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The Influence of Structure, Phase and Added Iodine on the Organic Yields of the $I^{127}(n,\gamma)I^{128}$ Reaction in Alkyl Iodides

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The organic yields[1] of I^{128} activated by the $I^{127}(n,\gamma)I^{128}$ process in eight purified alkyl iodides have been determined in the liquid phase, and in the solid phase at −190°. The following results of general significance in the development of the theory of reactions activated by radiative neutron capture in condensed organic systems have been obtained. (1) By using molecular iodine at different concentrations as a "scavenger" to compete with radicals for thermalized I^{128} atoms it has been possible to show that the organic yield observed in each of the pure alkyl iodides results from two or more types of elementary processes. (2) The organic yields of the liquid primary iodides (ethyl, *n*-propyl, *n*-butyl and isobutyl) are essentially equal, but different from the yields of the secondary iodides (isopropyl and *s*-butyl), giving the first reported evidence of a structural effect on processes of this type. (3) In contrast to most previous examples of phase effects on such processes, isobutyl, *s*-butyl and ethyl iodides do not give significantly higher organic yields in the solid phase at −190° than in the liquid phase. (4) The nature of the organic products found indicates that I^{128} atoms activated by radiative neutron capture can break carbon–hydrogen bonds in liquid and solid methyl iodide and carbon–carbon bonds in ethyl iodide.

INTRODUCTION

The purpose of this work was to obtain further evidence on the nature of the energy transfer processes and elementary reactions which lead to stable compounds of halogen atoms which have been activated by radiative neutron capture[2] in liquid and solid organic media.

EXPERIMENTAL

Purification of Alkyl Iodides.—The alkyl iodides used were the best grades obtainable from the Eastman Kodak Company and Matheson Chemical Company. All except the *s*-butyl, and isobutyl were further purified by vigorous mechanical agitation with concentrated sulfuric acid for at least five minutes. They were then washed with sulfite solution to remove free iodine, washed with water, dried over Mallinckrodt analytical reagent anhydrous magnesium sulfate, and distilled through a 16" Vigreux column, a 75% middle cut being retained. Those not treated with sulfuric acid (because they reacted with it too rapidly) were treated by the other operations in the procedure. The compounds with normal boiling points greater than 90° were fractionated at a pressure of 100 mm. The distillate was water white in each case except that of the yellow-green methylene iodide. Refractive indices of the purified compounds were in all cases in good agreement with the literature values.

Neutron Irradiations.—All irradiations were made with the alkyl iodide in the annular space between two large soft glass test-tubes, the neutrons being supplied by an antimony–beryllium photoneutron source[3] inserted in the smaller tube. The source contained about 2 curies of antimony and emitted about 6×10^6 neutrons per sec. Irradiation times varied from 0.2 to eight half-lives of the I^{128} (25 min.). All liquid samples were irradiated at room temperature and all solid samples at liquid air temperature. The sample volume was 20 ml.

Extraction and Counting.—Following neutron exposure of the pure alkyl iodides several crystals of elemental iodine were added to the irradiated liquid as carrier and it was extracted in an ungreased separatory funnel with an aqueous solution of 0.1 *M* sodium sulfite, 0.1 *M* sodium iodide. In several instances the walls of the bombardment vessel were washed with hot caustic solution which was then counted, to determine whether any of the inorganic activity had stuck to the walls. The results were negative, in agreement with previous evidence[2a,b] that free halogen added as carrier removes any such adsorbed activity.

Extraction of alkyl iodides which had been irradiated with elemental iodine present was done with an aqueous sulfite solution sufficiently concentrated to reduce all the iodine to iodide. In the cases of the more concentrated solutions appreciable heat was produced during extraction but tests showed that no significant exchange occurred between the aqueous iodide and the alkyl iodides during the extraction process. The low-boiling (42.5°) methyl iodide and the extraction solution used with it were cooled to reduce evaporation losses.

The aqueous extracting solution and the extracted organic layer were each counted in a solution type Geiger counter which had an annular jacket with a volume of 11 ml. Counting rates were corrected for radioactive decay, and

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[1] The "organic yield" is the fraction of the $I^{127}(n,\gamma)I^{128}$ events which result in organically bound I^{128}.

[2] For an introduction to the phenomena of chemical activation by nuclear processes, a discussion of possible elementary reactions available to particles so activated, and references to related work see: (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).

[3] Catalog and Price List No. 4, Isotopes Division, U. S. A. E. C., Oak Ridge, Tennessee, March 1951, p. 30.

also for differences in density of the counting media,[4] using curves determined for the particular counting tube used. For example, the relative specific counting rates of I^{128} in water (density 1.00), *s*-butyl iodide (d. 1.60) and methylene iodide (d. 3.33) were in the ratio 1 to 0.88 to 0.50.

