periments reported here establish the existence of reactions 1 to 5 without identifying the charge of the tritium atom at the time of reaction.

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The Effect of Bromine Scavenger on the Yields of Individual Organic Products of the $Br^{81}(n,\gamma)Br^{82}$ Process in Propyl Bromides

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The yields of eleven organic products of the $Br^{81}(n,\gamma)Br^{82}$ process in *n*-propyl bromide and in isopropyl bromide have been determined with and without 5×10^{-2} mole fraction of Br_2 present for the purpose of distinguishing the re-entry into organic combination which occurs by "hot" processes from that which results from "thermal" processes. The dibromopropanes and hexyl bromide are formed almost exclusively by hot processes. The parent propyl bromide is formed about equally by the two types and the other products involve the two in varying proportions. The ratios of products show correlation with the structure of the parent propyl bromide. The effect of increasing bromine concentration in decreasing the organic yields in the propyl bromides is the same for activation by each of the three processes, $Br^{79}(n,\gamma)Br^{80m}$, $Br^{79}(n,\gamma)Br^{80}$ and $Br^{80m} \xrightarrow{I.T.} Br^{80}$, indicating that in each case the same fraction of the new born energetic atoms enter stable organic combination before diffusing as thermal atoms.

Introduction

It is now well established[1,2] that when halogen atoms are activated by nuclear processes (such as (n,γ) $(n,2n)$ (n,p) and (I.T.)) in an organic medium, they can enter organic combination as a variety of products. Some of the tagged atoms enter organic combination as a result of "hot" processes (*i.e.*, before the activated atom has had opportunity to diffuse as a thermal atom) and some by thermal processes dependent on a thermalized atom encountering, by diffusion, a free radical which it formed while losing its energy.[1c,1g,2] The primary purpose of the present investigation has been to determine the separate contribution of hot and thermal processes to the formation of each of eleven organic products of the $Br^{81}(n,\gamma)Br^{82}$ process in the propyl bromides by determining the yields of these products with and without bromine scavenger added to eliminate the thermal processes. This information is needed for further clarification of existing theories[2] of such reactions. Another part of the investigation has been the determination of whether the ratio of hot to thermal processes is the same for activation of bromine in the propyl bromides by the three different processes: $Br^{79}(n,\gamma)Br^{80m}$, $Br^{79}(n,\gamma)Br^{80}$, and $Br^{80m} \xrightarrow{I.T.} Br^{80}$.

Experimental[3]

Materials.—Eastman Kodak white label organic chemicals were used throughout this work. The normal and isopropyl bromides were purified by bubbling a stream of oxygen containing 5% of ozone through them for one hour, followed by shaking with dilute hydrogen peroxide solution, neutralizing with sodium carbonate solution, washing with distilled water, and drying. They were then stirred vigorously with 95% sulfuric acid, the colored acid being replaced by fresh acid at half-day intervals until the fresh acid was not colored after 12 hours of stirring. After separation, the propyl bromide was neutralized, washed, dried over anhydrous magnesium sulfate and fractionated through a 12″ Vigreux column. A 75% center cut of the distillate with a boiling point range of less than ±0.2° was collected and stored in darkness. The chemicals used only as carriers were not subjected to any purification procedure.

Neutron Irradiation.—Samples of the propyl bromides to be used for carrier fractionation of the products of the (n,γ) reaction were irradiated in the CP3′ reactor of the Argonne National Laboratory for 15 minutes at a flux of 10^{10} neutrons cm.$^{-2}$ sec.$^{-1}$ and a radiation dose, as determined by ferrous sulfate dosimetry, of less than 5×10^4 roentgens. During irradiation they were sealed in blackened quartz ampoules. These contained 40 cm. pressure of oxygen to ensure against an increase in organic yield resulting from products of radiation damage.[4]

Neutron irradiations for the purpose of determining the effect of varied scavenger concentrations on the gross organic yield were made with a 10 curie Sb–Be photoneutron source.

