
4. The product distribution for the ^{82}Br -labeled species was approximately the same for the IBr-benzene and Br_2 -benzene systems in both the solid and liquid phases.

TABLE IV

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

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

TABLE V

ORGANIC YIELD OF THE $^{127}\text{I}(n,\gamma)^{128}\text{I}$ PROCESS IN POLYCRYSTALLINE
 BIPHENYL AND NAPHTHALENE AT ROOM TEMPERATURE

mf I ₂	Biphenyl	Naphthalene
10^{-2}	1.0%	0.5%
10^{-3}	4.5%	9.0%
10^{-4}	11.6%	14.0%

V. APPLICATION OF ISOTOPICALLY LABELED BROMINE FOR THE DETERMINATION OF TRACE UNSATURATION IN ALKANES

(O. Gadeken and R. L. Ayres)

SUMMARY OF PROGRESS

Tracer techniques have been successfully applied to the quantitative and qualitative analysis of trace quantities of olefinic unsaturate in pure alkane solvents. Utilizing the direct addition of ^{82}Br -labeled bromine to the carbon to carbon double bond; olefin impurities in a pure alkane solvent can be accurately determined in concentrations $\leq 6.4 \times 10^{-7}$ moles of unsaturate per ml of alkane.

Using ^{82}Br labeled bromine possessing a high specific activity (≤ 950 mC/g) the identity of individual olefin impurities can be determined by radiogas chromatography. Qualitative identification of unsaturates present in concentrations greater than 5×10^{-6} moles per ml of alkane are readily achieved.

INTRODUCTION

The addition of bromine to a double bond and subsequent analysis of the quantity of reagent consumed is one of the more widely accepted techniques for the determination of olefinic unsaturation. The numerous bromine addition methods developed, vary as to nature of the bromination reagents employed and, to a lesser extent, the type of analysis utilized for the determination of reagent consumed. In most instances a titrimetric procedure is employed. Palger and Jungnickel (25) have extensively reviewed the numerous methods reported prior to 1956.

There has been little effort or success in this early work in the determination of very small concentrations of olefinic unsaturation. However, Fritz and

Wood(26) have reported values for the determination of olefinic unsaturation in the concentration range of 2×10^{-6} to 2.2×10^{-5} moles of unsaturation per ml of solvent. Their method utilizes an indirect spectrometric determination of simple organic unsaturation based on the decrease in absorbance resulting from the reaction of the carbon-carbon double bond with excess bromine in 90% acetic acid-10% water.

Trace amounts of unsaturation in hydrocarbon solvents, used in the study of the radiative neutron capture induced organic yields of iodine (20) and bromine (19) in hydrocarbon matrices, have been shown to be important. Thus, the purpose of this investigation is to develop a sensitive technique for the analysis of trace quantities of unsaturation in pure hydrocarbon solvents.

EXPERIMENTAL

Samples containing 50, 100, and 500 microliters of bromine were prepared by vacuum-line techniques and sealed in quartz ampoules. Irradiation of the samples with thermal neutrons was carried out in the Omaha, Nebraska V.A. Hospital TRIGA reactor described in Chapter 1 of this progress report. The samples were irradiated for 5, 10, 120, and 600 minutes and then allowed to decay for a minimum of 48 hrs. in order to eliminate all short-lived isotopes. The respective ^{82}Br specific activities were 8, 14, 172, and 950 mC/g after the samples had been allowed to decay for forty-eight hours.

The ^{82}Br labeled bromine was then mixed with 10 or 20ml. solutions of repurified Phillips research grade n-hexane containing known amounts of added unsaturate (1-pentene or diisobutylene). The concentration of added bromine was kept constant at 9.16×10^{-4} moles per ml solution, while unsaturate concentration was varied from 0 to 9.132×10^{-5} moles per ml of solvent.

The addition of bromine was performed in the absence of light to prevent light induced bromine side reactions with the unsaturate and solvent. Complete addition to the double-bond was further insured by allowing the mixture to sit in an ice bath in the dark for 30 minutes.

The mixture was then extracted with an equal volume of aqueous sulfite solution. The organic phase was dried with anhydrous calcium chloride and a three ml aliquot of each phase was counted in a 2" x 2" NaI(Tl) scintillation well counter. The organic yield was then calculated by the following relationship:

$$\% \text{ Organic Yield} = \frac{\text{Organic Activity}}{\text{Organic Activity} + \text{Aqueous Activity}} \times 100$$

Where 100% organic yield would represent equal molar quantities of bromine and unsaturate.

RESULTS & DISCUSSION

Tables VI, VII, and IX present the observed and theoretical organic yields (i.e., the theoretical O.Y. would be 100% for equal molar concentrations of Br_2 and unsaturate) of 1, 2-dibromopentene and 1, 2 dibromo-diisobutane, resulting from the addition of ^{82}Br labeled Br_2 to 1-pentene and diisobutylene, respectively, in n-hexane solvent. All experimental values were corrected for the 0.084 ± 0.0427 contribution to the total organic yield, due to the thermal pickup of bromine by the pure n-hexane solvent shown in tables VIII and IX. In figure 5, the experimental values are compared with the calculated values, assuming 100% addition. The experimental values for 1-pentene were found to be consistently low. This is attributed to loss of the highly volatile 1-pentene from the standard solution by evaporation.

As can be seen in table IX and Fig. 5, the analysis technique described in the experimental section gives, in nearly all cases, the correct results over the entire concentration range shown (9.1×10^{-5} to 6.4×10^{-8} moles of olefin per

Fig. 5. Organic yields of n-hexane solution as a function of added olefin concentration.
 —, Calculated Values   ■, Diisobutylene   ●, 1-Pentene

ml of n-hexene). In most cases the percent error in experimental values for olefin concentration determination were $\leq 8\%$. This compares favorably with the results represented by Fritz and Wood (25) for higher concentrations of unsaturate. Refinement of the experimental technique is expected to yield even greater precision.

A number of determinations were carried out where the unsaturate concentration was held constant and the specific activity of the added bromine was varied. It was found that increasing the activity of the added bromine had little or no effect on increasing the sensitivity of the analysis, although increasing the added bromine activity resulted in increased activity in the bromine addition products. Corresponding increases in the activities of the pure n-hexene solvent with no added unsaturates were observed. Thus, the correction for increased activity of the solvent blank effectively cancelled any increase in the activity of the sample being analyzed.

On the basis of the above, and for reasons of convenience and economy, the optimum bromine specific activity for quantitative unsaturate analysis was determined to be equal to or less than 8 millicuries of ^{82}Br per gram of total bromine.

Our results indicate the use isotopically-labeled bromine for the determination of trace unsaturation in alkane solvents minimizes or eliminates many of the problems encountered in a number of the currently employed techniques. For example, standardization of the bromine reagent is completely eliminated, the unsaturate concentration can be determined directly in a hydrocarbon media without prior dissolution in a suitable solvent, and the limits of detection are lower than any previously reported. The ready availability of commercially produced ^{82}Br and the simplicity and sensitivity of this method merits careful consideration as to its applicability to routine determination of olefinic unsaturation in various non-polar solvents.

The method described above will yield only quantitative results for the analysis of unsaturates in alkanes. In many instances it is desirable to qualitatively identify the olefinic impurity. Successful qualitative identifications of olefinic impurities in alkane solvents have been performed in this laboratory by employing a modification of the technique described above.

The n-alkane solvent containing the olefinic impurities is treated with ^{82}Br labeled Br_2 exactly as described in the experimental section. However, the added bromine employed has a much greater specific activity than that used for quantitative analysis (>950 mC/g as compared to ≤ 15 mC/g). The extracted organic phase is then analyzed by gas chromatography, using a flow through window-proportional counter for the detection of the labeled organic products.

The GC radiation detector employed in these determinations has been described previously (1,2). The proportional type counter was selected because of its well known counting efficiency (i.e., sensitivity). The use of a thin window is necessary to prevent mixing of the eluting organic bromides and the counting gas, thus, preventing quenching of the counter by the organic bromides.

By employing radiogas chromatography as described above qualitative identification of various olefinic impurities tested (i-pentene and diisobutylene) was achieved for samples containing less than 5×10^{-6} moles of individual olefin per ml of solvent. Simultaneous quantitative analysis was also possible by comparison of unknown peak areas with the observed peak area of a standard of known concentration. However, this technique yielded less satisfactory results, for total unsaturate content in a sample, than the simple extraction and counting method.

One of the principal reasons for this was that quantitative addition of bromine to the double bond was not observed for the samples used for qualitative analysis. In fact, little or no addition products were observed. The principle

product (>95%) was found to result from the substitution of bromine at the allylic position of the olefin.

The brominations of the samples used for both the qualitative and quantitative analysis were performed identically, with the exception of using bromine having a much greater specific activity in the qualitative analyses. This difference in specific activities of the bromine must then be responsible for the observed bromine substitution samples containing high activities of ^{82}Br , in place of the expected addition to the olefin.

This postulate is not unreasonable, in that, the increased internal radiolysis of the sample from the higher activity bromine could initiate a free radical substitution process.

Although, quantitative addition of bromine would be more desirable in terms of increased sensitivity (2 bromines added instead of 1), the resultant bromine substitution products that are detected and identified uniquely characterize the unknown olefin present in the sample.

