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

Effect of Bromine Concentration on the Products of the Reactions of Carbon Tetrachloride with Bromine Activated by Radiative Neutron Capture and by Isomeric Transition[1]

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The yields of radioactive CCl_3Br, CCl_2Br_2 and higher boiling compounds resulting from radiative neutron capture and isomeric transition of bromine dissolved in CCl_4 have been studied as a function of bromine concentration. The total organic yield[2] from each mode of activation decreases very rapidly from about 35% at 0.01 mole % bromine to about 20% at 15 mole % bromine. This decrease in organic yield is primarily at the expense of the CCl_3Br product. In the same concentration range the yield of CCl_2Br_2 increases, while the yield of higher boiling activity decreases. After 15 mole % of bromine has been added the total and individual yields of organic products decrease almost linearly to zero at 100% bromine. The relative yield of the various organic products is, within experimental error, independent of whether the initial activation was by radiative neutron capture or isomeric transition. The total organic yield is slightly higher for the isomeric transition. At high bromine concentrations part of the radioactive bromine formed by both isomeric transition and radiative neutron capture enters combination as CBr_4.

Introduction

It has been shown[3-5] that bromine activated by nuclear isomeric transition or by radiative neutron capture is able to react with liquid carbon tetrachloride to form CCl_3Br, CCl_2Br_2 and higher boiling bromides. Negligible organic combination occurs in the gas phase, however. Both the complexity of the products and the absence of reactions in the gaseous state indicate that the organic bromides are not formed by a simple inversion type of mechanism between a bromine atom and a carbon tetrachloride molecule. They must result from the fact that the high energy imparted to the bromine atom by the nuclear event is dissipated by a more or less random breaking of bonds in the molecules in the immediate vicinity. The fragments so formed may then combine with each other and with the tagged halogen atom in a variety[6] of ways to form the different compounds observed.

It has been the purpose of the work of this paper to obtain a more detailed knowledge of the fragments formed and the competing reactions which they may undergo by studying the effect of changes in the bromine concentration on the relative yields of the products.

Experimental

Sources of Radioactivity.—Most of the (n,γ) experiments were carried out using an antimony–beryllium photoneutron source of about two curies, giving a total of about 6×10^6 neutrons per second. For experiments at very high and very low bromine concentrations samples were sealed in quartz tubes and irradiated in the CP-3′ heavy water pile at the Argonne National Laboratory. The latter reactions were traced by counting the Br^{82} (35.9 hr.) activity, while for those conducted with the antimony–beryllium source the Br^{80} (4.4 hr.) activity was used.

Br^{80} (4.4 hr.) for the isomeric transition experiments was obtained by irradiating quartz tubes of bromine in the Argonne pile for four hours.

Reagents and Purification.—Mallinckrodt Research Grade bromine and Low Sulfur carbon tetrachloride, Michigan Chemical Co. bromotrichloromethane and dibromodichloromethane, Dow Chemical Co. tribromochloromethane, and Eastman Kodak Co. carbon tetrabromide were used.

The bromotrichloromethane and dibromodichloromethane were used only as carriers in distillations, and hence were adequately purified by a single distillation through a 12″-Vigreux column to remove most of the 0.1% of phenyl glycidal ether added as an antioxidant by the manufacturer. The tribromochloromethane and carbon tetrabromide were used directly.

Experiments in which the carbon tetrachloride was allowed to stand in contact with bromine containing Br^{82} (35.9 hr.) as tracer showed that the carbon tetrachloride was capable of reacting with about 10^{-5} mole of bromine per liter. To render this impurity incapable of reacting with bromine, the CCl_4 was saturated with chlorine and chlorine dioxide and illuminated about 48 hours with a 1000-watt Mazda lamp. Just before use the chlorine and chlorine dioxide were removed by extracting twice with sodium sulfite solution and by several rinses with water, using an ungreased separatory funnel. The preparation was completed by drying with P_2O_5 and two fractional distillations through a 12″-Vigreux column.

Carbon tetrachloride so prepared still appeared to react with about 10^{-6} mole of bromine per liter, but gave the same experimental results in (n,γ) experiments as the untreated reagent. In the isomeric transition experiments, however, the impurity caused difficulty. The only activity to be expected in organic combination as a result of isomeric transition would be Br^{80} (18 min.). Any purely chemical bromination of the medium, however, would also introduce the 4.4- and 35.9-hr. species into organic form. Since bromine having a rather high specific activity of all three species necessarily was used to compensate for the decay of the 18-minute species during fractionation, the traces of bromine entering combination by ordinary chemical reactions caused an undesirably high long-lived background.

