[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, PRINCETON UNIVERSITY AND UNIVERSITY OF KANSAS]

Studies of the Tritium Labeling Reaction. III. Alcohols and Acetone[1]

BY WILFORD J. HOFF, JR., AND F. S. ROWLAND[2]

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The reactions of tritium from the $Li^6(n,\alpha)H^3$ nuclear reaction have been studied in methyl alcohol, ethyl alcohol and acetone. All of the important non-gaseous products can be formed in a reaction involving the tritium atom and a single solvent molecule. In these solvents, the most important reactions leading to non-gaseous products are

(1) $T + \equiv C{-}H \rightarrow \equiv C{-}T + \ldots$; (2) $T + \equiv C{-}CH_3 \rightarrow \equiv C{-}T + \ldots$;

(3) $T + {-}CH_2OH \rightarrow {-}CTO + \ldots$; (4) $T + {>}C{=}O \rightarrow T{-}\overset{|}{\underset{|}{C}}{-}OH$; (5) $T + {=}O \rightarrow {-}OT,\ T + {-}O{-} \rightarrow {-}OT.$

Introduction

Tritium atoms, recoiling with 2.7 Mev. energy from the $Li^6(n,\alpha)H^3$ reaction and brought to rest in an organic medium, become incorporated into the otherwise unchanged organic molecule in yields of from 10–50% for a wide variety of organic compounds. Most of the organic compounds in which this reaction has been investigated have been sufficiently complex that isolation and identification of all of the labeled species produced has not been attempted. In most cases, investigation has been restricted to the parent organic molecule itself, and to the distribution of activity within this molecule.[3]

The reactions of these "hot" tritium atoms have been investigated, however, in liquid methane and ethane.[4] In these compounds, the primary labeled tritium products are hydrogen and the parent compound in roughly equal proportion, and totaling 88 and 79% of the tritum activity, respectively. The remainder of the radioactivity has been distributed among non-parent hydrocarbons, both saturated and unsaturated, with molecular size up to C_4 hydrocarbons, and larger.

The 80+% yield of very simple products in the methane and ethane cases, together with the high yield of labeled parent compound in complex organic systems, has led to the hypothesis that the final chemical combination for an important fraction of the tritium occurs at rather low energies, and involves only the tritium atom and one disrupted molecule.[3b]

In order to verify or supplement this hypothesis, we have extended the investigation of these tritium atom reactions to further simple molecules: methyl alcohol, ethyl alcohol and acetone. We have attempted to account chemically for all of the non-gaseous tritium produced in neutron irradiations of solutions of lithium salts in these solvents.

Experimental

Irradiation.—All of the irradiations were carried out on liquid solutions of either $LiNO_3$ or LiCl, with the exception of one run on a solid solution of $LiNO_3$ in acetone. Irradiation times of 1 or 2 hours produced sufficient tritium activity to allow easy detection, without causing undue radiation damage in the solutions.

The irradiations were carried out under a variety of experimental conditions. The most important of the variables are listed in Tables I and II, together with the results of each experiment. All of the irradiations except experiment 12 were carried out in the same water-cooled location in the Brookhaven reactor; experiment 12 was carried out in the special liquid nitrogen-cooled facility. The nominal neutron flux in the former was 1.8×10^{12} n/cm.^{2}/sec.; the flux in the liquid nitrogen facility, 4.0×10^{12} n/cm.^{2}/sec.

Experiments 1 and 2 were carried out with ethyl alcohol solutions sealed off, in the presence of air, in glass tubes equipped with break-offs. These were cracked open in the presence of additional ethyl alcohol carrier. Experiments 10 and 13 were carried out with solutions sealed off in the absence of air. Prior to sealing, the acetone had been distilled back and forth several times in a U-tube, and the frozen solvent pumped on after each distillation. After irradiation, each sealed tube was cracked open while the contents were frozen down with liquid nitrogen, and then allowed to warm and transferred to a stoppered bottle.

Experiments 11 and 12 were carried out with solutions which were irradiated in aluminum tubes approximately 5" long and $^1/_4$" in diameter. In experiment 11, the tubes were packed in powdered Dry Ice throughout the irradiation period.