Fractionation of Products.—In order to determine the compounds formed by I^{128} produced by radiative neutron capture in methyl iodide the extracted organic layer was first dried over anhydrous magnesium sulfate. An aliquot was then fractionally distilled with an equal volume of methylene iodide as carrier. Methyl iodide was collected at atmospheric pressure and methylene iodide at about 112° and 95 mm. pressure. A sharp separation was obtained and the specific activity of each carrier was constant throughout all its fractions. The distribution of the I^{128} was computed from the counting rates of the fractions. Products higher boiling than methylene iodide were indicated by a higher specific activity in the pot residue than in the methylene iodide distillate.

In the tests made to characterize the products of the (n,γ) reaction on ethyl iodide, methyl iodide was used as carrier and the composition of the fractions was determined by refractive index measurements, since the rapid distillation demanded by the short half-life of I^{128} did not give perfect separation. The last fraction collected in both experiments was pure ethyl iodide so its specific activity could be accurately determined.

No significant exchange of iodine between alkyl iodides occurred during fractionation, in agreement with observations of others.[5]

Density Determinations.—The densities of the solids reported in Table I were determined by a simplified form of the method used earlier[2a] for similar determinations. A 25-ml. bulb with a small-bore neck was filled to a known volume with the alkyl halide. The bulk of the halide was then frozen very slowly from the bottom upward by gradually immersing it in liquid air. From the height of the solid in the neck, the weight of the compound used, and the known volume calibration of the system, the density of the solid at liquid air temperatures was computed. This method proved to give reproducible values to three significant figures. The liquid densities were determined by weighing measured volumes. "International Critical Tables" reports a density of 2.405 for ethyl iodide at −118°, and densities of 2.334, 1.980, 1.784 and 1.74 at 0° for liquid methyl, ethyl, *n*-propyl and isopropyl iodides, respectively. The most probable errors in our method of determining the density of the solids would make the values slightly low but would not alter their significance for the purposes of this paper.

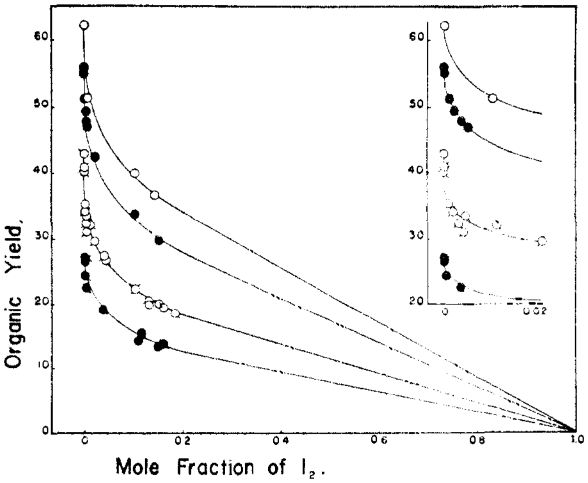

Fig. 1.—Effect of iodine concentration on the organic yields of the $I^{127}(n,\gamma)I^{128}$ reaction on alkyl iodides: ○, methylene iodide; ●, methyl iodide; ,○, ethyl iodide; ○', *n*-propyl iodide; ○͵, *n*-butyl iodide; `○, isobutyl iodide; ●', isopropyl iodide; ●͵ *s*-butyl iodide.

RESULTS AND DISCUSSION

I. Structure Effect

The data of Table I and Fig. 1 show that the organic yields from the $I^{127}(n,\gamma)I^{128}$ reaction in the eight liquid alkyl halides studied fall into three distinct groups: *i.e.*, about 60% for the iodomethanes; about 41% for the primary iodides higher than methyl, and 27% for the secondary iodides.

TABLE I

ORGANIC YIELDS OF I^{128} FROM THE $I^{127}(n,\gamma)I^{128}$ REACTION ON ALKYL IODIDES

	Organic yield, %		Density, g./ml.	
	Liquid (R.T.)	Solid (−190°)	Liquid (R.T.)	Solid (−190°)
CH_3I	56	65	2.279	2.80
CH_2I_2	62	70	3.325	3.76
C_2H_5I	41[a]	43	1.933	2.40
n-C_3H_7I	41	54	1.745	2.14
i-C_3H_7I	27	46	1.703	2.08
n-C_4H_9I	40	60	1.617	1.93
i-C_4H_9I	43	39	1.605	1.90
s-C_4H_9I	27	25	1.595	1.90

[a] The agreement between independent determinations of the liquid phase yield from ethyl iodide is indicated in Table II. This reproducibility is typical of that observed with duplicate samples of the other species. The experiments were made at a flux of 10^5 to 10^6/neutrons/$cm.^2$/sec. with the liquid in contact with air. Two experiments[b] with degassed ethyl iodide in sealed quartz tubes at a neutron flux of 10^7 gave yields of 42.5 and 40.3%. [b] Performed in the thermal column of the C.P. 3 pile which was made available by the Argonne National Laboratory as part of the Participating Institution Program. We should like to express our especial appreciation to Dr. S. Wexler and Dr. W. H. McCorkle for their coöperation in arranging for these experiments.

