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## The Influence of Structure, Phase and Added Chlorine on the Organic Yields of the $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$ Reaction in Alkyl Chlorides

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The organic yields of  $\text{Cl}^{38}$  from the  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  process in ten liquid alkyl chlorides are all *ca.* 21%, independent of structure and chain length. The same yield was obtained for dilute solutions of *n*-butyl chloride in hexane. For gaseous *n*-butyl chloride the yield is about 11% with or without hydrogen chloride scavenger present, and that from hydrogen chloride in butane is about 7%. These facts indicate that some of the  $\text{Cl}^{38}$  atoms produced by the  $(n,\gamma)$  process are activated in such a way that they can react with a hydrocarbon chain in a one step reaction to become organically bound, rather than to form hydrogen chloride as normal chlorine atoms would do. The organic yields of the liquid hydrogenous alkyl chlorides are not changed by the presence of elemental chlorine up to several mole %, whereas that of carbon tetrachloride is reduced. These results support the hypothesis proposed earlier to explain the scavenger effect of added halogen on  $(n,\gamma)$  induced reactions in alkyl bromides and iodides. The organic yields from seven alkyl chlorides tested in the solid phase at liquid air temperature are all higher than in the liquid but the ratio to the liquid results varies from 1.4 to 2.7. It has been demonstrated that highly purified pentene-2 may be used as a reagent to distinguish between tracer amounts of chlorine and hydrogen chloride. By means of this reagent it has been shown that about 8% of the  $\text{Cl}^{38}$  from the  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  reaction on butyl chloride appears as  $\text{Cl}_2$  and 70% as hydrogen chloride.

### Introduction

When an alkyl halide is irradiated with neutrons, some of the halogen atoms undergo a nuclear reaction of the type  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  (37 min.),  $\text{Br}^{81}(n,\gamma)\text{Br}^{82}$  (36 hr.) or  $\text{I}^{127}(n,\gamma)\text{I}^{128}$  (25 min.). In each case the new atom may have a kinetic energy of the order of thousands of kcal./mole<sup>1</sup> as a result of recoil from the emitted  $\gamma$ -ray or rays. This energy ruptures the bond of the halogen to the alkyl group and is further dissipated in collisions of the atom with molecules of the medium. A number of investigations<sup>2-6</sup> have led to the theory that the highly energetic atom produces a high concentration of a variety of radicals in a small volume element of the solution, and that after it has been moderated to an energy below bond energies, it may either combine with one of these radicals to form a stable molecule or react with a solvent molecule. If the atom enters stable combination immediately after its energy has been reduced below bond energies and before it has diffused in thermal equilibrium with the solvent the process has been called a "high energy process" to distinguish it from the "thermal processes" which involve those atoms which reach thermal equilibrium and undergo many collisions with the medium without entering combination.

The "high energy processes" may be distinguished experimentally from the "thermal processes" by the fact that they are not affected significantly by the presence of as much as 1 mole % of added halogen during neutron irradiation of the alkyl halide. By contrast halogen greatly reduces the probability of thermalized atoms combining with radicals to form stable organic products. It does so by furnishing low activation energy processes for fixing the atom in inorganic combination ( $\text{Br}^* + \text{Br}_2 \rightarrow \text{BrBr}^* + \text{Br}$ ) and also by removing the radicals ( $\text{R}\cdot + \text{Br}_2 \rightarrow \text{RBr} + \text{Br}$ ). Halogens added for this purpose are termed "scavengers."

(1) See, for example, W. F. Libby, *THIS JOURNAL*, **69**, 2523 (1947); R. R. Edwards and T. H. Davies, *Nucleonics*, **2**, No. 6, 44 (1948).

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

(3) G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

(4) J. F. Hornig and J. E. Willard, *ibid.*, **75**, 461 (1953).

(5) For further discussion and references see: J. E. Willard, "Ann. Rev. Nuclear Science," Vol. III, in press.

The work of the present paper was initiated to test the prediction,<sup>2</sup> arising out of the hypotheses outlined above, that all chlorine atoms activated by the  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  process in hydrogenous organic chlorides must enter stable combination by high energy processes which would not be affected by added halogen at concentrations of 1 mole % or so. This prediction is based on the fact that chlorine atoms react extremely readily with carbon-hydrogen bonds to form hydrogen chloride. Consequently the atoms produced by radiative neutron capture would not be expected to have a chance to reach thermal equilibrium with the medium as atoms. A corollary of this prediction is that thermal as well as high energy processes should be important in determining the fate of atoms produced by the radiative neutron capture reaction in carbon tetrachloride, and that the fraction of the  $\text{Cl}^{38}$  which becomes stabilized in organic combination should therefore be sensitive to scavengers.

A further purpose of the work has been to determine whether the reactions activated by the  $(n,\gamma)$  process in the homologous series of alkyl chlorides exhibit structural effects and phase effects similar to those observed with the series of iodides.<sup>3</sup> During the investigation the striking observation has been made that the fraction of the  $\text{Cl}^{38}$  atoms which become stabilized in organic combination is independent of the chain length of the alkyl chloride and of dilution with hydrocarbon.