The rest of the irradiations were carried out in one or more 15-ml. aluminum cups, equipped with tops in which a hole had been punched to prevent pressure build-up. After irradiation, the solutions were immediately transferred to stoppered glass bottles. Loss of solution during this type of irradiation was negligible.

The acetone solutions usually turned light yellow in color during the irradiation, with the exception of experiment 9 in which the dark blue DPPH solution tended toward a reddish-brown color after irradiation. The yellow color was very much lighter in experiments 8 (20% water by weight) and 12 (solid). The alcoholic solutions all were colorless following irradiation.

Derivatives.—After each irradiation, appropriate carriers were added to the irradiated solution, usually in separate experiments for each carrier. The carriers were often separated from the parent compound by vacuum distillation, followed by the precipitation of a characteristic derivative. In some cases, the derivative was precipitated directly from the solution of both carrier and sample. These derivatives were then recrystallized first to the correct melting point, and then to constant specific radioactivity through several successive crystallizations. The particular derivatives used were chosen because very little exchange of labile hydrogen took place during their formation, as well as for their relative ease of formation. Most form readily at room temperature or require only slight heating.

The derivatives were prepared as follows.

1. **Alcohols.**—The alcohols were first distilled from a solution of 1-ml. sample, 1 ml. of the appropriate alcohol as carrier, and 25–500 ml. of water, collecting approximately 1 ml. in the appropriate temperature range. This distillate was added to 3,5-dinitrobenzoyl chloride; the precipitate of 3,5-dinitrobenzoate was washed with 2% Na_2CO_3 solution and water, and recrystallized from ethanol–water and/or methanol–water solution.

Isopropyl alcohol was isolated from the ethyl alcohol

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[2] University of Kansas, Lawrence, Kansas.

[3] (a) R. Wolfgang, F. S. Rowland and C. N. Turton. *Science*, **121**, 715 (1955); (b) F. S. Rowland, C. N. Turton and R. Wolfgang, THIS JOURNAL, **78**, 2354 (1956); (c) F. S. Rowland and R. Wolfgang, *Nucleonics*, **14**, No. 8, 58 (1956).

[4] R. Wolfgang, J. Eigner and F. S. Rowland, *J. Phys. Chem.*, **60**, 1137 (1956).

TABLE I

	Ethyl alcohol				Methyl alcohol
Irradiation no.	1	2	3	14	4
Wt. organic, g.	1.34	1.0	19.2	19.8	19.2
Wt. Li salt, g.	0.20 LiCl	0.16 LiCl	0.60 $LiNO_3$	0.60 $LiNO_3$	0.61 $LiNO_3$
Irradiation conditions	1 hr. in sealed tube	6 hr. in sealed tube	1 hr. in vented Al cup	2 hr. in vented Al cup	1 hr. in vented Al cup
C–T activity in parent compd. dpm./mg.	2600 ± 150[a]	20400 ± 300[a]	3120 ± 50	5100 ± 100	3110 ± 70
Calcd. total activity produced	[c]	[c]	13,500	26,300	13,700
% Total T as C–T in parent	[c]	[c]	23	20	23
Activity relative to C–T in parent					
H_2O exchangeable	[c]	[c]	0.90 ± 0.10	0.85 ± 0.05	1.24 ± 0.04
Methyl alcohol	[c]	0.06 ± 0.01	0.08 ± 0.01	0.06 ± 0.01	
Ethyl alcohol					0.01
i-Propyl alcohol[b]	[c]	≤0.02	0.02	0.02	[c]
Ethylene glycol	[c]	[c]	0.01	[c]	0.01
Formaldehyde	[c]	[c]	0.01	[c]	0.05 ± 0.01
Acetaldehyde	0.06 ± 0.01	0.05 ± 0.01	0.09 ± 0.01	0.12 ± 0.01	[c]
B.p. >100°	[c]	[c]	[c]	0.01	[c]
Total non-gaseous	1.86 ± 0.10	1.91 ± 0.04	1.88 ± 0.05	1.88 ± 0.05	2.25 ± 0.05

[a] Some loss of solution in adding to carrier; hence, specific activity of original unknown. [b] Primary hydrogens only. [c] Not measured.

solutions by oxidation to acetone with $KMnO_4$ and $MgSO_4$, followed by formation of the 2,4-dinitrophenylhydrazone.[5] This, of course, gives only the tritium activity present in the primary hydrogens of isopropyl alcohol.

