γ-Radiolysis of Crystalline Oleic Acid

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The γ-radiolysis of crystalline oleic acid has been studied at −78 °C by e.s.r. spectroscopy and product analysis. The e.s.r. spectra of samples irradiated at −196 °C show the presence of the radical anion (I) doublet superimposed on a structure probably arising in part from the radical (II). At −78 °C most of the radicals formed at −196 °C undergo transformation into allylic radicals (III), suggesting that hydrogen abstractions are favoured in the crystalline lattice of oleic acid even at −78 °C. The e.s.r. measurements with the urea adduct of oleic acid suggest that the radical anion (I) may be the precursor of the σ-type radical (V). Neither the radicals (I) nor (IV) seems to play a major role in the radiolytic decarboxylation of oleic acid. The product analysis reveals that dimerization, decarboxylation, and hydrogenation are important radiolytic processes in the solid state; much less important are the reactions involving C–C bond rupture at positions at least twice removed from the carboxy-group and the reactions leading to *trans*-unsaturations. Comparison with the liquid-state experiments suggests that the mechanism of radiolysis of oleic acid is significantly influenced by the phase state and temperature.

THE radiation chemistry of crystalline organic compounds can be much influenced by the geometry of the lattice, number and type of lattice imperfections, and other factors related to the solid state. As suggested by Cohen,[1,2] the reaction path in a crystalline matrix may be determined by the relatively fixed distances and orientations of the potentially reactive centres and, for each reaction type, there may be an upper limit for such distances beyond which reaction can no longer occur; further, bimolecular reactions are expected to occur between nearest neighbours, which suggests that the molecular structure of the products might be a function of the lattice geometry of the reactant molecules.

In this paper we report a study of γ-ray induced decomposition of crystalline oleic acid. The liquid-state radiolysis of oleic acid has been studied,[3] but we preferred to repeat part of these experiments in order to facilitate the comparison with our results for the solid state.

EXPERIMENTAL

Sample Preparation and Irradiation for the Product Analysis.—Samples of 99% Fluka oleic acid (2 g) were sealed under high vacuum (10^{-5} mmHg) in Pyrex ampoules and irradiated in a ^{60}Co γ-source with total γ-doses ranging from 56 to 220 Mrad. The solid- and liquid-state radiolyses were performed at −78 and +35 °C (the normal source temperature) respectively. A few experiments were made also at −196 °C. The solid samples of oleic acid to be irradiated were prepared from the melt following the procedure described by Lutton [4] which gives oleic acid in the low-melting crystalline form. This form is pseudo-orthorhombic [5] with four molecules per unit cell; the acid dimers are held together by hydrogen bonds around centres of symmetry and form a layer structure. The molecules are bent at the *cis*-double bond and the two chain parts, which have the usual planar zig-zag structure, are tilted at 56·5° in opposite directions to 001 planes.

The dosimetry was performed with a Fricke dosimeter, and a $G_{\mathrm{Fe}^{3+}}$ value [6] of 15·6 was used.

Product Analysis.—The analytical scheme described by Hotown and Wu [3] has been most used. After irradiation the samples were allowed to melt in their glass containers still sealed; 1—2 g of material was then treated with diazomethane and applied in a n-pentane solution to a 25 × 4 cm Merck 0·02—0·05 silica gel column. Elution was performed with, successively, n-pentane, 5% ether in n-pentane, and pure ethyl ether, thus separating three fractions of increasing polarity, which after evaporation of the solvent were weighed and then submitted to g.l.c. and i.r. analysis.

The g.l.c. analysis of the monocarboxylic acid and hydrocarbon fractions were performed isothermally at 240 °C on an Apiezon L 0·3 mm × 50 m capillary column with a C. Erba Fractovap GT apparatus equipped with a flame ionization detector. I.r. measurements were made with a Perkin-Elmer 257 spectrometer, with the film technique.

The degree of unsaturation of the polymer fractions obtained from the solid-state radiolysis was estimated from the hydrogen uptake by 1 g samples dissolved in acetic acid in presence of a C–Pd catalyst. The carbon dioxide and hydrogen yields were determined approximately by measuring the volume of radiolytic gases condensable and not condensable at −196 °C. The use of this method was justified by the fact that preliminary mass spectrometric analysis revealed that CO_2 and H_2 accounted for more than 98% of the gaseous products arising from the oleic acid radiolysis, the remaining 2% consisting of C_1—C_4 hydrocarbons. The gas-volumetric measurements were made with a modified Russel and Taylor apparatus.[7]

E.s.r. Measurements.—These were carried out with polycrystalline samples of oleic acid and its urea adduct by using an *X*-band V 4500 Varian spectrometer. The samples were sealed under vacuum in Pyrex tubes of special design [8] and irradiated at −196 °C with total doses of about 10 Mrad. The radical concentrations were measured by comparison with a standard diphenylpicrylhydrazyl solution of known spin concentration.