TABLE VI

1-Pentene in n-hexane

Sample Number	λ_1 of Unsaturate per ml. of solvent	Moles of Unsaturate per ml. of solvent	Organic Yield %	Theoretical Yield %	Deviation From Average	Deviation From Theoretical
105	10	9.132×10^{-5}	95.02	99.69	-0.02	-5.67
106			95.04		0.00	-5.65
107			95.03		-0.01	-5.66
108			95.07		+0.03	-5.62
97	5	4.566×10^{-5}	45.60	49.84	+1.05	-4.24
98			45.46		+0.91	-4.38
99			45.36		+0.84	-4.48
100			45.18		+0.63	-4.66
101			44.23		-0.32	-5.65
102			44.34		-0.21	-5.50
103			43.45		-1.10	-6.39
104			42.81		-1.94	-7.03
117	2.5	2.283×10^{-5}	21.68	24.92	+0.06	-3.24
118			21.56		-0.06	-3.36
89	1	9.132×10^{-6}	8.60	9.97	+0.36	-1.37
90			8.67		+0.43	-1.30
91			8.03		-0.21	-1.94
92			7.25		-0.99	-2.72
93			7.93		-0.31	-2.04
94			8.07		-0.17	-1.90
95			7.96		-0.28	-2.01
119			8.84		+0.60	-1.13
120			8.83		+0.59	-1.14

TABLE VI (cont'd)

Sample Number	% of Unsaturate per ml. of solvent	Moles of Unsaturate per ml. of solvent	Organic Yield %	Theoretical Yield %	Deviation From Average	Deviation From Theoretical
69	0.1	9.132×10^{-7}	1.031	0.997	+0.183	+0.202
70			1.013		+0.165	+0.184
71			0.950		+0.102	-0.121
72			0.807		-0.041	-0.190
73			0.803		-0.045	-0.194
74			0.792		-0.56	-0.205
75			0.745		-0.103	-0.252
76			0.644		-0.204	-0.353
80	0.01	9.132×10^{-8}	0.178	0.100	+0.070	-0.078
81			0.117		+0.009	-0.017
82			0.121		+0.013	-0.021
83			0.101		-0.007	-0.001
84			0.021		-0.087	-0.079

TABLE VII

Diisobutylene in n-hexane

Sample Number	λ of Unsaturate per ml. of solvent	Moles of Unsaturate per ml. of solvent	Organic Yield %	Theoretical Yield %	Deviation From Average	Deviation From Theoretical
172	10	6.402×10^{-5}	64.57	69.89	-5.89	-5.32
192			78.48		+8.02	+8.59
193			78.63		+8.17	+8.74
196			74.91		+4.45	+5.02
197			75.19		+4.73	+5.30
200			59.32		-11.14	-10.57
201			59.22		-11.24	-10.67
209			71.92		+ 1.46	+ 2.03
210			71.92		+ 1.46	+ 2.03
170	7.5	4.802×10^{-5}	52.56	52.42	0	+ 0.14
135	2.5	1.601×10^{-5}	13.64	17.47	- 5.02	- 3.83
136			13.05		- 5.61	- 4.42
166			12.80		- 5.86	- 4.67
167			13.15		- 5.51	- 4.32
221			29.81		+11.15	+12.34
222			29.44		+10.78	+11.97
182	1	6.402×10^{-6}	7.66	6.99	+ 0.59	+ 0.67
183			7.51		+ 0.44	+ 0.52
204			8.16		+ 1.09	+ 1.17
207			6.04		- 1.03	- 0.95
208			6.00		- 1.07	- 0.99
127	0.5	3.201×10^{-6}	2.50	3.49	- .70	- 0.99
128			2.44		- .70	- 1.05
178			3.93		+ 0.73	+ 0.44

TABLE VII (Cont'd)

Sample Number	λ of Unsaturate per ml. of solvent	Moles of Unsaturate per ml. of solvent	Organic Yield %	Theoretical Yield %	Deviation From Average	Deviation From Theoretical
179			3.94		+0.74	+0.45
176	0.25	1.601×10^{-6}	1.54	1.75	+0.04	-0.21
177			1.45		-0.05	-0.30
213	0.1	6.402×10^{-7}	0.644	0.699	+0.18	-0.55
214			0.607		-0.19	-0.92
219	0.05	3.201×10^{-7}	0.315	0.349	-0.39	-0.34
220			0.392		+0.38	+0.43
145	0.01	6.402×10^{-8}	0.124	0.070	+0.059	+0.054
146			0.064		-0.001	-0.006
152			0.073		+0.008	+0.003
153			0.037		-0.028	-0.033
186			0.056		-0.009	-0.014
187			0.036		-0.029	-0.034

TABLE VIII

n-Hexane Solvent Blanks

Sample Number	λ of Unsaturate per ml. of solvent	Moles of Unsaturate per ml. of solvent	Organic Yield %	Theoretical Yield %	Deviation From Average
5	0	0	0.067	0	-0.017
6			0.027		-0.057
7			0.107		+0.023
8			0.078		-0.006
9			0.047		-0.037
10			0.023		-0.061
19			0.095		+0.011
21			0.121		+0.037
33			0.092		+0.008
45			0.064		-0.020
46			0.054		-0.030
109			0.088		+0.004
110			0.059		-0.025
111			0.084		0.000
112			0.060		-0.024
126			0.190		+0.106
141			0.044		-0.040
142			0.055		-0.029
143			0.182		+0.098
144			0.051		-0.033
161			0.140		+0.056
174			0.106		+0.022
175			0.052		-0.032
211			0.121		+0.037
212			0.085		+0.001

TABLE IX
Summary of Results

λ of Unsaturate per ml. of solvent	Type of Unsaturate	Moles of Unsaturate per ml. of solvent	Average Organic Yield %	Theoretical Yield	Standard Deviation
10	Pentene	9.132×10^{-5}	95.04	99.69	±0.02
10	Diisobutylene	6.402×10^{-5}	70.46	69.89	±7.60
7.5		4.802×10^{-5}	52.56	52.42	--
5	Pentene	4.566×10^{-5}	44.55	49.84	±1.08
2.5		2.283×10^{-5}	21.62	24.92	--
2.5	Diisobutylene	1.601×10^{-5}	18.66	17.47	±8.51
1	Pentene	9.132×10^{-6}	8.24	9.97	±0.53
1	Diisobutylene	6.402×10^{-6}	7.07	6.99	±0.99
0.5		3.201×10^{-6}	3.20	3.49	±0.83
0.25		1.601×10^{-6}	1.50	1.75	--
0.1	Pentene	9.132×10^{-7}	0.848	0.997	±0.138
0.1	Diisobutylene	6.402×10^{-7}	0.626	0.699	--
0.05		3.201×10^{-7}	0.354	0.349	--
0.01	Pentene	9.132×10^{-8}	0.108	0.100	±0.062
0.01	Diisobutylene	6.402×10^{-8}	0.065	0.070	±0.032
0	0	0	0.084	--	±0.042

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

(E. J. Kennitz)

I. THE IODINE ($^{127}\text{I}_2$ and $^{129}\text{I}_2$)-CYCLOPENTANE SYSTEM

SUMMARY OF PROGRESS

From our studies the following conclusions may be drawn: (1) The distribution of ^{130}I -labelled products is essentially the same whether produced from the $^{129}\text{I}(n,\gamma)^{130}\text{I}$ or the $^{130}\text{I}^m(\text{IT})^{130}\text{I}$ process. Phase also seems to have no effect on the distribution. Polymers and/or diiodo derivatives appear at 10^{-3} mf I_2 and higher, but do not appear to increase significantly with concentration of I_2 . (2) The major product is the monoiodo derivative of the parent molecule, cyclopentane. (3) The limiting organic yield is $44 \pm 1\%$ in the liquid or solid phase for this system. (4) The ^{130}I organic yield from the $^{129}\text{I}(n,\gamma)^{130}\text{I}$ process is somewhat lower, approximately 5%, than from the $^{130}\text{I}^m(\text{IT})^{130}\text{I}$ process.

INTRODUCTION

Several studies (27,28) involving the radiation of cyclopentane systems have indicated extensive ring fragmentation and possible mechanisms for the formation of major products. The mechanisms given by Hughes (27) are as follows:

* Underlined products are the main products of the reaction.

It is postulated (28) that the dissolved iodine in a I_2 -cyclopentane system scavenges hydrogen atoms and reduced the number of cyclopentyl radicals produced during the radiolysis.

In the present study we attempted to explore these postulates with scavenger studies and improved techniques of product identification. In addition, we attempted to probe the system with the use of iodine-129 and the freeze-thaw technique in order to compare this system with cyclohexane and straight chain hydrocarbons.

Lambrecht and Rack (29) found that the organic yield from the $^{129}\text{I}(\text{n},\gamma)^{130}\text{I} + ^{129}\text{I}(\text{n},\gamma)^{130}\text{I}^{\text{m}}$ processes in the I_2 -cyclohexane and I_2 -n-hexane systems was 4-6% lower than from the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ and $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ processes, which gave nearly identical yields. In both systems they found that hexyliodides were the major product while in the I_2 -cyclopentane system, iodocyclopentane was found to be the major product.

EXPERIMENTAL

Phillips research grade cyclopentane was used throughout without further purification. The preparation of the iodine-127, extraction of the iodine-129, preparation of samples, extraction and counting procedures and neutron irradiation facilities have been described earlier (15).

Irradiation times for organic yield determinations ranged from four to thirty seconds. Organic yields did not increase, within experimental error, with increased irradiation time for our experimental conditions. Irradiation time for gas chromatography ranged from six to thirty minutes. Organic yields were run under the same conditions to reflect the effect of longer irradiation time.

Samples were usually run within twenty-four hours after preparation. All samples were quick-frozen and stored under liquid nitrogen in the dark until run.

The basic features of the radiogas chromatograph have been described earlier (1). A 2.1-m. spiral column, 4-mm i.d., filled with 42-60 mesh Wilkens Instrument firebrick coated with 40% of its weight of Gen. Elec. SF-81(50) silicone vil was used, with He as the mobil phase. The general procedures have been described earlier (15).

RESULTS AND DISCUSSION

The organic yields of the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ process at various concentrations of iodine in cyclopentane, both liquid and solid (77°K) phases, are depicted in Fig. 6. In the liquid phase, the ^{128}I organic yield extrapolates to $44 \pm 0.5\%$; and in the solid phase extrapolates to approximately 54% at zero mole fraction iodine. Phase separation at 77°K appears to be quite significant at 5×10^{-5} and higher mf I_2 . At 2×10^{-5} and lower mf I_2 it appears that monomolecular dispersion has occurred. In the liquid phase, the scavenging action of I_2 can be seen to be effective at concentrations of 10^{-4} and higher mf. Since the solubility of iodine in cyclopentane is a limiting factor, the "hot" and "cold" portions of the reaction cannot be separated in this system. (See Table X).