2. **Aldehydes.**—Formaldehyde and acetaldehyde derivatives were formed from both ethyl alcohol and acetone by addition of 3-ml. sample, 1 ml. of aldehyde carrier, sodium acetate, and HCl in ethanol–water solution, to a large excess of dimedone solution. The aldehyde–dimedone precipitate was recrystallized from ethanol–water solution.

Acetaldehyde also was isolated in experiments 1 and 2 as the semicarbazide and in experiment 3 as the 2,4-dinitrophenylhydrazone.

3. **Acetone.**—Acetone was always isolated as the 2,4-dinitrophenylhydrazone by addition of 1-ml. sample to 100 ml. of a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* HCl, and recrystallization from ethanol.

4. **Ethylene Glycol.**—Three ml. of sample was added to 1 ml. of ethylene glycol carrier and 10 ml. of pyridine. After vacuum distillation of this solution to remove the alcohol and part of the pyridine, benzoyl chloride was added, the solution heated, and the dibenzoate precipitated by dilution with water. The precipitate was recrystallized from ethanol–water.

5. **Ethanol-to-acetate.**—Ethyl alcohol was oxidized to acetic acid with potassium dichromate in sulfuric acid. The acetic acid was distilled from the solution, neutralized with NaOH and evaporated to dryness. The sodium acetate was recrystallized from ethanol. A portion of the sodium acetate was dissolved in acidic ethanol and precipitated with *p*-bromophenacyl bromide. The *p*-bromophenacyl acetate was recrystallized from water.

6. **Acetaldehyde-to-acetate.**—Acetaldehyde was oxidized to acetic acid by (a) Benedict solution or (b) potassium dichromate, and the resulting solution treated as above to produce sodium acetate and *p*-bromophenacyl acetate.

Labile and High Boiling Tritium.—Several ml. of water was often added to a few ml. of the sample, and the solution fractionally distilled. The amount of labile tritium present was measured through the radioactivity of the next-to-last cut from this distillation. The excess tritium activity of the final cut (residue of undistilled liquid) over that of the pure water fraction was the measure of the activity bound in compounds with a boiling point greater than 100°. In those cases in which two water cuts other than the residue were measured, the agreement in specific activity was very satisfactory.

Counting.—The tritium activity was measured by gas proportional counting of the mixture of gases produced by treatment of the sample with zinc, nickelic oxide, and water at 700°.[6] The normal counter filling consisted of 34 cm. ethane plus the active gas (~1 cm.).

Results

The experimental results for the irradiated solutions in alcohols are given in Table I; for acetone, in Table II. The results have been expressed for the parent molecule in terms of the observed specific activity and the percentage this represents of the calculated total tritium production. The yields of other products have been expressed relative to that of the parent molecule, rather than in percentages of calculated total activity, in order to eliminate uncertainties in actual neutron flux for each irradiation. Any variation in this relative ratio could then, of course, be caused by variations in yield of either the labeled parent or non-parent molecule.

Comparison of the total non-gaseous activity with the sum of that found in each chemical species indicates, within the errors, that the major non-gaseous tritium products have been identified. Experiment 9 is an exception in which a large fraction of the activity carried with the DPPH residue and was not exchangeable readily with water.

Table III shows the intramolecular distribution of the tritium in two cases. Table IV summarizes the pertinent data on exchange reactions involved in derivative preparation, and lists the observed data from experiment 3 for comparison.

Discussion

There are two obvious paths by which tritium activity can be introduced into these compounds other than by direct reaction of an energetic atom or ion with the parent molecule. The first of these is by exchange reactions with labile tritium present in the system. Such exchange might take place either with the carrier material after it is added, or with the carrier or precipitating agent during derivative formation. All such exchange reactions have been shown to be slow under our conditions by the experiments listed in Table IV. The extent of these exchange reactions is sufficiently small that they can be considered negligible except for those constituents which appear to contain 0.5% or less of the total tritium produced by the nuclear reactions.