No such effect has been noted previously in reactions activated by radiative neutron capture. In fact, there is evidence that it does not occur with the bromides, for which the organic yields have been reported as: 32% for C_2H_5Br,[2] 38% for *n*-C_3H_7Br,[6] and 33% for *i*-C_3H_7Br.[6] Since the secondary iodides are known to be much less stable than the primary compounds with respect to decomposition to yield hydrogen iodide and the olefin, it seems quite possible that the lower yield which they give is due to decomposition of molecules which have just been formed from the I^{128} and have excess energy available. The higher yields of methyl and methylene iodide may be due, in part, to the fact that they cannot undergo dehydrohalogenation.

II. Scavenger Effect

As was the case for ethyl iodide and ethyl bromide,[2b] all of the iodides tested in the present work showed a rapid decrease in organic yield at low iodine concentrations as the concentration of iodine present during the neutron irradiation was increased (Fig. 1 and Table II). The yield was reduced by 15% or more of its value for the pure liquid by the presence of 0.01 mole fraction of I_2. Between about 0.01 mole fraction and 0.2 mole fraction it fell off much less rapidly. Experiments at higher concentrations were precluded by the limited solubility of iodine in the alkyl iodides. The curves of Fig. 1 have been extended as straight

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

(5) L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952).

(6) M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952).

TABLE II

ORGANIC YIELDS OF THE $I^{127}(n,\gamma)I^{128}$ REACTION ON ETHYL IODIDE AS A FUNCTION OF IODINE CONCENTRATION

I_2, mole fraction	Organic yield, % Individual determinations	Average
0	40.1, 40.8, 40.2, 40.5, 41.0, 40.6	40.5
6×10^{-6}	39.2, 39.0	39.1
1×10^{-5}	38.2, 39.6, 36.8, 38.0	38.2
6.9×10^{-5}	36.3, 36.7	36.5
9.4×10^{-4}	33.6, 33.9	33.8
1.9×10^{-3}	33.3	33.3
4.0×10^{-3}	33.2	33.2
1.7×10^{-2}	29.5	29.5
1.0×10^{-1}	22.4	22.4
1.3×10^{-1}	20.5	20.5

lines to show zero organic yield at 100 mole % iodine. A direct proportionality of the organic yield to iodine concentration in the high concentration regions is plausible and is in agreement with observations in this region with the bromine–carbon tetrachloride system.[7] Like those of the earlier work,[2b] the curves of Fig. 1 suggest that there are two or more types of processes by which I^{128} activated by radiative neutron capture in liquid alkyl iodides can enter organic combination. Added elemental iodine can compete with each of these processes by diverting the tagged atoms into inorganic form, but the processes differ in their sensitivity to such competition.

A. Low Concentration Region

The process most sensitive to added iodine and responsible for the very steep slopes at the left of Fig. 1 is essentially eliminated at a mole fraction of 0.01, or less. The ratio of iodine molecules to alkyl iodide molecules at this concentration is so low that the chance of a recoiling I^{128} atom encountering an iodine molecule before becoming thermalized is nearly negligible. Therefore, the effect of I_2 in the low concentration region must be to reduce the organic yield by competing with processes in which the I^{128} atoms normally enter organic combination after they have been thermalized and undergone many collisions with molecules of the medium. The nature of the reactions which these thermalized atoms may undergo in the absence of I_2 must be dependent on the relative *local* concentrations of the radicals and molecules with which they may react and on the relative rate constants for reactions with these species. Species to be considered are: (1) the alkyl iodide molecules of the medium; (2) impurities; (3) radicals produced by γ-radiation; and (4) radicals produced by the hot atom in losing its recoil energy. It is our conclusion that the thermalized I^{128} atoms in pure alkyl halides normally combine with radicals formed by the hot atom in losing its recoil energy. Reasons for eliminating the other possibilities are given below.

Possibility of Reaction with Alkyl Iodide Molecules.—Reaction of thermalized I^{128} atoms with the alkyl iodide molecules of the medium to form organically bound I^{128} is excluded both by activation energy considerations and by experimental evidence that photochemical exchange between iodine and ethyl iodide is not observed at room temperature.[8]

Question of Impurity Effects.—The pronounced decrease in organic yield caused by low concentrations of added iodine in the experiments of Fig. 1 immediately suggests the possibility that the added iodine removes impurities with which the I^{128} can otherwise react. Several lines of evidence seem to exclude this explanation of the results. Perhaps the most conclusive is the fact that the organic product which is reduced most rapidly in yield by increase in concentration of iodine scavenger is the parent molecule. This has been demonstrated for the case of methyl iodide (Table IV), and an analogous effect has been shown to exist with regard to the yield of CCl_3Br from the radiative neutron capture reaction on bromine dissolved in CCl_4.[7]

The striking agreement in yields between the four primary iodides tested (Table I and Fig. 1) is also evidence that the role of impurities is not important, since it would be highly improbable that impurities would remain in the different compounds in exactly the right quantities to give such agreement.