### Experimental

**Purification.**—It will be shown in a later section that when a pure alkyl chloride such as  $\text{C}_4\text{H}_9\text{Cl}$  is irradiated with neutrons about 21% of the  $\text{Cl}^{38}$  produced becomes stabilized in organic combination, about 8% as  $\text{Cl}_2$  and 71% as  $\text{HCl}$ . Consequently if the chloride which is irradiated contains even a small amount of an impurity such as an olefin or an alcohol which can react readily with  $\text{Cl}_2$  or  $\text{HCl}$  the apparent organic yield will be raised above its true value. Our results show that high and variable values are obtained with the Eastman Kodak Co. white label grade chlorides which were used in this work unless careful purification is carried out just prior to use. Purified samples which give satisfactory results immediately after purification again give high results after several days standing in the dark in contact with air in a glass stoppered bottle. This regeneration of impurity is presumably due to a slight dehydrohalogenation or hydrolysis of the chloride.

Two types of purification were found to give consistent results. The method used in most of the work was to sub-

ject the chloride to vigorous mechanical stirring with 95% sulfuric acid for several days, replacing acid when it became colored. Treatment was continued until this layer remained colorless after twelve hours of stirring. The compound was then washed with saturated sodium carbonate solution and with distilled water, and was dried with analytical grade anhydrous magnesium sulfate. After filtration it was distilled through a 10" Vigreux column and a 75% middle fraction was retained.

A second successful method of purification involved passing a stream of oxygen containing about 5% ozone through the chloride for a time three times longer than necessary to cause the first coloration of starch iodide paper by the exit gas. The liquid was then washed with sodium bicarbonate solution to hydrolyze ozonides and remove the organic acids thus produced. It was dried and fractionally distilled as in the sulfuric acid purification.

Because of its low boiling point the methyl chloride (Matheson Chemical Co., 99.5% purity) was purified by passing it through a sintered glass disc at the bottom of a 15" column of sulfuric acid on a vacuum system. It was condensed in a quartz tube and sealed off for neutron irradiation.

In a few cases samples were photochlorinated with a small amount of chlorine prior to use to ensure that all chlorinatable impurities had been removed. In the case of the tertiary chlorides this method was used exclusively, since they were decomposed by the other purification methods.

Infrared spectra taken on some of the samples before and after purification indicated that the purification procedures removed impurities with absorption peaks at 3 and 6  $\mu$  which might be attributed to olefinic compounds.

Mallinckrodt low-sulfur carbon tetrachloride was prepared for use by adding bromine, illuminating with a 1000-watt lamp for 24 hours at room temperature, washing with aqueous sulfite and with water and fractionally distilling.

**Neutron Irradiations.**—Purified organic liquids were usually irradiated by placing 15 ml. in the annular space between the walls of a vessel shaped like a dewar flask. A 10-curie Sb-Be photoneutron source<sup>6</sup> giving about  $2 \times 10^7$  neutrons per second was lowered into the center tube of the vessel. Irradiation times were of the order of an hour or two. The irradiation vessel was surrounded with water. In those cases where the liquid to be irradiated contained dissolved chlorine it was sealed off from a vacuum system in a quartz tube and placed next to the Sb-Be source in a tank of water. All liquid irradiations were done at room temperature except that of isopropyl chloride, which was done at 0°.

For solid phase irradiations the samples were contained in soft glass test-tubes immersed in a dewar of liquid air surrounded by water. The source was placed in the water adjacent to the dewar. This type of irradiation yielded activities of the order of 1000 c./min.

Because its low boiling point increased the time required to prepare methyl chloride for counting it was necessary to start with higher activity than in the case of the other halides. This was achieved by bombarding 5-g. samples of the liquid in sealed ampoules in the CP3' reactor of the Argonne National Laboratory for 30 min. at a flux of about  $10^{11}$  neutrons/cm.<sup>2</sup>/sec. Samples for gas phase experiments and experiments on solutions of butyl chloride in heptane were irradiated similarly at this reactor.

**Scavenger Experiments.**—When it was desired to irradiate an alkyl chloride containing a known concentration of elemental chlorine, the compound was first degassed by successive cycles of freezing, evacuating and thawing in a quartz tube attached to a vacuum system. While the substance was frozen with liquid air, a known amount of chlorine was admitted from a metering flask and the tube was sealed off following which it was placed in a vessel of water adjacent to the Sb-Be source. The chlorine used was admitted to the vacuum system and the metering flask of known volume directly from a tank, the pressure being measured by a mercury manometer protected with a layer of phosphoric acid. Care was taken not to expose the mixed reactants to any illumination other than dim red light.

Qualitative determinations of the solubility of chlorine in *n*-butyl and *n*-propyl chloride showed that essentially all

of the chlorine added to alkyl chloride samples for scavenger purposes in the experiments described below must have been in the solution phase rather than the gas phase.