The product distribution from the $^{129}\text{I}(n,\gamma)^{130}\text{I}$ and $^{129}\text{I}(n,\gamma)^{130}\text{I} + ^{130}\text{I}^m(\text{IT})^{130}\text{I}$ processes in cyclopentane are given in Table XI. No significant differences between modes of activation and I_2 concentrations showed up in the iodine derivatives except for a higher boiling fraction at 10^{-3} and higher mf I_2 , which was not detectable at 5×10^{-4} mf I_2 . The major product was iodocyclopentane which agrees with earlier work in this laboratory (28). Why there is relatively more ring fracture in the I_2 -cyclohexane system than the I_2 -cyclopentane system is not clear at this time.

TABLE X.
EFFECT OF I_2 CONCENTRATION ON ^{128}I ORGANIC YIELDS IN LIQUID
AND SOLID ($77^\circ K$) CYCLOPENTANE

$mf I_2$	Irrad. Time (sec)	Liquid Phase Organic Yield	Solid Phase Organic Yield
1.0×10^{-5}	30	44.2	53.8
2.1×10^{-5}	30	44.1	53.6
5.3×10^{-5}	16	43.5	32.8
1.7×10^{-4}	16	43.0	11.8
9.1×10^{-4}	16	37.9	4.2
4.4×10^{-3}	10	28.8	1.2
9.2×10^{-3}	4	12.4	0.4

Fig. 6. Organic Yield of ^{128}I as a function of $^{127}\text{I}_2$ concentration in liquid and solid (77°K) cyclopentane. Δ , liquid phase; $\circ$, solid phase.

TABLE XI.

PRODUCT DISTRIBUTION ^(a) FROM THE $^{129}\text{I}(\text{n}, \gamma)^{130}\text{I}$ AND THE $^{129}\text{I}(\text{n}, \gamma)^{130}\text{I} + ^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ PROCESSES IN LIQUID ($\sim 75^\circ\text{C}$) AND SOLID ($\sim 77^\circ\text{K}$) CYCLOPENTANE

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

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

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

(c) Pentyl iodides.

(d) Cyclopentyl iodide.

(e) Higher boiling fraction, possibly cyclopentyl diiodide.

(f) Only solid sample.

(g) 30 minute irradiation.

(h) 15 minute irradiation.

(i) 6 minute irradiation.

TABLE XII.

ORGANIC YIELD OF ^{130}I AS A FUNCTION OF TIME THE $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$
 PROCESS OCCURRED IN LIQUID CYCLOPENTANE PRIOR TO FREEZING AT 77°K

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

1. All samples were irradiated for 16 seconds.

Fig. 7. Organic yield of ^{130}I as a function of time the $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ process occurred in liquid cyclopentane prior to freezing at 77°K . All samples were irradiated at room temperature.

TABLE XIII.
GROWTH OF ^{130}I ORGANIC YIELDS BY THE $^{130}\text{I}^{\text{m}}(\text{IT})$ ^{130}I PROCESS
IN LIQUID CYCLOPENTANE

Time from Midpoint ⁽¹⁾ of Irradiation (min.)	Organic Yield ⁽²⁾
2	10.5
4	14.3
6	16.4
8	18.8
10	24.3
12	27.0
14	28.0
16	29.5
18	30.7
25	33.7
40	35.1
60	35.6
90	35.8
R^0	2.8
R	35.8

1. All samples were irradiated at approximately 77°K for 16 seconds and thawed within 25 seconds from the midpoint of irradiation.
2. Organic yields were calculated from the Freeze-Thaw Equation:

$$\text{O.Y. (IT)} = \frac{R - R^0}{e^{-t}} - \frac{(1 - e^{-t})R^0}{e^{-t}}$$

$$\alpha = 0.39$$

$$b = 0.61$$

R^m = O. Y. of sample irradiated solid (77°K), liquified immediately (usually within 25 sec. from midpoint of irradiation) and extracted after 90 minutes.

R^o = O. Y. of sample irradiated solid (77°K) and kept at this temperature for 90 minutes and then extracted.

Fig. 8. Organic yield of ^{130}I as a function of time that the $^{130}\text{I}^m(\text{IT})^{130}\text{I}$ process occurred in liquid cyclopentane prior to freezing at 77°K . All samples were irradiated at 77°K and thawed within 25 seconds from the midpoint of irradiation.

Fig. 7 and Table XII illustrate a growth curve of the $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ process in liquid cyclopentane. Extrapolation of the curve to zero time gives an organic yield of about 31%, which is due to the $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}$ and $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}^{\text{m}}$ processes. A similar value (29) was obtained earlier in this laboratory for the I_2 -cyclohexane system. Allowing the $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ process to occur for longer and longer times before freezing with liquid nitrogen results in an organic yield curve which approaches $35.6 \pm 0.5\%$ at 90 minutes or after 99.9% of the reaction is completed. The ^{130}I organic yields due to the $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ process alone are given in Table XIII and depicted in Fig. 8. The value obtained by the freeze-thaw technique for the ^{130}I organic yield by (IT) is only slightly higher, approximately 36% compared to 35.6%, than the organic yield due to the combined $^{129}\text{I}(\text{n},\gamma)^{130}\text{I}$ and $^{130}\text{I}^{\text{m}}(\text{IT})^{130}\text{I}$ processes. Interestingly, this higher yield of approximately 5% by (IT) over the (n, γ) process was also found in the I_2 -cyclohexane system.

II. THE SYSTEMS OF $^{127}\text{I}_2$ -ALKYLBENZENES, ICl -ALKYLBENZENE, AND ICl -CYCLOPENTANE AT 77°K

SUMMARY OF PROGRESS

Organic yield determinations at various mole fractions of I_2 and ICl were run in selected alkylbenzenes and cyclopentane at 77°K . In addition, product analysis was attempted with gas chromatography for several of the alkylbenzenes with success.

There appeared to be little or no effect on the ^{128}I organic yield due to the different alkyl groups on the benzene ring in either the I_2 -alkylbenzene or the ICl -alkylbenzene systems. However, ^{128}I organic yields were lower from the ICl than the I_2 solute, generally ten percent or more lower. The ^{38}Cl organic

yields were consistently between 18.8 and 21.8% except for the ICl-cyclopentane system, which was approximately 14%.

Gas chromatography revealed the major product or products to be alkyl iodides.

The work in this area represents another step in the preliminary work leading to an investigation of biological systems. The limits of gas chromatography and the effects of various substituted groups on the benzene ring are currently being investigated. It is hoped that exploratory work with certain amino acids can be started during the coming year.

INTRODUCTION

In an earlier study (15) a number of alkylbenzenes were investigated in the liquid state. Unlike benzene, there was a significant amount of iodine self-scavenging in these systems.

Benzene and iodine have been shown (30) to form a solid electron-donor-acceptor complex at 77°K. This model would explain the relatively high and constant ^{128}I (and ^{130}I) organic yields in this system in the range of 10^{-6} to 10^{-3} mf I_2 , found in an earlier study (15). Since organic yields induced by nuclear transformations have been shown (19,21) to give information concerning the state of aggregation and tendency toward complexing, I_2 - and ICl-alkylbenzene and ICl-cyclopentane systems at 77°K were studied in order to obtain this and possibly other information about these systems.

Chien and Willard (31) found that the reactions of ^{38}Cl activated by the (n,γ) process in liquid hydrogenous media gave a constant yield of 21% which was independent of hydrocarbon or alkyl chloride solvent studied. Although the organic yields in the same media at 77°K often gave higher values, some were the same. Miller and Dodson (32) found that the ^{38}Cl organic yield in the liquid CCl_4 -cyclohexane system from the (n,γ) process was a fairly consistent value of 11% whereas the value was around 20% for the liquid CCl_4 -benzene system.

EXPERIMENTAL

Phillips research grade alkylbenzenes and cyclopentane were used as received. Reagent grade iodine monochloride was used as received (Matheson, Coleman and Bell) and Mallinckrodt reagent grade iodine was sublimed from a mixture with CaO and KI.

The sample preparation, extraction and counting procedures and neutron irradiation facilities have been described earlier (1,15).

Irradiation time for organic yield determinations ranged from 2 to 10 seconds in the I_2 -hydrocarbon systems and was 10 seconds in the ICl-hydrocarbon systems.

Samples were usually run within twenty-four hours after preparation and kept in liquid nitrogen, wrapped in foil, until run.

The basic features of the radiogas chromatograph have been described earlier (1). A 2.1-m. spiral glass column, 4-mm. i.d., filled with 5% GE-SE-30 on 60/70 Anakrom ABS was used with He as the mobil phase. The general procedures for the chromatograph runs have been described earlier (15).

RESULTS AND DISCUSSION

The ^{128}I organic yields produced by the $^{127}I(n,\gamma)^{128}I$ process in the I_2 -alkylbenzene, -benzene and -cyclopentane systems are shown in Table XIV. The O. Y. plateau found earlier (15) in the I_2 -benzene system shows up in the same region, 10^{-3} mf I_2 and less, in the I_2 -alkylbenzene systems but not in the I_2 -cyclopentane system. Apparently the phase separation which occurs in a number of systems (19) even at I_2 mf as low as 5×10^{-5} does not occur in the alkylbenzenes except at rather high I_2 mf; above 10^{-3} mf I_2 . The behavior of the I_2 -cyclopentane system, on the other hand, seems to be quite similar to other I_2 -alkane systems.

The product distribution from the $^{127}I(n,\gamma)^{128}I$ process in several I_2 -alkylbenzene systems is presented in Table XV. The major product in each case was methyl iodide, except in the case of the I_2 -ethylbenzene system, which produced

equal quantities of methyl and ethyl iodide as the major products. It was somewhat unexpected that no iodobenzene was detected in any of the systems examined. No attempt was made to determine the position of the iodine in the iodinated parent molecules.

