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THE PREPARATION OF GAS FOR ASSAY OF
TRITIUM IN ORGANIC COMPOUNDS

by

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Summary

A simple method has been developed for the conversion of tritium in organic compounds to a mixture of hydrogen and methane, suitable for assay in an ionization chamber or internal gas counter. The compound is heated for three hours at 640°C with a mixture of zinc, nickel oxide and water in a sealed tube made of Pyrex 1720 glass. A wide variety of organic compounds has been analyzed with an accuracy and reproducibility of one per cent. Analysis over a wide range of tritium activities is facilitated since tritium is retained (to the extent of about 1.5 per cent) only in the glass tube, which is discarded after a single use. Manipulations required for an analysis can be performed with simple apparatus in less than thirty minutes.

Tritium in gaseous form may be measured accurately and efficiently by means of ionization chambers(1,2,3,4) or internal gas counters.(5,6,7,8,9,10) Previously reported procedures for converting the tritium in organic compounds to a gas suitable for such measurements have involved preliminary combustion to water, followed by reduction to hydrogen by a metal(1,2,3,6) or lithium aluminum hydride(4) or to a tritiated hydrocarbon by a Grignard reagent(7,8) or aluminum carbide.(9) In addition to being time-consuming and requiring rather elaborate apparatus, these procedures suffer from the fact that there is an exchange(11) of hydrogen between water and glass surfaces; the resulting "memory" necessitates either a preconditioning(12) of the apparatus when samples of varying specific activities are analyzed or a scavenging operation between analyses. The present paper describes a rapid, one-step procedure for obtaining the tritium from an organic compound as a mixture of hydrogen and methane, which has been used for ion current measurements, and should also be satisfactory for internal gas counting.(5,12)

The search for such a procedure was prompted by the development, by Professor T. S. Lee(13) of the University of Chicago, of a method for the determination of oxygen in organic compounds. In his method, the oxygen is converted to carbonate on heating the compound with a mixture of graphite

and strontium oxide or to oxide on heating with metallic zinc. His conclusion that hydrogen would appear as hydrogen gas or methane under these conditions suggested the possible applicability of such a method to tritium assay.

In preliminary experiments compounds containing tritium were heated at 640°C in evacuated and sealed tubes with the reagents used by Lee. The tubes were constructed of Pyrex 1720 glass because ordinary Pyrex 7740 glass is not sufficiently heat resistant while quartz and Vycor were found to be too permeable to hydrogen. The volatile product was pumped through a trap at -195°C into an ionization chamber for tritium assay. Any condensible material found in the trap was added to the gas in the chamber.

The decomposition of water by heating with zinc yielded non-condensable gas which contained the expected amount of tritium; the use of graphite with barium oxide or even with zinc invariably gave low results. Further investigation of systems containing graphite was therefore abandoned.

The decomposition of 2-propanol-2-t with zinc gave quantitative yields of non-condensable tritiated products. In the case of benzyl- α -t alcohol, however, the gas produced even after prolonged heating contained substantial quantities of benzene and less than 90% of the expected amount of tritium. In a search for reagents which might promote the decomposition of aromatic products, carbon tetrachloride, iron, nickel, chromic oxide, nickelous oxide, nickelic oxide and vanadium pentoxide were added, in separate experiments, to the reaction mixture. Quantitative recovery of tritium from benzyl alcohol without formation of condensible material was consistently obtained by heating for three hours at 640°C with a mixture of granulated zinc and powdered nickelic oxide. These conditions did not give satisfactory results with some of the compounds analyzed. Addition of water to the reaction mixture improved the results in these cases, and was therefore made a part of the standard procedure. The analysis of the gas was simplified by expanding a known fraction directly into the ionization chamber rather than making a complete transfer with a Toepler pump.

Procedure

Reaction tubes 17 cm. long with break-tips, as shown in Figure 1, are made from 1.1 cm. diameter Pyrex 1720 glass tubing.¹ In each tube are placed 1 gm. of zinc (Baker and Adamson, 30 mesh), 100 mg. of nickelic oxide (Baker's Analyzed, gray-black powder), 5-6 mg. of water and a 5-10 mg. sample of the tritium compound. Water and liquid samples

¹Available on special order from Corning Glass Works, Corning, N. Y.

Figure 1. Reaction Tube

are introduced in small sealed ampoules with bent tips, solid samples in porcelain boats. The reaction tubes are constricted, evacuated to 1 mm., sealed off, and agitated until the ampoules are broken and the contents are evenly distributed. Using asbestos-covered tongs, the tubes are placed horizontally in a furnace at $640 \pm 10^\circ\text{C}$ and removed after three hours.

The apparatus shown in Figure 2 is used for transfer of the gas samples. A reaction tube, A, is placed in tube B, which is then evacuated, closed off, and inverted to break the tip of tube A. The gas is expanded into an evacuated ionization chamber, C, of the Berkowski type.^(14,2,15) Methane is admitted to the chamber through stopcock 2, sweeping in the gas between stopcocks 2 and 1, until atmospheric pressure is reached. The ion current collected at a potential of 380 volts is measured with a vibrating reed electrometer.² The tritium content of the chamber in microcuries is calculated by multiplying the current in amperes by 9.0×10^{11} . The total amount of tritium is obtained by multiplying that in the chamber by the ratio of the volume of the whole system to that above stopcock 2. (The volume of the system is corrected for the volume of glass in tube A, using a density of 2.5; the volume of the reagents in the tube is inappreciable.)