Separation of the Radioactive Organic Products of the (n,γ) Reaction.—Following neutron irradiation, each 80-ml. sample of propyl bromide was washed with an aqueous

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[1] (a) E. Glueckauf and J. W. J. Fay, *J. Chem. Soc.*, 390 (1936); (b) E. G. Bohlmann and J. E. Willard, THIS JOURNAL, **64**, 1342 (1942); (c) S. Goldhaber, R. S. H. Chiang and J. E. Willard, *ibid.*, **73**, 2271 (1951); (d) J. F. Hornig and J. E. Willard, *ibid.*, **75**, 461 (1953); (e) M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952); (f) F. S. Rowland and W. F. Libby, *ibid.*, **21**, 1495 (1953); (g) G. Levey and J. E. Willard, THIS JOURNAL, **74**, 6161 (1952); (h) C. E. McCauley, G. J. Hilsdorf, P. R. Geissler and R. H. Schuler, *ibid.*, **78**, 3246 (1956); (i) R. H. Schuler and C. E. McCauley, *ibid.*, **79**, 821 (1957); (j) G. Levey and J. E. Willard, *ibid.*, **78**, 2351 (1956); (k) J. B. Evans and J. E. Willard, *ibid.*, **78**, 2908 (1956); (m) J. B. Evans, J. E. Quinlan and J. E. Willard, Abstracts of the 130th meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1956, page 27R; (n) A. A. Gordus and J. E. Willard, THIS JOURNAL, **79**, 4609 (1957); (o) M. Milman and P. F. D. Shaw; and M. Milman, P. F. D. Shaw and I. B. Simpson, *J. Chem. Soc.*, 1303 (1957).

[2] For reviews of the literature on chemical effects of nuclear transformations see: (a) J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953); (b) *Ann. Rev. Phys. Chem.*, **6**, 141 (1955).

[3] Further details of this work are given in the Ph.D. thesis of J. C. W. Chien filed with the University of Wisconsin Library in 1954.

[4] The organic yield of the $Br^{81}(n,\gamma)Br^{82}$ reaction in *n*-propyl bromide is higher than the normal value when degassed samples are exposed to more than about 2×10^4 r. at a flux of 1.6×10^5 r./hr.[5] In the present work 40 cm. of oxygen was found to maintain the normal organic yield during a neutron irradiation at a gamma flux of 2×10^5 r./hr. for a half hour.

[5] J. C. W. Chien and J. E. Willard, THIS JOURNAL, **77**, 3441 (1955).

solution of sodium sulfite and sodium bromide and placed in a 500-ml. distillation flask with ethyl bromide carrier. Forty ml. of liquid methyl bromide was then added on a vacuum line by condensation with the aid of liquid air, following which the mixture was melted and the flask was connected to a distillation assembly where successive fractions of the methyl bromide distillate (b.p. 3.86°) were condensed, as described below, and counted. The other carriers were then added. Ethyl, isopropyl and *n*-propyl bromides were fractionated under atmospheric pressure. Methylene and ethylene bromides and 1,2-dibromopropane were fractionated at 10 cm. pressure; *n*-hexyl bromide, 1,3-dibromopropane and 1,1,2-tribromoethane were fractionated at 5 cm. pressure.

The vapor pressure temperature data needed to fractionate organic bromides at reduced pressures were determined by measuring the boiling points of the compounds at five or six different pressures. The data are given in Table I in terms of the equation $\log p_{mm} = -A/T + B$ where p_{mm} is the vapor pressure in mm. of mercury, A and B are constants and T is the absolute temperature.

TABLE I

CONSTANTS FOR THE VAPOR PRESSURE–TEMPERATURE EQUATION

Compounds	$A \times 10^{-3}$	B
Methylene bromide	1.753	6.614
n-Butyl bromide	1.786	6.686
Ethylene bromide	1.825	6.381
1,2-Dibromopropane	1.884	6.482
n-Hexyl bromide	1.973	6.485
1,3-Dibromopropane	2.056	6.528
1,1,2-Tribromoethane	2.222	6.719

Fractionation and Counting Equipment.—A 3 foot long 15 mm. o.d. column packed with glass helices and provided with a heating jacket was used for the fractionation.[6] A take-off rate of 10–20 ml./hr. and a reflux ratio of about 1:20 were used. A mercury float type regulator maintained a constant pressure ± 1 mm. at all pressures from 30 to 760 mm. The stainless steel plate for supporting the helices in the column was replaced by an all-glass support to avoid catalyzed decomposition of the high boiling organic bromides during distillation.

