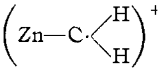
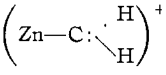
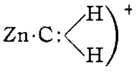
probably not be planar. If not planar, it would probably execute rapid inversion as does ammonia.

We now need only to replace an H by Zn^+ in the I and II forms of CH_3 above to account for the triplet spacing of the $(ZnCH_2)^+$ radical.


I


II


III

The tumbling or rotary motions would presumably average out the H coupling in I, and the splitting would arise mainly from II. The observed spread of 40 gauss indicates that structures with a one-electron CH bond contribute about 20% to the ground state or that the odd electron remains 4% of the time in the 1s orbital of each H. Again the contributions from II might arise from the tendency of the C to fill its 2s subshell.

Tetramethyl Tin.—The paramagnetic resonance obtained for irradiated $Sn(CH_3)_4$ is incompletely resolved and more complex than those for the divalent Zn and Hg compounds. The pattern obtained, see Fig. 3, is almost certainly a superposition of the resonances of two or more radicals. It is possible that the two stronger lines with the first weak one to their right belong to the quintet of $(C_2H_4)^+$ and that the other two components on the left are made unrecognizable by unresolved lines of some unidentified radical. With the second derivative presentation, a resolved line has a maximum at the center with a minimum on either side. This shape leads to confusing and varied contours when two or more lines are incompletely resolved. However, we detected the $Sn(CH_3)_4$ with different amounts of modulation and also as a first derivative. The various curves obtained seem to bear out the interpretation that there is a strong quintet of about 95 gauss spread incompletely resolved from other lines. Nevertheless, this interpretation is by no means certain. If there is a quintet due to $(C_2H_4)^+$, this radical could be produced from the ionized $Sn(CH_3)_4$ to leave $H_2Sn(CH_3)_2$ or two molecules of $HSn(CH_3)_3$.

The radicals detected above are either neutral or positively charged. We have assumed that they are produced as a result of ionization of a molecule of the solid by the X-rays. Because we have obtained no recognizable evidence for them, we have said nothing about the resonances of the electrons which are knocked away. Presumably these electrons are trapped somewhere in the solid, possibly at impurity centers or points of imperfection, and give a resonance which is too broad to detect with our method of small amplitude modulation. Some of the unidentified lines of Fig. 3 might, however, result from F center resonances.

Acknowledgment.—We wish to thank Mr. William B. Ard for valuable assistance in this work.

Durham, No. Carolina

[Contribution from the Departments of Chemistry, St. Peter's College, and Brookhaven National Laboratory]

Chemical Effects of (n,2n) Activation of Iodine in the Alkyl Iodides[1,2]

By Charles E. McCauley, George J. Hilsdorf, Paul R. Geissler and Robert H. Schuler

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The distribution of radioactive material between organic and inorganic products following the $I^{127}(n,2n)I^{126}$ activation of iodine by fast neutrons has been studied in both liquid and solid ethyl, *n*-propyl, isopropyl, *n*-butyl and *sec*-butyl iodides. The total organic retention has been found in all cases to be very similar to that found for (n,γ) activation. For each of the above materials, the distribution of I^{126} activity among the various alkyl iodides has been studied using carrier fractionation methods. In the case of ethyl iodide the product distribution observed for (n,2n) activation has been found to be very similar to that for (n,γ) activation. It is evident that the ultimate chemical fate of the radioactive nucleus is not dependent on the initial energy of the recoiling atom or on other variations which might be expected to result from the different nuclear processes. For all iodides, the activity is distributed among a number of components with the major fraction appearing in the parent material. The activity from solid *n*-propyl and *n*-butyl iodide is found to a considerable extent in the corresponding secondary iodide although in the case of the solid secondary iodides very little activity appears in the isomeric primary iodides. In general, products appear to be formed by reactions of the activated atom both in the epithermal region and, immediately after thermalization, with the radicals produced in the wake of the recoiling particle.

Previously it has been shown[3] that the retentions observed in the (d,p), (γ,n) and (n,2n) activation of iodine in methyl and ethyl iodide are nearly identical to those observed for (n,γ) activation.[4] The present work was undertaken in order to compare the retentions for the $I^{127}(n,\gamma)I^{128}$ and $I^{127}(n,2n)I^{126}$ processes in the solid alkyl iodides and to examine the distribution of activity among the various organic products resulting from the irradiation of both liquid and solid samples. More complete data on the values of the retention in the absence of scavenger iodine are also reported.

Levey and Willard[5] have measured the total organic retentions for the (n,γ) activation of eight lower alkyl iodides in both the liquid and solid phase and in the case of methyl and ethyl iodide have isolated the individual products using carrier fractionation techniques. In the present investigation, the use of the 13-day I^{126} activity produced by the fast neutron activation of the alkyl iodides makes it possible to carry out fractionation studies on more complex systems. Information on the distribution of

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[1] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 14, 1955.

