

Self-radiolysis of tritiated compounds

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SUMMARY

The self-radiolysis of a tritiated organic compound has been studied with particular attention to the determination of its percent decomposition, its $G(-M)$ value, as well as yields of the radiolysis products.

Reliable figures have been obtained with the use of accurate experimental techniques, in particular the reverse isotopic dilution method coupled to preparative gas-chromatography.

INTRODUCTION.

In two previous papers was reported the self-radiolysis of tritiated fatty acid esters; in particular, the major self-decomposition products were identified ⁽¹⁾, and the use of clathrates was tried in order to decrease self-radiolysis during storage ⁽²⁾.

In the present paper, a full set of experiments has been carried out to determine the fundamental factors influencing the self-radiolysis of methyl stearate-9, 10- H^3 , with the employ of the radiation chemistry achievements to interpret the obtained results. In fact, the main processes occurring in self-radiolysis should be divided according to the usual physical, physicochemical, and chemical stages, provided that the decomposition of the original labelled molecule, following the decay of the radioactive atom, accounts for only a minor fraction to the over all radiation effects. No use has been made of the special classification of Bayly and Weigel ⁽³⁾ which was particularly developed to find out different methods for controlling the self-decomposition of labelled compounds during storage.

Large discrepancies may be found in literature in self-radiolysis experiments. From one side, there are papers reporting the results on exceedingly radiation resistant labelled compounds ⁽⁴⁾; on the other hand, there are papers which describe significant radiation damage for similar labelled compounds ⁽⁵⁾.

The aim of this paper is particularly directed to the rather formidable problem of achieving accurate and reliable results, particularly in obtaining

the fundamental units of "per cent decomposition", and the G-values. In fact, too often a theoretical approach has been employed in the calculation of these values, without a sound application of the radiation chemistry achievements. But even the experimental approach has often suffered for the employ of unreliable techniques.

The experiments described in this paper were particularly performed in order to check the techniques, and the results were discussed with the utmost attention to the radiation chemistry processes.

However, no mechanism has been suggested for the self-radiolysis of the labelled ester, due the high conversion of initial compound, even at the lowest beta-irradiation; this fact eliminates any possibilities to obtain any but speculative pattern of the physicochemical and chemical stages of the radiation action.

EXPERIMENTAL PART.

1. — *Methyl stearate-9, $10^{-3}H$ preparation.*

A purified methyl oleate sample was hydrogenated with a mixture of hydrogen and tritium (ca 3 curies) on the Adams platinum oxide, in petroleum ether. The tritiated stearate was crystallized several times from water : ethanol. The specific activity of the purified ester was 303.960 mC/mmole, measured by ionization chamber-vibrating reed electrometer, with a standard deviation of $\pm 0.5\%$.

2. — *Sample storage.*

The tritiated ester was stored, at room temperature, under vacuum, within 10 ml Pyrex ampoules containing a break-seal; dilutions were carried out in order to store samples at different specific activities.

3. — *Analytical procedures.*

(i) *Radio-gas-chromatographic analysis of the gaseous self-radiolysis products.*

After the storage, the ampoules were connected to a vacuum line, the seals broken, and the gaseous products collected by a Toepler pump.

The gaseous fraction was then analyzed by G. S. C. on a 4 mm i.d. 2 m long column, containing molecular sieves 5 A⁰, at 100⁰ C, connected with a flow ionization chamber, coupled with a Cary mod. 32 vibrating reed electrometer. Mass and radioactive peaks were recorded.

(ii) *Reverse isotopic dilution-gas chromatographic collection method.*

The out-gassed tritiated methyl stearate of the ampoules was diluted with a known amount of the corresponding inactive ester, and the "per cent decomposition", as well as the different decomposition products measured by reverse

isotopic dilution. Owing to the rather similar properties of these compounds it was of the utmost importance to ensure their separation before performing the specific activity measurements.

A modified chromatograph was employed, according to Cacace *et al* ⁽⁶⁾. This apparatus, shown in Figure 1, possesses the outlet of the detector block so machined to obtain a female conical joint. Whenever a peak emerges from the column, a trap of 4 mm i.d. glass tubing with a male ground joint is fitted to the block joint. After the collection of the peak, the trap is withdrawn; different traps being used for different substances.