Previous[2b] work has shown that identical organic yields can be obtained from ethyl bromide purified by quite different methods. Related evidence is the fact that our yield for pure methyl iodide is in agreement with earlier work,[9] and that our yield for pure ethyl iodide is in agreement with similar measurements made independently in this Laboratory[2b] and elsewhere.[10]

Question of Radiation Effects. (1).—The neutron sources used in this work, as in all radiative neutron capture chemical studies reported to date, emitted a high ratio of γ-rays to neutrons. If the radicals produced in the organic medium by the γ-rays were present at a high enough concentration to compete with other species which might react with thermalized I^{128} atoms they would affect the observed organic yields. It may be estimated, however, that the steady state concentration[11] of such radicals in our experiments was 10^{-11} mole fraction whereas each thermalized I^{128} atom was present in a volume element of solution containing radicals which it itself had produced, at a mole

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[7] J. F. Hornig and J. E. Willard, THIS JOURNAL, in press.

[8] (a) W. H. Hamill and R. H. Schuler, *ibid.*, **73**, 3466 (1951); (b) C. T. Chmiel and R. H. Schuler, Paper 86, Division of Physical and Inorganic Chemistry, Cleveland Meeting of the American Chemical Society, April, 1951.

[9] E. Gluckauf and J. W. J. Fay, *J. Chem. Soc.*, 390 (1936).

[10] (a) J. W. J. Fay and F. Paneth, *ibid.*, 384 (1936); (b) W. F. Libby, THIS JOURNAL, **62**, 1941 (1940).

[11] The γ-radiation intensity from the 2 curie Sb–Be source used for most of the neutron irradiations was about 5000 roentgens/hr. at the distance of the sample, while ionization due to fast neutrons and beta particles was very much less and therefore can be neglected in the following estimate. If 83 ergs are absorbed per gram of alkyl iodide per roentgen and 32 e.v. are required per ion pair, then ion pairs were formed in the samples at a rate of 10^{13} per cc. per sec. The steady state concentration (n per cc.) of these radicals in the pure alkyl iodide may be estimated from the relation $dn/dt = 0 = 10^{13}/\text{sec.} - 4u\sigma^2n^2$, where $4u\sigma^2n^2$ equals the number of radicals which collide with each other per cc. per sec. For the purpose of this estimate the assumptions are made that the collision rate in solution may be calculated in the same way as for a gas and that every collision between radicals forms a stable compound. The speed of the radicals u has been taken as 5×10^4 cm./sec. and the diameter as 4×10^{-8} cm. This yields a value of 1×10^{11} organic radicals per cc. (a mole fraction of 10^{-11}) as the steady state concentration. When molecular iodine is present, the radical concentration is still lower.

fraction[12] of the order of 10^{-3}. On the basis of these estimates it would be predicted that the γ-ray intensity would have to be increased by a factor of about 10^8 squared in order for γ-produced radicals to compete for I^{128} atoms.

(2).—Reasoning similar to that above, based on competitive processes, may be used with regard to solutions at iodine concentrations of about 0.001 mole fraction, *i.e.*, in the steep portions of the curves of Fig. 1. The steep slope must result from the fact that there is a process leading to stabilization of I^{128} in organic combination which is competitive with I_2 at this concentration. Can γ-produced radicals be responsible for competition with the reaction $I_2 + I^{128} \rightarrow II^{128} + I$ at this concentration of iodine? A conservative estimate[14] indicates that such competition could have been important in our systems only if the activation energy for the exchange of I^{128} with I_2 were as high as 16 kcal./mole. Since the activation energy for the exchange is certainly much lower than this,[15] the competitive reaction of γ-produced radicals can be excluded.

(3).—Paragraphs (1) and (2) above, dealing with the question of radiation effects, have centered attention on the possibility of thermalized I^{128} atoms combining directly with radicals produced by γ-radiation, and the probability of such processes has been shown to be very small. Another route by which I^{128} might enter organic combination would be reactions of the type $R + II^{128} \rightarrow RI^{128} + I$, between radicals and stable iodine molecules which had been formed by the I^{128}. Hamill and Schuler[8a] have shown that exchange with molecular iodine involving a step analogous to the above accompanies the photolysis of liquid methyl and ethyl iodides and Hamill and Williams[16] have pointed out that in principle reactions of this type, involving radicals produced by γ-radiation, may increase the apparent organic yield of (n,γ) reactions by returning I^{128} to organic form after it has been initially stabilized in inorganic form as I_2. If this occurs an increase in the iodine concentration of the system to levels in excess of the total radical production would decrease the I^{128} reacting in this way because the *fraction* of the total iodine so reacting would be decreased. In principle this might lead to a steep initial slope of curves such as those of Fig. 1. It is shown below, however, that the effect is negligible in this work, at least in the case of ethyl iodide on which specific tests have been made.

Table III shows that the rate at which I_2 (1×10^{-5} mole fraction) tagged with I^{131} enters organic combination under the influence of the highest radiation levels used in any of the work reported here is about 7×10^{-9} mole fraction per minute or 4×10^{-8} mole fraction in five minutes. Table II shows the organic yield from the (n,γ) reaction as a function of iodine concentration in ethyl iodide for similar five minute irradiations. Since the organic yield is very sensitive to iodine concentration at concentrations (5×10^{-6} to 10^{-2} mole fraction) far above the total amount known to react with radicals (4×10^{-8} mole fraction) it may be concluded that the scavenger effect is not due to competition with reactions of the type $C_2H_5 + II^{128} \rightarrow C_2H_5I^{128} + I$ involving radicals produced by γ-rays.