RESULTS AND DISCUSSION

E.s.r. Measurements.—*Pure oleic acid.* The irradiation at −196 °C of polycrystalline oleic acid yields a spectrum

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[1] M. O. Cohen and G. M. J. Schmidt, *J. phys. Chem.*, 1966, **66**, 2422.

[2] M. O. Cohen, *Mol. Cryst. and Liq. Cryst.*, 1969, **9**, 287.

[3] D. R. Hotown and G. Shuang Wu, *J. Amer. Chem. Soc.*, 1967, **89**, 516.

[4] E. S. Lutton, *Oil and Soap*, 1964, **23**, 265.

[5] S. Abrahamson and I. Ryderstedt-Nahringbauer, *Acta Cryst.*, 1962, **15**, 1261.

[6] ASTM Method D-1671-63.

[7] J. Weiss *et al.*, *Ind. and Eng. Chem.* (*Products Res. and Development*), 1964, 773.

[8] G. Adler, D. S. Ballantine, and B. Baysal, *J. Polymer Sci.*, 1960, **48**, 195.

(Figure 1, A) which is composed of a doublet of 23—24 G superimposed on a poorly resolved pattern with an overall splitting of *ca.* 156 G. The doublet is most likely generated by the radical anion (I), a species which is thought to arise from the electron capture by carboxy-groups;[9] the underlying structure reveals the presence of some other radicals, among which the radical (II) may be tentatively identified from the two external lines at *ca.* ±78 G, which are present also in the low-temperature spectrum of n-hexadecane.[10] At −196 °C the spectrum shown in Figure 1, A is stable indefinitely but after annealing for 24 h at −78 °C it changes irreversibly with a 60—70% yield into a seven-line pattern with an average hyperfine splitting of 14—15 G (Figure 1, B). A splitting of 14—15 G is generally associated with allyl radicals;[11] on this basis we suggest that the spectrum of Figure 1, B should be attributed to structure (III). This interpretation implies that part of the radical reaction taking place at −78 °C results ultimately in the formation of radicals (III). For some of the radicals already present at −196 °C or arising from the decay of radical (I), the conversion into allyl radicals may proceed *via* intermolecular hydrogen atom transfers, a mechanism which does not require a translational motion of the reactants and may proceed topotactically within the lattice with the least amount of distortion and strain. Radicals (III) are very stable at −78 °C but start decaying at the m.p. yielding presumably doubly unsaturated dimers with branching at carbon atoms adjacent to the double bonds, as for instance (IV). Part of the unsaturation of these dimers may be of the *trans*-type provided that, as is expected,[3] elaidinization takes place before or following the recombination.

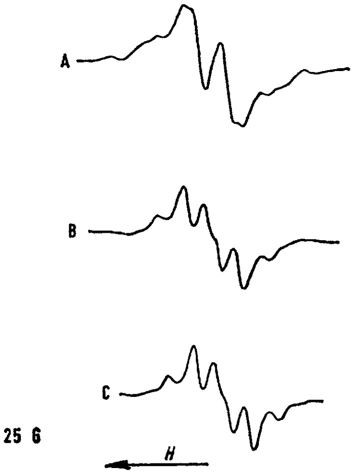
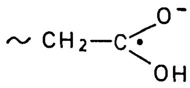
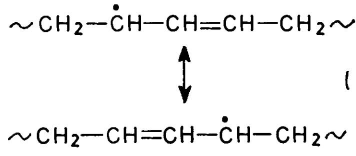
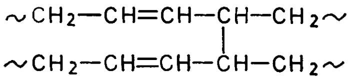


FIGURE 1 E.s.r. of γ-irradiated polycrystalline oleic acid: A, sample irradiated at −196 °C; B, sample irradiated at −196 °C and annealed for 24 h at −78 °C; C, sample irradiated at −78 °C


(I)

$\sim CH_2-\dot{C}H-CH_2\sim$ (II)


(III)


(IV)

$\sim CH_2-\dot{C}{=}O$ (V) $\sim CH_2-\dot{C}H-CO_2H$ (VI)

The irradiation at −78 °C yields almost exclusively allyl radicals (Figure 1, C) with a *G* value of 1·0. This radiolytic yield may be a lower limit because partial saturation may occur with a γ-dose of 10 Mrad; moreover it enables us to estimate a contribution of *ca.* 40% due to the post-irradiation allyl radical coupling to the overall process of oligomer formation (Table 1).