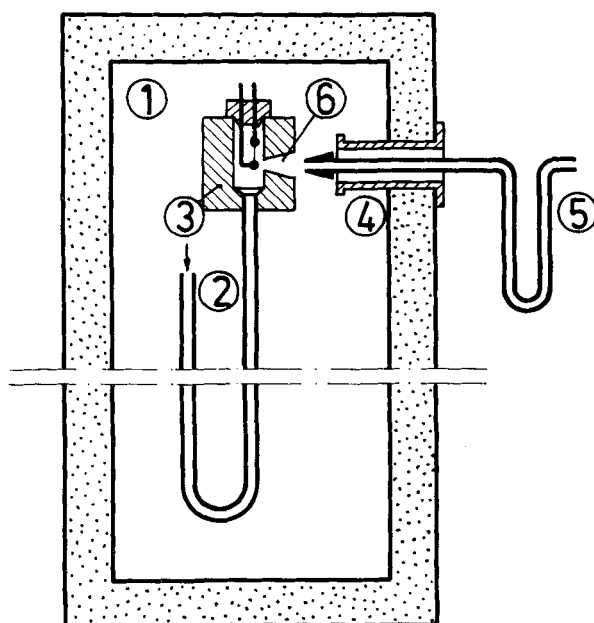


FIG. 1

In order to remove traces of stationary phase, every collected product was introduced into a special apparatus and distilled under vacuum. Only after this rather strict purification, the radioactivity measurements were carried out by ionization chamber- Cary 32 vibrating reed electrometer.

Other details on the product analysis were reported in the previous work ⁽¹⁾.

TABLE I. Per cent decomposition of methyl stearate-9-10-³H

Sample No	Quantity (mg)	Specific activity (mC/mmole)	Time (days)	Dose ^c (eV/g) × 10 ⁻¹⁸	Dose rate (eV/g/day) × 10 ⁻¹⁷	Per cent decomposition
1	100.385	303.960	142	252.00	177.46	23.4
2	98.525	303.960	142	252.00	177.46	25.9
3 ^a	314.150	314.000	71	137.00	192.96	24.9
6 ^b	86.340	130.100	120	90.40	75.33	18.9
7	94.260	130.100	120	90.40	75.33	20.5
8	98.110	3.400	262	5.14	1.96	9.8
9	102.620	2.488	250	3.49	1.40	8.8
10	102.040	1.684	265	2.57	0.97	7.2
11	106.670	0.756	224	0.98	0.44	2.3
12	106.125	0.756	214	0.94	0.44	2.0

^a This sample refers to data published in paper (1).

^b Samples 4 and 5 were not analyzed for per cent decomposition.

^c The absorbed doses for the "per cent decomposition" are higher than the figures of Table II, taking into account the days elapsed since the gases collection.

TABLE II. Gaseous products from methyl stearate-9, 10-³H

Sample No.	Dose (eV/g) 10 ⁻¹⁹	G molecules/100eV			Gas radioactivity (m μ C/mg of ester)			
		H ₂	CH ₄	C ₃ H ₆	HT	CH ₃ T	C ₂ H ₅ T	
—	624 ^a	1.55	0.72	0.040	—	—	—	
1	252	1.63	0.88	0.051	—	—	7.71	
2	252	1.64	0.85	0.052	750	21.9	5.69	
3	137 ^b	1.36	0.82	0.030	690	20.0	4.00	
4	92.3	1.55	1.16	0.047	108	3.90	1.29	
5	92.3	1.57	1.17	0.049	109	3.60	1.56	
6	45.2	1.05	0.74	N.D. ^c	64.2	3.38	0.78	
7	45.2	1.06	0.86	N.D.	57.2	2.43	0.65	
8	2.91	1.57	2.41	N.D.	28.2	N.D.	N.D.	
9	2.07	1.66	2.23	N.D.	24.6	N.D.	N.D.	
10	1.45	1.76	2.50	N.D.	N.D.	N.D.	N.D.	
11	1.45	1.79	2.48	N.D.	N.D.	N.D.	N.D.	

^a Gamma irradiated inactive stearate (2).^b Previous paper data (1).^c Not Detectable.

RESULTS.

Table I reports the per cent decomposition of the various samples of methyl stearate as obtained by reverse dilution-gas chromatographic collection method.

Table II gives the gaseous products. The G-values were determined by mass gas-chromatographic records, after suitable calibration. The gaseous activities were determined by the radiogaschromatographic record after calibration with a tritiated gas of known specific activity. Both calibration factors have a 5 % precision.

The other identified products are reported in Table III. They were determined by the reverse dilution-gas chromatographic collection method.

DISCUSSION.