[2] Research carried out in part under the auspices of the U. S. Atomic Energy Commission.

[3] R. H. Schuler, *J. Chem. Phys.*, **22**, 2026 (1954).

[4] The conventional term "retention" is used throughout this paper to describe the fraction of activity which appears in organic combination. The "retained" activity results from the reformation of organic species and not from non-rupture of the original bonds.

[5] G. Levey and J. E. Willard, This Journal, **75**, 6161 (1953).

products is of particular interest in the case of the propyl iodides since analogous data are available for the propyl bromides from the work of Fox and Libby.[6]

Experimental

Materials.—Matheson alkyl iodides were purified by treatment with elemental bromine, extraction of free halogen with sodium thiosulfate, thorough washing with water, drying and fractionation through a three foot helix-packed column. The middle fifth of the distillate was used for the irradiations and the second and fourth fifths for carrier materials.

Activations.—Samples of the alkyl iodides were exposed to the fast neutron flux produced by bombarding a thick beryllium target with 20 Mev. deuterons from the Brookhaven 60 inch cyclotron. Exposures were usually for 100 microampere-hours of deuteron bombardment. Except where noted all solutions contained dissolved air. Where the sample did not contain free iodine during the irradiation, iodine was added shortly after to minimize post-irradiation exchange. Ten-ml. samples were activated for retention measurements and 50-ml. samples were used for the fractionation experiments. Liquid samples were exposed in stoppered volumetric flasks. For irradiation of the frozen iodides the samples were contained in long necked flasks which were sealed with deKhotinsky cement and kept in liquid nitrogen during the entire irradiation.

Retentions.—After the 25-min. I^{128} activity had decayed out, the sample was diluted with carbon tetrachloride and a portion counted in an annular-jacketed Geiger counter. After extraction of the iodine with aqueous sodium thiosulfate, the organic material was counted and the ratio of the organic activity to the total activity taken as the retention.

Fractionation.—Known volumes of carrier materials (from 25 to 50 ml. of each component) were added to the irradiated sample, the free iodine was extracted with sodium thiosulfate, and the sample was dried over anhydrous $MgSO_4$. All of the components boiling below methylene iodide were rapidly stripped off at reduced pressure in a three-foot Vigreux column. A sample of pure methylene iodide was then distilled at 10 mm. The residual material was collected and the volume measured. The mixture of lower-boiling components was separated at reduced pressure in a six-foot helix-packed column. A 5-ml. sample from the central portion of each component was diluted to 50 ml. with hexane and counted. Because of the large dilution factor, variations in counting efficiencies due to the density difference of the various samples were minimized.

It has previously been shown[7,8] that mixtures of methyl, ethyl and the propyl iodides can be separated without appreciable exchange of activity. To test the separation of the butyl iodides, 40 ml. of active *n*-butyl iodide was added to 40 ml. of inactive *sec*-butyl iodide and the mixture refluxed at atmospheric pressure for 10 hours. After fractionation, less than 1% of the activity was found in the *sec*-butyl iodide.

The relative activity of each component was calculated as the product of its specific activity and the volume of carrier initially present. In the case of the heavy residue the specific activity is taken as the excess over that of the methylene iodide fraction. The volume here is that of the stillpot residue. The percentage activity appearing in each component was calculated as the product of the per cent. retention and the ratio of the relative activity of the component to the sum of the activities of all of the components. In several of the propyl iodide samples this sum was compared to the relative activity of the infractionated material and found to account for 97 to 101% of the organic activity.

Results

Retentions.—The retentions observed for various liquid and solid samples are given in Table I along with comparative data for (n,γ) activation. All retentions listed are for iodine-free air-saturated samples. Retentions observed for samples containing added iodine during the irradiation are given as the experimental points in Fig. 1 along with the curve representing the results of Levey and Willard on the same systems. The measurements on propyl iodide were made shortly after one microampere-hour irradiations. It has been pointed out earlier[3] that post-irradiation exchange accounts for an increase of 1–2% in the retention of the ethyl iodide samples.

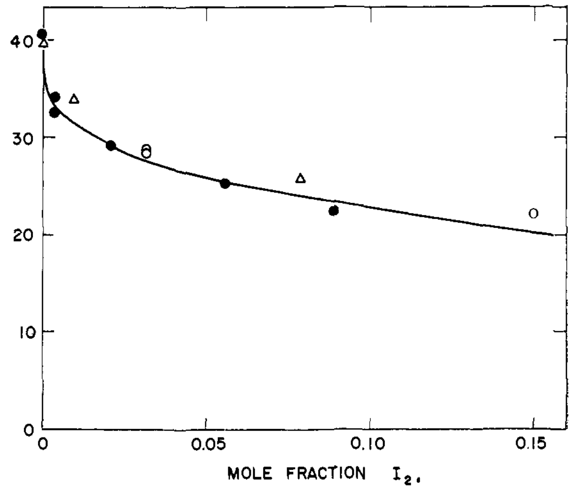

Fig. 1.—Effect of dissolved iodine on (n, 2n) retentions: of ethyl iodide, ○; *n*-propyl iodide, ●; *n*-butyl iodide, Δ. Solid curve represents the results of Levey and Willard (ref. 5) on (n, γ) activation.