TABLE 1

Silicic acid absorption chromatographic fractions from solid state (−78 and −196 °C) and liquid state (+35 °C) radiolysis of oleic acid

		Relative yields [a]		
Irradiation temp. (°C)	Dose/Mrad	Hydrocarbons	Monocarboxylic acids	Oligomers
−78	56·3	0·82	94·90	4·28
	116·0	2·00	91·20	6·80
	181·0	2·70	86·00	11·30
	226·0	3·00	84·00	13·00
+35	56·0	1·00	87·00	12·00
	111·0	1·76	73·50	24·74
	227·0	2·30	52·30	45·40
−196	56·0	0·00	97·04	2·72

[a] Calculated from the recovered material. Recoveries were quantitative within 1—2%.

Oleic acid–urea adduct. The e.s.r. spectrum obtained at −196 °C resembles that of Figure 1, A, except for the greater intensity of the doublet (Figure 2, A). Above −90 °C the doublet changes irreversibly and almost quantitatively (>85%) into a symmetrical singlet deviating toward the high-field region (Figure 2, B). This new signal is nearly identical in shape, position, and line-width to that obtained by γ-irradiation of palmitoyl chloride, a compound which is expected to undergo the dissociative electron capture reaction (1). On this basis we suggest that the radical arising from the decay of

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[9] (*a*) I. Miyagawa and W. Gordy, *J. Amer. Chem. Soc.*, 1961, **83**, 1036; (*b*) J. E. Bennet and L. H. Gale, *Trans. Faraday Soc.*, 1968, **64**, 1174; (*c*) R. N. Schwarz, M. W. Hanna, and B. L. Bales, *J. Chem. Phys.*, 1969, **51**, 4336; (*d*) H. M. Vyes, J. Janecka, and M. Fujimoto, *Canad. J. Chem.*, 1970, **48**, 2804; (*e*) H. C. Box, H. G. Freund, and K. T. Lilga, *J. Chem. Phys.*, 1965, **42**, 1471; (*f*) H. C. Box, H. G. Freund, K. T. Lilga, and F. E. Budinski, *J. Phys. Chem.*, 1970, **74**, 40; (*g*) A. Faucitano, A. Perotti, G. Allara, and F. Faucitano Martinotti, *J. Phys. Chem.*, 1972, **76**, 801; (*h*) refs. 13, 14.

[10] A. Faucitano, in preparation.

[11] P. B. Ayscough and H. E. Evans, *Trans. Faraday Soc.*, 1964, **60**, 801.

(I) is (V).* The hyperfine structure superimposed on the singlet is rather complex but progressive thermal annealing (Figure 2, B—E) suggests that it is composed of a sextet (a_{av} = *ca.* 27 G), a septet (a_{av} = *ca.* 14 G), and a quartet (a_{av} = *ca.* 28 G) attributable to the radicals (II), (III), and (VI) respectively. These radicals are probably formed during the irradiation and contribute to the hyperfine structure superimposed on the doublet (Figure 2, A). Above −50 °C the singlet decays at a rate which increases with increasing temperature; the decay is accompanied by a substantial decrease of the overall radical concentration and causes only minor changes in the shape of the rest of the spectrum consisting in a slight enhancement of the lines attributed to the radicals (III) and (VI) (Figure 2, C). At room temperature the sextet and the quartet disappear slowly, at different rates, leaving ultimately a septet of 13·8 hyperfine splitting and binomial intensity distribution attributed to the allyl radical (III) (Figures 2, D and E).