(i) *Per cent decomposition.*

In order to calculate this important value several formulas have been suggested; for example, an exponential equation has been reported by Rochlin ⁽⁷⁾ :

$$\% \text{ decomposition} = (1 - e^{-F\bar{E}G_{\text{tot}}}) 100$$

TABLE III. Total identified products from methyl stearate-9, 10^{-3}H

Products	Per cent of the initial ester activity		Technique employed
	Absorbed dose		
	2.52 10^{21} eV/g ^c	1.37 10^{21} eV/g ^d	
H ₂	0.075 ± 5 %	0.067	G.C. ^a
CH ₄	0.002 ± 5 %	0.002	G.C.
C ₂ H ₆	0.0007 ± 14 %	0.0004	G.C.
Heptadecane	0.765 ± 14 %	0.38	I.D.-G.C. ^b
Methyl palmitate	5.555 ± 8 %	7.22	I.D.-G.C.
Methyl heptadecanoate	4.50 ± 4 %	2.31	I.D.-G.C.
Stearic acid	9.09 ± 5 %	4.44	I.D.-G.C.
Palmitic acid	2.45 ± 5 %	1.07	I.D.-G.C.
Heptadecanoic acid	0.45 ± 5 %	0.52	I.D.-G.C.
Frac. b. 260° C	—	3.87	I.D.-G.C.
Total free acids	11.23 ± 7 %	7.30	I.D.-G.C.
Total % products identif.	22.12 ± 1 %	21.17	I.D.-G.C.
Total % decomposition	24.65 ± 5 %	24.90	I.D.-G.C.

^a Radio-gas-chromatographic.

^b Reverse isotopic dilution-gas chromatographic collection.

^c These figures refer to samples 1 and 2.

^d Figures of sample 3.

were F = fraction of its own radiation absorbed by the compound (in the case of ^3H -labelled compounds, $F = 1$); \bar{E} = mean energy of radiation : $5.6 \cdot 10^3$ eV; S_0 = initial specific activity of the compound, mcuries/mmole; t = time; G = molecules destroyed per 100 eV absorbed. For exponent values of about 0.10 (for 10 % decomposition), the approximate equation has been employed :

$$\% \text{ decomposition} = F \bar{E} G S_0 t$$

Tolbert ⁽⁸⁾ published in 1960 a table of calculated "per cent decomposition" for ^{14}C -labelled compounds of 125 molecular weight, at three different $G(-M)$ values.

However, rather unfortunately, any possible equation is highly dependent on the actual $G(-M)$ value; as it is well known in radiation chemistry, the composition of a system changes continuously during irradiation. Reactions between the radiolysis products and the active primary species (ions, radicals, excited molecules) cause a non-linear dependence to be expected between the destroyed product and the absorbed dose.

For the per cent decomposition normally found in self-radiolysis experiments, no linearity may be invoked. As shown in Figure 2 for a total dose range of 10^{18} - 10^{21} eV/g (the employed dose range in the present work), only a scarce linearity may be observed, and for the first part of the plot : Figure 3.

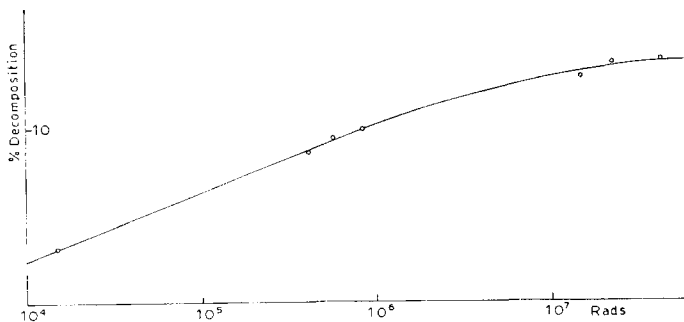


Fig. 2

Similar experiments ^(9, 10), confirm this statement.

The Rochlin attempt to employ a 2.97 value for $G(-M)$, the same theoretically for all compounds, on the assumption that an ion pair is formed with an average energy loss of 33.7 eV, all β -energy is absorbed by ionization, and no recombination occurs, has failed in most cases to match the experimental per cent decomposition values.