Both the ^{128}I and ^{38}Cl organic yields from the (n,γ) processes in the ICl -alkylbenzene, -benzene and -cyclopentane systems are presented in Table XVI. The ^{128}I O. Y. trends are essentially the same in these systems as in the above where I_2 was the solute, except for lower organic yields in the aromatic systems and higher organic yields in the cyclopentane system. It would appear the phase separation in the ICl -cyclopentane system is not as extensive as in the I_2 -cyclopentane system.

The ^{38}Cl organic yields seem to be independent of ICl concentration and are very close to the 21% found in liquid hydrocarbon media (31) except in the ICl -cyclopentane system where it is around 14%. Interestingly, the ^{38}Cl organic yield in the liquid ICl -cyclopentane system is also around 14%. At 10^{-5} mf ICl , the experimental scatter of the ^{38}Cl organic yields was so great, meaningful data could not be obtained.

III. THE I_2 -ETHYLBENZENE, I_2 -CUMENE, AND I_2 -t-BUTYLBENZENE SYSTEMS

Upon standing, the organic phase from the organic yield determinations of the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ process in solutions of iodine in ethylbenzene, cumene, and t-butylbenzene turned from colorless to pink. The color was found to be due to the presence of molecular iodine, which appeared whether the solution was subjected to light or left in the dark. The use of different organic solvents for the extraction of the organically bound iodine, initially produced as a consequence of the nuclear transformations, did not seem to affect the rate at which the iodine

TABLE XIV
EFFECT OF I_2 CONCENTRATION ON ^{128}I ORGANIC YIELDS IN VARIOUS ALKYL BENZENES
AND CYCLOPROPANE AT 77°K

Organic Solvent	mf $I_2^{(a)}$	O. Y.	mf $I_2^{(a)}$	O. Y.
Benzene	10^{-2}	46.2	10^{-3}	52.7
Toluene		49.1		59.9
Ethylbenzene		39.6		46.9
Cumene		17.0		51.0
t-Butylbenzene		19.6		54.8
n-Butylbenzene		17.3		49.0
Cyclopropane		0.4		4.2
Benzene	$10^{-4(a)}$	63.5	$10^{-5(a)}$	61.5
Toluene		59.9		57.9
Ethylbenzene		52.5		52.8
Cumene		50.7		51.6
t-Butylbenzene		55.2		55.7
n-Butylbenzene		51.4		52.6
Cyclopropane		11.8		32.8 ^(b)

(a) Irradiation time was 2 seconds for 10^{-2} and 10^{-3} mf, 10 seconds for 10^{-4} mf, and 16 seconds for 10^{-5} mf.

(b) 5.3×10^{-5} mf I_2 .

10^{-2} : o-xylene 3.6   p-xylene 0.4
         m-xylene 9.7   pseudocumene 2.6

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

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

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

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

mf ICl	Organic Solvent	^{128}I Organic Yield (1)	^{38}Cl Organic Yield (1)
10^{-2}	Benzene	29.3	21.5
	Toluene	23.6	20.2
	Ethylbenzene	24.0	20.1
	Cumene	22.6	19.4
	Pseudocumene	22.5	19.6
	n-Butylbenzene	21.8	18.8
	Cyclopentane	12.4	14.3
10^{-3}	Benzene	43.4	22.3
	Toluene	38.8	20.6
	Ethylbenzene	28.6	21.1
	Cumene	38.4	18.8
	Pseudocumene	38.4	20.1
	n-Butylbenzene	29.6	19.4
	Cyclopentane	38.0	14.1
10^{-4}	Benzene	45.7	21.8
	Toluene	40.2	21.1
	Ethylbenzene	38.6	20.6
	Cumene	41.3	19.4
	Pseudocumene	41.3	20.2
	n-Butylbenzene	37.8	18.8
	Cyclopentane	44.0	14.2
10^{-5}	Toluene	39.9	
	Ethylbenzene	38.4	
	Cumene	42.1	
	Pseudocumene	42.3	

Table XVI, continued

mf ICl	Organic Solvent	^{128}I Organic Yield (1)	^{38}Cl Organic Yield (1)
10^{-5}	n-Butylbenzene	38.2	
	Cyclopropane	59.6	

(1) All samples were irradiated for ten seconds.

was released as free iodine. Benzene and carbon tetrachloride were used in addition to the system solvents.

Since the degree of coloration indicated a relatively large amount of free iodine, $^{127}\text{I}_2$, attempts were made to measure it quantitatively and the rate at which it is released from the combined state. Preliminary studies have shown that the reaction(s) involved in the formation of molecular iodine in the iodine-ethylbenzene system is a first order reaction requiring several days to reach equilibrium. The other two systems appear to equilibrate much faster.

Very little difference was found in the amount of organically bound iodine produced at 77°K compared to that formed at 25°C . Considerably more organically bound iodine was found in the iodine-cumene and iodine-*t*-butylbenzene systems than in the iodine-ethylbenzene system, however.

Since this study is just underway and several difficulties have yet to be resolved, no data is being submitted at this time.

VII. GAS PHASE REACTIONS OF ^{128}I , $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$, AND ^{38}Cl ACTIVATED BY
 RADIATIVE NEUTRON CAPTURE AND ^{130}I ACTIVATED BY ISOMERIC TRANSITION
 IN CH_4 , CD_4 AND POLYHALOMETHANES

(D. W. Oates, J. B. Nicholas, and E. P. Rack)

SUMMARY OF PROGRESS

An extensive program has been initiated in gas phase reaction studies of ^{128}I , $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ and ^{38}Cl activated by radiative neutron capture and ^{130}I activated by isomeric transition in CH_4 , CD_4 and polyhalomethanes in an attempt to gain information concerning isotope effects and mode of activation effects, relative importance of positive charge, excitation energy and kinetic energy to the various reactions, applicability and evaluation of kinetic theory to the hot-atom reactions, the systematics of iodine reactions in CH_4 , CD_4 and polyhalomethanes, and the nature of ^{38}Cl reactions in CH_4 and CD_4 .

In our study of the gas phase reactions of ^{128}I , $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$, and ^{38}Cl activated by radiative neutron capture and ^{130}I activated by isomeric transition in CH_4 , CD_4 and polyhalomethanes we hope to gain information concerning (a) isotope effects and mode-of-activation effects in iodine reactions in CH_4 and CD_4 , (b) relative importance of positive charge, electronic excitation energy, and kinetic energy to $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ reactions activated by the (n,γ) process and ^{130}I activated by the (IT) process in CH_4 and CD_4 , (c) applicability of kinetic theory to ^{130}I reactions in CH_4 and CD_4 and ^{38}Cl reactions in CH_4 and CD_4 , (d) the systematics of iodine reactions in CH_4 , CD_4 and polyhalomethane and (e) the nature of ^{38}Cl reactions in CH_4 and CD_4 . Specifically we are determining (a) the effects of rare-gas moderators and molecular additives on the organic yields

and individual product yields of ^{128}I , $^{130}\text{I} + ^{130\text{m}}\text{I}$ and ^{38}Cl activated by the (n, γ) process and ^{130}I activated by the (IT) process in various organic systems, (b) organic yields and individual product yields of ^{128}I reactions in the various polyhalomethanes employing various molecular additives, (c) the effects of large pressure changes to iodine organic yields and individual product yields into reactions in various organic systems. We are also initiating studies involving the reactions of $^{127}\text{I}^+$ in the ground and electronically excited states in CH_4 , CD_4 and various organic systems employing an ion-cyclotron resonance mass spectrometer.

Since most of our studies are incomplete we will present in this report only a summary of our experimental results with pertinent tables and figures without any theoretical evaluation (at this time) of our data.

A. RARE GAS MODERATION OF THE IODINE-130 REACTIONS ACTIVATED BY RADIATIVE NEUTRON CAPTURE AND ISOMERIC TRANSITION WITH CH_4 AND CD_4

EXPERIMENTAL

Purity and Source of Reagents

Iodine was sublimed from a mixture of reagent grade I_2 , KI, and CaO. Iodine-129 was obtained from Oak Ridge National Laboratories in aqueous NaI^{129} solution. $\text{CH}_3\text{I}^{129}$ was prepared by extracting the NaI^{129} into $\text{CH}_3\text{I}^{127}$ with H_2O_2 catalyzed with a trace of HNO_3 . The solution was washed, dried, degassed four times and sealed under vacuum and allowed to undergo photochemical exchange for five days before using. Eastman Kodak white-label CH_3I was purified by distillation. Phillips Petroleum Company research-grade CH_4 (99.65 mole% purity), Matheson research grade CD_4 (99% purity by ion-cyclotron resonance, 1% CD_3H) and Airco assayed reagent argon, neon, krypton, and xenon were used directly.

Preparation and Irradiation of Reaction Systems

Over 1000 samples have been incorporated in the data presented here and Progress Report 3 (1) representing radiative neutron capture and isomeric transition activated gaseous reactions of ^{130}I with CH_4 and CD_4 in the presence of rare-gas moderators and I_2 and $\text{CH}_3\text{I}^{129}$ additives. All samples were irradiated in a thermal neutron flux of 1.1×10^{11} neutrons $\text{cm}^{-2} \cdot \text{sec}^{-1}$ at ambient temperature in the Omaha, Nebraska, V.A. Hospital TRIGA reactor. The accompanying gamma radiation flux was 3×10^{17} $\text{ev g}^{-1} \cdot \text{min}^{-1}$. Triplicate quartz ampoules, varying in size from 7 to 10 ml, were prewashed (33) and filled with the reactants using vacuum-line techniques and stored in liquid nitrogen (34). The total gas pressure of all systems was maintained at approximately 1 atmosphere.