TABLE III

γ-RADIATION INDUCED ENTRY OF IODINE INTO ORGANIC COMBINATION IN SOLUTIONS OF I_2^{131} IN ETHYL IODIDE

Concn. of $I_2 = 1 \times 10^{-5}$ mole fraction; 20 ml. of solution irradiated in annular ring around Sb–Be source containing about 8 curies of Sb^{127}; radiation intensity at position of sampe about 20,000 r./hr.; this radiation intensity is the same as that used in obtaining the data of Table II and about four times higher than used in the other experiments of Fig. 1.

Time of irradiation, min.	I^{131} organic, %	I^{131} reacted/min., mole fraction[a]
0	0.23	
28	2.5	8.1×10^9
48	3.7	7.3×10^9
60	4.6	7.2×10^9
132	6.3	6.3×10^9

[a] Mole fraction of total solution.

Possibility of Thermal Reaction of I^{128} with Radicals Produced in Losing its Recoil Energy.—If an I^{128} atom reaches thermal energies at a distance of one or more molecular diameters from the last radical which it forms in losing its recoil energy it will diffuse in the system until it encounters something with which it can react. It has been estimated that the *local* concentration[12] of radicals in the small volume element of 10^4 molecules or so immediately surrounding the atom is of the order of 10^{-3} mole fraction as contrasted to a mole fraction of about 10^{-11} in the solution as a whole.[11] This local concentration consists of radicals *produced by the atom itself* in losing its recoil energy. The concentration region of the steep slopes of Fig. 1 (0 to 0.01 mole fraction) is consistent with the

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(12) If an iodine atom emits an 8 Mev. γ-ray as a result of the $I^{127}(n,\gamma)I^{128}$ reaction it will receive a recoil energy of about 6000 kcal./mole, *i.e.*, a total energy sufficient to break some 100 bonds. The number of bonds broken will probably be considerably smaller than this, however, because it is likely that most of the neutron capture events release their energy as more than one γ-ray so that there is some cancellation[13] of recoil energy, and because part of the energy is dissipated as vibrational and kinetic energy without breaking bonds. It is plausible to assume that 10 to 20 radical pairs are formed. The *local concentration* of these radicals may be estimated as follows. About 15 collisions are required on the average for a recoiling I^{128} atom with 6000 kcal./mole to be reduced to thermal energy by collisions with isolated gaseous atoms of the same weight. It is reasonable to suppose therefore that a similar recoiling atom in a liquid alkyl halide will not travel more than fifteen molecular diameters on the average before reaching thermal energies; quite probably the distance will be much less because of the close packed nature of the molecular environment.[2b] It may be assumed, then, that a thermalized I^{128} and all the radicals formed by the dissipation of its recoil energy are present in a volume containing 10^4 molecules or less. If 10 radicals are formed and escape primary recombination, the radicals are present in this volume element at a mole fraction of 10^{-3}.

(13) (a) W. F. Libby, THIS JOURNAL, **69**, 2523 (1947); (b) J. W. Cobble and G. E. Boyd, *ibid.*, **74**, 1282 (1952).

(14) It may be estimated by reasoning similar to that of footnote (11) that the steady state concentration of organic radicals in the presence of a mole fraction of I_2 of 10^{-3} in C_2H_5I will be 4×10^8/cc. if the reaction $C_2H_5 + I_2 \rightarrow C_2H_5I + I$ has zero activation energy or 4×10^6/cc. if it has an activation energy of 4 kcal./mole. Assuming equal frequency factors, the radicals at these concentration ratios could compete for the I^{128} atoms only if the activation energy for the exchange of atoms with I_2 were higher than for their reaction with radicals by 21 kcal./mole and 16 kcal./mole, respectively. These estimates are made from the relation (concn. of I_2)/(concn. of radicals) = exp $(E_{I_2} - E_{rad.})/RT$.

(15) R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950).

(16) W. H. Hamill and R. R. Williams, Jr., private communication.

hypothesis that these slopes are due to competition between these radicals and the added I_2 for the I^{128}.

B. High Concentration Region

The relatively gradual slopes of the curves of Fig. 1 at iodine mole fractions greater than 0.01 indicate the existence of a process or processes by which I^{128} can enter organic combination which is much less sensitive to iodine concentration than the process indicated by the curves below 0.01. These are probably "high energy processes" and include: (1) reactions of I^{128} with radicals which it has formed and with which it reacts before escaping from the cage where formation took place; and (2) "hot radical reactions"[17] of the type $RI + I^* \rightarrow RI^* + I$. The hot radical reactions are high activation energy processes which occur after the I^{128} has dropped below the energy required to rupture molecules to form radical pairs, but before it has become completely thermalized. An increase in iodine concentration decreases the organic yield from hot radical reactions because it increases the probability that these will be of the type $I^* + I_2 \rightarrow I_2^* + I$. It likewise decreases the organic yield due to direct combination of the I^{128} with organic radicals by increasing the relative probability of formation of inorganic radicals (*i.e.*, iodine atoms).

