Anomalies in the Counting Rate of the Solid Thin Film of Tritiated Lauric Acid in Relation to its Film Structure[*]

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(Received February 20, 1963)

Recently, increasing attension has been drawn to the special application of tritium as a radiotracer, because of the extremely soft nature of its β-radiation. Especially in the field of surface chemistry, tritium has proved to be very useful for studying the details of adsorption and related surface phenomena[1,2]. For this purpose, several tritiated compounds were prepared in our laboratory, and the condition of their solid counting was examined precisely[3] since the counting rate of tritium is highly dependent on the detailed geometry of each of the solid surface. In the course of this observation, we have found peculiar phenomena with a thin solid film of tritiated lauric acid.

A thin film of this substance deposited from benzene on a stainless steel dish and put in a 2π gas-flow counter gave a counting rate which decreased far more rapidly than was to be expected from the natural decay of tritium β-activity. Moreover, we could observe a distinct break point in the decay curve ten days after the deposition of the film, independent of the amount of sample taken, provided that the film was sufficiently thin. The present paper describes the details of these studies.

Experimental

The α, β-ditritiated lauric acid $CH_3(CH_2)_8(CHT)_2$-$COOH$[4] was dissolved in benzene to give a 5.12×10^{-3} mol./l. solution, which was then spread on the stainless steel dish with a micro-pipette. The solid thin film of tritiated lauric acid left after the evaporation of the solvent was of a mean thickness of about 4～10 μg./cm². The β-counting rate of these films was then measured with a 2π gas-flow windowless counter ("Aloka DC-1001", a Nihon Musen Co. product), using propane[5] as a flow gas at the flow rate of 120 bubbles per minute. The results are shown in Fig. 1, where the counting rate is plotted against the time which elapsed after the formation of the thin film. We can notice in this figure that the radioactivity first decreases linearly with time, but its inclination is far steeper than is to be expected from the natural decay rate of tritium (half-life; 12.46 years), and that after ten days, a break point appears and another straight line of a smaller inclination follows. We can confirm that this behavior, especially the time of the appearance of the break point, is fairly reproducible, provided that the thickness of the sample film is sufficiently thin. At first, we presumed that this peculiarity comes from the extremely soft nature of the β-ray of tritium, but precise studies revealed that the phenomena are mainly due to the evaporation of the deposited film of an uneven structure. The following possibilities have been examined experimentally to arrive at the conclusion.

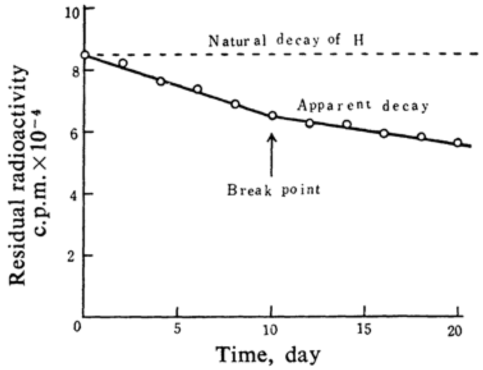

Fig. 1. The decrease in the radioactivity of the thin film of tritiated lauric acid with time.

Exchange with the Hydrogen from the Atmosphere Moisture and the Effect of Flow Gas.— First, as a possible cause of the anomalous rapid decay, we considered the labile position in the lauric acid molecule of the tritium atom, which can be removed by an exchange with a hydrogen atom of water vapor in the flow gas. To examine this possibility three similar tritium samples were prepared, two of which were allowed to come in contact with streams of dry and moist air respectively at the rate of 100 cc. per minute, while the remaining one was kept in a closed vessel without any air current. Changes in the counting rate with time were measured for these samples; the results are shown in Fig. 2. We can see in this figure that, as a whole, the curves are similar. This excludes the possibility that air flow and moisture can remove tritium. The possibility of flow gas itself producing the anomalous phenomena is also

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[*] Paper presented at the 4th International Congress of Radioactivity, Koyto, Japan, 1961; and at the Annual Meeting of Colloid Chemistry, Ueda, Japan, 1961.

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2) A. R. G. Lang and S. G. Mason, *Int. J. Appl. Radiation and Isotopes*, **7**, 251 (1960).