Since relatively small amounts of $\text{CH}_3\text{I}^{127}$ were shown to have an inhibiting effect on the ^{128}I organic yields (35) we were concerned with using too great a source pressure of $\text{CH}_3\text{I}^{129}$ in the moderator studies. To justify the use of 15 mm $\text{CH}_3\text{I}^{129}$ and 2 min. irradiation time for the moderation studies (to assure great enough activity in individual samples to eliminate statistical fluctuation), reported in Progress Report 3, additional experiments were performed. For samples containing rare-gases and methane we employed varying conditions ranging from amples contained only 0.1 mm $^{129}\text{I}_2$ to samples containing 0.1 mm $^{127}\text{I}_2$ and 2 mm to 15 mm $\text{CH}_3\text{I}^{129}$. Varying lengths of irradiation time (30 sec. to 5 min) were performed on the various component systems. Our results showed that the use of 15 mm $\text{CH}_3\text{I}^{129}$ as reported in Progress in Report 3 gave Iodine organic yields that were too low because of the complicating effect on activated iodine species. Therefore, we repeated our original CH_4 data and extended our work to the CD_4 system employing 5 mm and less of $\text{CH}_3\text{I}^{129}$ in the various reaction systems.

Extraction Procedure

All samples were broken in a separatory funnel beneath a two-phase layer of CCl_4 and I_2 and 0.5M aqueous Na_2SO_3 . For the (n, γ) + (IT) combined studies, the

samples were allowed to stand at ambient temperature in the dark for 90 min. to allow 99.9% of the ^{130m}I to decay to the ground state before extraction. Samples used in the (n, γ) studies were extracted 1 min. after the beginning of irradiation minimizing the effects of any isomeric transition to the organic yield. The separated phases were counted in a well-type gamma-ray scintillation counter. Due to the low activity it was not necessary to correct for coincidence loss or relative counting efficiencies.

Radiation Induced Reactions

Mixtures containing rare-gas, $\text{CH}_3\text{I}^{129}$, methane, and I_2 tagged with ^{131}I were irradiated for 2 min. so as to make a direct correlation with the moderator studies and to determine the extent of any radiation-induced reactions in the systems. Under the conditions of preparation and irradiation (35) negligible ^{131}I pickup was found in systems which did not contain a rare-gas additive. The best visual straight lines were drawn through the data (plotted as percent ^{131}I appearing in organic combination for the various systems vs. mole fraction additive) merging at zero mole fraction additive. At unit mole-fraction of rare gas (which corresponds to $760 \pm 40\text{mm}$) the data extrapolated to 9.98%, 5.8%, and 1.0% for Xe, Kr, and Ar-Ne, respectively. To determine the correction for radiation induced reactions in the moderator systems, a quantity equal to the product of the mole fraction of rare-gas and the extrapolated maximum extent of ^{131}I pickup was subtracted from the observed organic ^{130}I yield.

The reaction system under consideration is quite complex in nature. During the irradiation of ^{129}I several nuclear phenomena are taking place. By radiative neutron capture ^{130}I and ^{130m}I are born simultaneously and ^{130m}I is decaying by isomeric transition to ^{130}I . Because of these conflicting contributions to the formation of ^{130}I during irradiation it is impossible to accurately determine the absolute value for the (n, γ) activated ^{130}I and ^{130m}I . Instead, what we find is

a minimum value. The most easily obtainable data is the combined (n, γ) plus (IT) contributions to the formation of ^{130}I after the isomeric transition has been allowed to occur in the gas phase. This data, however does not lend itself to theoretical treatment. We employed an extraction after irradiation (1 min. after the beginning of a 30 sec. irradiation) in an attempt to obtain a value for the (n, γ)-activated process with a minimum amount of isomeric transition contribution to be used in comparison with the $^{128}\text{I}(\text{n},\gamma)$ -activated reaction and with the $^{130}\text{I}(\text{n},\gamma) + (\text{IT})$ -activated reaction.

Various studies have been performed to obtain data for comparison between the two isotopes ^{128}I and ^{130}I . These include establishing the limiting organic yield for ^{128}I and ^{130}I in a methane environment using $^{127}\text{I}_2$ and $^{129}\text{I}_2$ as well as $\text{CH}_3\text{I}^{127}$ and $\text{CH}_3\text{I}^{129}$ as sources for ^{128}I and ^{130}I .

Samples containing only 0.1mm of $^{127}\text{I}_2$ or $^{129}\text{I}_2$ with methane gave consistently low yields in the range of 10% or less. These low yields in the gas phase were attributed to micro crystallization of the I_2 on the sides of the reaction ampoule, not allowing the iodine to react in the gas phase. This complicating crystallization was an effect of reactor temperature (9°C) for irradiation times greater than 30 sec. To alleviate this problem of crystallization, $\text{CH}_3\text{I}^{129}$ was employed as the source of ^{129}I so as to achieve meaningful data.

It was important to have the maximum amount of $\text{CH}_3\text{I}^{129}$ present so as to have sufficient activity and minimize a lengthy irradiation but yet obtain a true representative organic yield. We found that the presence of 5mm $\text{CH}_3\text{I}^{129}$ with 0.1mm I_2 gave the best results.

Table XVII presents the observed and corrected organic yields for the (n, γ)-induced $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ reactions and (n, γ) + (IT) activated ^{130}I reactions in various CH_4 -rare gas or molecular additive reaction systems.

Table XVIII presents the observed and corrected organic yields for the (n, γ)-induced $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ reactions in various CD_4 -rare gas or molecular additive reaction systems.

In order to interpret properly the relative effects of the additives, it is necessary to correct the observed data as shown in Tables XVII and XVIII for (a) the 1.1% failure to bond-rupture of CH_3I , (b) any radiation-induced reactions, and (c) any ^{130}I which reacts with the molecular additive forming organic products.

By extrapolating the data in Table XVII on a log-log plot of ^{130}I organic yield vs. mole fraction of CH_4 at mole fraction additive less than 0.1, we find that at zero mole fraction additive the maximum extent of ^{130}I stabilized in organic combination (as a result of the (n, γ) process) is $42.0\% \pm 2\%$. Also by extrapolating the (n, γ) organic yield data of Table XVII on a log-log plot of ^{130}I organic yield vs. mole fraction of CD_4 at mole fraction additive less than 0.1, we find that at zero mole fraction additive the maximum extent of ^{130}I stabilized in organic combination (as a result of the (n, γ) process) is 42.0 ± 2 . Although there may be an isotope effect for $^{130}\text{I} + ^{130}\text{I}^{\text{m}}$ reactions in CH_4 and CD_4 , we could not observe these within the limits of our experimental error. It is interesting to point out that the extrapolation of the various moderator data, including $\text{CH}_3\text{I}^{129}$ additive data to the same point is an internal consistency test for the use of 5 mm $\text{CH}_3\text{I}^{129}$ in the various samples.

By extrapolating the (n, γ) + (IT) organic yield data of Tables XVII and XVIII vs. mole fraction of CH_4 or CD_4 in a manner similar to that described above we find that the organic yields of ^{130}I in CH_4 and CD_4 , at zero mole fraction additive are 32.0 ± 2 and 32.5 ± 2 , respectively. By employing the relationship $^{130}\text{I}(\text{observed}) = 0.39 ^{130}\text{I}(\text{n}, \gamma)\text{O.Y.} + 0.61 ^{130}\text{I}(\text{IT})\text{O.Y.}$ we calculate the (IT)-induced organic yields for ^{130}I in CH_4 and CD_4 as $25.6 \pm 2\%$ and 26.4% , respectively.

Table XVII

PERCENT ^{130}I STABILIZED IN ORGANIC COMBINATION IN CH_4 AND VARIOUS GASEOUS ADDITIVES ^(a)

Additive	Mole Fraction Additive	^(b)	% ^{130}I as Organic (obs) (n, γ)+(IT)- activated	% ^{130}I as Organic (cor) (n, γ)+(IT)- activated	% ^{130}I as Organic (obs) (n, γ)-activated	% ^{130}I as Organic (cor) (n, γ)-activated
CH_3I	0.0077				33.7 } 45.5 }	39.6 } 38.5 }
	0.0447				21.7 } 20.9 }	21.4 } 20.3 }
	0.0654				16.6 } 18.8 }	17.7 } 16.6 }
	0.0891				12.5 } 11.2 }	11.8 } 10.7 }
	0.2083				5.6 } 6.0 }	5.8 } 4.7 }
	0.2896				4.6 } 2.1 }	3.4 } 2.3 }
	0.4762				2.5 } 2.0 }	2.3 } 1.2 }
	0.7149				2.1 } 1.3 }	1.7 } 0.6 }
	0.0188		40.1 } 38.4 } 41.8 }	40.1		39.0
	0.0201		38.4 } 35.8 } 31.2 }	35.1		34.0
	0.0315		35.3 } 29.8 } 26.1 }	30.4		29.3

Table XVII (Cont)

PERCENT ^{130}I STABILIZED IN ORGANIC COMBINATION IN CH_4 AND VARIOUS GASEOUS ADDITIVES^(a)

Additive	Mole Fraction Additive ^(b)	% ^{130}I as Organic (obs) (n, γ)+(IT)- activated,	% ^{130}I as Organic (cor) (n, γ)+(IT)- Activated	% ^{130}I as Organic (obs) (n, γ)-activated	% ^{130}I as Organic (cor) (n, γ)-activated
	0.0447	26.9 19.9	23.5	22.4	
	0.0564			13.7	
	0.0654	16.8 16.1	16.4	15.3	
	0.0703	11.4 12.7	12.0	10.9	
	0.0873	11.3 10.1	10.7	9.6	
	0.1178	6.4 8.0	7.2	6.1	
	0.2083	5.6 5.9	5.8	4.7	
	0.2896	3.4 2.8	3.2	2.1	
	0.4762	2.6 2.2	2.4	1.3	
	0.7149	2.2 1.2	1.7	0.6	
Kr	0.0094			42.5	41.3
	0.0769			38.7	37.4
	0.2925			39.6 26.8	33.2 30.5
	0.4659			32.9	29.1

Table XVII (Cont)