Two further precautions were taken to avoid this difficulty. Inactive bromine was added to the CCl_4 about 24 hours before the experiment, then a small amount of the high specific activity bromine was added at the time of the experiment. This procedure reduced but did not eliminate the difficulty, so it appeared that perhaps an organic bromide was being introduced as an impurity in the bromine. This impurity might exchange with the radioactive inorganic bromine in the system and then be extracted into the organic layer. To check this, the bromine used was generated from NaBr, $NaBrO_3$ and H_3PO_4, rather than being introduced as the liquid. With this combined treatment the long-lived activity appearing in organic form corresponded to about 10^{-7} mole of bromine per liter, which was sufficiently low for the purpose of the experiment.

(n,γ) Experiments.—The solutions of bromine in CCl_4 were placed in the annular space of a soft glass dewar flask of a size such as to accommodate the antimony–beryllium source in the central tube. Water in the central tube and surrounding the flask was used as a moderator. After irradiation, the bromine was extracted with NaOH or Na_2SO_3 solutions about 0.05 molar in NaBr. Ten milliliters each of bromotrichloromethane and dibromodichlorometh-

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[1] Presented before the Nuclear Chemistry Section of the XII International Congress of Pure and Applied Chemistry in New York, September, 1951.

[2] The "organic yield" is the fraction of the $Br^{79}(n,\gamma)Br^{80}$ or Br^{80m} (4.4 hr.) $\rightarrow$ Br^{80} (18 min.) events which result in stable organic combination of the product atom.

[3] J. E. Willard, THIS JOURNAL, **62**, 256 (1940).

[4] J. E. Willard, *ibid.*, **62**, 3161 (1940).

[5] E. G. Bohlmann and J. E. Willard, *ibid.*, **64**, 1342 (1942).

[6] S. Goldhaber and J. E. Willard, *ibid.*, **74**, 318 (1952).

ane were introduced with the extracting solution. The organic layer was washed with water, then fractionated on a 12″-Vigreux column. When the temperature indicated that the carbon tetrachloride had been distilled over, successive 2-ml. samples were collected. About 4 ml. was left in the pot. The composition of each sample was determined by its refractive index. Counting was done with cylindrical glass Geiger tubes having annular glass jackets holding 10 to 12 ml. The inorganic layer was counted several times over a period of 48 hours, to allow a calculation of the counting rate due to Br^{80} (4.4 hr.) at any arbitrary reference time t_0, and a calculation of the ratio of the activities due to Br^{80} (4.4 hr.) and Br^{82} (35.9 hr.). The counting rate of each organic sample was then corrected for time of count, Br^{82} (35.9 hr.) activity, volume of sample and density of counting solution.

The material left in the still-pot always showed a higher specific activity than any of the immediately preceding fractions. This activity was attributed to tracer amounts of compounds boiling higher than dibromodichloromethane. Refractive index measurements showed this sample to be pure CCl_2Br_2, within the accuracy of such measurements. The counting rate in excess of what would have been expected from pure CCl_2Br_2 as determined from the distilled fractions was recorded as "higher boiling activity."

The corrected values of the specific activity of the various fractions, together with their composition as determined from refractive index measurements, were then combined by the method of least squares to give final values for the specific activity of Br^{80} (4.4 hr.) present as bromotrichloromethane, dibromodichloromethane and higher boiling compounds at the reference time t_0.

Isomeric Transition Experiments.—Solutions of purified carbon tetrachloride and bromine were prepared in glass stoppered bottles and allowed to stand 24 hours. Enough radioactive bromine was then added to give the desired concentration and specific activity. The solution was allowed to stand for 75 minutes, the calculated time for maximum 18-minute activity in the organic fraction. Extraction, fractionation, counting and calculation were then carried out as described for the (n,γ) experiments.