TABLE I

ORGANIC RETENTIONS (%)

Iodide	Liquid (25°) (n,2n)	(n,γ)[a]	Solid (−196°) (n,2n)	(n,γ)[a]
Ethyl	41.3,[b] 42.6[c]	41	40.2[c]	43
n-Propyl	44.1, 42.5	41	55.0, 60.1[d]	54
	44.0, 43.4[d]		55.7, 56.4[d,e]	
	40.8		61.3, 59.0	
Isopropyl	30.2, 31.6[d]	27	48.9, 47.6	46
			51.5,[d] 47.7	
			47.9, 48.8	
			52.6	
n-Butyl	44.8[d]	40	59.8[d]	60
sec-Butyl	28.5, 30.3[d]	27	25.3, 25.7[d]	25

[a] From the work of Levey and Willard (see ref. 5). [b] From ref. 3. [c] Sample fractionated (Table III). [d] Sample fractionated (Table IV). [e] Sample contained 52 mg. I_2 per 50 ml. to dilute active iodine upon melting.

In general, the I^{126} retentions for both the liquid and solid iodine-free iodides are nearly the same as those observed for the production of I^{128}. As described below, the effects of radiation undoubtedly account for a small increment to the retention. For the samples containing added iodine, where an increase in retention due to this radiation-induced exchange is minimized, the different modes of activation give results which agree within the experimental error in all cases.

In the solid propyl iodides, several retentions 5–6% higher than those reported by Levey and Willard[5] were observed. These are believed to be spuriously high since in other experiments the retentions were found to be in good agreement with the (n,γ) results. In one experiment on solid *n*-

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

(7) C. E. McCauley, W. H. Hamill and R. R. Williams, Jr., THIS JOURNAL, **76**, 6263 (1954).

(8) R. G. Badger, C. T. Chmiel and R. H. Schuler, *ibid.*, **75**, 2498 (1953).

propyl iodide, iodine was dissolved in the iodide before freezing so that when the sample was melted the free radio-iodine would be diluted with carrier iodine and be less liable to exchange with the parent material. Although the effect of iodine on solid phase retentions has not been studied, in the liquid state the low concentration of iodine added (0.004 *M*) would be sufficient to reduce the retention only a few per cent. The retention of this sample agrees with the other values observed for *n*-propyl iodide as well as the results of Levey and Willard.

Radiation Effects.—The samples during the course of activation receive an appreciable radiation dose, of the order of 10^5 roentgens during a 100 microampere-hour bombardment.[9] This is sufficient to cause the liberation of an observable quantity of free iodine and to increase the apparent retention by reaction of the radiation-produced radicals with the radioactive iodine present.[10] Originally it was thought that this radiation-induced exchange might completely vitiate attempts to obtain (n,2n) retentions for iodine-free solutions and particularly for the solid iodides. However, the effects of radiolysis, although real, appear to be much less than initially expected.

In the case of air-saturated samples, the increase in retention due to the presence of radiation is minimized by the competition of the oxygen with the iodine for the radicals produced. In the case of solutions containing added iodine, the competition of inactive iodine eliminates any increase in retention except for the most extreme doses.

In Table II, the retention of *n*-propyl iodide is given as a function of radiation dose. The retention is reasonably constant, although it increases observably as the concentration of radio-iodine builds up in the solution. In an air-free iodine-free sample, where the effect of competition of the dissolved oxygen is lost, the observed retention is considerably higher than for air-saturated systems. Correspondingly, the liberation of free iodine is considerably less than for air-saturated samples. In the (n,γ) activation of ethyl iodide, where the samples received a far smaller radiation dose, no difference in retention between air-free and air-saturated samples has been found.[5] In an air-free sample of *n*-propyl iodide initially containing 0.04 *M* free iodine, the observed retention was identical to that of a similar air-saturated sample.

Table II

Effect of Irradiation Period on the Retention in *n*-Propyl Iodide

Conditions	Irradiation (μmp. hr.)	Retention
Air satd.[a]	1	40.8
-iodine free	11	42.5
	37	43.4
	90	44.0
	108	44.1
Degassed-iodine free	108	54.7
Air satd. 0.04 *M* I_2	50	34.4
Degassed 0.04 *M* I_2	50	34.2

[a] In the air saturated iodine-free sample iodine is produced at approximately the rate of 3×10^{-6} mole/l./μamp. hr.

