

## SELF - RADIOLYSIS OF TRITIATED COMPOUNDS : IV - UNSATURATED FATTY ACID ESTERS .

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### SUMMARY

*The self-radiolysis of methyl oleate-9,10-T has been studied under different conditions of storage, i.e. under vacuum, in solution of benzene, of n-pentane, and of cyclohexene.*

*The influence of the storing conditions on the total yields of decomposition, as well as on the different self-radiolysis products formed, is discussed taking into account the processes and mechanisms observed in the radiation chemistry of this, and similar compounds.*

### INTRODUCTION

Three previous papers have been devoted to the self-radiolysis of saturated fatty acids, particularly to methyl stearate-9,10-T, (1-3). The self-radiolysis processes have been thoroughly studied in order to account for the decomposition products formed, their amount, and the influence of diluents on their formation.

These studies have been extended to an important unsaturated fatty acid ester, methyl oleate-9,10-T which is rather extensively employed in metabolism studies; in particular, has been studied the influence of different storing systems on the to-

tal percent decomposition as well as on the formation of the various products.

Particular attention has been paid, in this paper, to the study of the real significance of some of the most commercially employed storing systems for highly radioactive tritiated compounds.

In fact, it's common practice to store radioactive compounds in pentane or benzene solutions; the use of these hydrocarbons as storing systems relies substantially on the assumption that dilution, as well as the radiation chemical behaviour of these two compounds, can be useful to decrease self-radiolysis.

This paper shows how, in the case of the unsaturated tritiated compound checked, the effectiveness of these two hydrocarbons is rather poor; an additional point that has not received due attention up to now is the influence of these storing systems on the amount of the various self-radiolysis products formed. For example, it's quite significant that benzene has a "sponge effect" to radiation, giving a decrease on the over all decomposition, but it increases the cis/trans isomerization of an unsaturated compound; this is a well known phenomenon in photochemistry, coming from the energy transfer of the benzene excited triplet states to the unsaturated solute that it is supposed to "protect" against radiation.

Again, in this paper, as well as in the previous ones of this series, self-decomposition percent and G-values, are higher than the values often reported in literature, (4).

The need for reliable techniques to perform this kind of experiments has been stressed elsewhere (3,5). The opinion of the authors is that the formidably resistant radioactive compounds quoted in literature as well as the success of many storing systems, are the consequence of possible poor techni-

ques of separation, and identification of the decomposition products (27). The complaints of customers of commercial radioactive materials, recently appeared (6,78), are an indirect confirmation of this state of facts.

## EXPERIMENTAL PART

### Stearolic Acid and Methyl Stearolate.

Stearolic acid was synthesized according to K.S. Tenny et al. (9) from methyl oleate, Fluka reagent grade. The corresponding ester was prepared from the silver salt and methyl iodide.

### Methyl-oleate-9,10-T

It was prepared according to K.S. Tenny et al (9) from the synthesized methyl-stearolate. It was purified by GLPC as above. The specific activity was 50.2 mC/m mole.

### Inactive carriers

#### 8-Heptadecyne

It was prepared according to Ahmad et al. (10), from nonyne-1, K&K, and 1-Br-octane, K&K .

#### cis-8-Heptadecene

It was prepared from heptadecyne-8, according to Campbell et al. (11)

#### 1-Br-8-Hexadecyne

It was prepared from nonyne-1, K&K, and 1,7-dibromo-heptane, K&K.

### 9-Heptadecynoic- Acid

It was prepared according to Ahmad et al. (10) from 1-Br-8-Hexadecyne.

### cis-9-Heptadecenoic-Acid

It was prepared from 9-Heptadecynoic -acid according to Campbell et al. (11)

### Methyl-cis-9-Heptadecenoate

It was prepared from the corresponding acid by methylation with  $\text{CH}_2\text{N}_2$ .

Methyl-palmitoleate, methyl-oleate, methyl-stearate, methyl-elaidinate, palmitoleic-acid, elaidinic acid, stearic acid, and oleic acid were GLPC standard pure products, purchased from the C. Erba Co., Italy.

### GLPC Analysis

Synthesized methyl esters, halohydrocarbons and hydrocarbons, were analyzed and purified on DEGS columns (9), using a GT C.Erba chromatograph equipped with hot wire detector.