The distillate from the fractionation column passed through a spiral of 3.5 mm. o.d. glass tubing with a volume of 4 ml. which surrounded an Amperex 90-NB metal wall Geiger tube, shielded from the column and receiving pot by 4″ of lead. The distillate completely filled the spiral at all times. The output of the Geiger tube fed through a count rate meter to a two point chart recorder which also recorded the temperature measured by thermocouples in the still head of the distillation column.

In order to maintain the counting spiral and tube below the boiling point of CH_3Br (3.86°) during the distillation they were surrounded by a two walled glass jacket with evacuated annulus and were cooled to −10° or below with the vapor from boiling liquid air.

Since the walls of the counting spiral completely absorbed all of the Br^{82} β-particles, counting was dependent only on the γ-radiation and the counting efficiency was independent of the density of the carrier.

Determination of Organic Yields.—A small aliquot from each irradiated sample to be used for the fractionation experiments was used to determine the total organic yield by counting the aqueous ($SO_3^=$,Br^-) extract, and the organic layer, in a solution type Geiger counter. The yields of the individual organic products were determined from the deflection each produced on the radioactivity plot on the chart recorder when the spiral was full of a representative portion of the distillate. In general this plot gave a level plateau for each component suggesting that a pure fraction of constant specific activity was being measured. The relation between recorder deflection and percentage yield was determined from the deflection produced when the counting spiral was filled with the aqueous extract. Appropriate volume and decay corrections were made.

The organic yields of the (n,γ) process in tests of the effects of varied scavenger concentrations were obtained by methods described previously.[5,7]

The yields of the isomeric transition process in propyl bromides were determined by two methods. In the first, neutron irradiated propyl bromide was extracted free of inorganic activity, dried and allowed to stand in the dark for three hours, following which the inorganic activity was again extracted and counted immediately for comparison with the total activity. In the second method Br_2, containing Br^{80m}, was added to propyl bromide in an amount corresponding to the scavenger concentration desired and allowed to stand in the dark for three hours. The organic yield was calculated from counts made on the organic layer immediately after extraction and the aqueous layer after three hours of standing.

Results

Scavenger Effect on the Yields of the $Br^{79}(n,\gamma)Br^{80}$, $Br^{79}(n,\gamma)Br^{80m}$ and Isomeric Transition Processes.—From Fig. 1 it may be seen that within experimental error the organic yields of Br^{80} and Br^{80m} activated by radiative neutron capture and of Br^{80} activated by the isomeric transition process in normal propyl bromide are equivalent to each other and are reduced to the same extent by added Br_2 at all mole fractions from 10^{-5} to 10^{-1}. The same is true for isopropyl bromide which has a lower organic yield and lower scavenger effect.

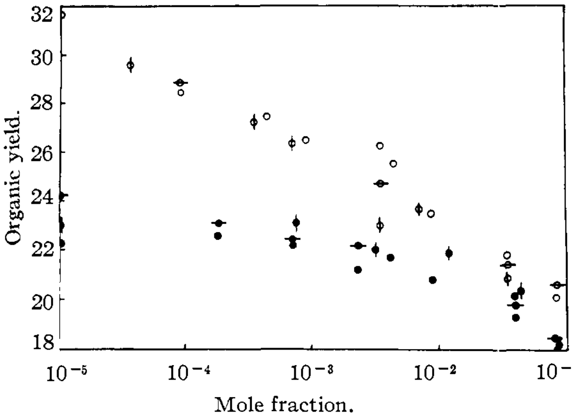

Fig. 1.—Scavenger effect on the yields of the $Br^{79}(n,\gamma)Br^{80}$, $Br^{79}(n,\gamma)Br^{80m}$ and isomeric transition processes. Open circles, *n*-propyl bromide; solid circles, isopropyl bromide; ○ and ●, $Br^{79}(n,\gamma)Br^{80}$; -⊖- and -●- $Br^{79}(n,\gamma)Br^{80m}$; ⦶ and ●, isomeric transition.

These data seem to indicate that the fraction of the activated atoms which enters organic combination by hot processes and the fraction which enters after diffusion as thermal atoms is the same for each of the three methods of activation. The data add still another type of evidence to the now extensive array[1f,1h,1i,1j,1k,1o,7] in support of the conclusion that the chemical fate of halogen atoms activated by nuclear processes in pure condensed liquid alkyl halides is remarkably independent of the type of process (*i.e.*, is insensitive to wide variations in the magnitude of the initial recoil energy and charge), although experiments have been reported which appear to give contrary results.[8] For recoil atoms with much higher energies than those used here

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(6) "Todd Precision Fractionation Assembly," Todd Scientific Co., Springfield, Pa.