The conclusion which should be drawn from this discussion is that no

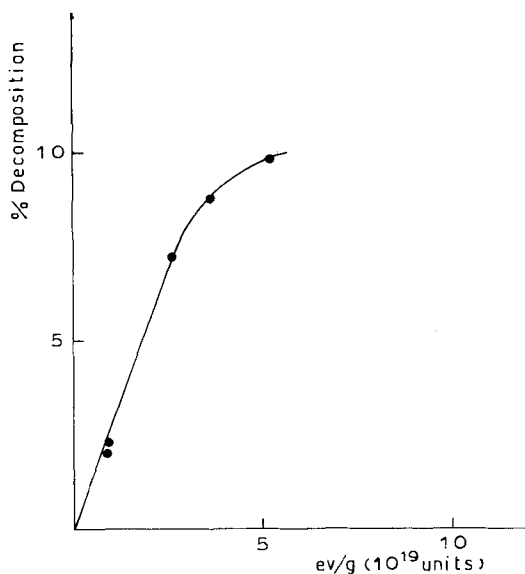


Fig. 3

theoretical approach to per cent decomposition seems reliable, owing to the fact that $G(-M)$ values change continuously with the dose absorbed by M .

But also the experimental approach should be performed with the utmost care, choosing the right technique.

In the case studied in this paper, the usual employ of the reverse dilution analysis, without the coupled gas-chromatographic separation of decomposition products, like palmitate and heptadecanoate esters, should have given unsatisfactory results, owing to the impossibility, by simple recrystallization, to separate these esters; it does mean that the found 24.7 % decomposition should have "decreased" to 14.7 %.

The exceedingly low "per cent decomposition" often found in literature, should be suspected being a consequence of uncomplete purification of the labelled compounds after the storage.

(ii) $G(-M)$ yield.

In the previous paragraph, it has been underscored why any theoretical attempt to calculate $G(-M)$ values should be discarded; and why the experimental approach should be carried out with utmost care.

In radiation chemistry, rather conventionally, has been introduced the "initial $G(-M)$ yield" by extrapolating the plot "per cent decomposition" vs. dose, at zero dose. Owing to the non-linearity of such plot, $G(-M)$ values decrease rather steady with dose.

A good check of the found G(-M) values, which should be made whenever possible, is the material balance of self-radiolysis products.

For example, according to Platzman ⁽¹¹⁾, (who takes as a radiosensitivity standard a G(-M) of ~ 10), the stoichiometry or material balance, expressed as molecules per 100 eV absorbed, is, in the case of methanol irradiation : $9.5 \text{ CH}_3\text{OH} = 4.1 \text{ H}_2 + 3.1 (\text{CH}_2\text{OH}) + 2.0 \text{ HCHO} + 1.2 \text{ H}_2\text{O} + 0.1 \text{ CO}$

Such a material balance, for the self-radiolysis of methyl stearate, for 100 eV absorbed, (at a total dose of 2.5×10^{21} eV/g), is : $18.7 (\text{Methyl stearate}) = 2.56 (\text{Gaseous products}) + 7.52 (\text{esters}) + 9.59 (\text{acids}) + 2 (\text{unidentified products}) + 0.69 (\text{heptadecane})$.

The G(-stearate) values are (at doses of 2.5×10^{21} eV/g) 18.7 and 20.7; at lower doses, G(-M) values increase up to ~ 500 .

Generally speaking, this inverse law has been demonstrated in radiation chemistry : however, the material balance has been carried out only at 2.5×10^{21} eV/g dose. The sensitivity of the employed techniques prevented a similar check to be brought about on samples irradiated at lower doses. As a consequence, no but speculative interpretation may be given for these results; one could argue that a labelled impurity (formed during the preparation of the ester, and not eliminated during its purification) could decompose at high rate, destroying itself completely at low dose. In this case, the over-all effect could not interfere for the samples which received higher doses.

The material balance at 2.5×10^{21} eV/g dose justifies, at least for this irradiated system, G(-M) values higher than 20.

Many other Authors have found similar values; particularly Tolbert ⁽¹²⁾ for the radiolysis of leucine, and Phillips ⁽¹³⁾ for the radiolysis and self-radiolysis of sugars.

Many attempts were made to relate these values with some solid state property of the irradiated substances, but unfortunately no clear-cut explanation has been given since now.

(iii) *G(gaseous products) yield.*

G(H₂) and G(CH₄) for methyl stearate-9, 10-³H are shown in Table II; even in their cases, they decrease at increasing dose. Samples of the same inactive ester, irradiated with a ⁶⁰Co source, gave similar figures.

The total radioactivity of hydrogen is highly dependent on the received dose, as may be seen in Figure 4.

The hydrogen and the fatty acid ester specific activities are strictly related. In some cases, shown in Table V, the specific activity of hydrogen corresponds to the theoretical value, taking into account the isotopic effects. Similar results were found in a previous paper ⁽¹⁾.

Unfortunately the study of gaseous products formed during self-radiolysis has received practically no attention since now ⁽¹⁵⁾, and no comparison may be found in literature.

