kcal. and Coughlin's free energy values show a probable error due to using an estimated entropy of germanic oxide. Table II shows the heat and entropy of formation of germanic oxide, both amorphous and hexagonal, together with the corresponding values of silica.[9] For germanium the comparison was made at 850°K. in order that the error due to the use of the estimated heat capacity may be avoided in the data for the hexagonal modification.

TABLE II

	State	H, kcal.	S, e.u.
GeO_2 (at 850°K.)	Amorphous	−127.6	−40.6 (calcd.)
	Hexagonal	−131.7	−41.4
SiO_2 (at 298°K.)	Amorphous	−202.5	−42.27
	Tridymite	−204.8	−43.11

Solubility of Oxygen.—In the above discussion it was assumed that germanium metal does not dissolve oxygen. However, if there is any solubility in this case, it would decrease the activity of germanium. Contrary to this apprehension, Candidus and Tuomi[10] have reported that the solubility is negligible, and Trumbore and his coworkers[11,12] have shown error in the work of Hoch and Johnston[13] who observed a large solubility of oxygen. It may be concluded, therefore, that germanium does not dissolve oxygen appreciably.

Supplement.—After the present experiment had finished, the authors found that Ono and coworkers[14] had investigated the same equilibrium by a flow method. They obtained −141.8 kcal./mole as the standard heat of formation of germanic oxide. They measured only from the reduction side, while the present measurement were carried out from both the reduction and oxidation sides with sufficient agreement. Besides, the present results seem to show that a circulation method is more suitable than a flow method, since hydrogen pressure is comparable to water vapor pressure in equilibrium. Then, the present results may be more accurate.

Acknowledgment.—The authors wish to express their thanks to Prof. Leo Brewer for his friendly criticism and to Prof. Isao Kayama, Hokkaido Teachers College, who persuaded them to participate in the research group studying germanium. The sample of germanic oxide was supplied by Mr. Hideo Baba, Electrical Communications Laboratory. The preliminary testing of this experiment was carried out by Mr. Satoshi Kado, to whom the authors are also indebted.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Halogen Atom Reactions Initiated by Nuclear Processes in Hydrocarbon Solutions

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RECEIVED FEBRUARY 4, 1957

The organic yields of I^{128} and Br^{80} activated as a result of the $I^{127}(n,\gamma)I^{128}$, $Br^{79}(n,\gamma)Br^{80}$ and $Br^{80m} \xrightarrow{I.T.} Br^{80}$ processes are higher in dilute hydrocarbon solutions than in pure organic halides. They increase with increasing chain length of the hydrocarbon. For the (n,γ) activations in hydrocarbon solutions they decrease by about one-fifth in going from 0 to 100°. These variations in yield are all rather insensitive to the addition of free halogen as scavenger and therefore involve "hot" processes. The results, correlated with those of other investigations, suggest that a number of previously unexplained facts about reactions of hydrogenous material with I^{128}, Br^{80} and Cl^{38} activated by the (n,γ) process may be explained by ionic reactions. The organic yields from the Br^{80m} isomeric transition in liquid hydrocarbons depend on the source molecule containing the Br^{80m} to an extent which is consistent with earlier observations of failure of the transition to rupture C–Br bonds in liquid bromine as the solvent.

Introduction

There are several reasons for studying the chemical consequences of activation of halogen atoms by nuclear processes[2] in each of a series of hydrocarbons: (1) the sizes and weights of the molecules with which the energetic halogen atom is surrounded while losing its energy can be varied without varying the types of bonds to be broken (*i.e.*, only C–C and C–H); (2) conservation of momentum requirements make it impossible for a halogen atom to enter organic combination in such a medium by a "billiard ball collision" mechanism; (3) preliminary observations[3] on such systems have shown changes in organic yields[4] dependent on the size of the hydrocarbon molecules; (4) such studies should contribute to a better understanding of the mechanisms of the various hydrogen replacement reactions cited in the next paragraph; (5) the mechanism of replacement of H^1 by H^3 in tritium recoil reactions[5a] (and possibly also in systems activated by the decay of tritium[5b] may be similar to

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(1) Fulbright–Smith–Mundt Scholar 1953–1954, Project Assoc. (1954–1955), Univ. of Wisconsin; Ravenshaw College, Cuttack, India.