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[5] L. Kaplan, THIS JOURNAL, **77**, 5469 (1955).

[6] K. Wilzbach, L. Kaplan and W. G. Brown, *Science*, **118**, 522 (1953).

TABLE II: CHEMICAL STATE OF TRITIUM PRODUCED BY NEUTRON IRRADIATION OF SOLUTIONS OF $LiNO_3$ IN ACETONE

Irradiation no.	5	6	10	13	11	12	7	8	9
Wt. organic, g.	19.7	19.8	4.0	7.9	7.9	15.8	7.6	6.3	7.9
Wt. $LiNO_3$, g.	0.60	0.60	0.12	0.24	0.24	0.48	0.23	0.19	0.24
Special conditions	None	None	No air present	No air present	−78° (liquid)	−196° (solid)	+0.1 g. H_2O	+1.95 g. H_2O	+11 mg. DPPH
Irradiation conditions	1 hr. in vented Al cup	1 hr. in vented Al cup	1 hr. in sealed Pyrex	2 hr. in sealed quartz	35 min. dry ice	1 hr. in liq. N_2 facility	1 hr. in vented Al cup	1 hr. in vented Al cup	1 hr. in vented Al cup
C–T activity in parent compd. (dpm./mg.)	4400 ± 150	3260 ± 40	2170 ± 30	6350 ± 50	2420 ± 25	7900 ± 120	3180 ± 60	2580 ± 40	3260 ± 40
Calcd. total activ. prod.	13,200	13,100	[a]	26,300	7700	29,300	13,000	10,400	13,200
% Total T as C–T in parent	33	25	20–30[a]	24	31	24	24	25	22[b]
Activity relative to C–T in parent									
H_2O exchange	0.39 ± 0.02	0.56 ± 0.03	.....	0.49 ± 0.02	.....	0.70 ± 0.03	.....	1.91 ± 0.08	1.02 ± 0.03
Formaldehyde	.....	0.01	.....	.....	.....	.....	.....	.....	.....
Acetaldehyde	0.28 ± 0.01	0.38 ± 0.01	0.17 ± 0.01	0.35 ± 0.01	0.27 ± 0.01	0.20 ± 0.01	0.29 ± 0.01	0.31 ± 0.01	0.43 ± 0.01
i-Propyl alc.	0.05 ± 0.01	0.05 ± 0.01	.....	0.05 ± 0.01	.....	0.12 ± 0.01	.....	.....	.....
B.p. >100°	0.04	0.06	.....	0.10	.....	0.08	.....	.....	.....
Total non-gaseous	1.9 ± 0.2	2.1 ± 0.1	2.3 ± 0.1	1.9 ± 0.2	2.8 ± 0.3	1.9 ± 0.2	2.2 ± 0.2	3.2 ± 0.1	4.5 ± 0.1

[a] Uncertainty in neutron absorption in Pyrex. . . . Not measured. DPPH = diphenyl picryl hydrazyl. [b] Total activity in solution exceeds calculated value; % listed is % total activity in solution.

It is also possible for the general radiation damage taking place in a system to produce labeled compounds other than the parent molecule. In considering the fate of any particular tritium atom, the term "general radiation damage" would include all destruction caused by radiation and by particles other than the tritium atom in question.

There are two important possible avenues for radiation damage influence: (a) subsequent destruction of a labeled molecule by the interaction of additional particles or radiation, and (b) reaction of an energetic tritium atom with one of the reactive fragments produced by prior irradiation, rather than with the parent molecule. Both of these mechanisms are important in long irradiations.

General radiation damage can occur from any of the variety of radiations present in an operating nuclear reactor, but, in these systems, the chief source of radiation damage is the $Li^6(n,\alpha)H^3$ reaction itself.[7] Since essentially all of the 4.8 Mev. reaction energy is absorbed in the solution, 4.4×10^{13} e.v. must be dissipated for every dpm. of tritium produced. It can be seen, by combining these data with the *G* value of 8.2 for destruction of ethyl alcohol irradiated with 28 Mev. He^{++} ions,[8] that approximately 1% of the ethyl alcohol molecules will be destroyed in a two-hour irradiation at the concentrations and fluxes used in these experiments. Since the *G* value for production of any particular chemical species is much less than 8.2, production of any labeled compound in ethanol solutions by destruction of the labeled parent can also be neglected except for those compounds containing 0.5% or less of the total tritium produced. The same conclusion can be reached for methanol and acetone solutions by similar calculations.