**Extraction and Counting.**—All of the chlorides which boil above room temperature were processed in the same manner following irradiation. Immediately after irradiation 1 ml. of 0.1 *M* bromine in carbon tetrachloride was added to the irradiation vessel to act as a halogen carrier and prevent tracer amounts of chlorine and hydrogen chloride from sticking to the walls. The inorganic halogen was then extracted with a solution 0.1 *M* in sodium sulfite and 0.1 *M* in sodium chloride. After separation of the organic and inorganic layers each was counted with an annular jacket-type of Geiger tube. The "organic yield" was computed as the ratio of the counting rate of the organic phase to the sum of the counting rates of the organic and inorganic phases after appropriate corrections for differences in density, volume and radioactive decay. Gaseous samples were prepared for counting in the same way as the liquid samples, after freezing them down in the irradiation flask and adding carriers.

Most samples were counted for a sufficient time so that the standard deviation was less than 1.4%. The usual time was 18 minutes. Since appreciable decay occurred during this period the series expansion  $N_0 = [S(1 - e^{-\lambda})]/[1 - e^{-(n+\lambda)}]$  (where *S* is the total number of counts recorded, *n* + 1 the number of minutes the sample was counted, and  $\lambda$  the decay constant) was used to calculate the initial counting rate  $N_0$ .

In order to prepare the irradiated ampoules of methyl chloride (b.p. -24°) for counting, they were frozen with liquid air, opened and connected to a system of traps where the liquid was allowed to vaporize. The gas was bubbled through two traps in series containing aqueous 0.1 *M* sodium sulfite and sodium chloride, and finally condensed in a flask containing 150 ml. of absolute methanol in which the gas is extremely soluble. The irradiation vessel was then flushed with chlorine gas to remove activity which might have stuck to the walls and the chlorine was caught in the aqueous traps. The aqueous and organic fractions were counted in the same manner as the other chlorides.

**Determination of Effect of Density on Counting Rate.**—In order to determine the influence of density of the counting solution on the relative counting rates of Cl<sup>38</sup> in different solutions a saturated solution of trichloroacetic acid was irradiated with neutrons, following which 10-ml. aliquots were mixed with 10 ml. of chloroform, acetone, ethanol and an aqueous solution of trichloroacetic acid, and counted. The counting rates of the solutions were determined and corrected to the same time. A similar set of determinations was made with an aliquot of irradiated butyl chloride in each of the same four solvents. A plot of the relative counting rates of the solutions against their densities gave a curve from which the counting correction factor for any density in the range could be read.

The effect of changing average atomic number of the medium was considered to be negligible since the counts observed were due predominately to  $\beta$ -rays. The specific counting rate fell off smoothly by about 11% in going from a density of 0.7 to a density of 1.3.

**Pentene-2 as a Reagent to Distinguish Tracer Quantities of Chlorine from Hydrogen Chloride.**—When alkyl halides are irradiated with neutrons the radiohalogen atoms which are produced may enter stable combination as elemental halogen, as hydrogen halide and as organic species. The amounts produced in experiments such as those described in this paper are of the order of  $10^{-18}$  mole, much too small to allow the ratio of the two inorganic substances to be determined by conventional means such as iodimetric titration. It is likewise impossible to determine them by adding macro amounts of hydrogen halide and halogen to serve as carriers for the tracer constituents, and then separating the carriers and determining the radioactivity in each, because of the rapid exchange between halogens and hydrogen halides. Earlier attempts to distinguish tracer bromine from tracer hydrogen bromide by selective reaction with freshly reduced copper were unsuccessful.<sup>7</sup> We have now found that tracer amounts of radiochlorine may be quantitatively distinguished from tracer amounts of hydrogen chloride by the fact that pentene-2 will react instantaneously with the former but only very slowly with the latter. The method

(6) Obtained from the Oak Ridge National Laboratory and activated by irradiation in the pile of the Brookhaven National Laboratory.

(7) G. Levey and J. E. Willard, *THIS JOURNAL*, **73**, 1866 (1951).

was evaluated by adding 0.002 mole of pentene-2 to tubes containing 0.15 mole of butyl chloride and either a small amount of  $\text{Cl}^{36}$  or a small amount of  $\text{HCl}^{36}$ .<sup>8</sup> The mixtures were shaken for different time intervals and then extracted with aqueous sulfite. In the case of the chlorine, all of the activity entered organic combination and became unextractable very rapidly while essentially all of the  $\text{HCl}$  was still extractable after 2 hours. Initial tests of the method gave variable results due to impurities in the pentene-2 which reacted with hydrogen chloride at an easily measurable rate. It was found that these could be removed by careful fractional distillation.

It is possible that the above technique or a modification of it using a different olefin may prove useful in distinguishing tracer amounts of bromine from hydrogen bromide.