(2) For a discussion of the physical processes involved and a review of earlier work on their chemical consequences see: J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953); *Ann. Rev. Phys. Chem.*, **6**, 141 (1955).

(3) (a) S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2271 (1951); (b) S. Goldhaber and J. E. Willard, *ibid.*, **74**, 318 (1952).

(4) The organic yield is the percentage of the atoms produced by nuclear transformation which become stabilized in organic rather than inorganic combination.

(5) (a) See, for example, and references: R. Wolfgang, J. Eigner and F. S. Rowland, *J. Chem. Phys.*, **60**, 1137 (1956); (b) K. E. Wilzbach, THIS JOURNAL, **79**, 1013 (1957).

that of replacement of hydrogen by halogens activated by nuclear processes.

It has been shown that both iodine[6] and bromine[7] atoms activated by the (n,γ) process can replace hydrogen in pentane, forming the amyl halide, that Cl^{38} atoms from the $Cl^{37}(n,\gamma)Cl^{38}$ process undergo similar reactions in heptane,[8] cyclohexane and benzene,[9] and that the $I^{127}(n,\gamma)I^{128}$ reaction in liquid CH_4 produces both CH_3I^{128} and $C_2H_5I^{128}$.[10a] Further evidence indicates that substitution for hydrogen can occur by a unique "hot" non-radical reaction; *i.e.*, I^{128} atoms or ions freshly formed by the $I^{127}(n,\gamma)I^{128}$ process react[10] with *gaseous* CH_4 in a process of the type $I^{128} + CH_4 \rightarrow CH_3I^{128} + H$, and freshly formed Cl^{38} atoms give a similar reaction with gaseous butane or butyl chloride.[8]

Experimental

Reagents.—Eastman white label C_2H_5Br was purified by mechanical stirring with successive portions of concentrated H_2SO_4 for 12 hours each until further portions showed no coloration. It was then washed with water, dried with $MgSO_4$ and fractionally distilled. Phillips "pure" grade pentane, hexane, heptane and nonane were used. The first three of these were treated with H_2SO_4 in the same way as the C_2H_5Br following which they were stirred with 0.5 *N* $KMnO_4$ solution 6 *N* in H_2SO_4 for 12 hours before drying and distillation. The nonane and decane (Matheson) were fractionally distilled and then subjected to the H_2SO_4 treatment, washing and drying. Following purification all of the hydrocarbons were tested by adding 10^{-3} cc. of elemental bromine labeled with Br^{82} (36 hr.) to 25 cc. of the liquid. The solution was allowed to stand in the dark for about two hours, following which the Br_2 was extracted with aqueous sulfite and the radioactivity in the aqueous and organic layers was determined by counting. The fraction of the bromine which entered organic combination was always less than 0.2%. Hydrocarbons purified only by passing through a column of silica gel showed a high bromine pick-up in similar tests. Michigan Chemical Co. CCl_3Br was freed from stabilizer by distillation, illuminated while containing dissolved Br_2, extracted with aqueous sulfite, washed with water and dried.

Preparation of Organic Compounds Containing Br^{80m}.—$C_2H_5Br^{80m}$ and $CHBr_2Br^{80m}$ were prepared by allowing vapors of the non-radioactive compounds to stand for a few minutes in a flask coated with freshly sublimed $AlBr_3$, which had been prepared by adding radioactive Br_2[11] to dry aluminum, using vacuum system techniques. CCl_3Br^{80m} was prepared by illuminating a mixture of CCl_3Br and radiobromine.

Neutron Irradiations.—All neutron irradiations for studies of the (n,γ) process were made with an Sb-Be photoneutron source[12] which contained about 10 curies of Sb^{127} and emitted about 10^7 neutrons/sec. when received. The liquids to be irradiated were contained either in soft glass test-tubes set in a paraffin block, or in the annular space between the walls of a vessel shaped like a wide mouthed dewar, which was surrounded with water. During irradiations the source was positioned in the center of the paraffin block or of the dewar-like vessel. The γ-ray dosage received by the samples was in the range of about 10^3 to 10^4 r./hr. Irradiations for the production of Br^{80m} (4.4 hr.) were of 8–12 hours duration and those for the production of I^{128} (25 min.) lasted 1–2 hr. The samples irradiated at temperatures above 25° were contained in sealed tubes in a bath of thermostated paraffin oil.