It is tempting to seek to assign a physical significance to the intercepts obtained when the high concentration portions of the curves of Fig. 1 are extrapolated to zero mole fraction of iodine. Perhaps these indicate the value for the organic yield due to combination of the recoil atom with an organic radical it has just formed, in the cage where it was formed and due to "hot radical reactions." If so, the difference between this value and the observed organic yield in the absence of scavenger is due to reactions of thermalized I^{128} atoms with radicals which they encounter by diffusion in the system.

III. Products from Methyl Iodide

The data of Table IV indicate that approximately 9% of the recoil iodine atoms produced by the radiative neutron capture process in liquid methyl iodide enter stable combination as CH_2I_2 while 47% are found as CH_3I.

TABLE IV

PRODUCTS OF THE $I^{127}(n,\gamma)I^{128}$ REACTION IN METHYL IODIDE

Phase	I_2, mole fract.	I^{128} activity, % of total			
		CH_3I	CH_2I_2	Higher boiling	Inorganic
Liquid (R.T.)	0	47.8	8.4	0	43.8
		46.4	9.8	0	43.8
	0.024	31.9	10.2	0	57.9
	.054	27.5	9.9	0.9	61.8
	.069	26.9	7.4	2.3	63.4
	.10	24.3	8.6	0.9	66.2
Solid (−190°)	0	43.5	18.2	3.3	35.0
		43.2	18.2	2.5	35.0
		43.6	19.0	2.3	35.0

It seemed possible that the CH_2I_2 might be formed by a process which did not involve the direct breaking of carbon–hydrogen bonds. Such a process could involve the following steps. (1) Formation of a CH_3 radical by collision of the recoil atom with the iodine of CH_3I. (2) Reaction of the excited CH_3 radical with CH_3I to form CH_4 and a CH_2I radical. (3) Reaction of the CH_2I radical with the thermalized tagged atom to form CH_2I_2. Reactions of methyl radicals such as (2) have been postulated[8a,17] to explain observations on the photolysis of alkyl iodides. If such a sequence of steps occurred in the reaction activated by radiative neutron capture, it might be expected that scavenger iodine would decrease the yield of tagged CH_2I_2. The data of Table IV indicate that there is very little decrease of this product up to a mole fraction of at least 0.1. This is evidence that iodine atoms activated by the $I^{127}(n,\gamma)I^{128}$ process can replace hydrogen atoms in methyl iodide. Similar replacement of hydrogen in methane has recently been observed.[18]

In contrast, the yield of CH_3I^{128} from irradiation of methyl iodide is decreased from 47 to 24% when 0.1 mole fraction of iodine is added. The decrease is important evidence on two points. First, it shows quite conclusively that the effect of added iodine in reducing the total organic yield is not accomplished by removing an impurity with which the recoil atoms react. This follows from the fact that no conceivable impurity would react with the recoil atom to give methyl iodide. In the second place, it shows that the yield of recoil atoms in the form of the parent molecule is more susceptible to scavenger action than the yield of molecules which require more serious rupture of the parent. This difference does not seem to be explained by the theory[6] which attributes the organic products of hot atom reactions solely to a combination of "hot processes," which yield primarily the parent compound, and "epithermal processes" which are responsible primarily for the more complex products.

The yields obtained from liquid methyl iodide (Table IV) are similar to those obtained much earlier by Gluckauf and Fay[9] (46% CH_3I and 11% CH_2I_2). They, however, observed the same yields in the solid phase as the liquid.

IV. Products from Ethyl Iodide

Evidence was obtained (Table V) that about 3% of the recoil iodine atoms in pure ethyl iodide become stabilized as methyl iodide, both in the liquid and solid phases, indicating carbon–carbon bond rupture. Another 3% or so are found in compounds higher boiling than ethyl iodide when liquid ethyl iodide is irradiated, and this increases to 10% when the solid is used. The third column of Table V shows the apparent percentage of a

TABLE V

PRODUCTS OF $I^{127}(n.\gamma)I^{128}$ REACTION ON ETHYL IODIDE

Phase	I^{128} activity, % of total				
	CH_3I	Intermediate	C_2H_5I	Higher boiling	Inorganic
Liquid (R.T.)	3.3	1.6	33.5	2.9	59
Solid (−190°)	2.6	3.0	27.0	10.3	57

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[17] W. H. Hamill, R. R. Williams, Jr., H. A. Schwarz and E. E. Voiland, Univ. of Notre Dame, Radiation Chemistry Project Report, March 1, 1951.

[18] J. F. Hornig, G. Levey and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).

compound intermediate in boiling point between CH_3I and C_2H_5I. This may be iodoethylene formed by the decomposition of newly formed excited diiodoethane molecules. The formation of a multiplicity of organic products is consistent with observations on other systems.[7,9,19,20]

V. Phase Effects

In the case of all compounds examined heretofore,[6,2a] except methyl iodide[9] and ethyl iodide,[2b] it has been observed that the organic yield from the radiative neutron capture process in the solid phase is greater than in the liquid phase. The data of Table I indicate that this is true for five of the iodides examined in the current work (including methyl iodide) but that little or no increase occurs for the other three. In fact, there appears to be a slight decrease in the cases of isobutyl and secondary butyl iodide.