Results

A number of tritiated compounds have been analyzed by the described procedure. The tritium content of these compounds was known from ion current measurements on the hydrogen obtained from them by methods known to be quantitative.^(2,16) The results obtained by the zinc fusion method are listed in Table 1 together with the expected values. The standard deviation of a single measurement is 0.6 per cent; the average ratio of the results found to those expected is 1.010 ± 0.011 . The precision and accuracy of the method thus compare favorably with those obtained^(1,2,4,6,12) by conventional procedures based on combustion.

The extensive exchange of hydrogen during fusion, evidenced by the formation of tritiated benzene and nonvolatile product from incomplete decomposition of benzyl- α - t alcohol in the absence of nickelic oxide, was utilized to obtain further information on the scope of the method. Experiments were performed in which reaction tubes contained tritiated water and various unlabeled organic compounds. The recovery of tritium, shown in Table 2, indicates that the conversion to volatile product is substantially complete for all of the compounds except urea and aromatic halides. With these, significant amounts of ammonia and benzene, respectively, were found in the gas, in contrast to the results of a normal analysis, such as that of benzyl alcohol, from which only methane (72%) and hydrogen (28%) were obtained.

²Applied Physics Corporation, Pasadena, California, Model 30.

Figure 2. Apparatus for Analysis of Gas Samples

Table 1

DETERMINATION OF TRITIUM IN ORGANIC COMPOUNDS

Compound*	Tritium, $\mu\text{c}/\text{mM}$	
	Found $\dagger$ by Zinc Fusion	Expected
HOT	325.9 ± 1.1	327.0
CH_3CHTOH	11.65 ± 0.06	11.59
$\text{CH}_3\text{CHTOOCC}_6\text{H}_4\text{NO}_2$	11.52 ± 0.05	11.59
$\text{CH}_3\text{CT}(\text{OH})\text{CH}_3$	19.74 ± 0.08	19.42
$\text{C}_5\text{H}_5\text{CHTOH}$	10.69 ± 0.05	10.53
$\text{C}_6\text{H}_5\text{CHTOOCC}_6\text{H}_3(\text{NO}_2)_2$	10.72 ± 0.04	10.53
$\text{C}_6\text{H}_4\text{TCH}_3-(\text{o})$	4.90 ± 0.01	4.87
$\text{C}_6\text{H}_5\text{CT}=\text{NNHC}_6\text{H}_3(\text{NO}_2)_2$	9.69 ± 0.01	- - -
$\text{BrCH}_2\text{CHTC}_6\text{H}_4\text{NO}_2$	19.89 ± 0.15	19.63
$\text{C}(\text{CH}_3)_2(\text{NO}_2)\text{CHTC}_6\text{H}_4\text{NO}_2$	11.09 ± 0.03	10.98
Cholesterol	15.54 ± 0.08	15.31
Estradiol	28.39 ± 0.23	27.52
Dihydroxypregnanedione	5.35 ± 0.01	5.23
$(\text{C}_6\text{H}_5)_3\text{SiT}$	182.4 ± 0.3	184.0

*We are indebted to Drs. T. F. Gallagher and D. K. Fukushima for the samples of tritium-labeled steroids.

$\dagger$ Results include a correction of 1.5% for retention of tritium in the reaction tube. Errors are standard deviation of several analyses of each compound.

Table 2

ANALYSIS OF TRITIATED WATER IN PRESENCE OF
ORGANIC COMPOUNDS

Compound	Condensable Product % of Total Gas	Tritium in Gas %
Octadecane	0.0	99.5
Anthracene	0.0	99.9
Biphenyl	0.0	99.8
Cholesterol	0.0	100.6
Propylene diamine	0.6	99.4
m-Phenylene diamine	0.1	99.3
Benzaldehyde		
2,4-dinitrophenylhydrazone	0.0	99.9
Pyridine	0.0	100.5
Thiophene	0.2	99.9
Butyl chloride	0.6	99.9
Butyl bromide	0.3	100.0
Butyl iodide	0.5	99.9
Chlorobenzene	2.4	96.5
Bromobenzene	1.0	99.0
Iodobenzene	3.1	95.3
m-Dichlorobenzene	1.7	95.2
Urea	1.0	97.8

To determine the extent of "memory" in the procedure, an analysis of a sample of triphenylsilane containing 5.35 microcuries was followed immediately by an analysis of an inactive sample. The value obtained, less than 10^{-4} microcuries, corresponds to a "memory" of less than 0.002%. Such an experiment gives no information concerning the retention of tritium in the reaction tube. The reaction tube used for the analysis of benzyl alcohol containing 4.40 microcuries was enclosed in a larger tube and heated with water and zinc. The resulting gas contained 0.068 microcuries (1.54% of that in the initial sample). In a similar experiment, the retention of tritium in a tube used for the analysis of a sample of tritiated water was 1.7%. Results obtained by the method are increased by 1.5% to compensate for the loss.

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