Extraction and Counting.—Following neutron exposure of solutions of the alkyl iodides, a small amount of elemental halogen was added to the irradiation vessel to prevent sticking of tracer amounts of inorganic halogen on the walls. The liquid was then extracted with aqueous sulfite–halide solution. Counting was done by placing the liquid in an annular jacket designed to slide over a type 90NB Amperex Geiger tube. All counts were corrected for the composition of the medium,[13] the relative counting efficiency of the jacket, the volumes of the solutions, and for radioactive decay. In the studies of the $Br^{79}(n,\gamma)Br^{80m}$ reaction, the aqueous and organic layers were allowed to stand 2 to 3 hours following separation, before counting, to allow the Br^{80m} (4.4 hr.) to re-establish equilibrium with the Br^{80} (18 min.) daughter which emits the radiation which is counted. When Br^{80m} was to be determined following irradiation of CCl_3Br, or of alkyl bromides scavenged with I_2, adequate time was allowed for the Cl^{38} (37 min.) or I^{128} (25 min.) activity to decay. Two or more experiments were run for each condition tested and the results given in the tables are the averages of the values obtained. The organic yields[3] of individual determinations regularly agreed within ±0.5% of the average for the (n,γ) studies and ±1% for the isomeric transition studies.

Isomeric Transition Experiments.—For the isomeric transition experiments, the Br_2 or organic compound containing the Br^{80m} was added to 25 ml. of the hydrocarbon to be tested in a glass-stoppered flask and allowed to stand for 2–3 hours. Extraction was carried out as described above. The time of separation was taken as the time when the Br_2 color had just disappeared from the organic layer. When the source of Br^{80m} was Br_2, the activity in the organic layer decayed with an 18 min. half-life. The aqueous layer was allowed to stand until parent–daughter equilibrium was reached, before counting to determine the total 4.4 hr. activity. When the Br^{80m} was in an organic compound the 18 min. activity was counted in the aqueous phase and the 4.4 hr. in the organic. In the latter case the organic yield was given by one minus the ratio of the aqueous 18 min. activity to the organic 4.4 hr. activity, both activities being corrected to the time of extraction.

I_2 as Scavenger for (n,γ) Reactions on Bromides.—Br_2 has been demonstrated[3b,14] to be a powerful tool as a scavenger for thermal atoms and radicals produced by the (n,γ) process in alkyl bromides and I_2 has been shown[15] to serve similarly for alkyl iodides. In the present work I_2 was used as a scavenger for the (n,γ) reaction on solutions of C_2H_5Br in various hydrocarbons in order to minimize the problems of the reactivity of Br_2 with hydrocarbons in the presence of light and γ-radiation. The data of Table I show that its scavenger effect on bromides is equivalent to that reported earlier[3b,14] for Br_2.

TABLE I

ORGANIC YIELDS OF THE (n,γ) PROCESS IN C_2H_5Br AND IN CCl_3Br AS A FUNCTION OF CONCENTRATION OF IODINE

C_2H_5Br		CCl_3Br	
I_2, mole fraction	Av. org. yield, %	I_2, mole fraction	Av. org. yield, %
0.000	32.0	0.000	39.0
.001	31.3	.001	37.5
.002	28.4	.002	33.5
.005	27.1	.004	31.5
.010	26.7	.0066	29.5
.015	24.5		
.020	23.0		

Results and Discussion

Effect of Dilution of Alkyl Halide with Hydrocarbon.—The data of Table II show that, consistent with results reported earlier for C_2H_5Br and C_2H_5I in hexane,[3b] the organic yield for the $Br^{79}(n,\gamma)Br^{80m}$ process on bromine in the form of C_2H_5Br is increased by dilution with either pentane or heptane, a limiting value characteristic of the pure hy-

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[6] A. F. Reid, *Phys. Rev.*, **69**, 530 (1946).

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[9] J. M. Miller and R. W. Dodson, *J. Chem. Phys.*, **18**, 865 (1950).

[10] (a) J. F. Hornig, G. Levey and J. E. Willard, *ibid.*, **20**, 1556 (1952); (b) G. Levey and J. E. Willard, *ibid.*, **25**, 904 (1956).