### Results and Discussion

**Absence of "Thermal" Reactions in Alkyl Chlorides.**—In contrast to the effect of added halogen on the alkyl iodides and ethyl bromide, and in accordance with predictions (see Introduction), the organic yields of nine alkyl chlorides tested are not altered by the presence of a few mole % of added chlorine (Table I). This we believe to be due to the fact that the tagged chlorine atoms are never able to reach thermal energies and diffuse in the system as thermal atoms. Those which escape combination by other "high energy" processes always react with carbon-hydrogen bonds to form hydrogen chloride.

TABLE I  
ORGANIC YIELDS FROM THE  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  PROCESS IN ALKYL CHLORIDES

Compound	[Cl <sub>2</sub> ], mole fraction	Organic yields, %	
		Liquid	Solid
Methyl	0	21.7, 20.0	
Ethyl	0	22.8, <sup>2</sup> 23.0 <sup>2</sup>	62.0 <sup>2</sup>
<i>n</i> -Propyl	0	22.7, 21.0, 23.2	62.8, 61.2
	.07	23.2	
Isopropyl	0	21.8	
	.11	19.6	
<i>n</i> -Butyl	0	21.2, 21.1, 21.7	35.0, 35.7
	.04	21.2	
	.11	19.2	
Isobutyl	0	22.1, 23.2	32.8, 33.3
<i>s</i> -Butyl	0	21.6	31.2, 32.2
	.03	21.2	
<i>t</i> -Butyl	0	34.6	
	.03	34.0	
	.06	33.8	
<i>n</i> -Amyl	0	22.1, 22.0, 21.2	
	.10	20.4	
Isoamyl	0	22.0	32.3
	.04	22.0	
<i>s</i> -Amyl	0	22.0	38.1
	.04	20.9	
<i>t</i> -Amyl	0	36.8, 37.4	
	.03	36.3	

In three cases where 10 mole % of chlorine was present in the alkyl chloride during irradiation the organic yield was reduced by about 10% of its normal value. At this chlorine concentration exchange with the chlorine molecule might be expected to replace 10% of each type of process by

(8) Obtained from the Oak Ridge National Laboratory.

which the atoms are consumed in the absence of chlorine.

**Evidence for Thermal Processes in Carbon Tetrachloride.**—In carbon tetrachloride a recoil chlorine atom which has been moderated cannot react readily with a molecule of the solvent to form a stable product as it can in the hydrogenous alkyl chlorides. (The reaction of chlorine atoms with carbon tetrachloride molecules to form elemental chlorine and trichloromethyl radicals has been demonstrated by F. Johnston of our laboratory to have an activation energy of 15 kcal./mole or higher). Therefore it would be expected, in terms of the hypothesis of the mechanism of such reactions summarized in the Introduction, that some of the  $\text{Cl}^{38}$  atoms formed in liquid carbon tetrachloride by radiative neutron capture would diffuse as thermal atoms before encountering and combining with radicals which they had formed. If this is the case the presence of low concentrations of chlorine during neutron irradiation should reduce the organic yield from carbon tetrachloride just as added iodine reduces the organic yield in the alkyl iodides, but in contrast to the effect of chlorine on alkyl chlorides which have carbon-hydrogen bonds in the molecule. The data of Table II verify this prediction. They yield the characteristic shape of "scavenger" curve observed with ethyl bromide<sup>2</sup> and the alkyl iodides,<sup>3</sup> thus giving further support to the concept that both high energy processes and thermal processes may contribute to chemical stabilization of the recoil atom produced by radiative neutron capture. The scavenger effect in carbon tetrachloride has been observed also by Hamill and Williams.<sup>9</sup>

TABLE II  
THE SCAVENGER EFFECT OF CHLORINE ON THE ORGANIC YIELD FROM THE  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  PROCESS IN CARBON TETRACHLORIDE

[Cl <sub>2</sub> ], mole fraction	Organic yield, %	[Cl <sub>2</sub> ], mole fraction	Organic yield, %
0	44.3	0.12	30.2
$1.58 \times 10^{-3}$	40.0	.22	22.5
$6.58 \times 10^{-3}$	35.2	.28	21.6
$8.23 \times 10^{-3}$	33.4		
$4.67 \times 10^{-2}$	31.6		

**Ratio of Chlorine to Hydrogen Chloride Produced by the  $(n,\gamma)$  Reaction on Butyl Chloride.**—When pentene-2 was added to butyl chloride either before or after neutron irradiation the  $\text{Cl}^{38}$  activity which was non-extractable with aqueous sulfite was always about 29% rather than the 21% regularly found (Table I) in the absence of pentene. The effect was independent of pentene concentration in the range tested (0.001 mole fraction to 0.1 mole fraction). The fact that the effect of pentene is the same whether it is added before or after the neutron irradiation indicates that its function is to react with stable product molecules containing the  $\text{Cl}^{38}$  rather than to react with  $\text{Cl}^{38}$  atoms before they have entered stable combination.