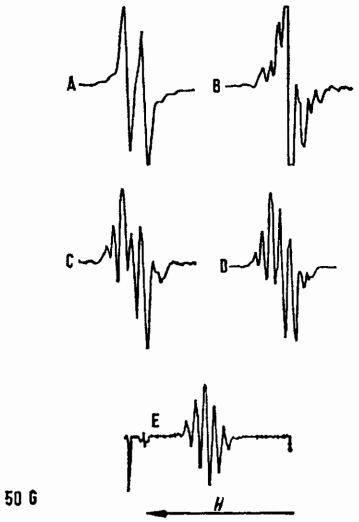

FIGURE 2 E.s.r. spectra of the polycrystalline urea adduct of oleic acid γ-irradiated at −196 °C: A, recorded at −196 °C, 15 min after irradiation; B, recorded at −85 °C; C, D, and E, recorded at room temperature. Samples annealed for 2 h (C) and two days (D) at room temperature, and for 2 h at 100 °C (F)

According to the observation made, the formation and the behaviour of (I) and its related species may be described in terms of reactions (2)—(4). An alternative mode of decomposition for (I) might be based on reactions (5) and (6).[13,14] We prefer the former mechanism because it seems more capable of accounting for the nearly quantitative conversion of (I) into (VI); in fact reaction (6) is expected to be in competition with at least two other energetically favoured processes, the addition to the double bond and the hydrogen abstraction from methylenes adjacent to the double bond, to form the radicals of type (II) and (III) respectively. The observations relating to the disappearance of the singlet suggest that the main mode of decomposition is not based on the well known reaction (7) but rather on a mechanism involving the formation of small radical fragments capable of diffusing and reacting within the clathrate lattice. The slight increase of the radical (VI) concentration observed at the end of the decay may be attributed to a participation of reaction (7) followed by (8) or to the direct hydrogen abstraction (9) by (V). Reaction (9) may acquire importance in pure oleic acid as a consequence of the parallel alignment of the chains. The e.s.r. changes taking place at room temperature (Figure 2, D and E) might be reckoned with the tendency of free spin to migrate toward allyl positions. This phenomenon is much less than that observed in pure oleic acid at +78 °C, presumably owing to the hindrance of intermolecular hydrogen atom transfers by the 'walls' of the tubular cavities.[15]

Solid-state Radiolysis Products.—Crystalline oleic acid undergoes extensive decomposition at −78 °C, *ca.* 6% of the initial amount being transformed with a dose of 56 Mrad. Silicic acid absorption chromatography of the condensed products reveals the presence of three fractions (Table 1), namely oligomers, monocarboxylic acids, and hydrocarbons, which were respectively eluted with pure ether, 5% ether in n-pentane, and pure n-pentane. The oligomer fraction contains also a small percentage of low-molecular weight compounds, presumably dicarboxylic acids, to judge from the fact that g.l.c. on a GESE 30 column shows the presence of a number of peaks with retention time lower than that of octadecenedicarboxylic acid. The gaseous products consist mostly (>98%) of CO_2 and H_2, and of less than 2% of C_1—C4 hydrocarbons.

The hydrocarbon fraction. The hydrocarbon fraction consists mostly (>85%) of heptadecene and heptadecane and contains a minor percentage of hydrocarbons with chain lengths other than C_{17} (Tables 2 and 3) and of *trans*-unsaturation, as indicated by the i.r. absorption

TABLE 2

Composition of the hydrocarbons fractions from the γ-radiolysis of oleic acid in the solid state (−78 °C) and in the liquid state (+35 °C)

	Relative yields/% (w/w)	
Hydrocarbons	Solid state (−78 °C) Dose 227 Mrad	Liquid state (+35 °C) Dose 227 Mrad
cis- and *trans*-Heptedecene	90·04	85·48
Heptadecane	6·73	6·27
Hydrocarbons with chain length > or < C_{17}	3·23	8·24

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* According to Bennet *et al.*[12] the average h.f. couplings of β hydrogens in radicals of the type (V) are *ca.* 5—6 G; this value is below the observed line width, so the e.s.r. signal is expected to appear as a singlet.