It is difficult to estimate what the effect of radiation on the solid phase retentions should be since data on the radiation-induced exchange in the solid state are not available. However, an increase in the amount of back reaction is indicated by a lower yield of iodine production in the solid. That complications due to back reaction are not very important is shown by the general agreement between the present results and those of (n,γ) activation.

Fractionation Experiments.—The results of the carrier identification of the individual products of the reactions of the active iodine atoms are reported in Table III and IV. In Table III a comparison is made of the product distribution of I^{126} and I^{128} activity in ethyl iodide. It is seen that the product distribution in the two cases is essentially the same, the small differences being of the order of the errors involved in the determinations. In the fractionation of the products from ethyl iodide small amounts of activity appear in the propyl iodide carriers. While activity in the propyl iodides from liquid ethyl iodide is marginal, that of the samples from solid ethyl iodide appears to be real and indicates carbon–carbon bond synthesis.

Table III

Products of (n,2n) and (n,γ) Activation of Iodine in Ethyl Iodide

Product	Liquid (25°) (n,2n)	Liquid (25°) (n,γ)[a]	Solid (−196°) (n,2n)	Solid (−196°) (n,γ)[a]
Methyl iodide	1.7	3.3	1.4	2.6
Vinyl iodide[b]	0.6	1.6	1.2	3.0
Ethyl iodide	35.2	33.5	27.2	27.0
Methylene iodide	3.7	2.9	6.4	10.3
Residue	1.4[c]		4.0[d]	
Total organic	42.6	41.3	40.2	42.9

[a] From Levey and Willard (ref. 5). [b] Taken as the activity of the fraction boiling between methyl and ethyl iodide which is in excess of that attributable to those components. [c] The sum of 0.3% of the activity found in the isopropyl iodide fraction, 0.3% in the *n*-propyl iodide fraction, and 0.8% in the heavy residue. [d] The sum of 1.6% of the activity found in the isopropyl iodide fraction, 0.7% in the *n*-propyl iodide fraction, and 1.7% in the heavy residue.

In Table IV are given the product distribution data for *n*-propyl, isopropyl, *n*-butyl and isobutyl iodide. It is seen, in comparing the two iodine-free liquid *n*-propyl iodide samples, that in the absence of dissolved oxygen the increased retention appears entirely in the parent material. This supports the inference made above, that the difference in the results of the two measurements is due to a radiation-induced exchange since such an exchange has been found to result almost entirely in the formation of the parent species.[11] Comparison between the air-saturated and degassed samples containing added iodine shows not only that the retentions but also the product distributions are indistinguishable. The agreement between these two samples is an indication of the precision obtained in the fractionations. In the case of liquid *n*-butyl iodide the presence of 0.007 *M* iodine affects only the activity appearing in the parent material. As

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(9) This bombardment oxidizes ferrous ion (in the Fricke dosimeter) to the extent of 10^{-3} mole/liter. From this we estimate an energy absorption from the fast neutron flux of 6×10^{18} e.v. per cc. of solution.

(10) R. H. Schuler and W. H. Hamill, This Journal, **74**, 6171 (1952); R. C. Petry and R. H. Schuler, *ibid.*, **75**, 3796 (1953).

(11) R. C. Petry and R. H. Schuler, *ibid.*, in press.

TABLE IV

DISTRIBUTION OF PRODUCTS OF (n,2n) ACTIVATION OF IODINE IN THE ALKYL IODIDES

State	Carrier iodine, *M*	Organic retention, %	Products							
			CH_3I	C_2H_5I	*i*-C_3H_7I	*n*-C_3H_7I	*s*-C_4H_9I	*n*-C_4H_7I	CH_2I_2	Residue
			n-Propyl iodide							
Liquid	0	43.4	3.5	0.9	2.3	32.5	..	..	2.6	1.6
Liquid (degassed)	0	54.6	3.6	0.9	2.3	42.2	..	..	3.1	2.5
Liquid	0.04	34.4	3.2	1.0	1.4	24.5	..	..	2.9	1.4
Liquid (degassed)	0.04	34.1	3.2	0.8	1.0	24.7	..	..	3.5	0.9
Solid	0	61.5	9.7	1.8	18.8	21.3	..	..	4.8	5.1
Solid	.. [a]	56.4	5.8	0.9	13.3	21.7	..	..	7.9	6.8
			Isopropyl iodide							
Liquid	0	31.6	2.9	0.7	23.8	1.6	..	..	2.2	0.4
Liquid (degassed)	0.04	23.3	2.0	0.9	16.0	1.3	..	..	2.1	1.0
Solid	0	51.5	4.1	0.9	39.2	3.3	..	..	3.2	0.8
			n-Butyl iodide							
Liquid	0	44.8	2.2	2.8	0.1	0.4	2.3	30.1	2.6	4.3
Liquid	0.007	39.8	2.2	2.6	0.1	0.3	2.3	26.1	2.3	3.9
Liquid	0.09	33.9	1.9	2.5	0.1	0.3	1.3	23.2	1.9	2.7
Liquid	0.77	25.9	1.2	1.8	0.1	0.3	1.0	17.2	1.7	2.6
Solid	0	59.8	2.7	3.1	0.8	0.6	16.2	21.0	4.3	11.1
			sec-Butyl iodide							
Liquid	0	30.3	2.9	1.1	0.1	0.2	20.0	1.3	2.0	2.7
Solid	0	25.7	2.9	1.0	0.1	0.3	13.9	2.3	2.5	2.7