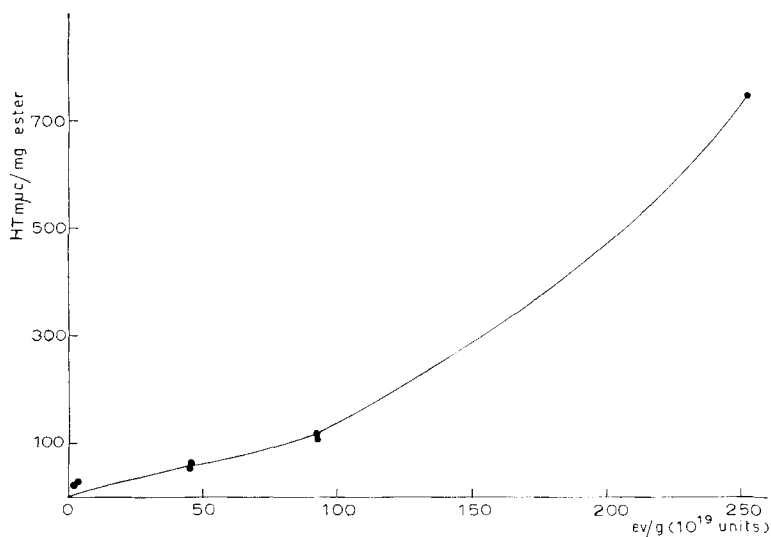


Fig. 4

TABLE IV. Material balance of self-radiolysis products

Products	G ^a molecules/100eV	Calculated methyl stearate consumed	
		molecules/100eV	
		Carbon basis	Hydrogen basis
H ₂	1.63	0.000	0.086
CH ₄	0.88	0.046	0.093
C ₂ H ₆	0.05	0.005	0.008
Methyl palmitate	4.06	3.630	3.635
Methyl heptadecanoate	3.46	3.278	3.467
Heptadecane	0.69	0.617	0.654
Stearic acid	7.26	6.970	6.995
Heptadecanoic acid	1.96	1.754	1.756
Palmitic acid	0.37	0.314	0.314
Total	20.36	16.614 ^b	17.008 ^b

^a G.-values refer to sample 1.

^b G(-stearate) found by isotopic dilution is 18.7.

(iv) *G(products)*.

The total per cent of identified activity is 22.12 %; the total per cent decomposition is 24.7 %. That is, only a 2.6 % of the initial activity has not been identified.

These results refer to samples 1 and 2 which received both the dose of 2.52×10^{21} eV/g, at the same dose-rate of 1.77×10^{19} eV/g/day.

The products were identified by isotope reverse dilution taking into account the radiolysis pattern of a fatty acid methyl ester.

Only scarce literature may be found on these compounds; and no attempt was made to follow any possible self-radiolysis product : particularly no olefin or polymeric fraction was detected.

Anyway, the identified products account for 89 % of the ester activity transformed during storage. Probably, the olefinic fraction — at the dose received by the system (2.5×10^{21} eV/g) — decrease rather steady.

The material balance of Table IV, for sample 1, gives a grand total of 20.4 product molecules per 100 eV absorbed vs. 16.6 molecules of methyl stearate per 100 eV absorbed. The found *G*(-stearate) was 18.7.

TABLE V. Specific activities of the gaseous products

Sample no	Methyl stearate-9, 10^{-3}H mC/mmoles	mC/mmoles			
		HT		CH_3T	$\text{C}_2\text{H}_5\text{T}$
		found	calculated		
1	303.96	—	—	—	3.65
2	303.96	10.92	16.6	0.62	2.67
4	108.20	4.52	5.7	0.22	1.79
5	108.20	4.55		0.20	2.09
6	130.10	8.09	6.9	0.64	N.D.
7	130.10	7.15		0.32	N.D.

CONCLUSIONS.

The purpose of this work was to contribute to the over all theories and procedures commonly employed in self-radiolysis studies.

The reverse isotopic dilution technique — which has found extensive employ in self-radiolysis experiments — is not without serious drawbacks. Whenever a labelled compound contains, after storage, impurities of similar molar radioactivity, large errors may be expected; taking, for instance, a compound A and a contaminant B of similar molar radioactivity, then conta-

minant B needs be present only to 0.1 mole per cent to cause a 10 % error in the molar radioactivity of A ⁽¹⁴⁾.

The second point stressed in this paper is the possibility to employ the radiation chemistry achievements to find out the possible self-radiolysis products, as well as their extent; it has been also emphasized the usefulness of material balances in checking the experimental results.

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