[11] Made by irradiation of ampoules of liquid bromine in the CP5 nuclear reactor of the Argonne National Laboratory.

[12] The source was obtained from the Oak Ridge National Laboratory (Radioisotopes Catalogue page 141 (1952)) and irradiated at the Brookhaven National Laboratory.

[13] R. S. H. Chiang and J. E. Willard, *Science*, **112**, 81 (1950).

[14] J. F. Hornig and J. E. Willard, THIS JOURNAL, **75**, 461 (1953).

[15] G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

drocarbon apparently being reached at concentrations between 0.1 and 0.01 mole fraction. The increase over the value in pure C_2H_5Br toward this limiting value is qualitatively proportional to the mole fraction of hydrocarbon. The increase is predominantly, and possibly wholly, the result of a type of chemical event which occurs to the tagged halogen atoms before they have had an opportunity to diffuse as thermal atoms in the system; that is it is the result of a "hot"[2,3b] process. This is illustrated by the fact that the difference in organic yields between pure C_2H_5I and hydrocarbon solutions containing 0.05 mole fraction C_2H_5I is, within the experimental error, independent of the concentration of I_2 scavenger present (Fig. 1).

TABLE II

ORGANIC YIELDS OF THE $Br^{79}(n,\gamma)Br^{80m}$ PROCESS IN SOLUTIONS OF C_2H_5Br IN *n*-PENTANE AND *n*-HEPTANE AT DIFFERENT CONCENTRATIONS

C_2H_5Br, mole fraction	Av. organic yield, % In pentane	In heptane
1.00	32.0	32.0
0.80	..	37.3
.75	..	37.7
.66	37.0	40.0
.50	37.5	42.0
.20	38.0	44.8
.10	40.4	46.0
.02	41.0	47.1
.01	42.2	47.4

Effects of Chain Length of Hydrocarbon and of Temperature.—From Table III and Fig. 1 it may be seen that the organic yields of I^{128} from the $I^{127}(n,\gamma)I^{128}$ process in solutions of 0.05 mole fraction of C_2H_5I in *n*-pentane, *n*-heptane and *n*-decane, and of Br^{80} from the $Br^{79}(n,\gamma)Br^{80}$ process on C_2H_5Br at 0.1 mole fraction in *n*-heptane and *n*-decane, increase with increasing chain length of the hydrocarbon. Because the difference persists even in the presence of sufficient scavenger to nearly eliminate encounters of the thermalized tagged atom with radicals by diffusion, it must be concluded that the chain length of the hydrocarbon molecules affects the probability that the tagged atom will enter organic combination before diffusion as a thermalized atom. The most probable cause of such an effect seems to be a difference in the effectiveness of the solvent cages for retaining the tagged atom in contact with an organic radical it has just formed long enough for a stable compound to be formed.

TABLE III

ORGANIC YIELDS OF THE (n,γ) PROCESS ON ETHYL HALIDES IN HYDROCARBONS IN THE PRESENCE OF IODINE SCAVENGER

I_2, mole fraction	Organic yield in Pentane	Heptane	Decane
	Yields from C_2H_5I,[a] %		
0.000	45.0	47.0	52.5
.001	..	44.2	48.2
.0013	39.0	..	..
.0019	37.0	..	..
.002	37.8	41.6	45.6
.004	35.0	..	..
.005	..	38.0	..
	Yields from C_2H_5Br[b]		
0.000	40.4	46.0	49.0
.007	..	34.1	39.0
.0015	..	33.3	37.8

[a] The mole fraction of C_2H_5I was 0.05. [b] The mole fraction of C_2H_5Br was 0.10.