[a] Sample contained 52 mg. of I_2 frozen into the lattice (in 50 ml.).

the retention is about 4% high in the iodine-free sample, the effect of the low iodine concentration appears to be largely due to the scavenging of the radiation-produced radicals. The true product distribution in *n*-butyl iodide is probably more closely given by the results on the sample 0.007 *M* in I_2 than by those from the iodine-free sample. In general the activity appearing in the parent fraction of any of the iodine-free samples may be slightly high due to radiation produced reactions. Other fractions should be unaffected.

Discussion

Effects of Recoil Energy.—Production of I^{126} by the fast neutron activation of iodine results in a nucleus which has an initial energy of the order of 100,000 e.v. This is contrasted to the recoil energy of approximately 100 e.v. available in the activation of iodine by thermal neutrons. However, in spite of this thousand-fold difference in recoil energy, the organic yields from the two processes and the product distributions observed in the case of ethyl iodide are essentially identical. It is evident therefore that the excess recoil energy is of little significance in determining the fate of the radioactive species. The various implications of the similarity of yields, including the dependence of retention on charge of the nucleus[12] and of variations in local radical concentration in the wake of the recoiling particle, have already been discussed.[3] The present work extends the previous studies to alkyl iodides in the absence of scavenger iodine and demonstrates that even in the solid state the recoil energy of the iodine atom has little influence on the over-all results.

Addition of elemental halogen or similar radical catchers to an alkyl halide prior to irradiation decreases the organically combined activity, the effect per mole of added halogen being greatest at small concentrations of halogen. Since it is expected that processes occurring while the recoil particle has considerable energy will not be subject to suppression by the presence of scavenger iodine, the similarity of the effect of added iodine on the I^{126} and I^{128} retentions again shows that we are concerned with processes that occur only after the recoil atom has lost most of its excess energy.

Because of the similarity in the yields, one is tempted to identify completely the results of the two different activation processes. We wish to be cautious in this regard, however, since work currently in progress in these laboratories has indicated that Br^{78} formed by fast-neutron activation of the propyl bromides has a higher retention than the products of (n,γ) activation in both the liquid and solid state. In the case of the iodides any differences, if such exist, are extremely small and represent only slight modifications of the considerations of the effect of recoil energy on the chemical processes.

Libby and co-workers[6,13] have reported that the retention observed for Br^{82} in the solid alkyl bromides is higher than that for Br^{80}. In a discussion of this isotope effect, they have proposed a model in which the essential feature is the effective melting of a zone in the crystal by the recoiling atom. It is reasoned that the more energetic recoils will melt a greater zone and behave as if they were in a more liquid-like environment in the subsequent reactions. However, it is shown in the present work that in the fast-neutron activation of *n*-propyl, isopropyl and *n*-butyl iodide, where the active species is known to have a large excess energy and where the retentions of the solid samples are appreciably above those of

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[12] G. Levey and J. E. Willard THIS JOURNAL **78**, 2351 (1956), have ecently shown that the product distribution resulting from the isomeric ransition in Br^{80} is very similar to that observed in (n,γ) activation.

[13] F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1495 (1953).

Table V

Comparison of the Products of the Activation of the Propyl Iodides and Propyl Bromides

	Activity (%) as							
	CH_3X	CH_2X_2	C_2H_5X	n-C_3H_7X	i-C_3H_7X	*vic*-Dihalides	Other organic activity	Total organic activity
Liquid *n*-propyl iodide	3.5	2.6	0.9	32.5	2.3	..	1.6	43.4
Liquid *n*-propyl bromide[a]	1–2	1.8	.7	17.1	1.7	5.9	4.2	34.7
Liquid isopropyl iodide	2.9	2.2	.7	1.6	23.8	..	0.4	31.6
Liquid isopropyl bromide[a]	1–2	..	.7	2.5	9.3	7.7	5.3	31.7
Solid *n*-propyl iodide	5.8	7.9	.9	21.7	13.3	..	6.8	56.4
Solid *n*-propyl bromide[a]	1–2	2.4	2.7	26.9	3.4	23.8	22.5	88.4
Solid isopropyl iodide	4.1	3.2	0.9	3.3	39.2	..	0.8	51.5
Solid isopropyl bromide[a]	1–2	..	1.7	31.8	11.7	23.0	21.2	94.3

[a] From the work of Fox and Libby (ref. 6).

the liquid, the retention does not decrease below that observed in (n,γ) activation. It seems, therefore, that the proposed energy dependent liquefaction of the crystal is of little bearing in the case of the iodides.