(7) J. C. W. Chien and J. E. Willard, THIS JOURNAL, **76**, 4735 (1954).

(8) D. J. Apers and P. C. Capron, *J. Inorg. Nucl. Chem.*, **2**, 219 (1956).

TABLE II

EFFECT OF BROMINE SCAVENGER ON THE PRODUCTS FROM ACTIVATION OF THE PROPYL BROMIDES BY THE $Br^{81}(n,\gamma)Br^{82}$ PROCESS

Product	Yield, % of total induced activity											
	n-Propyl bromide						Isopropyl bromide				Degassed *n*-propyl bromide[c]	
	No Br_2 added			Br_2 added[a,b]			No Br_2 added		Br_2 added[a,b]		No Br_2 added	Br_2 added[b]
	Fox and Libby (1)[d]	Present work[a] (2)	(3)	(4)	(5)	(6)	Fox and Libby (7)[d]	Present work (8)	(9)	(10)	(11)	(12)
CH_3Br		2.01	2.05	1.29	1.19	1.28		2.76	1.24	1.30		
C_2H_5Br	0.7	0.50	0.52	0.31	0.29	0.32	0.7	0.14	0.05	0.14	0.64	0.21
i-C_3H_7Br	1.7	1.87	1.94	0.68	0.80	0.71	9.3	10.06	5.77	5.37	2.15	0.7
n-C_3H_7Br	17.1	18.0	17.9	7.42	7.96	7.58	2.5	1.03	0.66	0.66	14.3	7.93
CH_2Br_2	1.8	1.27	1.31	0.90	0.99	1.07		0.63	0.54	0.56	1.51	1.80
"$C_2H_4Br_2$"[e]	3.1	1.68	1.61	1.39	1.36	1.41	5 4	2.52	0.23	0.27	23.9	14.3
1,2-$C_3H_6Br_2$	2.8	2.35	2.50	2.30	2.28	2.21	2.3	4.14	3.66	3.89		
n-$C_6H_{13}Br$			0.31		0.31			0.21	0.20	0.17		
1,3-$C_3H_6Br_2$	2.7	2.35	2.44	2.32	2.17	2.19	0.8	0.10	0.8	0.9	2.38	1.88
1,1,2-$C_2H_3Br_3$		0.28	0.27	1.05	0.89	0.88		0.12	1.03	0.91	0.22	0.91
Higher boiling	1.5	1.05	1.16	3.27	3.45	3.40	2.9	0.81	3.66	3.32		
Total org. yield	34.7	32.4	32.0	20.9	20.9	21.1	31.7	23.6	17.1	16.7	53.5	29.2

[a] Each of the columns gives the results of a separate irradiation and fractionation. [b] 5×10^{-2} mole fraction. [c] These degassed samples were irradiated at a flux of 10^{10} n cm.$^{-2}$ sec.$^{-1}$ for 30 min. and received a γ-radiation dose of about 10^5 roentgens while the samples in the columns to the left were irradiated half as long and under a pressure of 40 cm. of O_2. [d] Results of Fox and Libby.[1e] [e] This fraction may have included 1,1-dibromopropane; see text.

(*i.e.*, from the (n,2n) process) there is evidence of some increase in organic yield in selected chemical environments.[1i,9]

Relative Contributions of Hot and Thermal Processes to the Formation of Different Products.—Experimentally determined yields of Br^{82}, from the $Br^{81}(n,\gamma)Br^{82}$ process, in each of eleven products from each of the propyl bromides are given in Table II, and the ratios of the yields with scavenger to those without are shown in Table III. The concentration of scavenger used was sufficient to guarantee that only those tagged atoms which took part in hot replacement reactions, or which combined with a radical before diffusing more than a very few molecular diameters from the spot where the radical was formed, could appear in organic combination.