PERCENT ^{130}I STABILIZED IN ORGANIC COMBINATION IN CH_4 AND VARIOUS GASEOUS ADDITIVES (a)

Additive	Mole Fraction Additive (b)	% ^{130}I as Organic (obs) (n, γ)+(IT)- activated	% ^{130}I as Organic (cor) (n, γ)+(IT)- activated	% ^{130}I as Organic (obs) (n, γ)-activated	% ^{130}I as Organic (cor) (n, γ)-activated
	0.7687			32.3	26.8
Xe	0.0165			46.0 43.9 43.5 33.8	41.8 40.6
	0.0173				
	0.0976			37.9	
	0.0985			38.8	
	0.4003			27.8 31.9 29.2 30.4	29.8 25.1
	0.4068				
	0.7755			31.8 22.9 26.2 29.3	
	0.7992				
					27.5 19.4

Table XVIII

PERCENT ^{130}I STABILIZED IN ORGANIC COMBINATION IN CD_4 AND VARIOUS GASEOUS ADDITIVES ^(a)

Additive	Mole Fraction Additive ^(b)	% ^{130}I as Organic (obs) (n, γ)+(IT)- activated	% ^{130}I as Organic (cor) (n, γ)+(IT)- activated	% ^{130}I as Organic (obs) (n, γ)-activated	% ^{130}I as Organic (cor) (n, γ)-activated
CH_3I	0.0054			42.9 36.8 37.6 37.5 40.9	39.1 38.0
	0.0153			29.4 30.2 30.6 29.8	30.0 28.9
	0.0159				
	0.0590			17.1 14.1 16.1	15.8 14.7
	0.0991			12.8 10.5 10.6	11.3 10.2
	0.1373			8.3 7.6 8.4 7.8	8.0 6.9
	0.5310			2.1 3.0 2.1	3.6 2.5
	0.0054	41.8 39.1 40.2 41.6	40.7		39.6
	0.0056				
	0.0057	35.7 35.4	35.6		34.5
	0.0155	27.3 28.4 26.8 34.1	29.1		28.0
	0.0163				
	0.0524	17.7 13.1 11.9 12.2	13.7		12.6
	0.0548				

Table XVIII continued

PERCENT ^{130}I STABILIZED IN ORGANIC COMBINATION IN CD_4 AND VARIOUS GASEOUS ADDITIVES^(a)

Additive	Mole Fraction Additive ^(b)	% ^{130}I as Organic (obs) (n, γ)+(IT)- activated	% ^{130}I as Organic (cor) (n, γ)+(IT)- activated	% ^{130}I as Organic (obs) (n, γ)-Activated	% ^{130}I as Organic (cor) (n, γ)-activated
Ne	0.0957	8.1	10.8	9.7	
		12.8			
	0.1023	8.9			
		13.4			
	0.1361	7.3		6.2	
	0.6202	3.9	3.6	2.5	
	0.6373	3.3			
	0.7931	2.8	2.3	1.2	
	0.8352	1.8			
	0.0128	38.4	39.4	38.3	
		40.4			
	0.1103	43.0		41.9	
	0.2244	35.6	36.5	35.2	
		37.5			
	0.4718	38.2		36.6	
	0.0133			37.2	36.1
	0.2233			33.6	32.3
	0.0151			38.2	38.8
				37.4	
	0.0158			40.9	
				38.8	
	0.0143	38.5	38.5	37.4	
		37.6			
	0.0145	38.0			
		39.9			
	0.0429	37.0	36.6	35.5	
		36.3			

Table XVIII continued

PERCENT ^{130}I STABILIZED IN ORGANIC COMBINATION IN CD_4 AND VARIOUS GASEOUS ADDITIVES^(a)

Additive	Mole Fraction Additive ^(b)	$\%^{130}\text{I}$ as Organic (obs) (n, γ)+(IT)- activated	$\%^{130}\text{I}$ as Organic (cor) (n, γ)+(IT)- activated	$\%^{130}\text{I}$ as Organic (obs) (n, γ)-activated	$\%^{130}\text{I}$ as Organic (cor) (n, γ)-activated
	0.0454	30.6 32.8	31.7	30.6	
	0.0931	35.4 35.3	35.7	34.5	
	0.0966	36.5			
	0.2579	35.4 36.1	35.4	34.1	
	0.2636	34.6 35.5			
Kr	0.0548			46.8 39.4 39.9 40.4	41.6 40.2
	0.1900			36.2 35.1 35.8 41.0 37.1 56.6	40.4 38.2
	0.3051			40.4 37.5 38.0	38.6 35.8
	0.3936			41.0 34.5 41.3 37.2	37.6 34.2
	0.4940			34.5 38.2 34.9 37.8	36.3 32.4
	0.5994			36.4 37.2 35.3 35.8	36.2 31.6

Table XVIII continued

PERCENT ^{130}I STABILIZED IN ORGANIC COMBINATION IN CD_4 AND VARIOUS GASEOUS ADDITIVES^(a)

Additive	Mole Fraction Additive ^(b)	% ^{130}I as Organic (obs) (n, γ)+(IT)- activated	% ^{130}I as Organic (cor) (n, γ)+(IT)- activated	% ^{130}I as Organic (obs) (n, γ)-activated	% ^{130}I as Organic (cor) (n, γ)-activated
Xe	0.7189			36.8 37.1 36.3 34.4	36.2 31.0
	0.8535			37.5	31.5
	0.0119			35.7 35.8 36.8 36.6	36.3 35.2
	0.0554			29.7 30.5 30.4 28.2	30.1 29.0
	0.1163			29.2 26.8 28.1 26.6	27.7 25.7
	0.2918			23.4 24.0	23.7 20.0
	0.4821			27.7 22.9	22.8 17.4
	0.7336			22.6 20.2 25.8 24.4	23.2 15.7
	0.0118	31.8 29.3	30.5		29.4
	0.0182	32.6 30.8	31.7		30.4

Table XVIII continued

PERCENT ^{130}I STABILIZED IN ORGANIC COMBINATION IN CD_4 AND VARIOUS GASEOUS ADDITIVES^(a)

Additive	Mole Fraction Additive ^(b)	% ^{130}I as Organic (obs) (n, γ)+(IT)- activated	% ^{130}I as Organic (cor) (n, γ)+(IT)- activated	% ^{130}I as Organic (obs) (n, γ)-activated	% ^{130}I as Organic (cor) (n, γ)-activated
	0.0503	28.1 29.5 26.5 27.2	27.8	26.3	
	0.0617	27.1		25.5	
	0.0815	28.2 27.6 22.4	25.0	23.2	
	0.2923	22.3 17.8 21.7 18.9	20.2	16.4	
	0.4953	23.7 20.1 16.5	20.1	14.5	
	0.6996	22.5 20.2	20.8	13.4	
	0.7221	19.6			

Footnotes (a) and (b) same as Table XVII

It is interesting to note that our calculated value for the (IT)-induced organic yield of ^{130}I in CH_4 compares quite well to the value $26.2 \pm 3.0\%$ as determined experimentally by Wilkey (36). However Wilkey's value of 54.4% for the (n, γ) induced ^{130}I organic yield is much higher than our experimental value of $42.0 \pm 2\%$.

At this time our evaluation of the moderator data and the application of the kinetic theory is incomplete. It appears that the (n, γ)-induced organic yields for ^{130}I with CH_3I additive in CH_4 and CD_4 extrapolate to 0%, with Kr moderator to 30.0%, with Xe moderator to $15.0 \pm 2\%$. This would suggest that of the 42.0% ^{130}I organic yields in both CH_4 and CD_4 about 12.0% as the result of kinetic-energy activations, 15.0% is a result of thermal $\text{I}^+(\text{D}_2)$ reactions, and 15.0% as a result of thermal reactions involving other iodine species.

B. REACTIONS OF (n, γ)-ACTIVATED ^{128}I AND ^{38}Cl WITH CH_4 AND CD_4

EXPERIMENTAL

Samples were prepared in a minimum of light using normal vacuum line techniques. The reaction vessels were 7-10 ml. quartz ampoules which were sealed, wrapped in foil, and stored in liquid N_2 until irradiated. Reaction systems containing CH_3I were scavenged with 0.1 mm I_2 and contained sufficient CD_4 to give each sample a comparable total pressure (700 mm Hg). The partial pressure of CH_3I was also kept comparable from sample to sample (3 mm Hg) in the moderated systems. ICl reaction systems contained varying amounts of ICl , rare gas moderators, CH_4 or CD_4 . No I_2 was required as a radical scavenger. Because of the low ambient vapor pressure of ICl , in order to obtain mole fractions of ICl approaching one, it was necessary to reduce the total pressure of the system to as low as 22 torr. The moderated systems contained comparable ICl and total system pressures. (3 torr and 700 torr respectively)

Eastman Kodak white label CH_3I was distilled and stored above clean copper to decrease decomposition. I_2 was sublimed from a mixture of reagent grade I_2 , CaO , and KI . Matheson, Coleman and Bell ICl , Phillips Petroleum Company research grade CH_4 (99.65 mole percent purity), and Matheson research grade CD_4 , (99% purity using Ion Cyclotron Resonance, 1% CHD_3) were used directly. The rare gases, Airco-assayed reagent grade, neon, argon, krypton, and xenon were also used directly.

Samples were irradiated from 20 seconds to 2 minutes at the TRIGA reactor at the Omaha Veterans Administration Hospital (See Chapter I this report).

Organic yields were determined by initially separating the organic and inorganic activity in a two phase extraction mixture of $\text{CCl}_4\text{-I}_2$ and aqueous sulfite. A small amount of NaCl was added to the ICl systems to act as a Cl^- carrier. The activities of the two phases were determined using a 400-channel RIDL analyzer with a punch-tape printout. Counting times were one minute and ten minutes for the CH_3I and ICl systems respectively. Data were compiled and corrected on a 1620 IBM computer using programs 1 and 2 which may be found in Progress Report #3.