Liquid Alkyl Iodides.—The major fraction of the organic activity, in the irradiation of liquid alkyl iodides, appears as the parent material with about 25% distributed among other products. In Table V a comparison is made between the product distribution from the propyl iodides with that from the bromides as reported by Fox and Libby.[6] In the liquid iodide samples activity in the minor components occurs to about the same extent as in the bromides but the parent iodide has about twice the activity of the bromide. A considerable difference exists between the behavior of the dihalide products; dibromides account for a considerable fraction of the propyl bromide retention but vicinal diiodides, since they are unstable, do not contribute to the organically bound activity in the case of the propyl iodides.

Structural factors which might influence product formation are somewhat obscured by the relatively small yields of the various species other than the parent material. However, the data of Table IV do indicate that structural factors play an important part in determining minor products. Random molecular disruption would result in the formation of twice as many methyl fragments from isopropyl and *sec*-butyl as from *n*-propyl and *n*-butyl iodide. This is evidently not the case. The disproportionately large yield of methyl from *n*-propyl iodide and of ethyl from *n*-butyl iodide suggests that radicals are produced with excess energy and rupture along paths similar to reaction 1.

$$R—CH_2—CH_2\cdot \longrightarrow R\cdot + CH_2{=}CH_2 \qquad (1)$$

Analogous fragmentation has been observed to occur to a small extent in the photochemical[7] and radiation chemical[11] decomposition of the iodides. In a similar manner the *sec*-butyl radical can decompose to yield methyl radical and account for at least part of the observed high methyl iodide yield. As is again demonstrated in the results of the photolysis and radiolysis[7,11] the bulk of the radicals are probably formed by the simple rupture of the C—I bond so that the activity should predominate in the parent species.

While the vicinal diiodides are unstable, the 1,1-diiodo-, 2,2-diiodo- and 1,3-diiodopropanes and analogous butanes are not. These diiodides will appear in the high boiling residue and perhaps as contamination in the methylene iodide fraction. As might be expected, the residue accounts for a much larger fraction of the activity in the normal iodides; for example, of the diiodide products of isopropyl iodide only 2,2-diiodopropane is stable whereas 1,1- and 1,3-diiodopropane can be produced from *n*-propyl iodide. If we give equal weight to the replacement of each of the hydrogen atoms, then the ratio of diiodide product from *n*-propyl iodide to that from isopropyl iodide should be 5 to 1 and similarly from *n*-butyl iodide to that from *sec*-butyl iodide should be 7 to 4. The data of Table IV are unexpectedly near to these ratios.

In studies of the gross retentions of the iodides, Levey and Willard have shown that the liquid primary iodides, ethyl, *n*-propyl, *n*-butyl and isobutyl iodide all behave similarly.[5] The retentions are about 41% and are decreased by the same amount upon the addition of a given mole fraction of iodine to the system. A similar situation exists for the secondary iodides where the retentions are about 27%. This constancy of retention within a given series might well have been expected if the organic activity appeared in a single component, but is a little surprising in view of the diversity of products formed.

It is interesting to note in the case of *n*-butyl iodide that the added iodine decreases each individual component. In fact each compound is affected to about the same degree although this may be somewhat fortuitous. This is in contrast to the observations on the methyl iodide system where addition of 10 mole per cent. iodine halves the activity found in methyl iodide while causing virtually no effect on the methylene iodide component.[5] The present results on *n*-propyl iodide are somewhat intermediate; upon the addition of 4 mole per cent. iodine the parent and methyl iodide activities drop slightly while the methylene iodide actually increases. It would seem that in the simpler systems the presence of iodine stabilizes diiodide products. In more complex systems this effect is lost in the general decrease in organic products.

The decrease in organic activity in the presence of added halogen has often been thought of as taking place in two regions: the first occurring at low concentrations where the halogen scavenges thermal radicals and the second at high concentrations where the halogen interferes in epithermal processes.[14] The similarity of the product distribution in the presence and absence of iodine would argue that there is no essential difference between these two regions but rather that the retention has a greater functional dependence on a given change in iodine concentration at low concentrations. This is in accord with theories presently being developed for diffusion controlled reactions. In fact, Roy, Williams and Hamill[15] have quantitatively described a diffusion-recombination mechanism for the scavenger effect in ethyl bromide.