A column packed with E-301 silicon grease was used to separate the components of the tritiated mixtures after storage.

Tritiated hydrogen and methane were checked by flow radio gas-chromatography; the samples were analyzed on a P. Elmer Fractometer connected with an ionization chamber and a Victoreen reed electrometer.

A GAL capillary column, mounted on a P. Elmer 226 flame ionization instrument, was used to determine methyl elaidinate-9,10-T.

### TLC

TLC was carried out using Merck F<sub>254</sub> silica gel thin layer strips,

using either iodine or U.V. light for developing the spots. The radio assays were checked by a Radiochromatogramm Scanner, model RSC-363, Baird Atomic, Co.

#### Column chromatography

It was carried out according to Howton and Wu<sup>(12)</sup> using 70-325 mesh ASTM silica gel, (Merck). The solvents were Merck reagent-grade pure.

#### Scintillation counting

The activity of each substance was determined by scintillation counting in toluene solution of PPO + POPOP, by a Nuclear Chicago Co. Mark I apparatus.

#### Solvents for storage

Particular care was given to purification of the storing solvents.<sup>(13)</sup> n-Pentane, and cyclohexene were Merck reagent grade pure. They were redistilled and fractionated on a Todd apparatus, equipped with a tantalum wire column. The purity was checked by GLPC. Benzene, Merck reagent grade pure, was obtained anhydrous by normal procedure; then it was fractionated on the Todd column and its purity checked by GLPC.

#### Sample Preparation, Storage, Analysis.

Methyl oleate-9,10-T, after purification by GLPC, was put into ampoules with break-seals.

One sample was carefully outgassed and stored under vacuum. Benzene, c-hexene, n-pentane were added to the other three samples. After outgassing the ampoules were sealed and stored in the dark, at room temperature. The four ampoules contained the following quantity of methyl oleate-9,10-T:

- 1) 204.18 mg under vacuum
- 2) 97.66 mg, in 1.0 cc of benzene (0.328 mmole/ml)
- 3) 57.71 mg, in 1.0 cc of n-pentane (0.194 mmole/ml)
- 4) 65.21 mg, in 1.0 cc of c-hexene (0.219 mmole/ml)

After a storage of  $\sim 300$  days, the ampoules were connected to the vacuum line, the seals broken and by a Toepler pump gases collected and analyzed by flow radio-gaschromatography. The solid and liquid components of the mixtures were analyzed by reverse isotopic dilution method, diluting them with inactive known amounts of carriers.

The various substances were then collected in U glass-tubes, connected directly to the detector chamber of a C. Erba gas-chromatograph, modified according to Cacace et al<sup>(14)</sup>, in order to avoid any contamination among the various effluents.

## RESULTS

The results for the different storage experiments are summarized in Table I and Table II. The analytical procedure to obtain these values have been described in the experimental part, or in previous papers of this series, (1-3).

In particular, in Table II are not reported the polymeric G-values, because it was not possible to identify the dimers or higher molecular weight products; as a consequence only the overall percent of polymeric material is reported.

*The material balance is shown in Table III.*

**Table I**  
Per Cent Decomposition

Product	Under vacuum	Benzene solution	Pentane solution	Cyclohexene solution
cis-8-heptadecene	0.12	0.12	0.20	0.79
Me-cis-9-heptadecenoate	0.09	0.28	0.27	0.24
Me-palmitoleate	0.16	0.13	0.30	0.49
Me-stearate	0.25	0.14	1.38	2.64
Oleic acid	2.12	2.78	2.10	3.34
Palmitoleic acid	0.017	0.02	0.01	0.013
cis-9-Heptadecenoic acid	0.014	0.06	0.02	0.05
Stearic acid	1.99	0.66	0.25	0.14
Me-elaidinate	3.6	3.98	2.87	1.19
Unknown polymer	trace	0.26	4.00	0.80
Dose (ev/g $10^{-20}$ )	8.44	8.42	9.39	9.47
Dose (Mrad)	13.52	13.49	15.04	15.17
Percent decomposition	10.84	9.17	12.31	9.37
Unidentified percent	2.48	0.74	0.91	0.08