Since pentene-2 reacts very rapidly with chlorine, but not with hydrogen chloride under the condi-

(9) W. H. Hamill and R. R. Williams, Jr., Abstracts 123rd Meeting Am. Chem. Soc., p. 41P, paper 99, April, 1953.

tions of these experiments (see Experimental section) the observed increase in organic yield from 21 to 29% as a result of pentene addition must be due to reaction of pentene with  $\text{Cl}^{38}$  in the form of  $\text{Cl}_2$ . Thus it may be concluded that, of the total  $\text{Cl}^{38}$  produced in liquid butyl chloride, about 21% enters organic combination, 8% forms  $\text{Cl}_2$  and 71% forms  $\text{HCl}$ . It is probable that the ratio of  $\text{Cl}_2$  to  $\text{HCl}$  would decrease with increasing chain length in the series of alkyl chlorides and with dilution with hydrocarbons.

As a further check on the interpretation of the experiments with pentene, butyl chloride which had been irradiated with neutrons was illuminated with light from a 1000-watt G.E. H-6 mercury arc, filtered with a Corning 5534 filter which cuts off all wave lengths below 3400 Å. Both butyl chloride and hydrogen chloride are transparent in the wave length range transmitted by the filter but chlorine absorbs. It was found that the organic yield of irradiated samples was about 25% in contrast to 21% in the absence of illumination. Addition of pentene after illumination did not increase the organic yield further, thus indicating that the chlorine formed by the  $(n, \gamma)$  process had all reacted as a result of the illumination, about half of it entering organic combination and half inorganic combination as hydrogen chloride. The fact that half of the chlorine entered organic combination was consistent with what would be expected for an ordinary photochlorination but was somewhat unexpected for the system containing only tracer amounts of chlorine because of the improbability of the third step in the sequence: (1)  $\text{Cl}_2 \xrightarrow{h\nu} 2\text{Cl}$ , (2)  $\text{Cl} + \text{RH} \rightarrow \text{R}\cdot + \text{HCl}$ , (3)  $\text{R}\cdot + \text{Cl}_2 \rightarrow \text{RCl} + \text{Cl}$ .

In accordance with expectations the 29% organic yield observed when pentene-2 was added to the butyl chloride following neutron irradiation was not altered if the system was illuminated subsequent to the pentene addition but before extraction.

The only type of inorganic product containing  $\text{Cl}^{38}$  which can be formed by the  $(n, \gamma)$  reaction on carbon tetrachloride is  $\text{Cl}_2$ . Therefore, if pentene-2 is present in the solution during irradiation, all of the  $\text{Cl}^{38}$  should be found as organic activity as a result of addition of the chlorine to the pentene. In two such experiments with 2.5 and 6.5 mole % of pentene-2 the organic yields were 94 and 96%. The small remaining fraction of inorganic activity was presumably due to reaction of the recoil atoms with carbon-hydrogen bonds of the pentene to form hydrogen chloride.

**Structure Effects.**—It is notable (Table I) that all of the organic chlorides except the tertiary compounds give essentially the same organic yield. This is in contrast to the iodides<sup>3</sup> where the yields fall in the order methyl, other primary iodides, secondary iodides. No data are available for the tertiary iodides. It may be that the decrease in organic yield in going from primary iodides to the secondary iodides is due to the increasing ease with which hydrogen iodide can be split out of a highly excited molecule just formed by the recoil atom. The absence of a parallel effect of structure in the chloride series is consistent with this explanation since the chlorides are relatively stable with respect

to decomposition into hydrogen chloride and an olefin.

The fact that *t*-butyl and *t*-amyl chloride give much higher organic yields than the primary and secondary chlorides may be due to the fact that such molecules are more apt to fragment into several organic radicals when struck by a recoil atom and thus increase the probability that the tagged atom will combine with a radical rather than removing a hydrogen atom from a carbon-hydrogen bond.

**Organic Yield from Butyl Chloride in Heptane Solutions.**—From the fact that the organic yields of the chlorides are independent of chain length from methyl through amyl (Table I), and hence of the ratio of C-Cl bonds to other bonds, it might be predicted that the organic yield of any one of the chlorides would be unaffected by dilution with a hydrocarbon. This has been found to be the case for solutions of butyl chloride in heptane down to concentrations at least as low as  $5.6 \times 10^{-4}$  mole fraction (Table III).

TABLE III

ORGANIC YIELDS OF THE  $\text{Cl}^{37}(n, \gamma)\text{Cl}^{38}$  PROCESS IN *n*-HEPTANE

<i>n</i> -BuCl, mole frac.	1	0.81	0.58	0.065	0.014	0.0006
Org. yield, %	21.7	21.3	22.5	20.6	22.2	20.7