It has been shown earlier[2a] that an increase in density of bromotrichloromethane on freezing and cooling parallels the increase in organic yield of Br^{80} from radiative neutron capture which occurs over the same temperature range. It, therefore, seemed possible that the different phase effects observed for different compounds in Table I might be due to differences in the density changes of these compounds when they are frozen and cooled. Consequently we have determined the densities of the compounds both in the liquid and solid phase and have listed them in columns 4 and 5 of Table I. It may be seen that the differences in phase effect cannot be attributed to differences in density change.

The data of Tables IV and V show that neutron irradiation of solid methyl iodide or ethyl iodide at $-190°$ produces a slightly lower yield of I^{128} in the parent molecule than irradiation of the liquid. The yield of more complex products increases as a result of solidification in each case. The failure of the yield of the parent molecule to increase is in contrast to observations on normal propyl bromide[6] and on bromotrichloromethane.[2a] It is illustrative of the indications coming from this work that phase effects are conditioned by the properties of specific compounds and that it is impossible as yet to predict them on any simple basis.

SUMMARY AND CONCLUSIONS

The work of this paper and a related earlier paper[2b] has produced several new facts of general significance about reactions activated by radiative neutron capture in liquid media, with which any satisfactory theory of such phenomena must be consistent. They are: (1) A significant fraction of the organic yield of I^{128} in liquid alkyl iodides (or of Br^{80} in ethyl bromide) is due to processes which are eliminated by the presence of 0.01 mole fraction of molecular halogen. (2) A significant fraction of the tagged atoms which enter *inorganic* combination, as well as of those which enter organic combination, does so by *high energy processes*.[2b] (3) Low concentrations of free halogens present in methyl iodide during neutron irradiation preferentially decrease the organic yield of the parent molecule relative to more complex products. (4) The ratio of the organic yield of alkyl iodides in the solid phase to that in the liquid phase varies from species to species and is not always greater than one. (5) Structural isomers with similar densities may give different organic yields and different effects of phase change on the organic yield.

These observations appear to be inconsistent with the theory suggested by Libby and coworkers,[6,21] which postulates that organic combination to form the parent molecule occurs predominantly as a result of billiard ball collisions in the "hot region" and that the more complex products are formed predominantly in an epithermal energy region which is especially sensitive to phase effects. This concept of "hot" and "epithermal" reaction regions, each responsible for certain types of products and certain effects, was first invoked to rationalize the increase in organic yield in the solid phase as compared to the liquid phase, and the multiplicity of products observed in the (n,γ) reaction of the propyl bromides. It does not appear to be necessary for this purpose, however, if note is taken of the fact that liquid and solid media consist of closely packed aggregations of molecules where the results of transfer of energy from the hot atom to the surroundings must be much different than in a gas. When an iodine atom with high kinetic energy in a liquid or solid alkyl iodide strikes a molecule which is in its path, it is striking an assemblage of atoms which is surrounded by and backed by a wall of other molecules. The result must be a more or less random fragmentation of the surroundings rather than a "billiard ball" transfer of energy to one atom at a time such as would occur between atoms colliding in the gas phase. The relative numbers and specific types of organic and inorganic fragments formed must depend on the chemical nature, density and crystal structure of the medium. Consequently the relative yields of the activated atom in different product species will depend on these factors; it will also depend, in part, on the activation energy for its reaction with stable molecules of the medium. This concept of the mechanism of (n,γ) activated reactions in condensed systems is broad enough to rationalize the observed facts. A more detailed hypothesis capable of leading to prediction of the relative amounts of specific products in new systems must await a greater background of fact and theory on the behavior of condensed systems.

It should be noted that there is a possibility that a positive charge on the iodine atom activated by the (n,γ) process plays a role in its reaction with the medium, just as such a charge must be responsible for reactions of Br^{80} activated by isomeric transition.[22] There is experimental evidence[23a] that some 45% of the I^{128} atoms formed by the I^{127}

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(19) R. G. Bohlmann and J. E. Willard, THIS JOURNAL, **64**, 1342 (1942).

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

(21) L. Friedman and W. F. Libby, *ibid.*, **17**, 647 (1949).

(22) J. E. Willard, THIS JOURNAL, **62**, 256 (1940).

(23) (a) S. Wexler and T. H. Davies, private communication; (b) S. Wexler and T. H. Davies, Brookhaven National Laboratory Report No. C-7-AECU-50 (1948); (c) S. Yosim and T. H. Davies, *J. Chem. Phys.*, **56**, 599 (1952).

$(n,\gamma)I^{128}$ reaction in gaseous ethyl iodide at low pressure are positively charged as a result of internal conversion of some of the capture γ-rays. Similar evidence has been reported for a positive charge on Br^{80},[23b] Br^{82},[23b] Au^{107},[23c] and In^{116},[23c] follow-radiative neutron capture.

