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Self-radiolysis of Tritiated Long-chain Compounds

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Much work has been made by many investigators studying on the self-radiolysis of ^{14}C-labelled organic compounds (1-2). Additional light has recently been thrown on the similar radiolysis of organic compounds labelled with tritium whose beta particles are of rather strong reactivity with matters (3). Guarino *et al.* have thus reported strong self-radiolysis of tritiated methyl stearate, when its specific activity is in the order of magnitude of 10^2 to 10^3 C/mol (4). We have compared gaschromatograms and radiogaschromatograms of tritiated compounds of (A) low specific activity kept for storage for long time, (B) high specific activity for short time, and (C) high specific activity for long time.

All tritiated samples were thoroughly purified (5-7) and stored in glass ampoules or in paraffin-sealed vessels for a given time, *t*. They included (A) octadecane-[1-^{3}H] (16 mC/mol in its specific activity at $t = 0$) (4), (B) dodecan-[2,3-^{3}H, ^{3}H]-ol (15 C/mol) (6), and (C) stearic-[9,10-^{3}H, ^{3}H] acid (9.5 C/mol) (7). Then, all the samples were taken out for examination without further treatment. In the case of stearic acid (C), additional experiments were carried out with its methyl ester obtained by treating the stored sample with diazomethane in ethyl ether.

Mass- and radiogaschromatograms were simultaneously taken with Yanagimoto-Aloka GCG-5DH gaschromatograph which comprised an activated CuO-Fe system to convert the sample gases into tritiated hydrogen for counting in gaseous phase. Practically no memory effect has been observed throughout the experiments.

Practically no self-radiolysis was recognized over the chromatographic charts for (A) and (B), as shown in Figure 1, while the high specific activity sample stored for long time has given considerable radiation damage due evidently to self-radiolysis, as is seen in Figure 1 (C). It is noteworthy that the chromatograms, though not specifically be shown, of the stored acid without esterification have given no peaks over the chart. This fact suggests that the self-radiolysis products in Figure 1 (C) are mostly carboxylic acids of hydrocarbon chain shorter than stearic acid. All these acids seem to be adsorbed at the CuO-Fe surfaces before getting into the counting device. They seem also to have more or less the same specific activity which is estimated by comparing the activity peak to the mass peak. These facts suggest that the self-radiolysis of tritiated stearic acid results in a degradation of the molecules at the nonpolar position rather than the polar one. Similar conclusion has been obtained in the case of tritiated methyl stearate (4).

Figure 1 (C) informs also that the self-radiolysis products occupy ca. 5% of the whole area of peaks in the mass- and radiochromatograms. If we assume

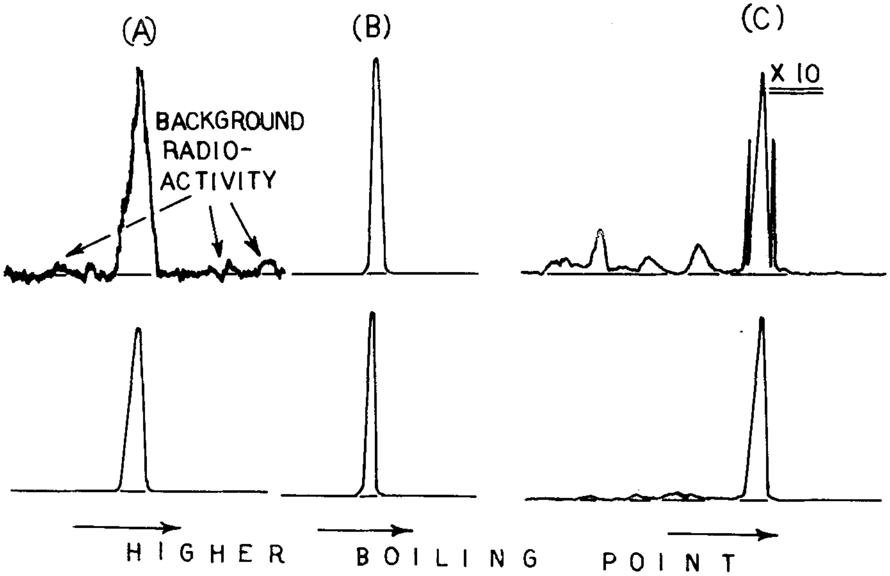

FIG. 1. Mass- (lower) and radiogaschromatograms (upper) of (A) octadecane stored for $t = 91$ months, (B) dodecanol stored for $t = 7$ days, and (C) fresh methyl ester of stearic acid stored for $t = 78$ months.

no more products other than those in the figure and complete absorption of β-rays energy by the stored acid, the absorbed dose is estimated to be 22 Mrad and G value be 7.8, approximately. Rather low G value is due probably to the neglected products in gaseous and polymer forms which could not be detected by the present method.

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Methyl esters of unsaturated fatty acids labeled with tritium in the methyl group

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Methyl esters of unsaturated acids have been labeled with tritium in the methyl group by a microtechnique which is a modification and refinement of the methylation procedure of Metcalf and Schmitz (1). About 30 µl of 15% boron trifluoride methanol reagent (1) were placed in a reaction flask and frozen rapidly in liquid nitrogen (—196° C).

The flask was attached to a simple glass vacuum manifold and evacuated to 10^{-3} Torr. A glass reservoir flask containing 100 mC of tritium labeled methanol (80 mc/mM) was likewise frozen and evacuated simultaneously. The flasks were isolated from the vacuum pump and the methanol-^{3}H was vacuum distilled into the reaction flask. After the flask was closed the reagents were allowed to come to room temperature for equilibration. The flask was opened and the pressure was raised to atmospheric with N_2. Fatty acid (50 mg) was added and the solution was refluxed for 15 min. After being cooled, the

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