**Organic Yields in the Gas Phase.**—The unexpected constancy of organic yield at about 21% shown by a variety of compounds and over a wide range of concentration in hydrocarbon solution by the data of Tables I and III required consideration of the possibility that there is 21% failure of the C-Cl bond to rupture following the  $\text{Cl}^{37}(n, \gamma)\text{Cl}^{38}$  process. This could be the case if there is a high multiplicity in the  $\gamma$ -spectrum and substantial cancellation of recoil momentum. Earlier work on chlorates and perchlorates has, however, shown complete rupture of the parent bond following the  $(n, \gamma)$  reaction on the chlorine of these radicals.<sup>10</sup> In order to test the completeness of carbon-chlorine bond rupture, samples of both butyl chloride vapor and propyl chloride vapor were irradiated with neutrons and the organic yields determined. The results, given in Table IV, indicate that even in the gas phase with equimolar quantities of hydrogen chloride present as a carrier for the inorganic activity the  $\text{Cl}^{37}(n, \gamma)\text{Cl}^{38}$  process yields about 11% of the activity in organic combination. Most  $(n, \gamma)$  reactions on gaseous alkyl halides show a much lower organic yield than this.<sup>11,5</sup>

The fact that less than 2% of the  $\text{Cl}^{38}$  appeared as the parent compound in experiments where *n*-butyl chloride was irradiated (Table IV) proves that the high organic yield in such systems is due primarily to re-entry of the  $\text{Cl}^{38}$  into organic combination after splitting its parent bond, *i.e.*, that there is little or no failure of the parent bond to rupture following the  $(n, \gamma)$  process.

Additional observations of interest in these experiments are: (1) in the irradiations of *n*-butyl chloride which showed only 1.0 and 1.3% of the

(10) (a) R. Daudel, *Compt. rend.*, **214**, 547 (1942); (b) P. J. Von Heerden and Ninck-Blok, *Physica*, **10**, 13 (1943).

(11) S. Wexler and T. H. Davies, *J. Chem. Phys.*, **20**, 1688 (1952).

TABLE IV  
ORGANIC YIELD OF THE  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  PROCESS IN GASEOUS  
PROPYL CHLORIDE, BUTYL CHLORIDE AND BUTANE

	Composition of irradiated gas		Organic yield, %	
	Org. cpd., mm.	[HCl], mm.	Total	$\text{As}$ $n\text{-C}_4\text{H}_9\text{Cl}^a$
$n\text{-C}_3\text{H}_7\text{Cl}$	103	0	9.4	
	103	0	11.3	
	103	0	12.1	
	107	102	10.6	1.3
	95	95	11.5	1.0
$n\text{-C}_4\text{H}_{10}$	980	1040	6.8	5.0
	1040	1040	7.8	5.6
$n\text{-C}_3\text{H}_7\text{Cl}$	207	10	11.4	
	207	10	12.4	
	241	0	11.8	
	241	0	15.5	

<sup>a</sup> The organic yield of *n*-butyl chloride was determined qualitatively by comparing the activity in a 50% center cut from a fractional distillation of the organic layer with the total activity. The specific activity in the material left in the still pot was higher than the center cut.

$\text{Cl}^{38}$  as *n*-butyl chloride there was an additional 8% present as higher boiling compounds; (2) a  $\text{Cl}^{38}$  atom activated by the  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  process seems to have a higher probability of forming *n*-butyl chloride by reaction with butane than with gaseous *n*-butyl chloride; (3) the organic yields of reactions of the type of Table IV are independent of hydrogen chloride concentration up to a mole fraction of at least 0.5.

#### Implications of Liquid and Gas Phase Yields.—

From the data presented above it must be concluded that in the liquid phase a  $\text{Cl}^{38}$  atom produced by the  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  process has *ca.* a 21% chance of replacing a hydrogen atom or a radical on a hydrocarbon chain, regardless of whether the medium is  $\text{CH}_3\text{Cl}$ , or any one of the other primary or secondary alkyl chlorides, or even heptane.

This result means that the probability of the  $\text{Cl}^{38}$  entering organic combination is independent of the mass of the molecule and of the presence or absence in the molecule of atoms of mass equal to that of the reactive atom. It indicates that a newly formed  $\text{Cl}^{38}$  atom which has lost sufficient of its kinetic energy and charge to be able to form a stable bond has a specialized type of reactivity which allows it to react with a hydrocarbon chain to enter organic combination rather than abstracting a hydrogen atom to form HCl, as photochemically produced chlorine atoms would be expected to do.

This peculiar reactivity is further illustrated by the fact that  $\text{Cl}^{38}$  formed in a *gaseous* mixture of  $\text{C}_4\text{H}_9\text{Cl}$  and HCl, or of  $\text{C}_4\text{H}_{10}$  and HCl has a significant probability of entering organic combination (Table IV). The reaction in the gas phase in the presence of HCl scavenger must be a one-step, bimolecular elementary reaction between the  $\text{Cl}^{38}$  atom and the alkyl chloride or the butane, rather than a combination with a free radical. This conclusion is supported both by the fact that the  $\text{Cl}^{38}$  would be expected to exchange with HCl before having a chance to encounter a free radical in the system, and by the fact that ethyl bromide<sup>11</sup> and other gases<sup>5</sup> which have been investigated show a relatively negligible organic yield thus proving that

radicals produced by the  $\gamma$ -radiation from the neutron source are not important in determining the fate of the tagged atom

The fact that the yields in the liquid phase are somewhat higher than the gas may indicate that in the liquid there is some reaction of the  $\text{Cl}^{38}$  with "caged" radicals which it itself has just formed, or it may indicate that the close-packed arrangement in the liquid is more favorable to reactive encounters of the same type which occurs in the gas.