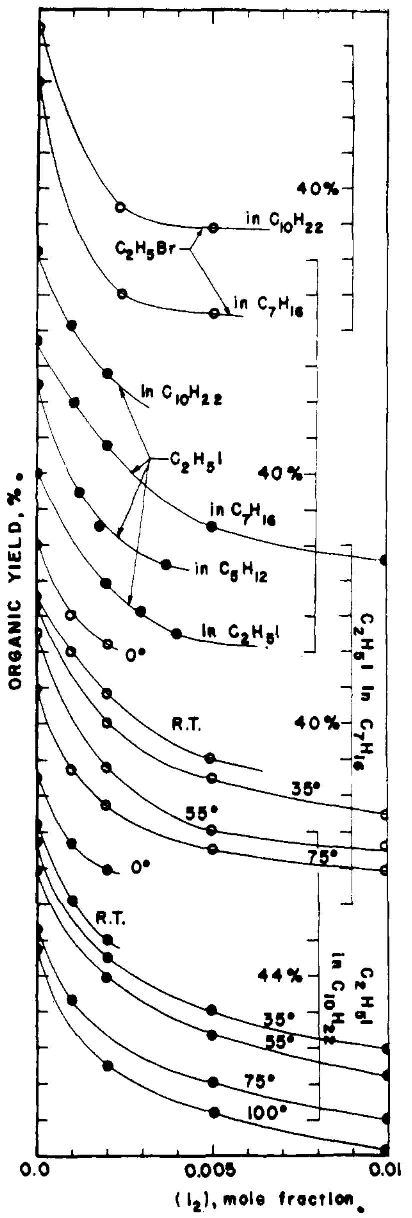

Fig. 1.—Effect of iodine scavenger on the organic yields of the $Br^{79}(n,\gamma)Br^{80}$ and $I^{127}(n,\gamma)I^{128}$ processes in hydrocarbon solutions as a function of solvent and temperature. Concentration of C_2H_5Br for upper two curves 0.10 mole fraction; concentration of C_2H_5I for lower three groups of curves 0.05 mole fraction. Each division on the scales at the right represents 2% in organic yield. The scale for each group of curves is labeled with a single percentage value opposite the center of the curves to which it applies.

Because the effectiveness of the solvent cages might be expected to decrease with increasing temperature, and also because the higher solubility of iodine at higher temperatures makes it possible to use higher concentrations of iodine scavenger, determinations were made of the organic yields of the (n,γ) reaction on ethyl iodide in decane and in heptane at five temperatures and at a series of iodine concentrations. The results, given in Table IV and Fig. 1 indicate a decrease by about one fifth in organic yield for a 100° increase in temperature at all iodine concentrations in both solvents. The fact that the temperature coefficient is observed in the presence of 0.01 mole fraction I_2 scavenger indicates that the change in temperature alters the probability of some process by which the I^{128} enters organic combination before it has undergone many collisions subsequent to being moderated to thermal energies. As in the case of the effect of chain length it seems most plausible to ascribe this to a change in the effectiveness of solvent cages for preventing the I^{128} atom from escaping from a radical which it has just formed.

TABLE IV

ORGANIC YIELDS OF THE (n,γ) PROCESS ON C_6H_5I[a] IN HEPTANE AND DECANE AS A FUNCTION OF TEMPERATURE

	I_2, mole fraction	Organic yield in % at 0°	35°	55°	75°	100°
Heptane	0.000	50.0	46.5	45.0	41.0	
	.001	46.0	..	..	37.5	
	.002	44.2	40.2	37.5	35.5	
	.005	..	38.0	34.0	33.0	
	.010	..	35.0	33.4	31.0	
Decane	.000	55.0	51.5	50.0	46.5	45.5
	.001	51.4	48.2	..	42.6	..
	.002	50.0	45.4	44.8	40.5	39.0
	.005	..	42.0	40.5	37.8	36.5
	.010	..	40.0	38.5	36.0	34.4

[a] The mole fraction of C_2H_5I was 0.05.

The caging effect concept[16] used above has been quantitatively demonstrated[17–19] for the photochemical dissociation of I_2 in solution. Lampe and Noyes[18] have shown that the primary quantum yield for this dissociation changes with solvent from 66% for hexane to 14% for carbon tetrachloride to 4% for hexachlorobutadiene at 25°, the trend being for the dissociation yield to decrease with increase in molecular weight of the solvent. Both the primary quantum yield,[18] and the rate constant for the atom recombination reaction[20] have been shown to increase with increase in temperature.

The only report in the literature on the effect of temperature on the organic yields of the (n,γ) process in pure liquid ethyl halides,[21] of which we are aware gives values of 37.0 and 38.6% for C_2H_5I at −78 and 20° and of 34.5 and 31.8% for C_2H_5Br at −78 and 0° indicating less temperature sensitivity than that shown in the present work for hydrocarbon solutions at higher temperatures. Limited data[3a] indicate a small negative temperature coefficient for the organic yield of Br^{80} from the (n,γ) and isomeric transition processes in CCl_3Br and little or no temperature effect for Cl^{38} in CCl_4.