RESULTS

Contained in Table XIX are the observed and corrected ^{128}I organic yields activated by radiative neutron capture in mixtures of CD_4 and various rare gases. The organic yields were corrected for 1.1% which is the failure for bond rupture of ^{128}I in CH_3I and radiation-induced pickup of organically-bound ^{128}I in moderated systems. By extrapolating the data in Table XIX on a log-log plot of ^{128}I organic yield vs. mole fraction of CD_4 at mole fraction additive less than 0.1, we find that at zero mole fraction additive the maximum extent of ^{128}I stabilized in organic combination is $51.5 \pm 0.5\%$. This value is less than the value 54.4% for the $^{128}\text{I}\text{-CH}_4$ system indicating the existence of a small isotope effect between CH_4 and CD_4 . Presented in Figure 9 are the plotted data of Table XIX.

At unit mole fraction additive, the ^{128}I organic yields extrapolate, for neon and krypton, to a value of $36 \pm 2\%$ and, for xenon, to $11 \pm 2\%$. Because of the small isotope effect between CH_4 and CD_4 and the errors in the unit-mole-fraction additive extrapolation, it is not possible with certainty to identify the nature of the isotope effect. However it appears that it is due to the kinetic energy contribution to the organic yields and not to those from the thermal contribution. We are planning additional experiments and will employ the kinetic theory to the kinetic-energy activated yields.

By employing ICl as a source for iodine in CH_4 and CD_4 we found the same effect on iodine organic yields that we reported previously (1) for CH_3F . In the $\text{CH}_3\text{F-ICl}$, $\text{CD}_4\text{-ICl}$ and $\text{CH}_4\text{-ICl}$ systems the ^{128}I organic yield dropped to essentially 0.0% at mole fractions of ICl between 0.02 and 0.03%. (See Figures 10 and 11 and Fig. 16 of reference (1)). We are presently employing radiogas chromatography in these systems.

Presented in Table XX and XXI are the experimental ^{128}I and ^{38}Cl data for the $\text{CH}_4\text{-ICl}$ and $\text{CD}_4\text{-ICl}$ reaction systems. It is interesting to note for the ^{38}Cl organic yields in both CH_4 and CD_4 that they are $2.0\% \pm 0.5\%$ at unit mole fraction ICl . We are presently studying the nature of this thermal contribution. By extrapolating the ^{38}Cl data on a log-log plot in the usual manner at zero mole fraction ICl the limiting ^{38}Cl organic yields are $23.3\% \pm 0.5\%$ for the CH_4 system and $15.2 \pm 1\%$ in the CD_4 systems. It is interesting to note that the ^{38}Cl isotope effect between CH_4 and CD_4 is larger on both an absolute and relative basis than in the ^{128}I systems. We are presently studying the ^{38}Cl reactions employing rare gas moderators and radiogas chromatography.

TABLE XIX

PERCENT ^{128}I STABILIZED IN ORGANIC COMBINATION IN VARIOUS GASEOUS MIXTURES^(a)

Additive	Mole Fraction Additive ^(b)	% ^{128}I as Organic (observed)	% ^{128}I as Organic (corrected)
Krypton	0.105	52.7	51.5
	0.152	52.9	51.6
	0.285	52.7	51.4
	0.432	41.9	40.5
	0.514	47.1	45.5
	0.663	49.2	47.5
Xenon	0.0113	46.7	45.6
	0.0199	46.6	45.4
	0.0324	46.5	45.3
	0.131	41.0	39.7
	0.289	29.7	28.2
	0.430	27.9	26.2
	0.897	9.9	7.5
	0.968	11.3	8.8
Neon	0.007	52.7	51.6
	0.035	47.7	46.6
	0.036	45.9	44.8
	0.060	41.8	40.7
	0.138	50.7	49.6
	0.170	50.5	49.4
	0.176	48.3	47.2
	0.256	50.8	49.7
	0.323	51.8	50.7
	0.335	54.7	53.6
	0.414	42.7	41.6
	0.430	44.0	42.9
	0.521	46.1	45.0
	0.536	46.6	45.5

TABLE XIX Continued

Additive	Mole Fraction Additive (b)	% ^{128}I as Organic (observed)	% ^{128}I as Organic (corrected)
Neon	0.624	46.8	45.7
	0.643	44.1	43.0
	0.767	38.4	37.2
CH_3I	0.003	52.7	51.6
	0.0035	48.5	47.4
	0.0043	41.7	40.6
	0.0070	47.0	45.9
	0.0073	48.5	47.4
	0.0098	35.4	34.3
	0.0101	44.1	43.0
	0.0182	35.3	34.2
	0.0187	39.8	38.7
	0.0192	35.4	34.3
	0.0201	35.8	34.7
	0.0298	24.6	23.5
	0.0422	26.4	25.3
	0.0436	23.3	22.2
	0.0624	19.8	18.7
	0.099	12.9	11.8
	0.108	8.7	7.6
	0.451	5.8	4.7
	0.500	8.9	7.8

(a) All samples contained 0.1 ± 0.02 mm I_2 and 3.0 ± 1.0 mm $\text{CH}_3\text{I}^{127}$ and were irradiated for 20 seconds.

(b) Calculated assuming additive pressures.

Fig. 9. Effect of ICl additive on the (n, γ) activated reaction of I^{128} with CD_4 .

Fig. 10. Effect of ICl additive on the (n, γ) activated reaction of ^{128}I with CH_4 .

Fig. 11. Percent I^{128} formed as organic activity in CD_4 additive mixtures containing CH_3I and I_2 .
Moderators: Ne, ●; Kr, ◻; Xe Δ.

TABLE XX

PERCENT ^{128}I AND ^{38}Cl IN ORGANIC COMBINATION IN $\text{CH}_4\text{-ICl}$ REACTION SYSTEM

Mole Fraction (ICl)	Mole Fraction (CH_4)	-Log Mole Fraction (CH_4)	% O.Y. (^{128}I)	Log % O.Y. (^{128}I)	% O.Y. (^{38}Cl)	Log % O.Y. (^{38}Cl)
0.0042	0.9958	0.0019	45.1	1.654	12.3	1.090
0.0072	0.9928	0.0031	33.9	1.530	23.7	1.375
0.0169	0.9831	0.0074	21.5	1.333	20.1	1.303
0.0333	0.9967	0.0147	0.80	-0.097	19.7	1.295
0.0395	0.9605	0.0175	0.54	--	17.2	1.234
0.0643	0.9357	0.0289	4.3	--	15.4	1.188
0.0955	0.9045	0.0436	0.0	--	8.62	0.936
0.100	0.900	0.0458	0.1	--	9.61	0.883
0.192	0.808	0.0926	0.8	--	7.9	0.897
0.304	0.696	0.1572	0.1	--	7.8	0.892
0.321	0.679	0.168	0.2	--	8.4	0.926
0.456	0.544	0.264	1.3	--	8.2	0.914
0.658	0.342	0.467	0.5	--	4.6	--
0.800	0.700	0.699	0.5	--	2.9	--
0.0058	0.9942	0.0025	45.3	1.656	14.1	1.149
0.0214	0.9786	0.0100	1.7	0.2304	13.6	1.134
0.0350	0.9650	0.0155	0.4	--	8.4	0.924
0.060	0.940	0.0750	0.6	--	7.8	0.894
0.194	0.806	0.0937	0.6	--	6.8	0.834
0.422	0.578	0.2381	3.5	--	4.0	0.602
0.907	0.093	1.0315	0.4	--	2.5	0.398

VII. SZILARD-CHALMERS ORGANIC YIELDS IN LIQUID AND SOLID ALKYL IODIDES

(R. L. Ayres and E. P. Rack)

SUMMARY OF PROGRESS

The radiative neutron capture induced yields of organically bound iodine in the liquid alkyl iodides showed, to varying degrees, a dependence on exchange reactions, accompanying γ -radiolysis, and phase. In the absence of and/or corrected for the contributions of exchange and radiolysis, the $^{127}\text{I}(\text{n}, \gamma)^{128}\text{I}$ induced organic yields in liquid methyl, ethyl, n-propyl, and n-butyl iodide are 57, 41, 48, and 48% respectively. The corresponding yields of the polycrystalline alkyl iodide solids at 77°K are identical to the liquid state values; however, the yields for glassy normal propyl and butyl iodide are 8 to 12% higher than their corresponding polycrystalline and liquid state values.

INTRODUCTION

A number of conflicting values have been reported for the organic yields induced by various nuclear processes in pure alkyl iodides. For the $^{127}\text{I}(\text{n}, \gamma)^{128}\text{I}$ activation process, the reported organic yield values range from 56-100% (37,42-44), 37-95% (38-40,43), 41-55% (42,44,49), and 41-53% (38,42,44) for pure methyl, ethyl, n-propyl, and n-butyl iodide, respectively. Similar, but less scattered, values have been reported for the Szilard-Chalmers yields, induced by other nuclear activation processes of iodine, (45-48) in these systems. A partial explanation for these varied results is suggested by studies of the exchange reactions of $^{131}\text{I}_2$ with the corresponding alkyl iodides (50-54).

Svoboda (50) studied the exchange of $^{131}\text{I}_2$ in pure methyl, ethyl, n-propyl, and n-butyl iodide as a function of temperature and iodine concentration. He suggested that a pseudomonomolecular exchange of iodine with alkyl iodides could be responsible for the higher values of organic yields reported in the literature. Cohen and Trumbore (51,53) in a study of iodine exchange with ethyl iodide, confirmed the importance of exchange in the determination of Szilard-Chalmers yields in alkyl iodides. Both (50,51) studies showed that, although the rate law is independent of iodine concentration, the apparent isotopic exchange (as measured by organic retention of activity) is dependent on it. At the very low concentrations of iodine expected in the Szilard-Chalmers experiments, exchange was found to be very rapid. Thus, previously reported values of organic "retention", obtained in studies of Szilard-Chalmers reactions in alkyl iodides, are placed in doubt.