TABLE III

RATIO OF ORGANIC YIELDS OF Br^{82} IN PROPYL BROMIDES WITH AND WITHOUT 5×10^{-2} MOLE FRACTION Br_2 PRESENT

Product	Ratio in *n*-propyl bromide	Ratio in isopropyl bromide
Methyl bromide	0.61	0.46
Ethyl bromide	.60	
i-Propyl bromide	.38	.55
n-Propyl bromide	.42	.64
Methylene bromide	.77	.90
Ethylene bromide	.85	.10
1,2-Dibromopropane	.93	.93
n-Hexyl bromide	1.0	.85
1,3-Dibromopropane	0.93	.85
1,1,2-Tribromoethane	3.4	8.1
Higher boiling	3.1	4.3

The compounds formed may be divided into three classes with respect to the effect of scavenger on the yield: (1) those for which the yield is raised three fold or more, *i.e.*, 1,1,2-tribromoethane and higher boiling compounds[10]; (2) those for which the yield is reduced by 15% or less, *i.e.*, 1,3-dibromopropane, 1,2-dibromopropane, *n*-hexyl bromide, ethylene bromide (from *n*-propyl bromide) and methylene bromide (from isopropyl bromide); (3) those for which the yield is reduced by 35% or more, *i.e.*, *n*-propyl bromide, isopropyl bromide, ethyl bromide, methyl bromide and ethylene bromide (from isopropyl bromide).

This division indicates that in general those compounds which may result from the reaction of a thermalized Br^{82} atom with a radical formed by the breaking of a C–Br or C–C bond are more susceptible to reduction in yield by scavengers than those which involve the breaking of C–H bonds. From the low scavenger effect on the latter it may be inferred that they are formed by a one step replacement reaction,[1m,11] or by combination with a radical immediately after thermalization, rather than by reaction of the radioactive species after it has diffused away from the site of formation. The ability of iodine,[11,12] bromine[1n] and chlorine[1m,13] to undergo non-radical one step bimolecular hydrogen replacement reactions when activated by radiative neutron capture has been clearly demonstrated by the results of the neutron irradiation of gaseous mixtures of halogens with hydrocarbons. Similar replacement reactions have been observed for tritium activated by the $He^3(n,p)H^3$ process[14] in gaseous alkanes, and the probability that ion-molecule reaction steps may be involved in these and similar reactions has been discussed.[1n,12,14,15]

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(9) R. H. Schuler and C. E. McCauley, *J. Chem. Phys.* **25**, 1080 (1956).

(10) The higher boiling compounds are the mixture which remained in the still pot at the end of distillation. By means of gas chromatography,[1k] using a scintillation counter as the detector for the trace amounts of radioactive compounds, James B. Evans of our laboratory has now observed peaks for at least six compounds which come off a silicone oil-firebrick column at higher temperatures than 1,1,2-tribromoethane (b.p. 187°).

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

(12) G. Levey and J. E. Willard, *ibid.*, **25**, 904 (1956).

(13) J. C. W. Chien and J. E. Willard, THIS JOURNAL, **75**, 6160 (1953).

(14) (a) A. A. Gordus, M. C. Sauer, Jr., and J. E. Willard, *ibid.*, **79**, in press (1957); (b) R. Wolfgang, *ibid.*, **79**, 3284 (1957).

(15) S. Aditya and J. E. Willard, *ibid.*, **79**, 3367 (1957).

The large increases in the yields of 1,1,2-tribromoethane and of the high boiling fraction caused by the presence of 5 mole % bromine during neutron irradiation may be due to the fairly high probability of a bromine molecule being present at the site where the Br^{82} enters combination by a hot process and to the possibility of the Br_2 becoming involved in this process with consequent formation of a polybrominated product. Alternatively, it may be the result of reaction of bromine with bromo-olefins containing Br^{82}. In this work no carriers for the bromo-olefins were added and since some of these have boiling points close to carriers which were used (*e.g.*, allyl bromide boils at 71.3° and *n*-propyl bromide at 70.9°) they might not have been distinguished.

Fox and Libby[1e] have determined the Br^{82} yield for five organic products from the (n,γ) activation of solid *n*-propyl bromide at liquid air temperatures. The ratio of the solid phase to liquid phase yield varies greatly from product to product. This ratio is highest for products which are formed by hydrogen replacement (3 for $C_2H_4Br_2$, using our value for the liquid phase yield; 4.0 for 1,2-$C_3H_6Br_2$; 3.1 for 1,3-$C_3H_6Br_2$). These are the same products which show little or no scavenger effect in the liquid phase (Table III), *i.e.*, are produced almost entirely by hot reactions rather than by Br^{82} atoms which have diffused in thermal equilibrium with the medium.