Consideration of Mechanisms.—The "hot" reactions observed as described above must involve one of the following mechanisms: (a) combination of a neutral recoil atom with an organic radical it had just formed, and with which it combines either before escaping from their common solvent cage or after only a few diffusive encounters with solvent molecules; (b) attack of an energetic neutral recoil atom on a solvent molecule in a displacement reaction in which it replaces a radical or atom; (c) formation of a molecule–ion by reaction of a recoil halogen ion with a solvent molecule, followed by neutralization or reaction of the molecule–ion to yield a stable organic halide molecule. It is impossible, at present, to distinguish between these mechanisms for liquid systems. Gas phase studies have shown, however, that I^{128}, Br^{80} and Cl^{38} when activated as a result of formation by the (n,γ) process can all enter organic combination by displacement reactions between the halogen atom or ion and hydrocarbon molecules, under conditions where the possibility of reaction of the tagged species with free radicals is eliminated.[8,10,22] There is evidence that the atom must have a charge for this type of reaction to occur.[10b] It is probable, therefore, that reactions of ions contribute to the "hot" portions of the reactions discussed in this paper and to many other "hot" reactions initiated by nuclear transformations in both the gas and condensed phases. It is reasonable to assume that these ionic reactions are related in type to the highly efficient ion–molecule reactions[23] currently under intensive study by mass spectrometric techniques. It seems probable that the formation of carbon chains by recoil tritium atoms in methane,[5a] and the other highly efficient reactions of tritium atoms activated by recoil and by tritium decay[5b] are due to ionic reactions of the type revealed by the mass spectrometric studies.

The organic yield of 50% observed for the gas phase reactions of methane with iodine activated by the $I^{127}(n,\gamma)I^{128}$ process is drastically lowered by a few mole per cent. of C_2H_5I and the yield in pure C_2H_5I gas is only about 1%.[10] Because the ionization potential of the C_2H_5I (9.5 e.v.) is lower than that of the I atom (10.4 e.v.) the effect of C_2H_5I in lowering the yield with CH_4 has been ascribed to neutralization of the I^{128+} ions by C_2H_5I before their kinetic energy has been sufficiently reduced to allow them to form a stable combination. It is possible that similar factors may play some role in the reactions of mixtures of liquid alkyl halides and hydrocarbons with halogens activated by the (n,γ) processes. Major differences from the gas phase results might be expected, however, due to caging effects, differences in charge transfer potentials, and differences in the nature and stability of the molecule ions formed. Among the experimentally observed differences are the low organic yields of I^{128} in gaseous $C_2H_5I(1\%)$[10] as compared to liquid C_2-

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H_5I(42%),[24] and in gaseous C_2H_6(3%), C_3H_8(4%) and C_4H_{10}(5%)[22] as compared to the liquid hydrocarbons tested in the work of this paper (Table III). Likewise the organic yield of I^{128} reacting with CH_4 in the gas phase is much more sensitive to added C_2H_5I (*i.e.*, 5 mole % C_2H_5I reduces the yield in gaseous CH_4 by more than 50%)[10b] than are the yields from the hydrocarbons of this paper in the liquid phase. In all probability these differences are due in part to the fact that non-ionic reactions in which the recoil atom can combine with a radical it has formed are made possible by the caging effect and greater probability of diffusive recombination in the liquid.