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[CONTRIBUTION FROM THE BEACON LABORATORIES OF THE TEXAS COMPANY]

Isotopic Exchange Rates as Criteria of Surface Heterogeneity[1]

BY R. P. EISCHENS

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The exchange between gaseous CO and CO chemisorbed on iron has been studied. The most weakly bonded CO exchanges the fastest. The exchange data show that the iron is heterogeneous. Kinetic treatment of the data indicates that the heterogeneity is due to differences between a relatively few homogeneous portions rather than to a spectrum of chemisorption bond strengths. In some cases it is not possible to distinguish between the two types of heterogeneity.

Introduction

The question of the degree of heterogeneity of catalyst surfaces has long been of interest to those concerned with fundamental catalyst studies. Despite the considerable attention this problem has received, there remains a wide divergence of opinion concerning this basic surface property. This disagreement stems from the fact that the adsorption of gases, the primary tool of surface chemistry, is inherently unsuited to resolve the question.

When attempts are made to study surface heterogeneity by means of rates of adsorption, heats of adsorption or related methods, the results are such that it is practically impossible to differentiate between heterogeneity as a true surface property and an apparent heterogeneity introduced by variation in the amount of gas on the surface.

The study of the exchange between adsorbed and non-adsorbed gas is not subject to the uncertainties caused by variation in the amount of gas on the surface. During the exchange the adsorbed molecule is displaced by another from the gaseous phase and the amount of gas on the surface remains constant.

When reduced iron is exposed to carbon monoxide at low temperature the gas is rapidly adsorbed.[2] That part of the adsorbed carbon monoxide which is not easily removed by pumping is designated as chemisorbed. Although the chemisorbed carbon monoxide is not easily removed by pumping, it does exchange with carbon monoxide from the gaseous phase. This exchange was first observed over synthetic ammonia catalysts.[3]

The work to be described in this paper is concerned with the study of the exchange between chemisorbed and gaseous carbon monoxide over unpromoted iron. The exchange was followed by introducing radioactive carbon monoxide as the chemisorbed phase and measuring the rate of its appearance in the gaseous phase.

Experimental

Apparatus—A functional sketch of the chemisorption-exchange apparatus is shown in Fig. 1.

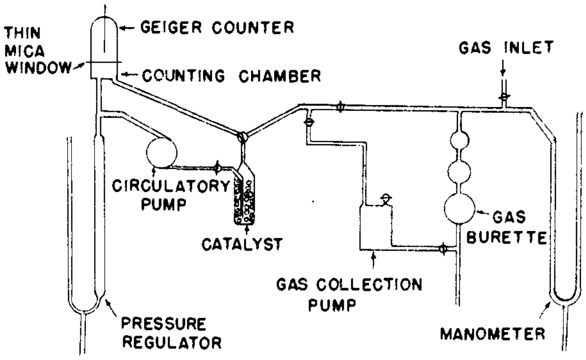

Fig. 1.—Functional sketch of chemisorption-exchange apparatus.

The Geiger counter was assembled from a commercial kit.[4] The counter was modified for gas counting by replacing the sealing ring with a brass chamber.[5] A non-recording Tracerlab Autoscaler was used.

A combination mercury diffusion-Sprengel pump was used to collect the gas pumped off at low pressure.[6] The circulating pump is of the magnetically activated plunger type. It operates at 500 cc./min. The volume of the gaseous phase was approximately 200 cc. The circulating pump was found to be essential to ensure uniformity of the isotopic composition of the gaseous phase. Uniformity of the gaseous phase could be attained in about one minute with the pump whereas it required several hours without it.

The pressure regulator is operated by changing the level of the contained mercury. It is used to adjust the initial pressure to the predetermined level and to compensate for small changes of pressure during the exchange run.

The inlet tube of the catalyst chamber extends to the bottom. The lower part is packed with glass beads so the entering gas can attain temperature equilibrium before reaching the catalyst. Both inlet and outlet of the catalyst chamber are protected from mercury vapor by gold leaf traps.

Materials.—The iron samples were prepared from the oxide by hydrogen reduction. The oxide was prepared by heating the hydroxides obtained by precipitation from a nitrate solution with ammonium hydroxide.[7] The chemicals

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[1] Parts of this paper were presented at the 1951 Gordon Research Conference on Catalysis and the Symposium on Colloid Chemistry of Catalysts at the 1951 A.C.S. Meeting in New York.

[2] S. Brunauer and P. H. Emmett, THIS JOURNAL, **62**, 1732 (1940).

[3] J. T. Kummer and P. H. Emmett, *ibid.*, **73**, 2886 (1951).

[4] Mark 7, Model 1, Radiation Counter Laboratories, Inc., Chicago, Illinois.

[5] J. T. Kummer, *Nucleonics*, **3**, 27 (1948).

[6] I. E. Puddington, *Ind. Eng. Chem., Anal. Ed.*, **16**, 592 (1944).

[7] The oxide was prepared by Mr. L. W. Cook of this Laboratory.