Identification of Carbon Tetrabromide as Reaction Product.—The presence of carbon tetrabromide as one of the reaction products was verified by two methods, successive crystallization to constant specific activity of carbon tetrabromide carrier, and partition between immiscible solvents. (a) **Successive Crystallization Method**: Reaction solutions containing 5 ml. of carbon tetrachloride and 75 mole % bromine were used. After reaction and extraction, CCl_3Br, CCl_2Br_2 and $CClBr_3$ were added in small amounts as hold-back carriers and known larger amounts of CBr_4 were added as a separation carrier. The CBr_4 was crystallized out by cooling in an ice-bath and centrifuging. The supernatant liquid was pipetted off and the procedure repeated. After several such recrystallizations, some of the crystals were removed, dried with an aspirator, dissolved in CCl_4 and counted. The amount of CBr_4 counted was determined by taking the refractive index of the CBr_4–CCl_4 solution. This procedure was repeated after successive recrystallizations. (b) **Solvent Partition Method**: Because the rapid radioactive decay imposed limitations on the crystallization technique, and because of the possibility of small amounts of radioactive contaminants being carried with the large amounts of carbon tetrabromide, a solvent partition technique was devised as an independent check. The sample of carbon tetrabromide was prepared and treated as for the crystallization experiments, but after the fourth crystallization, the entire sample was dried and weighed. Then it was partitioned between the immiscible layers formed when methyl alcohol and petroleum ether (b.p. 90–100°) are mixed. For partitioning, 10 ml. of each layer was used for each 0.1 g. of dried CBr_4. Top and bottom layers were then counted in the same counting tube and the counting rates compared at some reference time.

The correct value of the partition coefficient was determined by preparing carbon tetrabromide tagged with Br^{82} (35.9 hr.). A mixture of carbon tetrabromide and bromine tagged with Br^{82} was placed on a vacuum line and illuminated for 15 minutes with a 1000-watt Mazda lamp, then the bromine was removed by passing over freshly reduced copper wire. In two experiments the counting rate of the bottom layer, uncorrected for the effect of density on counting rate, was 1.26 ± 0.02 times that of the top layer. Similar experiments showed that the coefficient did not vary when the concentration of carbon tetrabromide was made 59% higher and 88% lower than normal. The partition coefficients of CCl_3Br and CCl_2Br_2 were determined under similar conditions to be 0.80 ± 0.02 and 0.98 ± 0.02. The coefficient for C_2Cl_6 was found by crude gravimetric determination to be 0.45 ± 0.1.

Results and Discussion

Total Organic Yields.[2]—An incidental purpose of the work of this paper was to recheck earlier values[5] of total organic yields from nuclear activation of bromine in carbon tetrachloride. These earlier

TABLE I

YIELD[2] OF ORGANIC PRODUCTS FROM RADIATIVE NEUTRON CAPTURE OF BROMINE IN CARBON TETRACHLORIDE

Mole % Br_2 in CCl_4	Per cent. of total activity CCl_3Br	CCl_2Br_2	Higher boiling	Total organic[a]
0.01	24	4	8	36
1.0	19.6	7.8	3.9	31.3
	17.4	6.7	2.3	26.4
5.0	15.0	9.7	2.3	27.0
	12.5	9.9	1.1	23.5
10	8.8	8.3	2.3	19.4
50	3.6	4.0	2.1	9.7
53	3.4	4.2	1.5	9.1
90	0.56	0.63	0.52	1.71
	.59	.76	.48	1.83
99	.04	.04	.025	0.11

[a] Obtained by adding the values in columns 2, 3 and 4. In two cases where the total organic yield was determined from a count of the organic liquid before fractionation the value was within 1% of that obtained by the summation method.

TABLE II

YIELD[2] OF ORGANIC PRODUCTS FROM ISOMERIC TRANSITION OF BROMINE IN CARBON TETRACHLORIDE

Mole % Br_2 in CCl_4	Per cent. of total activity CCl_3Br	CCl_2Br_2	Higher boiling	Total organic
0.01	23.7	2.63	4.22	30.6
	23.2	2.28	3.94	29.4
	22.6	2.0	6.50	31.1
				36.7[a]
0.1	23.8	4.4	5.0	33.4
				38.0[a]
1.0	20.3	6.2	5.9	32.4
				35.0[a]
				38.0[a]
5	16.2	12.2	2.8	31.2
				33.5[a]
10	11.3	9.2	2.7	23.2
				25.8[a]
25	6.8	8.7	2.9	18.4
				18.7[a]
50				11.5
				12.3[a]
75	3.1	4.3	2.0	9.5
				6.8[a]
				6.0[a]
90	0.77	1.1	0.61	2.48
				3.1[a]
				1.0[a]
99	0.14	0.17	0.097	0.41

[a] In these cases the total organic yields were determined directly from the counting rate of the extracted organic liquid, and no fractionation was carried out. In the other cases listed the total yields were obtained as the sum of the yields in columns 2, 3 and 4.