Correlation with Reactions of Cl^{38}.—Unlike the reactions of I^{128} and Br^{80}, the reactions of Cl^{38} activated by the (n,γ) process in liquid hydrogenous media give a constant organic yield (21%) which is independent of whether the solvent is an alkyl chloride or a hydrocarbon or a mixture of the two, and is independent of the chain length.[8] This unexpected independence of the yield on environment has had no satisfactory explanation. Consistent with the discussion in the preceding paragraphs it may now be explained tentatively by the hypothesis that only ionic reactions lead to organically bound Cl^{38} in liquid hydrogenous media, that 21% of the $Cl^{37}(n,\gamma)Cl^{38}$ events occur with internal conversion which produces ions,[25] and that all such ions result in organically bound chlorine. Chlorine atoms, unlike bromine and iodine atoms abstract H from C–H bonds with very low activation energy. In media where such bonds are available, every neutral chlorine atom would be expected to be fixed in inorganic combination as HCl. Br^{80} and I^{128} atoms, which do not abstract hydrogen as readily, have a greater opportunity to react with radicals which they form in losing the energy from the (n,γ) process. Consequently they may be expected to show organic yields which vary with the varying fragmentation and caging characteristics of different media. Similar variations are to be expected for Cl^{38} in non-hydrogenous solvents where the activation energy for reaction of chlorine atoms with the solvent is high. This is illustrated by the relatively high organic yield (44% total, *ca.* 32% "hot") and scavenger effect observed[8] with carbon tetrachloride in contrast to the 21% total organic yield with no scavenger effect for hydrogenous solvents.

Reaction of Hydrocarbons with Bromine Activated by the Br^{80} Isomeric Transition.—The data of Table V show that the organic yields of bromine activated by the isomeric transition process in hydrocarbons increase with increasing chain length of hydrocarbon regardless of scavenger concentration, as in the case of (n,γ) activation. Although the two nuclear processes are very different both can contribute both charge and recoil energy to the atoms involved. These data add further to the growing evidence[14,26,27] that the chemical events induced by the two types of activation are largely identical.

TABLE V

ORGANIC YIELDS OF THE $Br^{80m} \rightarrow Br^{80}$ ISOMERIC TRANSITION IN SOLUTIONS OF BROMINE IN HYDROCARBONS

Br_2, mole fraction	Organic yield, %, in Pentane	Hexane	Heptane	Nonane	Decane
9×10^{-6}	39.5	..	..	..	..
1×10^{-5}	..	42.5	..	..	..
9×10^{-5}	39.0	..	..	..	..
0.0001	..	41.0	42.3	45.5	49.1
.0009	33.0	..	..	..	..
.001	..	37.4	39.2	..	..
.005	..	..	35.0	40.5	42.0
.01	..	..	..	..	40.5
.02	..	..	27.4	30.8	..

Table VI shows further that the organic yields from the isomeric transition of bromine in hydrocarbons vary with the compound which is used as the source of bromine even when its mole fraction is as low as 1×10^{-5}. The differences between different source compounds are, to a first approximation, independent of the hydrocarbon solvent and of the concentration of bromine scavenger. It appears that they are the result of partial failure of the C–Br bond to rupture following isomeric transition, as observed earlier[28] for CCl_3Br, C_6H_5Br and CH_3Br in liquid bromine as the solvent. The differences between the organic yields from CCl_3Br and from Br_2 observed for the solvents of Table VI are 12.5, 11.0 and 11.0%, in striking agreement with the bond rupture failure of 10–13%[22,28] observed for CCl_3Br in the previous work; the differences between C_2H_5Br and Br_2 of 5, 9.5 and 6% are similar to the failure value of 6.5% for CH_3Br[28]; and the differences between CH_2Br_2 and Br_2 of 3.4, 8.5, 5.5 and 5.0% correspond to the failure value of 4.3%.[22] If the interpretation here is correct, it is of particular interest that the retention, in the parent molecule, of bromine atoms which have undergone isomeric transition, is so similar in hydrocarbon solvents and in liquid bromine.

TABLE VI

ORGANIC YIELDS OF THE $Br^{80m} \rightarrow Br^{80}$ ISOMERIC TRANSITION IN HYDROCARBONS WITH DIFFERENT COMPOUNDS AS THE SOURCE OF BROMINE

	Organic yield, in %, with $CHBr_3$[a]	CCl_3Br[a]	C_2H_5Br[a]	Br_2[a]
Pentane	43.0	..	44.5	39.5
Heptane	51.0	55.0	52.0	42.5
	40.5[b]	46.0[b]	..	35.0[b]
Decane	54.0	60.0	55.0	49.0

[a] The concentration of the bromine containing compound was 1×10^{-5} mole fraction in each case except for the second row of values for heptane. [b] Reaction solution contained 5×10^{-3} mole fraction of Br_2.

Acknowledgment.—This work was supported in part by the United States Atomic Energy Commission and in part by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation.

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