The importance of reactions of the energetic tritium atom with reactive products of radiation destruction is shown to be small by experiment 9, in which the radical scavenger, DPPH (diphenyl picryl hydrazyl), was present during the irradiation. Although the reactive species were greatly reduced in concentration by the rapid reaction with DPPH,[9] the yields of tritium as acetone and acetaldehyde were not affected within the errors of measurement.

There are several non-gaseous labeled compounds produced in these solutions with yields well above the possible level of activity from radiation damage and/or exchange reactions. These may be summarized for alcohols and acetone under the following general reactions, listing the approximate percentage of the tritium involved in each reaction in Table V.

Furthermore, there are gaseous labeled products from each of these systems. In a single experiment,[10] it has been shown that the gaseous prod-

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[7] S. Markowitz and F. S. Rowland, unpublished.

[8] W. R. McDonnell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

[9] A. Prevot-Bernas, A. Chapiro, C. Cousin, Y. Landler and M. Magat, *Disc. Faraday Soc.*, **12**, 98 (1952).

[10] R. Wolfgang, J. Eigner and F. S. Rowland, unpublished results.

TABLE III

INTRAMOLECULAR TRITIUM DISTRIBUTION

Expt. no.	Compd.	dpm./mg. Parent	dpm./mg. Oxidized derivative NaAc	dpm./mg. Oxidized derivative p-BrPhAc	dpm./mmole	% Parent
3	C_2H_5OH	3120 ± 50			14.3×10^4	100
			1325 ± 12		11.0×10^4	77
				388 ± 11	10.0×10^4	70
6	CH_3CHO (From acetone irradiation)	2460 ± 60			10.8×10^4	100
a			80 ± 8		6.6×10^3	6
				24 ± 6	6.2×10^3	6
b			47 ± 7		3.7×10^3	4
				17 ± 6	4.4×10^3	4

TABLE IV

EXCHANGE REACTIONS IN COMPOUNDS AND DERIVATIVES

Compd.	Solvent	Derivative	Exchange expt., dpm./mg. Labile T	Exchange expt., dpm./mg. Derivative	Expt. 3, dpm./mg. Labile	Expt. 3, dpm./mg. Derivative
CH_3OH	ROH	3,5-DNB	500,000	20[a]	3000	100
C_2H_5OH i-C_3H_7OH	ROH	3,5-DNB	300,000	300 30[a]	3000	600
i-C_3H_7OH	C_2H_5OH	2,4-DNPH of acetone	18,000	15	3000	35
$(CH_2OH)_2$	C_2H_5OH	Dibenzoate	18,000	12	3000	25
HCHO	C_2H_5OH	Dimedone	18,000	30	3000	55
CH_3CHO	C_2H_5OH	2,4-DNPH	18,000	140	3000	170
CH_3CHO	C_2H_5OH	Semicarbazide	500,000	400	..	..
CH_3CHO	CH_3COCH_3	Dimedone	90,000	25	..	..
CH_3COCH_3	CH_3COCH_3	2,4-DNPH	400,000	20	..	..

[a] Distilled from $\geq$20 volumes of water.

TABLE V

APPROXIMATE PERCENTAGES OF TOTAL TRITIUM REACHING STABLE CHEMICAL COMBINATION BY EACH REACTION IN THE PURE SOLVENT AT ROOM TEMPERATURE

Reaction	Ethyl alcohol, %	Methyl alcohol, %	Acetone, %
T for H	22	23	25
T for CH_3	1	..	9
$RCHO$ from RCH_2OH	2	1	..
C–OH from C=O	..	..	1
Labile T	20	29	12

(1) Substitution of T for H

$$C_2H_5OH + T \longrightarrow C_2H_4TOH + \ldots$$
$$CH_3OH + T \longrightarrow CH_2TOH + \ldots$$
$$CH_3COCH_3 + T \longrightarrow CH_2TCOCH_3 + \ldots$$