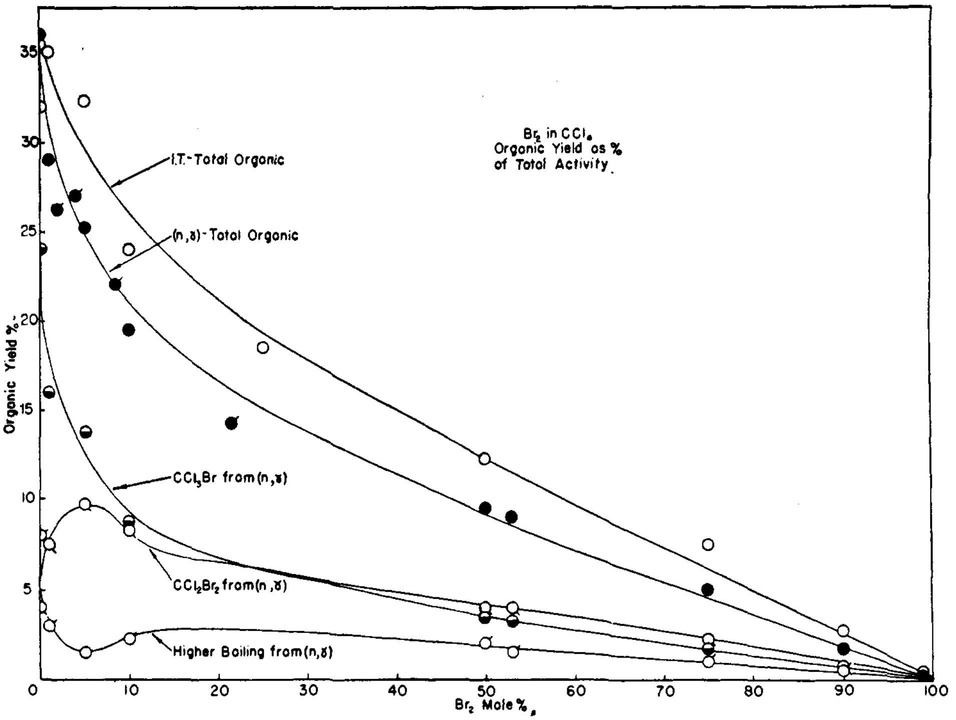

Fig. 1.—Organic yields[2] of reactions of bromine with carbon tetrachloride following radiative neutron capture and isomeric transition at different bromine concentrations. Tagged solid circles on second curve from top represent data taken independently by R. S. H. Chiang in our laboratory.

values were obtained in exploratory work done when less satisfactory equipment was available. The newer values are given in the last columns of Tables I and II and the averages of the individual values are plotted in the upper two curves of Fig. 1. These curves are in general agreement with those of the earlier work except for the (n,γ) reaction at concentrations below 10 mole % where the newer and more extensive data indicate a steep portion of the curve starting at higher yields than previously observed. This steep portion is analogous to that observed for bromine activated by the (n,γ) reaction in ethyl bromide[6] and iodine activated by the (n,γ) reaction in eight alkyl iodides.[7]

The data are insufficient to determine whether the yields from isomeric transition are different from those from the (n,γ) reaction at the lowest concentrations studied but it appears that the former are higher over a considerable portion of the concentration range. Analogously, it has been observed that the yield from the isomeric transition reaction in pure bromotrichloromethane is higher than that from the (n,γ) reaction.[8]

Yields of Individual Products.—Table I and Table II show the experimental results for the percentage of the atoms activated by radiative neutron capture and by the isomeric transition, respectively, which become stabilized as bromotrichloromethane, dibromodichloromethane and higher boiling compounds at different bromine concentrations. It may be seen that as the bromine concentration increases the yield of bromotrichloromethane decreases continuously while that of dibromodichloromethane goes through a maximum and that of the higher boiling products decreases rapidly by an amount about equivalent to the increase in the dibromodichloromethane yield. This behavior, which occurs for both methods of activation, is shown graphically for the (n,γ) reaction in Fig. 1.