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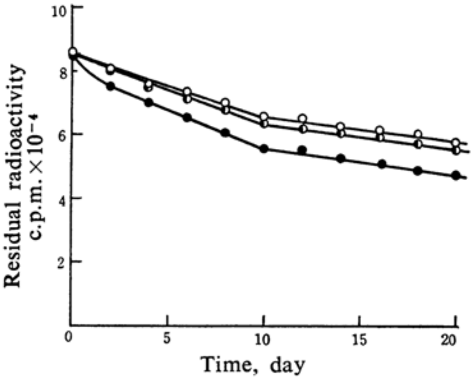

Fig. 2. The effect of the air current on the decrease in the counting rate.
● Dry air flow ◐ Humid air flow
○ Dry air without flow

excluded, since the tritiated stearic acid showed no such anomalies under similar conditions.

The Surface Migration of the Film Substance on the Dish. — If the film substance moves along the surface and clusters, it may decrease the surface area effective for counting. To examine this possibility, two tritium samples were prepared; in one of them tritiated lauric acid was spread in a uniform film, while in the other the substance was mounted as separate twenty-five small spots or clusters. The counting rate-agaist-time curves for these samples, as plotted in Fig. 3, failed to eliminate the anomalies, even for the spotted sample. This excludes the surface migration as an explanation.

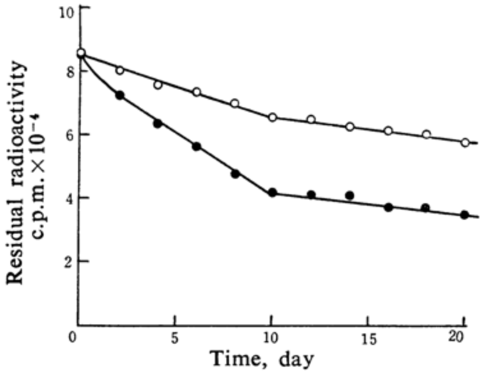

Fig. 3. The effect of the difference in mounting on the counting-rate-versus-time curve.
○ Uniform thin film
● Sample mounted in twenty-five spots

Chemical and Radiochemical Impurities. — Tritiated lauric acid may contain, for instance, other tritiated impurities which give rise to a rapid decrease in counting rate due to its evaporation. Such a possibility can, however, be excluded on the basis of the following experiments.

(1) We prepared at one time twenty samples of the film similar to that of Fig. 1, measured their weights, each on a different day, and constructed a diagram of weight loss due to evaporation versus time. Here the sample weight was determined by the monolayer method, that is, by dissolving the remaining sample film in 1 cc. of benzene, spreading the aliquot of the solution on a slightly acidified aqueous substrate, and determining, under a constant surface pressure, its limiting area, which is proportional to the amount of the remaining sample film. The results are shown in Fig. 4. We can see a break point on the 10th day similar to that found in Fig. 1. Thus we confirm that the evaporation is the main cause of these phenomena, as will be more precisely established later. Here the question arises as to whether this is exclusively due to the evaporation of the impurity. However, the weight loss during ten days is too large to explain the impurity, considering the m. p. of 43.5°C observed for the lauric acid and that of 75.5°C for the lauryl amide used. The presence of a volatile impurity has also been denied since in such a case we should have a simple horizontal straight line instead of the curve of Fig. 4, on account of the rapid evaporation of any such impurity from a spread monolayer for all samples.

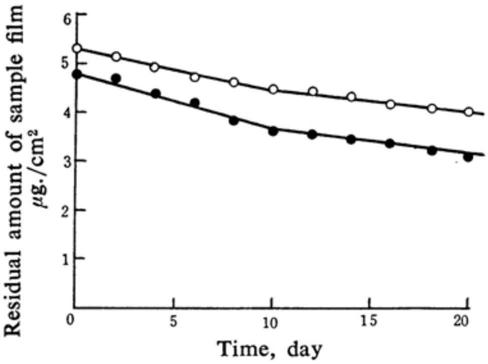

Fig. 4. The measurement of evaporation by radiotracer and surface trough experiment.
○ Surface trough measurement
● Radioactive measurement

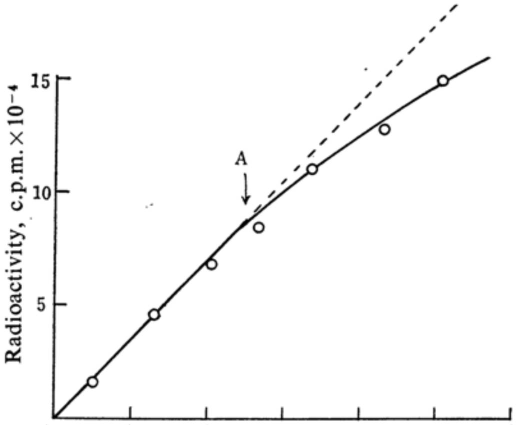

Fig. 5. The counting-rate-versus-sample-thickness curve.
A, Upper limit of linearity

However, the results did not agree with this expectation.