Solid Alkyl Iodides.—For any given iodide the change in retention in going from the liquid to the solid state seems to vary in a quite unpredictable fashion.[5] If, however, we focus attention not on the magnitude of the retention but on the distribution of products, several striking regularities become apparent. The secondary iodides follow one pattern, the primary iodides another. Except for a change in the parent species both isopropyl and *sec*-butyl iodide have almost the same product distribution in the solid and liquid phases. The product distribution from the primary iodides, on the other hand, changes markedly upon solidification. Both *n*-propyl and *n*-butyl iodide show a very large production of the isomeric secondary iodide in the solid. A relatively large increase in the yields of methyl iodide and of diiodide product is also observed. In the case of methyl iodide it is known that the methylene iodide produced increases from 9 to 18% upon solidification of the sample.[5]

Fox and Libby have made the generalization that solidification of the sample will favor organic combination.[6] It has already been pointed out by Levey and Willard that there is little difference in the retention values of liquid and solid ethyl, isobutyl and *sec*-butyl iodides and that the activity found in the parent species from methyl and ethyl iodide is less in the solid than in the liquid.[5] The present data show that *n*-propyl, *n*-butyl and *sec*-butyl iodide exhibit a similar decrease in the activity found in the parent species. The ratio of activities upon change of phase does not appear to be a criterion, as proposed by Fox and Libby,[6] on which to base the classification of the type of process by which a given product is formed.

The effect of phase change in the iodides is much smaller than in the bromides. The results given in Table V show that the increase in parent activity accounts for only a small fraction of the difference observed between the retention of the liquid and the solid propyl bromides. The major effect of solidification is the enhancement of the dibromide products. The lack of stability of diiodides accounts for at least a part of the smaller effect of phase change in the iodides. However, even where the diiodides are stable they are produced in much smaller yields than the corresponding dibromides. The secondary iodides show practically no increase in these products upon solidification.

The observation that solid primary iodides largely isomerize to the corresponding secondary ones, but that solid secondary iodides do not produce any large amounts of their primary analogs contrasts interestingly with the data of Fox and Libby[6] on the (n,γ) activation of the propyl bromides. In Table V it is seen that it is the isopropyl bromide which rearranges in the solid state to *n*-propyl bromide and not the converse. This difference of behavior finds a parallel in the addition of the hydrogen halides to unsymmetrical olefins: where hydrogen iodide adds as a molecule to form the secondary iodide, hydrogen bromide after oxidation in the presence of peroxides undergoes atomic addition to form the primary bromide. In the present instance it is possible that the recoil produces hydrogen iodide as an intermediate which in the solid is constrained by the crystal lattice until it can react with propylene. In the liquid the effect would be minimized by diffusion.

Considerations on the Reaction Mechanism.—Three models currently exist to explain the observed chemistry following nuclear activation.[16] These include the billiard-ball collision theory,[17-19] the epithermal reaction model[20,21] and the random-fragmentation model.[5,16] It is clear that the mechanistic picture is most complex and that progress toward a complete description will be slow. We wish to consider here the specific case of the possible reaction paths available to an energetic iodine atom as it loses energy and comes to rest in an alkyl iodide medium.

The recoil atom at first loses energy principally by collision with individual atoms of the alkyl iodide molecules. Apart from the small amount of energy required to break the bond or bonds holding the struck atom in the molecule, these collisions are essentially elastic. The target atoms so expelled may often have sufficient energy to disrupt nearby molecules, and this cascade effect will leave a widening cylinder of molecular fragments in the wake of the original recoil. Complete momentum transfer is possible only in collisions with iodine atoms, and then only under unusually favorable circumstances. If the energy needed to escape through the liquid cage barrier is ϵ, the probability that a recoil atom of initial energy E will be trapped after a single collision with a stationary iodine atom is ϵ/E. Evidently such sudden stoppages will occur in only a small fraction of the energetic collisions. However, as the recoil approaches thermal energies the momentum transfer requirement is less and it becomes more probable that the recoil atom will undergo collisions which result in the substitution of the active atom for inactive atoms of the parent species.[22]

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[14] S. Goldhaber and J. E. Willard, THIS JOURNAL, **74**, 318 (1952).

[15] J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **76**, 3274 (1954).

[16] Discussed in detail by J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953).

[17] W. F. Libby, THIS JOURNAL, **69**, 2523 (1947).

[18] J. M. Miller, J. W. Gryder and R. W. Dodson, *J. Chem. Phys.*, **18**, 579 (1950).

[19] P. C. Capron and Y. Oshima, *ibid.*, **20**, 1403 (1952).

[20] L. Friedman and W. F. Libby, *ibid.*, **17**, 647 (1949).

[21] J. M. Miller and R. W. Dodson, *ibid.*, **18**, 865 (1950).

[22] A. P. Wolf and R. C. Anderson, THIS JOURNAL, **77**, 1608 (1955), have demonstrated the substitution of C^{14} for N^{14} in the neutron activation of nitrogen heterocycles. A yield of 0.2% of anthracene-9-C^{14} and 3.5% of acridines was observed for irradiated acridine. These yields are quite significant when it is remembered that two bonds to specific carbon atoms have to be re-established. Presumably such a substitution can happen only in a billiard-ball process. It would be interesting to have comparative data on such reactions for the liquid as well as the solid phase.