Why does an increase in bromine concentration affect the yields of the different products so differently? This question may be answered in terms of the concept of the mechanisms of reactions of this type advanced earlier.[6,7] The earlier concepts are further strengthened by the evidence of extremely high molecular excitation offered by the experimental verification of carbon tetrabromide as a product in the present work.

When a bromine atom in a bromine molecule acquires kinetic energy equivalent to several thousand kcal./mole it starts moving rapidly but after having traveled much less than a molecular diameter encounters a solvent molecule. If this were an isolated molecule in the gas phase the energetic atom would "push it out of the way," that is, transfer momentum to the molecule in an elastic collision, and would continue on its way. In the liquid phase this cannot happen because the struck molecule is backed by and surrounded by a close packed wall of other molecules. The result is that the energy will be dissipated by breaking bonds in a rather indiscriminate fashion in the immediate vicinity of the energetic atom. When the energy of the atom has been reduced below bond breaking energies, it will find itself in or adjacent to a pocket of high local concentration of organic and inorganic radicals. If it combines with one of these radicals, after it has been moderated to an energy where this is

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(7) G. Levey and J. E. Willard, THIS JOURNAL, **75**, 6161 (1953).

(8) S. Goldhaber, R. S. H. Chiang and J. E. Willard, *ibid.*, **73**, 2271 (1951).

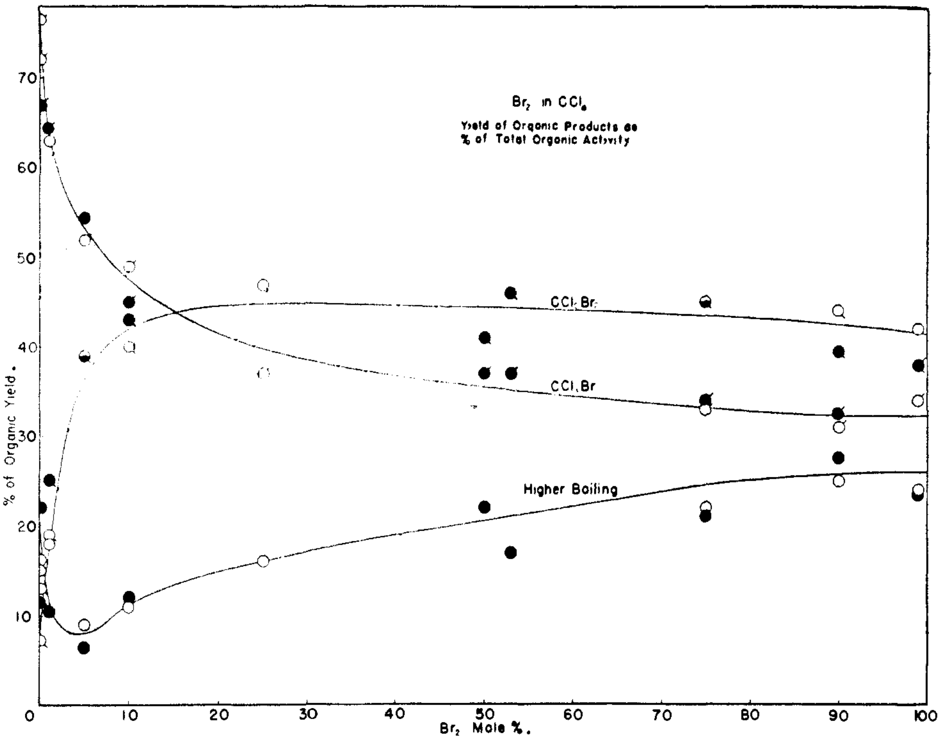

Fig. 2.—Relative yields of different organic products of the reaction of bromine with carbon tetrachloride at different bromine concentrations. The ordinates show the percentage of the total *organic* activity present as each product species. Open circles are for isomeric transition experiments and blackened circles for (n,γ) experiments. Circles with tags directed upward show the percentage of CCl_3Br, those with tags directed downward the percentage of CCl_2Br_2, and those without tags the percentage of higher boiling activity. Half blackened circles are used where the data for the isomeric transition and the neutron capture experiments fell at the same point.

possible but before it has had opportunity to diffuse in the system as a thermal atom, we say it has entered combination by a "high energy process."