Table II

G - VALUES

Products	Under vacuum	Benzene solution	n-Pentane solution	Cyclohexene solution
cis-8-Heptadecene	0.36	0.36	0.54	2.11
Me-cis-9-heptadecenoate	0.23	0.71	0.61	0.54
Me-palmitoleate	0.43	0.35	0.72	1.16
Me-stearate	0.60	0.34	2.79	5.63
Oleic Acid	5.36	7.05	4.77	7.53
Palmitoleic Acid	0.05	0.06	0.03	0.03
cis-9-Heptadecenoic acid	0.04	0.16	0.05	0.12
Stearic Acid	4.50	1.66	0.56	0.31
Me-elaidinate	8.36	9.56	6.18	2.35
G (identified products)	19.84	20.25	16.43	19.78
G-(Methyl oleate)	26.1	24.1	26.7	21.0
G (unidentified products)	6.26	3.85	10.27	1.22



Table III

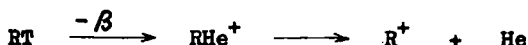
## MATERIAL BALANCE

	Under vacuum		Benzene solution		n-Pentane solution		Cyclohexene solution	
	C	H	C	H	C	H	C	H
cis-8-Heptadecene	0.32	0.34	0.32	0.34	0.48	0.51	1.89	1.99
Me-cis-9-septadecenoate	0.22	0.22	0.67	0.67	0.58	0.58	0.51	0.51
Me-palmitoleate	0.38	0.38	0.31	0.31	0.64	0.64	1.04	1.03
Me-stearate	0.60	0.63	0.34	0.36	2.97	3.13	5.63	5.94
Oleic acid	5.07	5.06	6.68	6.66	4.52	4.50	7.13	7.11
Palmitoleic acid	0.04	0.04	0.05	0.05	0.03	0.023	0.03	0.023
cis-9-Heptadecenoic acid	0.04	0.036	0.14	0.14	0.04	0.04	0.11	0.11
Stearic acid	4.26	4.50	1.57	1.66	0.53	0.56	0.29	0.31
Me-elaidinate	8.63	8.63	9.56	9.56	6.18	6.18	2.35	2.35
Total	19.56	19.84	19.64	19.65	15.97	16.16	18.98	19.37
G (identified products)	19.84		20.25		16.43		19.78	
G- (Me-oleate)	26.1		24.1		26.7		21.0	

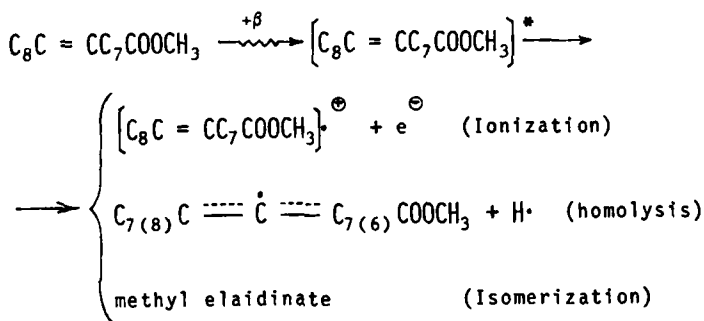
## DISCUSSION

I - Self-radiolysis of methyl oleate-9,10-T

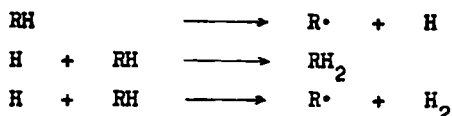
Rather unfortunately, the radiation chemistry of fatty acids has not received the same attention of other compounds, like hydrocarbons. However, taking into account the published literature, it is possible to get a reliable picture of the various mechanisms of self-radiolysis for this fatty acid methyl ester (12,15,18). Of the two primary effects (16), the obviously neglected one is the decay of the tritiated species, which create ionic non-labeled fragments, owing to their secondary significance as a source of radioactive final products:



The other primary effect - the absorption of the tritium decay betas by the labeled methyl oleate - leads to intermediates which can be summarized to the following three main processes, according to Howton and Wu (12).



Hyde and Verdin (17) observed the fragmentation of the excited methyl oleate molecules, and measured a radical yield (homolysis) of the "initiating radicals" with a G-value of 5.36.