Other Structural Correlations.—It is interesting to note in Table II that the yields of 1,2- and 1,3-dibromopropane from *n*-propyl bromide are equal whereas the yield of the 1,2-isomer from isopropyl is 40 times that of the 1,3. This is consistent with the fact that it is not possible to form the latter by simple hydrogen substitution.

The formation of *n*-hexyl bromide involves the rupture of two C–Br bonds, on adjacent molecules, and of a C–H bond. As might be expected its yield is low and insensitive to scavenger. Its formation is analogous to that of $C_2H_5I^{128}$ by the $I^{127}(n,\gamma)I^{128}$ activation of iodine in liquid methane[11] and of $C_2Cl_5Cl^{38}$ following the $Cl^{37}(n,\gamma)Cl^{38}$ process in CCl_4.[1m]

Effects of High γ-Dosage.—When degassed samples of *n*-propyl bromide were irradiated in the CP3′ reactor long enough to receive a γ-dosage of about 10^5 r. the organic yields increased, consistent with earlier observations.[4] Carrier fractionations showed that the increase was nearly all due to a species which distilled with the ethylene bromide carrier (column 11, Table II). This suggested that the main radiolysis product of *n*-propyl bromide was ethylene which reacted with Br^{82} or $BrBr^{82}$ formed as a result of the (n,γ) process. This is not an acceptable explanation, however, since the presence of 5×10^{-2} mole fraction of Br_2 during irradiation (column 12, Table II) did not reduce the yield of Br^{82} as "$C_2H_4Br_2$" to its normal value. In order for addition of Br_2 to an olefin to account for the 14% yield as "$C_2H_4Br_2$," some 20% of the Br_2 would have had to react in this way. In order to produce enough olefin to give this result the *G* value for its formation in the radiolysis of *n*-propyl bromide would have to be of the order of 10^3, which is inconceivably high. The conclusion that the reaction of $BrBr^{82}$ with ethylene cannot account for the increased yield is further substantiated by the fact observed by R. J. Neddenriep in our laboratory that when radiobromine is present in *n*-propyl bromide undergoing radiolysis the chief radioactive organic product formed is a dibromopropane.

Additional evidence indicates that the "$C_2H_4Br_2$" of Table II may be in part a dibromopropane. In analyses by gas chromatography of neutron-irradiated *n*-propyl bromide containing 5 mole % bromine the organic yield of ethylene bromide (b.p. 132°) has been found by J. B. Evans[1k,10] to be 0.21, in contrast to the values of 1.39 found in the present work. An adjacent peak for a component with a yield of about 1.2% appears on the chromatogram. This is tentatively assigned to 1,1-dibromopropane (b.p. *ca.* 135°), for which no carrier was added in our distillation and which probably would not have been separated from ethylene bromide.

It is not difficult to rationalize[4] the observation that high levels of γ-radiation in the absence of oxygen lead to an increase in the organic yield of pure degassed propyl bromide, as indicated by column 11 of Table II. One would predict, however, that the presence of 5 mole % of bromine (column 12) would negate all such effects and return the organic yield to the typical scavenged value of about 21% (columns 4–6) observed in the absence of radiation effects. The added bromine would be expected to remove the small amounts of reactive impurities and radicals produced by the radiation which might otherwise react with the trace amounts of Br^{82}, HBr^{82} and $BrBr^{82}$ produced as a result of the (n,γ) process. Thermalized Br^{82} and HBr^{82} would be expected to exchange with the added bromine before having opportunity to undergo any other reaction.

The properties required of the "olefin impurity" produced by radiation if it is to account for the substantially increased yield caused by the radiation in the presence of bromine are: (1) it must not be rapidly removed by Br_2. (2) Br^{82} atoms or HBr^{82} must have a much higher rate constant for reaction with it than for exchange with Br_2. (3) dissolved oxygen at a concentration of 10^{-3}–10^{-2} molar must be much more effective in reducing the formation of this species during radiolysis than is 5 mole % Br_2. These properties are similar to those which seem to be required of the impurities which are responsible for the fact that scavengers do not reduce the organic yield of unpurified *n*-propyl bromide to the value obtained for the purified compound.[7,16] They are sufficiently improbable to suggest that some radically new concept is needed to explain correctly the observations.