Since the organic yields of the homologous series of alkyl chlorides are independent of chain length or dilution with heptane they are not influenced by the probability of collisions of the  $\text{Cl}^{38}$  with a chlorine atom relative to collisions with parts of the hydrocarbon chain. Thus it appears that the moderating or momentum transfer properties of the medium are not significant and consequently the observed reaction cannot be a result of the kinetic energy with which the  $\text{Cl}^{38}$  is born. If this is a valid conclusion the reaction must result from the positive charge acquired by the  $\text{Cl}^{38}$  as a result of internal conversion of some of the energy of the  $(n,\gamma)$  process. As far as we know no attempt has been made to demonstrate internal conversion in the  $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$  process but the phenomenon has been found to accompany every  $(n,\gamma)$  reaction where it has been sought and is probably quite general.<sup>11,12</sup>

The mechanism of the  $\text{Cl}^{38}$  reactions described may be similar to that of the gas phase reaction of methane with  $\text{I}^{128}$  formed by the  $\text{I}^{127}(n,\gamma)\text{I}^{128}$  reaction, which has been ascribed to the charge on the  $\text{I}^{128}$  atom.<sup>13</sup>

There is a striking parallel between the results reported here for the alkyl chlorides and those observed by Miller and Dodson<sup>14</sup> for neutron irradiated mixtures of carbon tetrachloride with either benzene or cyclohexane. These authors found that the organic yield in the form of chlorobenzene or cyclohexyl chloride is independent of the concentration of the hydrocarbon from 1 to 99 mole %. The absolute value of the yield which they found was, as in the case of the alkyl chlorides, about 20%. Their results seem to indicate that a  $\text{Cl}^{38}$  atom which is born in a medium of 99 mole %  $\text{CCl}_4$  and 1 mole %  $\text{C}_6\text{H}_6$  has as good a chance of forming  $\text{C}_6\text{H}_5\text{Cl}$  as one born in 99 mole %  $\text{C}_6\text{H}_6$  and 1 mole %  $\text{CCl}_4$ . This is difficult to explain since nearly every  $\text{Cl}^{38}$  in the former solution would be expected to lose both its kinetic energy and its charge before encountering a  $\text{C}_6\text{H}_6$  molecule. (The ionization potential of Cl is 12.95 e.v. and that of  $\text{CCl}_4$  11.0 e.v.<sup>15</sup>)

**Organic Yields in the Solid Phase.**—Although the organic yields of all the primary and secondary organic chlorides tested are essentially the same (*ca.* 22%) in the liquid phase they vary greatly in the solid phase, those for ethyl and *n*-propyl being about 62% and those for the other halides tested being 32–38%. There is as yet no plausible theory to explain the variations in magnitude of the phase effect from compound to

(12) C. T. Hibdon and C. O. Muehlhaue, *Phys. Rev.*, **83**, 943 (1952).

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

(14) J. M. Miller and R. W. Dodson, *ibid.*, **13**, 865 (1950).

(15) R. F. Baker and J. T. Tate, *Phys. Rev.*, **53**, 683 (1938).

compound as illustrated by these results and others reported in the literature. Solidification has been observed to increase the yield in a number of cases<sup>16-18</sup> but to have little or no effect on it in others.<sup>2,3</sup> Since the scavenger studies reported in a preceding section have shown that the stable products of the Cl<sup>37</sup>(*n*, $\gamma$ )Cl<sup>38</sup> reaction in liquid hydrogen-containing organic chlorides are all produced by "high energy processes" it would not have been surprising if the yield had not changed on solidification. The fact that it does must be related either to a higher density of radicals formed by the high

(16) L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 617 (1949).

(17) S. Goldhaber, R. S. H. Chiang and J. E. Willard, *THIS JOURNAL*, **73**, 2271 (1951).

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

energy atom in losing their energy to a solid medium or to a different relative yield of different types of radicals when the medium is solid. These effects might result from either the higher density of the solid or a different average orientation of its molecules as compared to the liquid, or both. They may increase the probability that the tagged atom will become stabilized by combination with an organic radical rather than by reaction with a carbon-hydrogen bond to form hydrogen chloride.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

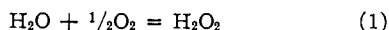
## Free Radical-Initiated O<sup>16</sup>O<sup>18</sup>-H<sub>2</sub>O<sup>16</sup> Exchange Reaction in Aqueous Solution