An increase in the concentration of bromine in carbon tetrachloride would be expected to reduce the organic yield by high energy processes because of the increased probability that radicals formed would be formed from bromine and hence be inorganic. We believe that the nearly straight line portions of the curves of Fig. 1 above about 10% are due to this type of competition by the increasing bromine concentration.

There is evidence that some of the tagged bromine atoms[6,8] in systems such as the one under discussion escape combination by high energy processes and consequently diffuse in the system as thermal atoms until they encounter one of the radicals which they have formed or some other species with which they can react. Added bromine can reduce the chance of such atoms entering organic combination by exchanging with them to fix them in inorganic combination and also by reacting with the organic radicals. Such *thermal processes* are much more sensitive to added bromine concentration than the *high energy processes*. We interpret the rapid change in bromotrichloromethane yield with bromine concentration, at low concentrations, to be due to this type of competition. The fact that the competition continues effectively over a hundred-fold range of bromine concentration indicates that different thermalized tagged atoms diffuse to regions of different local radical concentration before combining. Those which escape farthest from the center of the pocket of radicals which they formed, before combining with one of them, are most likely to be fixed in inorganic form by low concentrations of bromine "scavenger."

It is not surprising that the radicals which diffuse farthest from the site of formation are $CCl_3\cdot$ radicals rather than, for example, $CCl_2\cdot$ since it would be expected that $CCl_2\cdot$ radicals would be converted to $CCl_3\cdot$ by the reaction $CCl_2\cdot + CCl_4 \rightarrow 2CCl_3\cdot$, after only a few collisions with the medium. Thus the initial scavenging is at the expense of the CCl_3Br product.

The interesting rapid increase in dibromodichloromethane yield and corresponding rapid decrease in the yield of the higher boiling fraction (Tables I and II, Fig. 1) can be explained if it is assumed that some of the tagged atoms combine by a high energy process with $CCl_2\cdot$ radicals which they have formed, to produce $CCl_2Br\cdot$ radicals. At very low bromine concentrations such a radical will exist as such until it encounters another radical, for example a $CCl_3\cdot$ with which it will react to form a molecule containing two carbon atoms, such as C_2Cl_5Br. Such molecules would appear in our "higher boiling fraction." As the bromine concentration in such a system is increased the $CCl_2Br\cdot$ radicals have increasing chance to be used up by a reaction of the type $CCl_2Br\cdot + Br_2 \rightarrow CCl_2Br_2 + Br$ and less chance to form molecules containing two carbon atoms.

The fact that the ratio of higher boiling products to CCl_3Br and CCl_2Br_2 increases with increasing bromine concentration above about 10 mole % (Figs. 1 and 2) may be attributed to the increasing probability that additional bromine will be incorporated in the stable organic molecules which are formed by the combination of the tagged atom with excited organic radicals in the hot region.

TABLE III

CHARACTERIZATION OF CBr_4

Mole % Br_2 in CCl_4	Nuclear activation	Number of crystallizations	Activity as CBr_4, %	Partition coefficient[a]
75	I.T.	3	1.26	
75	I.T.	5	1.14	
75	I.T.	5	1.48	
		6	0.69	
		7	1.31	
75	I.T.	4		1.29
90	(n,γ)	4		1.27

[a] Ratio of counting rate in bottom layer to counting rate in top layer. The experimentally determined coefficient for CBr_4 is 1.27 ± 0.02.

The data of Table III indicate that about 1% of the activity produced by isomeric transition in solutions 75 mole % in bromine and 25 mole % in carbon tetrachloride enters stable combination as carbon tetrabromide and that this compound can also be formed by activation by the (n,γ) process in similar solutions. This means that four carbon–chlorine bonds in a single molecule must be broken and replaced by carbon–bromine bonds, one of the latter involving the tagged atom. The breaking of the four chlorine bonds may possibly occur in one step followed by combination of the carbon atom with the bromine of the medium, or, more probably a partially brominated, partially chlorinated highly excited molecule is first formed which then reacts with the surrounding bromine to form carbon tetrabromide. The presence of this product emphasizes the extremely high energy available to individual molecules when nuclear processes of activation are used, and the complexity of the elementary processes which may occur.