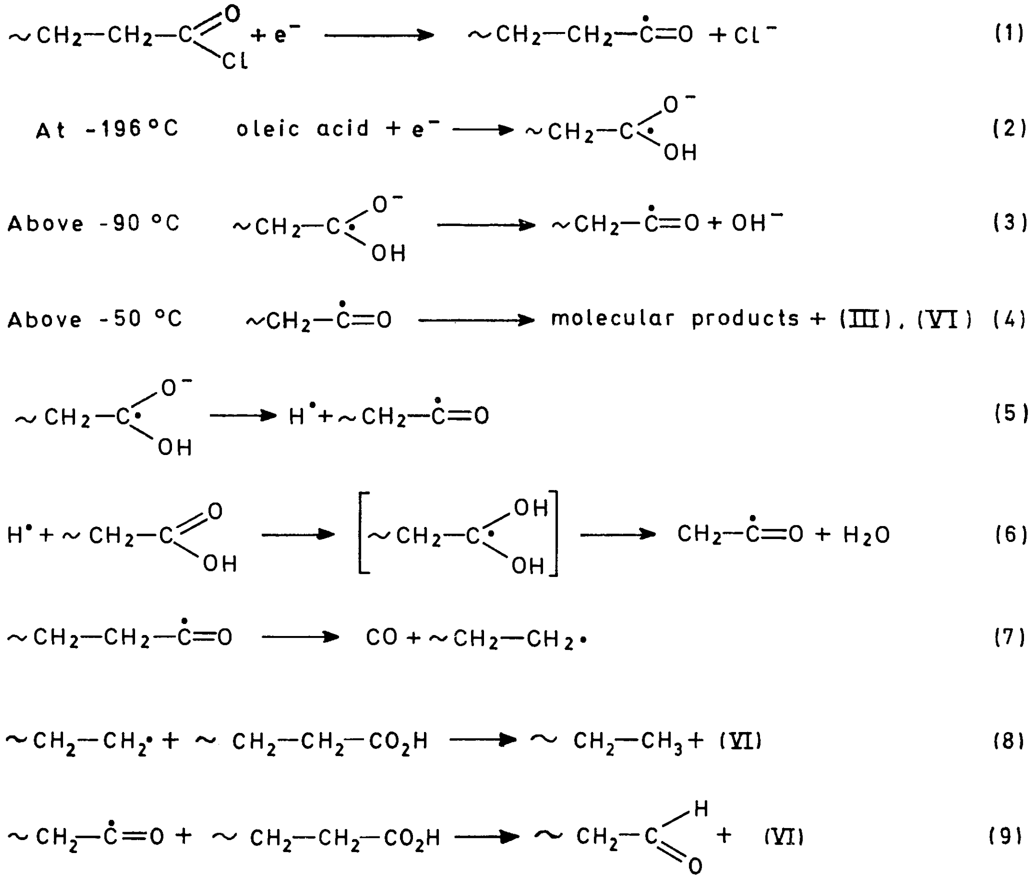
[12] J. Bennet, B. Mile, and K. Ward, *Chem. Comm.*, 1969, 13.

[13] P. B. Ayscough, K. Mach, J. P. Oversby, and R. K. Roy, *Trans. Faraday Soc.*, 1971, **67**, 360.

[14] P. B. Ayscough and J. P. Oversby, *Trans. Faraday Soc.*, 1971, **67**, 1365.

[15] A. Faucitano, P. Locatelli, F. Faucitano Martinotti, and A. Perotti, *Atti Accad. naz. Lincei, Rend. Clase Sci. fis. mat. nat.*, 1970, **48**, 523.

band at 10·35 μm. The radiolysis yield of C_{17} hydrocarbons ($\Sigma G_{C_{17}} = 0{\cdot}56$) compares fairly well with that of CO_2 ($G_{CO_2} = 0{\cdot}61$) pointing to the formation of C_{17} hydrocarbons at −78 °C being stoicheiometrically represented by the reaction $R\text{-}CO_2H \longrightarrow RH + CO_2$.



$$\sim CH_2-CH_2-C(=O)Cl + e^- \longrightarrow \sim CH_2-CH_2-\dot{C}=O + Cl^- \qquad (1)$$

$$\text{At } -196\ ^\circ\text{C} \quad \text{oleic acid} + e^- \longrightarrow \sim CH_2-\dot{C}(O^-)(OH) \qquad (2)$$

$$\text{Above } -90\ ^\circ\text{C} \quad \sim CH_2-\dot{C}(O^-)(OH) \longrightarrow \sim CH_2-\dot{C}=O + OH^- \qquad (3)$$

$$\text{Above } -50\ ^\circ\text{C} \quad \sim CH_2-\dot{C}=O \longrightarrow \text{molecular products} + (\text{III}), (\text{VI}) \qquad (4)$$

$$\sim CH_2-\dot{C}(O^-)(OH) \longrightarrow H^\bullet + \sim CH_2-\dot{C}=O \qquad (5)$$