(2) If the phenomena are mainly due to the evaporation of volatile tritiated impurities, the slow decreasing curve attained after ten days, as shown in Fig. 1, is to be explained by the evaporation loss of impurities extending far deep from the solid surface contributing only a little to the actual loss in the β-counting rate. This critical depth roughly corresponds to point A of the counting rate curve shown in Fig. 5. This would indicate that the anomalies shown in Fig. 1 are largely independent of the film thickness, at least for a sufficiently thick film. However, the diagram for the extremely thick film of 530 μg./cm^2 proved to be practically a horizontal line, without a break, even after 10 days or more. These findings are contrary to the above expectation. The possibility of any other short-life radio-nuclide causing these phenomena can be excluded, since the radioactivity of the sample was completely absorbed with a sheet of thin polyethylene or paraffin paper about 3 mg./cm^2 thick.

The Evaporation of Lauric Acid and the Possible Explanation of the Phenomena. — According to the reasoning of the preceding section, the anomalies shown in Fig. 1 can reasonably be explained on the basis of the evaporation of the lauric acid film itself. This is further confirmed by comparing the β-counting rate of the samples of lauric acid films prepared from a benzene solution by evaporating it at 16.5 and 50°C. The marked evaporation at the higher temperature is evident, as may be seen in Fig. 6. As to the detailed explanation of the phenomena in terms of the evaporation of the lauric acid film, the heterogeneity of the deposited film should be pointed out, since a homogeous film and a uniform evaporation result, rather, in a simple straight line of a negative slope, without a break point. In fact, when a drop of lauric acid is put on the dish, most of it spreads as a thin film, while some portion remains as minute droplets. The solvent then evaporates, leaving lauric acid in a thin, uniform film with many clusters scattered upon it. Some of those can even be traced by the naked eyes. This behavior is quite similar to oleic acid on the water surface, which results in a monolayer and liquid droplets.

Therefore, a brief consideration indicates that the radioactive thin film of the thickness of a simple Gaussian-like distribution, as shown by A or B in Fig. 7(II), when exposed to the uniform evaporation, shows a decrease in radioactivity, as is illustrated by A or B in Fig. 7(I), according to whether the thickness is smaller or larger than the critical thickness of the self-absorption of tritium β-radiation, as is shown in Fig. 7(II). Neither of these curves can alone explain the observed curves of Fig. 1.

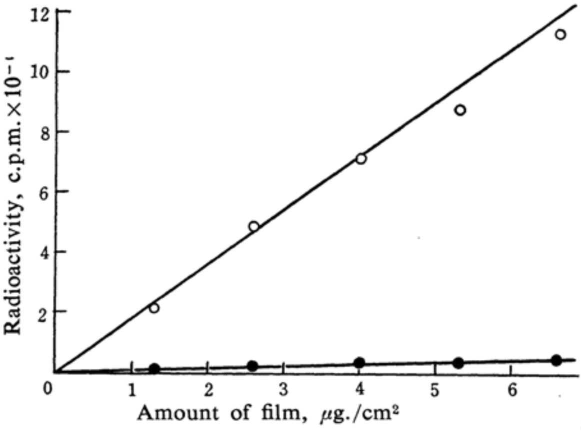

Fig. 6. The effect of the drying temperature on the counting rate of film.
○ Film prepared at 16.5°C
● Film prepared at 50°C

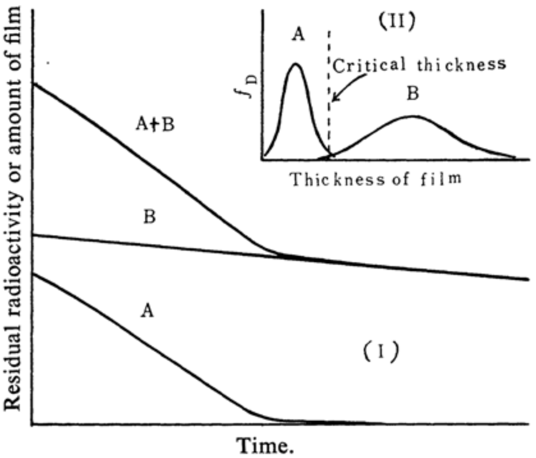

Fig. 7. A diagram showing the decrease in the counting rate depending on the thickness distribution of thin film. (I)A and (I)B indicate the c.p.m.-versus-time curves for the evaporation of films of the f_D thickness-distribution curve shown in (II)A (steep and narrow) and (II)B (flat and broad) respectively. (I)A+B represents c.p.m.-versus-time curve for the film composed of A and B. The dotted line represents the critical thickness for self-absorption.