Comparison of the Radiative Neutron Capture and Isomeric Transition Processes.—Since a Br^{80} (18 min.) atom produced by the isomeric transition is believed to be activated by virtue of its charge[3,9] and to have negligible recoil energy, whereas a bromine atom which has just been produced by the (n,γ) process has high recoil energy, the nature of the radicals produced by the two processes and hence the relative yields of stable products might well be quite different. However, Fig. 2 shows that within our experimental error the same relative yields of organic products are obtained by both processes at all bromine concentrations. This may be due to one of three causes. (1) The fragmentation of simple molecules like carbon tetrachloride may occur in an equally random fashion whether it results from charge neutralization processes or from the dissipation of recoil energy. (2) The atoms produced by isomeric transition may acquire sufficient recoil energy to break bonds, as a result of coulombic repulsion between the Br^{80} (18 min.) atom and its parent radical. Such repulsion would occur following distribution over the molecule of the high charge resulting from the emission of Auger electrons. (3) The atoms activated by the (n,γ) process may emit conversion electrons[10] and thereafter react as a result of their charge. No one of these three processes can be excluded on the basis of currently available evidence. If experiments in media consisting of more complicated molecules than carbon tetrachloride show the same product distribution from the (n,γ) and isomeric transition processes it will be evidence against the first suggested cause given above for our observations.

Question of Radiation and Impurity Effects.—The carbon tetrachloride used in this work was purified to an extent where it was proven that less than 10^{-6} mole fraction of bromine entered organic combination when the two were allowed to stand together. Since the lowest concentration of bromine in the experiments of Table I and II was 100-fold higher than the impurity reaction level, impurities cannot have had a significant effect on the observed results.

It may be estimated that if all the γ-radiation energy from the antimony–beryllium source which was absorbed in the bromine carbon tetrachloride solutions during a neutron irradiation was used efficiently in rupturing carbon–chlorine bonds the total mole fraction of $CCl_3\cdot$ radicals formed in the system would have been about 4×10^{-2} (the mole fraction of ion pairs, estimated on the basis of 32 ev./ion pair would have been *ca.* 4×10^{-3}). Not enough is known about the radiation chemistry of carbon tetrachloride to allow a valid prediction as to the efficiency of radical production and as to whether these radicals would have appreciable opportunity to combine with inorganic bromine in the system or would predominately recombine with the chlorine from which they were split. Insofar as they combine with bromine they would tend to raise the apparent organic yield of the (n,γ) reaction. In order to test the importance of this effect Mr. Richard Firestone of our laboratory has subjected solutions of bromine tagged with Br^{82} (35.9 hr.) in carbon tetrachloride to γ-radiation exposures similar to those received by the solutions of Table I during neutron irradiation. The results show that at a mole fraction of bromine of 10^{-2} to 10^{-8} the fraction of the bromine which enters organic combination is less than 1%. It may therefore be said with confidence that radiation effects on the observed organic yields of Table I, of the type discussed above, must have been completely negligible at bromine concentrations of 1 mole % and above and possibly at much lower concentrations.

In appraising the possibility of radiation effects on the organic yield it is necessary to consider not only the total consumption of elementary halogen by radicals as done above, but also the possibility that thermalized tagged atoms will react directly with radicals produced by radiation rather than entering stable combination by other processes. Such estimates[7] indicate that the probability of such an event is negligible compared to the proba-

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(9) G. T. Seaborg, G. Friedlander and J. W. Kennedy, THIS JOURNAL, **62**, 1309 (1940).

(10) (a) S. Wexler and T. H. Davies, Brookhaven National Laboratory Report C-7-AECU-50 (1948); (b) S. Yosim and T. H. Davies, *J. Phys. Chem.*, **56**, 599 (1952); (c) S. Wexler and T. H. Davies, *J. Chem. Phys.*, **20**, 1688 (1952).

bility of the tagged atom reacting with radicals which it has formed in losing its recoil energy.