The purpose of this study is to investigate the influence of exchange and other experimental parameters on the radiative neutron capture induced organic yields in "pure" alkyl iodides. Thus, by eliminating and/or correcting for any observed effects due to competing processes, the ^{128}I organic yields due solely to the nuclear activation process may be determined. This information is quite essential in order to employ the various alkyl iodides as sources of iodine in studies of the (n, γ)-activated processes of iodine in systems that are complicated by spontaneous thermal reactions with molecular iodine (55).

EXPERIMENTAL

Approximately 350 samples in quartz ampoules were degassed four times and irradiated for one second at a thermal neutron flux of 1.1×10^{11} neutron cm^{-2} sec^{-1} , or for varying times at lower neutron flux, in the Omaha, Nebraska V. A. Hospital TRIGA reactor. The accompanying γ -radiation flux was 3×10^{17} ev. g^{-1} min^{-1} .

Matheson, Coleman & Bell methyl iodide, Fisher ethyl iodide, and Eastman n-propyl and n-butyl reagent grade iodide were purified by shaking with aqueous sulfite and drying over silica gel, and by fractional distillation. All repurified iodides were stabilized by storage over copper turnings until use. No impurities were detected by gas chromatographic analysis in the repurified reagents. Iodine was sublimed from a mixture of reagent grade I_2 , KI and CaO.

All liquid samples were irradiated at $23 \pm 3^\circ\text{C}$ and maintained at this temperature, in the presence of normal interior illumination, for varying lengths of time prior to extraction. Solid samples were irradiated at 77°K and stored in liquid nitrogen until extraction. Extraction techniques have been described previously (56).

Radiolysis studies were performed by varying the duration of irradiation and/or reactor power.

RESULTS AND DISCUSSION

In order to measure the true $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ induced organic yields in the alkyl iodides studied we investigated (1) the effects of exchange in reactor irradiated samples by measuring the increase in organic yield as a function of time after irradiation, (2) the influence of accompanying γ -radiolysis and dose rate by varying reactor power and/or length of irradiation, (3) the influence of phase, particularly the form of the solid when frozen at 77°K , on the observed organic yields, and (4) compared degassed vs. air-saturated samples in order to determine the effect of oxygen scavenger on the observed organic yields.

Shown in Figure 1 are the $^{127}\text{I}(\text{n},\gamma)^{128}\text{I}$ induced organic yields obtained for liquid methyl, ethyl, n-propyl, and n-butyl iodide as a function of time of extraction after a one second irradiation. We found the respective liquid state organic yields to be 57, 41, 48, and 48% after correcting, for any exchange which occurred by extrapolating organic yields to zero -time.

The exponential increase of organic yield with time illustrates the dependence of the observed organic yield on thermal exchange of the alkyl iodide with inorganic ^{128}I produced by the nuclear activation. This dependence of organic yield on time of extraction or extent of exchange decreases in the order $\text{MeI} > \text{EtI} > \text{n-PrI} > \text{n-BuI}$, consistent with the reported values (50-54) for the exchange rates of the above alkyl iodides.

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

Using our values for the exchange half-times and the values for exchange rates reported by Svoboda (50) we calculated the concentrations of I_2 present in the samples to be of the order of 5×10^{-6} mole/l. Since this is approximately one to two orders of magnitude greater than what we would expect to be produced by radiolysis (57), iodine of approximately 5×10^{-6} mole/l concentration must have been present in the samples prior to irradiation. Iodine present at this very low concentration would not be expected to scavenge appreciably the (n, γ) induced yields of iodine, but to control the exchange rate of iodine with the alkyl iodide. The reported independence of organic yield between 2×10^{-5} and 2×10^{-7} mole fraction added iodine in methyl iodide after correction for exchange (49) supports this contention.

Our values for the liquid state organic yields of n-propyl and n-butyl iodide are approximately 7% higher than the values reported in earlier studies (38,40,47). However the earlier determinations were performed with air-saturated samples;

Fig. 12. Alkyl iodide organic yields as a function of time of extraction after irradiation. MeI, Δ ; EtI, $\square$; n-PrI, $\circ$; n-BuI, $\circ$. Solid points represent crystalline state values for the respective alkyl iodides.

whereas, degassed samples were used in this study. McCauley, et.al. (48), reported an increase in the organic yields of n-propyl iodide for the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ activation, when samples were degassed. We found a corresponding decrease of 7% for the organic yields of n-butyl iodide, while employing air-saturated samples. McCauley, et.al., suggested the lower yields observed for the air-saturated samples were a result of oxygen scavenging of the accompanying γ -radiolysis induced pick-up of the activated iodine.

Investigating the effects of radiolysis on the observed ^{128}I organic yields of the alkyl iodides studied we found no evidence that the accompanying 5×10^{15} ev. g^{-1} radiation received by the samples contributed appreciably to the observed yields. By varying the reactor power from 1.7 Kw to 17 Kw and the total γ -dose received by the alkyl iodide samples from 1×10^{14} to 1×10^{17} ev. g^{-1} we found no dependence of the observed organic yields on dose rate and total dose received when less than 1×10^{16} ev. g^{-1} . However, a ten-fold increase in total dose received by the samples from 5×10^{15} to 5×10^{16} ev. g^{-1} resulted in a 2 to 6% increase in the measured ^{128}I organic yields for normal propyl and butyl iodide. Similar results were reported for other n-propyl halides (48) and indicate that under certain conditions (i.e., total doses equal to or greater than 1×10^{16} ev. g^{-1}) the observed organic yields in the alkyl iodides studies are dependent on the accompanying γ -radiolysis.

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

We found the radiative neutron capture induced organic yields of ^{128}I to be 57, 41, 56 and 60% respectively for methyl, ethyl, n-propyl and n-butyl iodide at 77°K. These values are in agreement, within experimental error, with those in the literature (38,43,48). The solid state organic yields are the same as the corresponding liquid state values for the methyl and ethyl iodides but not for the n-propyl and butyl iodides which are higher by 8 to 12%. The methyl and ethyl iodides form a polycrystalline solid when rapidly frozen in liquid nitrogen; whereas, n-propyl and n-butyl iodide form glassy solids. The failure of the normal propyl and butyl iodides to follow the trend established by the methyl and ethyl iodides (i.e. solid and liquid state yields being equal) is due to the nature of the solid formed and not to structural differences. We obtained the polycrystalline form of n-butyl iodide by freezing the sample in liquid nitrogen, allowing it to warm slowly to its melting point (where the glass converts to the polycrystalline form), and cooling rapidly to 77°K. For the reactor irradiation of the polycrystalline form of the n-butyl iodide we found the organic yield to be 48%, identical to the liquid state value. Thus the differences reported earlier (38,48) between the solid state and liquid state yields of the alkyl iodides containing more than two carbon atoms is due to the type of solid formed and not to structural differences for the alkyl iodides studied.

Several conclusions can be drawn from this study. (1) The observed organic yields for the alkyl iodides are dependent on the amount of exchange reactions prior to extraction. (2) The contribution to the organic yields by exchange reactions decreases in magnitude with increasing chain length of the alkyl iodide. (3) The alkyl iodide organic yields are independent of the dose rate employed in this study but depend on the total dose in excess of 1×10^{16} ev. g⁻¹. (4) The organic yields in the polycrystalline solid alkyl iodides are the same as the respective liquid state yields. (5) The direct correspondence between the liquid

and polycrystalline state alkyl iodide yields may be used to determine simultaneously polycrystalline state yields and the corresponding liquid state yields in the absence of exchange and/or radiolysis.

PERSONNEL, PUBLICATIONS, TALKS AND MEETINGS

A. PERSONNEL LISTING:

1. Project Director

E. P. Rack

2. Graduate Students

R. L. Ayres

H. K. J. Hahn

E. J. Kemnitz

R. M. Lambrecht (Ph.D., June, 1969)

D. Oates

J. B. Nicholas

N. J. Parks (Ph.D., January, 1970)

R. Pettijohn

K. Swartz

M. Yoong

3. Undergraduate Students

O. Gadeken

4. Manuscript Typing and Progress Report Preparations

Miss J. Brichacek

B. PUBLICATIONS:

1. R. L. Ayres, E. J. Kemnitz, R. M. Lambrecht, and E. P. Rack, Iodine Organic Yields in Hydrocarbon Matrices as an Indication of Clustering, Complexing and Fractional Crystallization at 77°K. *Radiochim. Acta*, 11, 1 (1969).
2. R. M. Lambrecht, H. K. J. Hahn, and E. P. Rack, Radiative Neutron Capture Organic Yields as an Indication of the State of Aggregation of IO and I₂ in C₆-Hydrocarbon Matrices at 77°K. *J. Phys. Chem.*, 73, 2779 (1969).
3. E. J. Kemnitz and E. P. Rack, Isotope and Concentration Effects of Bromine in Polycrystalline Benzene at 77°K. *Radiochim. Acta* (In Press)
4. H. K. J. Hahn and E. P. Rack, Radiometric Analysis of Serum and Tissue Proteins. *Radiochim. Acta*, submitted for publication.

C. TALKS:

1. N. J. Parks (with E. P. Rack), "Reactions of I-128 Induced by Radiative Neutron Capture in Homologous Gas-Phase Halomethane Systems." Minneapolis, Minnesota, April 14-18, 1969. Division of Nuclear Chemistry and Technology, American Chemical Society.
2. J. B. Nicholas (with E. P. Rack), "Influence of Rare Gas and Molecular Additives on the ¹³⁰I Reactions Activated by Radiative Neutron Capture and Isomeric Transition in CH₄." Minneapolis, Minnesota, April 14-18, 1969. Division of Nuclear Chemistry and Technology, American Chemical Society.
3. R. L. Ayres (with E. P. Rack), "Iodine Organic Yields in Hydrocarbon Matrices as an Indication of Clustering, Complexing and Fractional Crystallization at 77°K." Minneapolis, Minnesota, April 14-18, 1969. Division of Nuclear Chemistry and Technology, American Chemical Society.

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