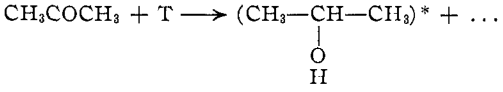
(2) Substitution of T for CH_3

$$C_2H_5OH + T \longrightarrow CH_2TOH + \ldots$$
$$CH_3COCH_3 + T \longrightarrow CH_3CTO + \ldots$$

(3) Formation of aldehyde from alcohol

$$CH_3OH + T \longrightarrow HCTO + \ldots$$
$$C_2H_5OH + T \longrightarrow (CH_3CHO)^* + \ldots$$

(4) Formation of alcohol from ketone



$$CH_3COCH_3 + T \longrightarrow (CH_3\text{—}\underset{\substack{|\\ O\\ H}}{CH}\text{—}CH_3)^* + \ldots$$

(5) Formation of labile tritium compounds

$$\text{-OH} + T \longrightarrow \text{-OT} + \ldots$$
$$\text{=O} + T \longrightarrow \text{-OT} + \ldots$$

ucts from an ethyl alcohol solution of LiCl include

HT	51.4%
CH_3T	3.5%
C_2H_5T $(+C_2H_3T)$	1.7%
$C_3H_7T + C_4H_9T$	0.4%
Carried by C_2H_5OH	43.0%

The activity carried by ethyl alcohol in this experiment is in excellent agreement with the total non-gaseous percentages listed for ethyl alcohol in Table V.

Reaction 1, the substitution of tritium for ordinary hydrogen without other change in the molecule, has been observed in yields from 10 to 50% for every organic compound yet tested.[3] In these three solvents, this reaction is again a very important one. The room temperature yields appear to be independent of all the variables tested within the limits of error.

Reaction 2 represents a rather large percentage of the yield for acetone solutions, and a lesser, but still significant, percentage in ethanol solutions. The intramolecular tritium distribution in the former case shows that almost all of the activity in the acetaldehyde is present in the aldehyde group, consistent with the reaction as written above. The non-zero yield of tritium in the methyl group falls within the range of activity possible from radiation damage and/or exchange reactions. The yield of reaction 2 in acetone solutions is also essentially independent of reactive solutes or diluents.

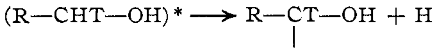
Reaction 4 proceeds in comparatively low yield and can be explained plausibly as tritium attack on the carbonyl carbon. Such an attack should place all of the tritium on the central carbon of the isopropyl alcohol. The intramolecular distribution was not checked by degradation because of the low levels of activity involved.

Reactions 1, 2 and 4, as well as 5 can be written as occurring by breaking one bond in the parent molecule and attaching tritium in its place. Reaction 3 is an exception and requires the breaking of at least two bonds in the parent molecule. However, it has been observed that aldehydes are frequently among the products of radiation processes in alcohols. For example, Newton and McDonell have shown that formaldehyde is produced in the radiolysis of CH_3OH with 28 Mev. He^{++} ions,[8] and McDonell and Gordon have shown similar production with Co^{60} γ-radiation.[11] Moreover, McDonell has demonstrated that the yield of formaldehyde from methyl alcohol–water solutions is directly proportional to the methyl alcohol concentration, and is presumably a characteristic product of the radiolytically excited molecule.[12] Formaldehyde also has been observed at high temperatures in the photolysis of methyl alcohol, as well as being present at low temperatures in the same experiments in low yields.[13] Recently, Burr has shown that the $-CH_2-$ carbon of ethyl alcohol is much more likely to lose a hydrogen atom than the CH_3- carbon, both in radiolysis with Co^{60} γ-radiation and in ionization in a mass spectrometer.[14] A similar conclusion was reached previously by McDonell and Newton from the large observed production of vicinal glycols in the radiolysis of a series of aliphatic alcohols.[8]

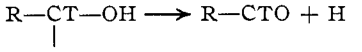
Our observed production of labeled aldehyde from the corresponding alcohol can be explained in a manner consistent with these observations by postulating that the initial substitution of T for H on the $-CH_2-$ carbon leaves an excited molecule

$$T + R—CH_2—OH \longrightarrow (R—CHT—OH)^* + \ldots \qquad (a)$$

which subsequently decomposes by two further steps to give the aldehyde



$$(R—CHT—OH)^* \longrightarrow R—\underset{|}{C}T—OH + H \qquad (b)$$



$$R—\underset{|}{C}T—OH \longrightarrow R—CTO + H \qquad (c)$$

Both (b) and (c) have been postulated previously by others in explanation of the experiments summarized above.