BY EDWIN J. HART, SHEFFIELD GORDON AND DWIGHT A. HUTCHISON

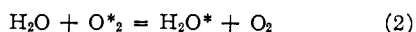
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A  $\gamma$ -ray-initiated chain exchange reaction of isotopically enriched dissolved oxygen with normal oxygen of the water has been found in alkaline solutions. The yield of this reaction is independent of dosage rate of  $\gamma$ -rays or intensity of ultraviolet light, increases with pH and concentration of enriched dissolved oxygen, and decreases with increasing concentration of hydrogen peroxide. The kinetic study provides evidence for the existence of the equilibrium: OH = H<sup>+</sup> + O<sup>-</sup>. The propagation steps are concluded to be: O<sup>-</sup> + O\*<sub>2</sub> = O\*<sup>-</sup> + O<sub>2</sub> and O\*<sup>-</sup> + OH<sup>-</sup> = O<sup>-</sup> + O\*H<sup>-</sup>, and the termination steps postulated as: O<sup>-</sup> + H<sub>2</sub>O<sub>2</sub> = OH<sup>-</sup> + HO<sub>2</sub> and O\*<sup>-</sup> + H<sub>2</sub>O<sub>2</sub> = O\*H<sup>-</sup> + HO<sub>2</sub>.

Hydrogen peroxide is produced by  $\gamma$ -ray irradiation of aqueous solutions containing dissolved oxygen. In the pH range below 9.0 the reaction proceeds with a yield,  $G_{H_2O_2}$ , of two molecules of hydrogen peroxide per 100 e.v. of absorbed  $\gamma$ -ray energy. Above a pH of 11,  $G_{H_2O_2}$  is one.<sup>1</sup> The net reaction is



During the course of an investigation using enriched oxygen to study reaction 1, a  $\gamma$ -ray-initiated chain exchange reaction between dissolved enriched oxygen and water has been found. In the region of high pH where the yield of the chain reaction is high and the yield of the hydrogen peroxide is negligible, the reaction is



(O\* is used throughout this paper to designate oxygen of 1.4 atomic per cent. O<sup>18</sup>).

The effect of dosage rate of  $\gamma$ -rays, intensity of ultraviolet light, and concentration of enriched oxygen, hydrogen ion and hydrogen peroxide on exchange reaction 2 is reported in the present paper. Additional evidence is provided to support the previously postulated ionization of the hydroxyl radical<sup>2,3</sup> in alkaline solution, and a simple mechanism is given for the chain exchange propagation steps.

### Experimental

A triply distilled water purified by distillation succes-

(1) H. Fricke, *J. Chem. Phys.*, **2**, 556 (1934).

(2) S. Gordon, E. J. Hart and P. D. Walsh, AECU-1534; S. Gordon and E. J. Hart, paper presented at Sept., 1952, ACS Meeting.

(3) E. J. Hart, S. Gordon and D. A. Hutchison, *THIS JOURNAL*, **74**, 5548 (1952).

sively from alkaline potassium permanganate and acid potassium dichromate solution, followed each time by passage through a silica tube heated to 800° was used in these experiments. The enriched oxygen was obtained by electrolysis of Stuart Oxygen Company 1.4 atomic % O<sup>18</sup> water. The oxygen was purified by recycling through activated platinized asbestos heated to 300° in order to remove traces of hydrogen and finally through an activated charcoal trap cooled by liquid nitrogen. Mass spectrometer analysis showed that no impurities of mass less than 100 are present to an extent more than 0.01%.

The aqueous solution was first degassed by pumping with a Hyvac and mercury diffusion pump backed by carbon dioxide and liquid nitrogen traps. The solution was then saturated with enriched oxygen gas at the desired pressure and forced into a specially designed 100-ml. syringe which served as the irradiation chamber. Suitable precautions were taken to ensure that all air was removed from the syringe by introducing and expelling two 10-ml. portions of the oxygenated solution before the addition of 100 ml. of solution used for the irradiation. Solutions prepared in this manner contained no gas phase and were irradiated by exposure in specially designed chambers<sup>4</sup> to Co<sup>60</sup>  $\gamma$ -rays. The dosage rates were measured by use of the ferrous sulfate actinometer, and a value of 15.5 Fe<sup>+++</sup>/100 e.v. was used to convert chemical yield to electron volts/liter.<sup>5</sup> After irradiation, the gas was extracted from the solution in a Van Slyke apparatus, and the isotopic analyses were run on a 60-degree sector-type direction-focusing mass spectrometer recently designed by Hutchison.<sup>6</sup> It was then assumed that the isotopic dilution taking place in the dissolved oxygen during irradiation was due to replacement of enriched dissolved oxygen by normal oxygen of water. The estimated enrichment of the water by exchange of enriched oxygen in all cases amounted to less than 0.002% and in the present experiments was neglected.

Equation 3 was used to calculate the molarity,  $M_o$ , of the enriched oxygen component in the dissolved gas as obtained

(4) R. A. Blomgren, E. J. Hart and L. S. Markheim, *Rev. Sci. Instruments*, **24**, 298 (1953).

(5) C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

(6) Description of instrument to be published.