Other differences between the yields of samples receiving high radiation dosage in the absence of oxygen and normal samples are the apparent decrease in the yield of *n*-propyl bromide without scavenger and the increase of that of methylene bromide with scavenger. The explanation for these is not obvious.

[16] P. C. Capron and E. Crevecoeur, *J. Chem. Phys.*, **21**, 1843 (1953).

Comparison with Previous Work.—Comparison of the yields from *n*-propyl bromide given in columns 2 and 3 of Table II, with those of Fox and Libby[1e] given in column 1 shows excellent agreement in most cases except that of ethylene bromide. The relatively high value observed for this compound by the previous workers may have been the result of a small radiation effect of the type illustrated in column 11 and discussed above. Less satisfactory agreement is observed for isopropyl bromide (columns 7 and 8). In particular we have observed, as previously noted,[1j] that the organic yield of Br^{82} from pure isopropyl bromide is about 23% rather than 32%.[1e] Our initial determinations gave values of 32% but after further experience with the purification procedures the lower values have been obtained regularly. Schuler and McCauley[11] likewise obtain 23%. As they point out, the difference between *n*-propyl bromide and isopropyl bromide is similar to that observed for the corresponding iodides.[1g]

McCauley, Hilsdorf, Geissler and Schuler[1h] have compared the yields of five products from the (n,2n) activation of iodine in *n*-propyl iodide with the analogous products of (n,γ) activation of *n*-propyl bromide as reported by Fox and Libby. In both cases the yield in the form of the parent material is much larger than any other, but it is much higher in the case of the iodide than the bromide. This may be due to the fact that bromine atoms can react with the medium to form HBr with an activation energy of only about 10 kcal./mole whereas such reaction is negligibly small in the case of iodine atoms, and hence they have a greater opportunity of encountering thermalized radicals and entering organic combination. A further similarity between the iodide work and the bromide work is that the organic yield is increased by high radiation doses in the absence of oxygen.[1h,7] By contrast with the *n*-propyl bromide results, where the increase appears in the $C_2H_4Br_2$ fraction (column 11, Table II), the increase appears as *n*-propyl iodide in irradiations of the latter, and is reduced to its normal value by a concentration of iodine scavenger as low as 0.04 *M*.

Whereas it has been suggested[1h] that in the case of the iodides there is no essential difference in the mode of formation of products in the hot and thermal regions, as differentiated by the scavenger technique, it is clear that there is a difference in the case of products resulting by hydrogen substitution by Br^{82} in the propyl bromides, as discussed in this paper, and by hydrogen substitution by other halogens in other media.[1n,11-13] If, as seems probable, the hot reactions are in part non-radical replacement reactions such differences would be expected. It seems probable that these replacement reactions may be of both the ion–molecule and neutral atom types.

As this manuscript was being completed we have had opportunity to read relevant papers of Milman and Shaw, and Milman, Shaw and Simpson[10] on the effect of added bromine on the relative yields of tagged products from the (n,γ) activation of bromine in C_2H_5Br and $C_2H_4Br_2$.

They have centered attention on the fact that the major portion of the thermal yield is due to the parent compound, which is likewise the case for the propyl bromides discussed above and for iodides.[1h] Their data seem to indicate that the yields of the minor products are, as in the case of the propyl bromides, subject to the influence of bromine scavenger to varying degrees. Excellent earlier evidence that competitive thermal radical reactions are involved in the formation of such polysubstituted minor components has been found in the study of the products of the (n,γ) activation of Br_2 in CCl_4 as a function of bromine concentration.[1d]

Milman and Shaw have suggested the hypothesis that the hot yield of the parent molecule resulting from (n,γ) activation of the alkyl halides should increase with increasing ratio of halogen atoms to other atoms in the organic compound. They find a slight trend in the predicted direction in comparing C_2H_5Br and $C_2H_4Br_2$. It is interesting in this connection to note that the total hot yields in dilute solutions of alkyl halides in hydrocarbons are higher than for the pure alkyl halides, but that they increase with increasing molecular weight of the hydrocarbon.[15] Identification of the individual products in the latter systems would be helpful in considering this problem further.

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