One result of such a series of reactions would be the depletion of activity in the $-CH_2-$ group of the parent alcohol. This is consistent with the higher specific activity per H atom observed for the methyl group of ethyl alcohol, as shown in Table III.

A substantial fraction of the tritium activity reaches stable chemical combination as tritium bound to oxygen. The reactions listed under (5) are probably the most important in the production of labile tritium. However, the rapidity of exchange of this tritium makes information as to the actual original reaction very difficult to obtain.

The effects of temperature and phase upon these reactions are demonstrated in experiments 11 and 12. In the liquid irradiated at −78°, and in the solid solution irradiated at −196°, there is no change in the amounts of acetone and acetaldehyde produced. There is an increase in labile activity in experiment 12 and probably so in experiment 11 in which the total non-gaseous yield has increased. However, the qualitative picture of the reactions taking place in these two experiments is the same as in the room temperature irradiations.

The introduction of either DPPH or water into the acetone solutions produces significant changes in the yields of both labile activity and total non-gaseous activity. These increases correspond to a reduction in total gaseous activity, and presumably represent tritium reaction with DPPH and water in preference to reaction to form HT.

On the other hand, reactions 1 and 2 are essentially independent of the concentration of dissolved solutes. Reactions 3 and 4 are probably also unaffected by these solutes, although this conclusion has not been tested by experiment. It is quite possible that *some* of the reactions forming labile tritium are also unaffected by H_2O or DPPH; the contribution of such reactions to the total yield of labile tritium is unknown.

The general course of reaction in these systems can be interpreted as occurring in this order: (a) reaction at comparatively high energy by reactions 1, 2 and probably 3 and 4, by a mechanism uninfluenced by dissolved substances; (b) reaction at a lower energy, perhaps essentially thermal, to form either labile tritium or gaseous HT. The yield of particular products will be dependent upon competitive reactions involving dissolved species as well as the solvent molecules.

The products of the reactions listed under (a) are all simple relatives of the parent molecule, and can be obtained by the reaction of the recoil tritium atom with a single solvent molecule, in agreement with the previously postulated mechanism.[3b] There does not appear to be any reason for requiring that these reactions take place in the presence of a very high concentration of radicals. Indeed, the absence of influence on reaction yields of DPPH would indicate that diffusing radicals have no important part in the reactions at all.

The nature of the reactions involved in (a) is not clear—they may presumably involve either a "hot" radical which immediately reacts with a tritium atom without opportunity for diffusion (and reaction with solutes), or formation of a complex which decomposes to products without going through radical formation. Such an intermediate complex is not that of the Walden inversion mechanism, as shown by experiments with molecules containing asymmetric centers.[3b,15] Further experiments, especially in the gas phase, should make the nature of these mechanisms clearer.

Although throughout we have described these reactions in terms of a tritium atom, we do not intend to imply that the reacting species is necessarily the uncharged atom. Stevenson and others have pointed out the importance of ion–molecule reactions in similar systems,[16] and possible reactions of T^+ certainly need to be considered. The ex-

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[11] W. R. McDonell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955).

[12] W. R. McDonell, *ibid.*, **23**, 208 (1955).

[13] M. K. Phibbs and B. deB. Darwent, *ibid.*, **18**, 495 (1950).

[14] J. G. Burr, Jr., THIS JOURNAL, **79**, 751 (1957).

[15] F. S. Rowland and R. P. Malsan, A. C. S. Meeting, Atlantic City, Sept., 1956.

[16] D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955).

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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PRINCETON, N. J.
LAWRENCE, KANSAS

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

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

BY J. C. W. CHIEN AND J. E. WILLARD

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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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(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.

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