This mechanism gives a  $G_{\text{R}\cdot} = 2.68$ . However, apart from the C-H homolysis, the splitting of carbon-carbon bonds in the liquid phase cannot be excluded.

In fact the presence, in our case, of methyl cis-9-heptadecanoate, methyl palmitoleate, and the corresponding acids, with a total yield of  $G = 0.75$  shows that, in the self-radiolysis, a certain homolytic C-C bond dissociation occurs. Similar results were obtained by Mac Farlane and Sweeting, who irradiated methyl dodecanoate, in the liquid phase (18). They obtained  $\text{C}_{11}$ ,  $\text{C}_{10}$ ,  $\text{C}_9$ ,  $\text{C}_8$ , and  $\text{C}_7$  methyl esters.

Actually, the most of the identified products in the self-radiolysis of methyl oleate, can be explained as coming from the homolysis of the ester molecule at the final  $\text{CH}_3$  as well as at the  $-\text{COOCH}_3$  sites. A similar pattern has been suggested by Mac Farlane and Sweeting. However, other routes, for example ionic intermediates, cannot be ruled out, for the reported uncertainty about primary species.

The  $G$ - values measured by Howton and Wu for oleic acid irradiation were determined at different total doses, from 50 to 420 MRad. Significant amounts of polymeric materials was found at doses in the range 200-420 MRad.

There are basic differences between linear energy transfers in self-radiolysis and gamma radiolysis (19,27). However certain similarities can be found. The polymeric fraction which is significant at gamma radiation doses of 200-420 MRad doses, giving a  $G(\text{polymeric}) = \text{ca.} 11$  oleate units, decreases to much lower values in the self-radiolysis experiment. Its

identification was impossible in our case, owing to the insufficient amounts of compounds; however a certain amount of methyl oleate units were used up to polymerize, (TLC Tests). The yields found by Howton and Wu for oleic acid irradiation (extrapolated at zero conversion) are: for elaidinization 4.4; for hydrogenation (stearic acid) 0.4;  $G^*$ (-oleic acid) = 17. These Authors conclude that the major product is polymeric,  $G^*(\text{polymers}) \sim 11$  oleate units.

## II - Self-radiolysis of methyl oleate in the presence of diluents.

The following diluents were employed: benzene, cyclohexene, and n-pentane. Tritiated methyl oleate, as well as other similar fatty acid esters, are commercially stored diluted in benzene or n-pentane.

The effectiveness of these diluents has been recommended, particularly benzene; the use of pentane is recommended on the basis of a simple dilution effect (20).

The use of cyclohexene has been checked in this work on the assumption that this molecule could significantly interfere with self-radiolysis mechanism. In fact, it has been shown that it alters the radiolysis mechanism, due to its scavenging effects \* (21).

The comparison of the  $G$  (-M) values in all the storing experiments, with the  $G$  (-M) value of the labeled compound stored under vacuum, as well as the different distribution of self-radiolysis products, gives a better understanding of the self-radiolytic processes.

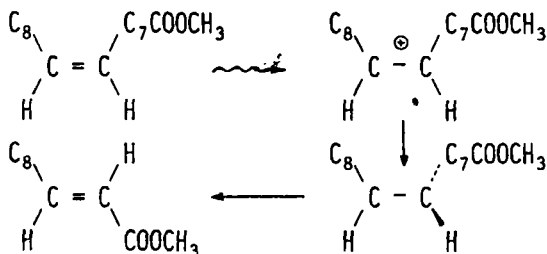
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\* The purity of the diluents has been recently shown to play an important rôle in the self-radiolysis products. Impurities can even enhance self-radiolysis (13).

### III - Cis-trans isomerization

The self-radiolysis of pure methyl oleate-9,10-T gives methyl elaidinate as the major product.

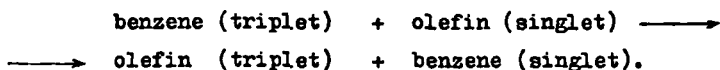
It is conceivable, according to Howton and Wu, that the isomerization mechanism is the following:



Its G-value, 8.63 is higher than the G-value found for the radiolysis of oleic acid, i.e. 4.2. This may depend on the different total doses, and on the difference on the energy deposition.