Alternative Theory of Product Formation Following (n,γ) Activation.—Friedman and Libby and Fox and Libby[11] have interpreted their important data on the products of the (n,γ) reaction of bromine in liquid and solid propyl bromides to indicate that the parent molecule is the favored product when bonds are broken by high energy bromine atoms, and other products are favored when bonds are broken by recoiling atoms with energies only a few times greater than bond energies ("epithermal" energy range). We feel that there are a variety of theoretical reasons and types of experimental evidence which preclude the possibility that this subdivision of reaction probability which they have outlined is generally applicable. Some of these have been discussed earlier.[7] They include a consideration of: (1) the differences in collisions and in fragmentation probability in condensed phases as compared to the gas phase; (2) the low probability of "head-on" collisions in which a recoil atom can lose all of its energy to a target atom; (3) the fact that inorganic combination as well as organic combination has been shown to occur in the high energy region[6]; (4) the fact that a considerable fraction of both the organic and inorganic yield from the (n, γ) reaction on the alkyl bromides and alkyl iodides occurs after the recoil atoms have reached thermal equilibrium with the medium[6,7]; (5) the fact that the increase in organic yield in the solid phase as compared to the liquid which would be expected from the epithermal region theory does not occur in certain alkyl iodides[7]; (6) the fact that in the work of the present paper and in the case of methyl iodide it has been found that added elemental halogen reduces the yield of the simplest organic product molecules resulting from (n,γ) activation more rapidly than the yield of more complex products.

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[11] (a) L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949); (b) Fox and W. F. Libby, *ibid.*, **20**, 487 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY, DEPARTMENT OF NEUROSURGERY OF NEW ENGLAND CENTER HOSPITAL, AND BIOPHYSICAL LABORATORY OF HARVARD MEDICAL SCHOOL]

Self-diffusion and Structure of Liquid Water. III. Measurement of the Self-diffusion of Liquid Water with H^2, H^3 and O^{18} as Tracers[1]

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Measurements of the diffusion of small amounts of deuterium hydroxide and tritium hydroxide in ordinary water were made at several temperatures. Previous data on the diffusion of $H_2^1O^{18}$ in ordinary water have been revised. The results confirm previous conclusions regarding the structure of water and the mechanism of self-diffusion, dipole orientation and viscous flow in water. The effect of the differences in the moments of inertia of various water molecules is discussed.

In previous work the self-diffusion coefficients of liquid water at different temperatures were determined with $H_2^2O^{16}$ and $H_2^1O^{18}$ as tracers, respectively.[1] But since in the former case when deuterium oxide (99.8%) was allowed to diffuse into ordinary water the measurements yielded only integral diffusion coefficients, direct comparison of these values with the tracer diffusion coefficients for other labeled water molecules (*e.g.*, $H_2^1O^{18}$ with average O^{18}-enrichment at or below 1 atom per cent.) is difficult. In the present work the diffusion coefficients of $H^1H^2O^{16}$ and $H^1H^3O^{16}$ in ordinary water are determined at several temperatures. The average enrichment of H^2 in the diffusion capillaries was about 1 atom per cent., that of H^3 about 0.0001 atom per cent. Consequently we may consider the measured diffusion processes as the diffusion of individual labeled water molecules in ordinary water and take the so obtained diffusion coefficients as the tracer diffusion coefficients for the corresponding molecules in ordinary water.[3] It is hoped that these tracer diffusion coefficients, taken together, will be as useful for theoretical studies on the structure of water as the true self-diffusion coefficient of liquid water which cannot be measured directly. Previous data on the diffusion of H_2O^{18} in ordinary water contained a systematic numerical error. This has been corrected and the revised values are included in the present article.

Experimental

Tracer Solutions.—The deuterium oxide used was supplied by Stuart Oxygen Company, San Francisco, Calif., and obtained on allocation from the Isotopes Division, U. S. Atomic Energy Commission. The deuterium oxide as shipped, 99.8% in deuterium oxide, was redistilled and diluted with ordinary conductivity water before use. The diluted heavy water contained about 2.5 atom per cent. excess of deuterium before diffusion. After diffusion the average concentration of deuterium left in the capillaries is about 0.5 atom per cent. excess.

The tritium was obtained in the form of hydrogen gas from the Isotopes Division, U. S. Atomic Energy Commission, Oak Ridge, Tennessee. The radioactive hydrogen gas was equilibrated with distilled water in the presence of platinum oxide as catalyst. The tritiated water so prepared had a specific activity of about 1 mc. per g. Thus the atom fraction of tritium in this radioactive water is less than 10^{-6}. This tritiated water was redistilled before use.

The O^{18}-enriched water contained, before diffusion, about

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[1] Paper I, THIS JOURNAL, **73**, 510 (1951); paper II, *ibid.*, **73**, 4181 (1951).

[2] Research Fellow of American Heart Association.

[3] For the definition of the term "tracer-diffusion," see J. H. Wang, THIS JOURNAL, **74**, 1182 (1952).