To explain the observed characteristics of the evaporation curve, a film having at least two peaks in the thickness-distribution curve, as in Fig. 7(II), should be taken into account. The composite evaporation curve of such a film is illustrated by curve A+B in Fig. 7(I), which closely resembles the actual evaporation curve. The abrupt decrease with time in surface area and, accordingly, in the slope of the counting-rate-versus-time curve is produced after the complete evaporation of the thinner film, A. The fact that the time of the appearance of the break point is largely independent of the amount of film taken is an indication of the relative constancy of the thickness distribution of the thinner film, which requires about ten days for complete evaporation.

The smaller inclination after the break point corresponds to the rate of evaporation only from the thicker portion of film B. The disappearance of the break point for the film 530 μg./cm² thick may be explained as resulting from the initial deposit being sufficiently thick and consisting exclusively of film B. According to the results of our experiment, the thickness distribution of film A is considered to be constant, at least in the region of apparent thickness from 4 to 10 μg./cm². The thickness distribution presumably shifts towards a thinner region for a film of a much smaller apparent thickness, since the break point for the film of, say, 1 μg./cm² appeared five days earlier than the above film, as is shown in Fig. 8. It should also be mentioned that the film already in the stage of a slow decrease in counting rate beyond the break point, when dissolved completely with benzene and redeposited by evaporation, again repeats all the changes of the curve of Fig. 1, as is shown in Fig. 9. This can be explained by the fact that the portion of film B still remaining thicker than the critical thickness at this stage and not contributing to the counting rate, when redeposited, produces a considerable amount of film A again, as is shown in Fig. 7(II). The slight increase in the counting rate (shown by the arrow in Fig. 9) when the film is redeposited can also be explained by the appearance of film A. It must be added that the experimental results showing the absence of the gas-flowing effect on the evaporation of the sample (cf. Fig. 2) seems, at first sight, to contradict our conclusion. However, it may be that the air current is insufficient to show the effect of evaporation in any perceptible amount in the case of such a small vapor pressure and rate of evaporation as those of lauric acid.

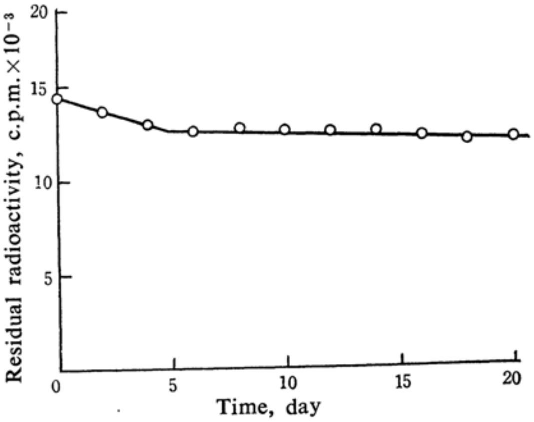

Fig. 8. The counting-rate-versus-time curve for the thinner film of 1 μg./cm².

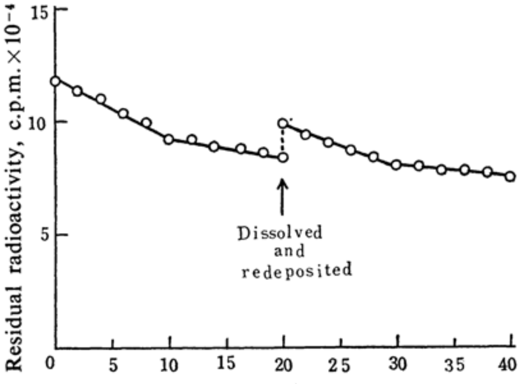

Fig. 9. The effect of the dissolution and redeposition of film on the counting-rate-versus-time curve.

Summary

A thin film of α,β-ditritiated lauric acid $CH_3(CH_2)_8(CHT)_2COOH$ deposited from benzene on a stainless steel dish and put in a 2π gas-flow windowless counter gave a counting rate which decreased far more rapidly than was expected from the natural decay of the β-activity of tritium. We observed a distinct break point in the decay curve ten days after the deposition of the film, independent of the amount of sample taken, provided that the film was sufficiently thin.

Various factors, such as impurities, surface migration, exchange reaction and evaporation, were considered to explain the phenomena; among these the evaporation of the lauric acid from the deposited surface film of the composite structure was proved to be the main factor responsible for these phenomena.

In conclusion, the authors wish to express their thanks to the Ministry of Education for the Scientific Research Expenditure Grant given to Tsunetaka Sasaki.

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