As the energy of the activated atom approaches thermal energies, the collisions become more inelastic in character[23] and result in epithermal reactions which form a variety of products which cannot be produced directly in the billiard-ball mechanism.

At energies not far above thermal, the recoil atom can effect various reactions, analogous to the hot reactions observed in photochemical systems.[24] Abstraction reactions of moderate activation energy such as

$$\mathrm{I}\cdot + \mathrm{CH_3{-}CH_2I} \longrightarrow \mathrm{CH_3I} + \cdot\mathrm{CH_2I} \qquad (2)$$

and

$$\mathrm{I}\cdot + \mathrm{I{-}CH_2CH_3} \longrightarrow \mathrm{I_2} + \mathrm{CH_3CH_2}\cdot \qquad (3)$$

are examples of this. The products observed from this type of reaction might be expected, at least as a first approximation, to be formed in a random statistical fashion.

The iodine atom, immediately after it has been fully thermalized, will begin diffusing through a medium in which there is initially an extremely high concentration of radicals which it itself has produced. It will have a high probability of reacting with these radicals to form both organic and inorganic ($\mathrm{I_2}$) activity. Such reactions, although involving thermal atoms, will be peculiar to the nuclear process; *i.e.*, because the reactants are inhomogeneously distributed throughout the system, the reactions will not be subject to ordinary scavenging effects. In general the radicals produced along the track might be expected to resemble those observed in the radiation chemistry of the same system.[25] One would expect a relatively high yield of products which can be formed by low energy modes of radical decomposition.

Finally, after the unreacted iodine atoms have been thermalized and have diffused out of the zone of high radical concentration, they will be fixed as inorganic activity by exchange with the free iodine unavoidably present in the medium.

Inorganic activity will be formed by reactions of epithermal atoms with solvent molecules (such as 3), by reactions of the active atoms with iodine in the recoil track, and by atoms which have been thermalized without undergoing reaction.[26] Organic activity will be formed by billiard-ball processes (probably to a rather small extent), by reactions of epithermal atoms, and by thermalized atoms with radicals produced in their immediate vicinity. Although it is clearly difficult to distinguish between products formed in epithermal processes and those which result from random-fragmentation of the medium, details such as the relatively high methyl iodide yield from *n*-propyl iodide give considerable weight to the importance of the latter mechanism.

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(23) The time required for a 10 e.v. iodine atom to pass through a butyl iodide molecule is of the order of 10^{-13} seconds. Time is available, therefore, for considerable vibrational energy to be transferred.

(24) W. H. Hamill, R. R. Williams, H. A. Schwarz and E. E. Voiland, Document AECU-1321, Technical Information Service, Oak Ridge, Tenn.

(25) Actually the energy loss processes are extremely different being due to ionization in the radiation chemical case and to knock-on effects in the recoil cases.

(26) By using dibromoethylene to scavenge thermal bromine atoms, it has been shown (ref. 15; R. R. Williams, Jr., W. H. Hamill, H. A. Schwarz, and E. J. Burrell, THIS JOURNAL, **74**, 5737 (1952)) in studies of (n,γ) activation of ethyl bromide that the inorganic bromine is produced both by thermal and hot processes.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Oxygen Isotope Effects at Anodes

BY MICHAEL ANBAR AND HENRY TAUBE

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The isotope fractionation factor for $\mathrm{O_2}$ liberated from water at an anode shows considerable variation with the nature of the electrode material, but is independent, at least over a limited range, of the current density. Mechanisms of the reaction are discussed. Tracer experiments using $\mathrm{PbO_2}$ and $\mathrm{MnO_2}$ as electrode material showed that none of the anode oxygen appears as $\mathrm{O_2}$. They showed also that rapid exchange of the oxide electrode with water is induced when the material functions as an anode.

A study of oxygen isotope fractionation effects on the electrolysis of water would appear to have significance in relation to theories of the mechanism of oxygen evolution, quite apart from the usefulness the effects might have in separation of isotopes. Nevertheless a systematic exploration of the isotope fractionation effects seems not to have been reported in the literature. Individual values have been cited,[1] but the agreement among various authors is unsatisfactory, and certain of the values, in the light of experience subsequent to the early work, appear to be unreasonably high. We are reporting the results of an investigation in which attention was paid to the influence of the nature of electrode material, temperature and of certain other parameters, on the magnitude of the isotope fractionation, as well as the results of some tracer experiments using metal oxide anodes.

Procedure.—The solutions described in Table I as "acid" or "basic" contained 0.1 M $\mathrm{HClO_4}$ or 0.1 M NaOH. The metal impurity content of the sample of Ni, Fe, Pd and Co used[2] did not exceed

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(1) The bibliography provided by L. Tronstad and J. Brun, *Trans. Faraday Soc.*, **34**, 766 (1938) is complete and still up to date.

(2) We are grateful to Prof. N. Nachtrieb for making certain of the electrode materials available to us.