Generally speaking, olefin isomerization has been studied by many Authors (22) and the found G-values range from ca. 2 for cis-butene-2, (22,a), up to 9 for cis-stilbene, (22,b). Very interesting is the behaviour of benzene as a solvent of tritiated methyl oleate. According to the well known behaviour of this compound, which is a photo and radiation sensitizer of cis-trans isomerization of olefins, the G-value of elaidinization increases with respect to the storage under vacuum.

The triplet energy of benzene has been found 85 kcal mole<sup>-1</sup> whilst the energies of olefin triplets are probably about 70 kcal mole<sup>-1</sup> (23); as a consequence, a triplet-triplet transfer has been postulated of the type:



The G-values of elaidinization goes from 8.63 (vacuum storage) to 9.56 (benzene solution storage).

The rather low increase, in this case, of the G-value in the benzene *sensitized* process can be explained, according to a similar mechanism discussed by Hammond et al (24), on the basis of a competition, between benzene triplets among themselves and the olefin molecules. The bimolecular  $(C_6H_6)^3 - (C_6H_6)^3$  annihilation can reduce the number of triplets available for transfer reaction to the olefin molecules, at their low concentration. The

fact that in the olefin under vacuum the yield of elaidinization is quite high could be a proof that  $(olefin)^3 - (olefin)^3$  bimolecular annihilation is a less important energy-wasting process than in the case of benzene, leaving the olefin triplets for cis/trans isomerization. A similar behaviour, has been found by Hammond et al for the gamma irradiation of various olefins.

In n-pentane, the methyl oleate gives a quite high polymeric fraction and a G-value for elaidinization of 6.18. n-Pentane transfers very *poorly* energy useful for elaidinization. In the cyclohexene dilution, methyl oleate elaidinization is practically *prevented* giving a G-value of 2.35.

#### IV - Formation of acids.

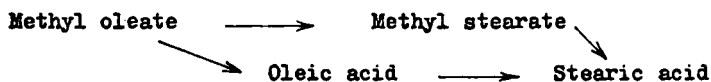
One of the major products formed during irradiation of an ester is the corresponding acid (15). In the self-radiolysis experiments, oleic acid is, after the isomerization product, the other major product coming from methyl oleate.

The formation of  $C_{(n-1)}$  and  $C_{(n-2)}$  acids, seems to involve a two step process: the fission of a C-C bond, as well as the demethylation of the ester group. As a consequence, their yields are very low: quite obviously, for all the storing systems, they are even lower than the corresponding  $C_{(n-1)}$  and  $C_{(n-2)}$  esters.

## V - Hydrogenation.

The hydrogenation of tritiated methyl oleate, as well as of the formed oleic acid, are the other two major products found. Quite large differences are shown, however, according to the different storing conditions.

Two main paths may be postulated which bring to hydrogenated products.



The changes found in the hydrogenation of tritiated methyl oleate, as well as that of tritiated oleic acid, are rather difficult to rationalize.

There is, anyway, a general trend to an increase of methyl stearate formed from methyl oleate in the following order of storage condition: cyclohexene, n-pentane, benzene, under vacuum; the formed stearic acid shows just the inverse sequence.

## VI- Polymerization products.

Howton and Wu studied rather extensively the polymer production in oleic acid irradiated under vacuum.

In order to get significant amounts of material they irradiated at rather higher doses than the ones employed in this paper. This fact prevents any study, in our case, of the polymerization products. At the lower doses employed (10 Mrads) in the self-radiolysis of methyl-oleate, it has been found, by T.L.C. and by V.P.C. some unknown high boiling material. According to the retention times on V.P.C. columns, it may be tentatively attributed to methyl oleate dimers.

This should be, according to Howton and Wu, a doubly unsaturated dimer. Looking at the percent of this unknown polymer fraction formed under different storing conditions. only in

the storage with n-pentane a significant amount of polymers, about 4% of the total decomposition, is formed.

## VII - Homolysis products.

Fragmentation products, arising from homolytic scission of carbon-carbon bonds, with  $C_{(n-1)}$  and  $C_{(n-2)}$  chains were found. Similar C-C bond scission has been observed by MacFarlane and Sweeting (18) in radiolysis products from n- $C_{12}$  and n- $C_{14}$  saturated fatty acid methyl esters, in the liquid phase.

It is worth pointing out the different behaviour of the liquid and solid phase toward the C-C homolysis. MacFarlane and Sweeting found an enhancement of demethylated product going from the liquid phase to the solid phase.

A quite similar phenomenon has been found in our self-radiolysis experiments. That is :

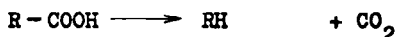
G-values (3)			
Methyl stearate-9,10-T		Methyl oleate-9,10-T	
Solid phase		Liquid phase	
Methyl palmitate	4.06	Methyl-palmitoleate	0.23
Methyl cis-9-hepta- decanoate	3.46	Methyl cis-9-heptade- cenoate	0.43
Dose 25. $10^{20}$ ev/g		Dose 8.4 $10^{20}$ ev/g	

MacFarlane and Sweeting suggest that the special packing of the ester molecules in the solid state could be critical for this kind of effect. One possible reason for the increased radiation effect in the solid state may come from the easier transfer of energy through the lattice, particularly for crystalline solids; the exciton theory, has been postulated for instance, by Phillips to explain the energy transfer in dry-freezed, and in crystalline glucose, (25).

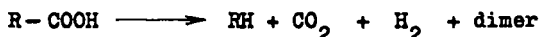


VIII - Hydrocarbons.

A rather sensitive point of cleavage of carboxylic acids is the linking of the carboxyl group to the main chain, (28). However the formation of the hydrocarbon with one carbon atom less than the original acid may occur by means of the so called "molecular reaction" :



as well as by a three molecules mechanism, giving rise also to a dimer (29).



In our case, only the presence of *cis*-8-heptadecene has been checked. However, Howton and Wu found, starting from 50 Mrad doses, a rather larger spectrum of hydrocarbons from irradiated oleic acid. It included double unsaturated as well as completely saturated hydrocarbons, from 15 to 17 carbon atoms.

The yields found were quite lower than that of *cis*-8-heptadecene.

A G-value of 0.36 was found in the self-radiolysis experiment for *cis*-8-heptadecene, under vacuum. The G-values of the possible other hydrocarbons are, as a consequence, too low to be detected.

The storage in cyclohexane of tritiated methyl oleate gives a G-value for *cis*-8-heptadecene of 2.11. Owing to the dimer formation inhibition effect of cyclohexane, it can be argued that, in this case, the most of the decarboxylated fragments give the corresponding hydrocarbon.

Practically no HT, and no tritiated methane was detected for the four storage experiments.

## CONCLUSIONS

- 1 - The self-radiolysis of an organic compound like methyl oleate-9,10-T follows with rather good approximation gamma radiolysis.

Large discrepancies, however, must be expected in the G-values, as a consequence of the differences in energy deposition. Generally speaking, the G-values in the self-radiolysis experiment are higher than the corresponding values for the radiolysis; this is probably due to a better energy transfer from the soft tritium betas to the unsaturated ester molecules.

- 2 - Provided good techniques are employed, like inverse isotopic dilution and gas-chromatographic separation, the G-values and the decomposition percent become reliable units to establish the self-radiolytic behaviour of an organic compound.

- 3 - Dissolution of the ester molecules in suitable diluents is a much more difficult task than expected: in fact, in the case of a solution, it is conceivable that the solvent is directly radiolysed, and only these radiolysis primary species act on the radioactive solute, giving rise to its decomposition. As a consequence, a rather good knowledge of the possible radiolysis processes and mechanisms of the solvent molecules is necessary, before choosing a diluent suitable for a given radioactive molecule.

For instance, benzene, even if rather extensively employed, is not suitable for storage of an unsaturated radioactive molecule, because it can increase radiolysis products coming from the cis/trans isomerization, even if giving an overall decrease of decomposition.

A better choice seems to be a solvent which is a scavenger

of primary radiolysis species, either ionic or radical, like cyclohexene.

- 4 - Whatever solvent can be tried, practically no inert compound can be thought of, as can be guessed from the preceding discussions. As a consequence the effectiveness of these solvents, even if perfectly pure, is rather poor and questionable in the broadest sense of the word, and it is debatable whether it should be better to store highly radioactive compounds simply under vacuum, in very clean and neutral glass vessels, and at room temperature, to avoid excitation transfers in the solid lattices.

#### ACKNOWLEDGMENTS

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