$$H^\bullet + \sim CH_2-C(=O)OH \longrightarrow \left[\sim CH_2-\dot{C}(OH)(OH)\right] \longrightarrow CH_2-\dot{C}=O + H_2O \qquad (6)$$

$$\sim CH_2-CH_2-\dot{C}=O \longrightarrow CO + \sim CH_2-CH_2^\bullet \qquad (7)$$

$$\sim CH_2-CH_2^\bullet + \sim CH_2-CH_2-CO_2H \longrightarrow \sim CH_2-CH_3 + (\text{VI}) \qquad (8)$$

$$\sim CH_2-\dot{C}=O + \sim CH_2-CH_2-CO_2H \longrightarrow \sim CH_2-C(=O)H + (\text{VI}) \qquad (9)$$

This gives further experimental support to the hypothesis that the participation of reaction (7) and consequently of the radical anion (I) to the mechanism of radiolytic decarboxylation of oleic acid is of minor importance. The general mechanism of radiolysis of olefins and carboxylic acids is thought to involve primary ionization, by ejection of electrons from molecular orbitals, followed by migration of positive charges towards the double bonds and the carboxy-groups respectively; as oleic acid has both a double bond and a carboxy-group in each molecule, it might be suggested that both the positive molecular ions (A) and (B) are formed, as in reactions (10). Ion (B) is expected to react according to reactions (11)—(13) yielding equimolecular amounts of CO_2 and C_{17} hydrocarbons.[3,13,14] The non-paramagnetic cation (VII) is simply the protonated form of oleic acid and may be presumed to undergo neutralization with OH^- ions resulting from the decay of (I) [reaction (3)] to form water and oleic acid. The presence of smaller amounts of hydrocarbons with molecular weight not consistent with C_{17} suggests that C–C bond scission occurs at some stages, possibly with a mechanism similar to that operating in the radiolysis of paraffins.[16]

TABLE 3

Solid-state γ-radiolysis of oleic acid at −78 °C; radiolytic yields (*G*)

Compounds	*G* values[a] solid state (−78 °C)
Oleic acid ⟶ dimers	2·49
Octadecanoic (stearic) acid	0·32
Octadecadienoic acid	0·04
cis- and *trans*-Heptadecene	0·53
Heptadecane	0·03
Oleic acid ⟶ hydrocarbons > or < C_{17}	0·01
Oleic acid ⟶ monocarboxylic acids > or < C_{17}	0·01
CO_2	0·61
H_2	0·29

[a] Calculated from a γ-dose of 56 Mrad.

The oligomer fraction. Oligomers are the most important radiolysis products, since they account for *ca.* 75% of the overall oleic acid decomposed (Table 3) ($G_{\text{oleic acid} \rightarrow \text{oligomers}} = 2{\cdot}49$). These compounds have an average molecular weight, as estimated by the Rast camphor method, almost exactly twice that of pure oleic acid; the i.r. spectrum resembles closely that of pure oleic acid except for the presence of a strong *trans*-unsaturation band at a wavelength significantly shorter

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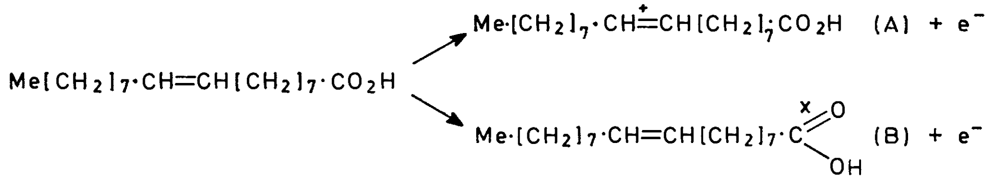
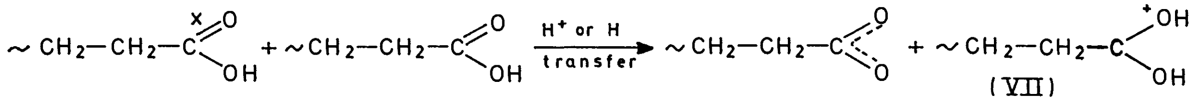
[16] W. E. Falconer and R. Salovey, *J. Phys. Chem.*, 1966, **44**, 3151.

than normal (10·32 μm), a phenomenon known to be due to branching at carbon atoms adjacent to the double bond;[3] this band, however, is less intense than that of pure oleic acid, suggesting that not all the unsaturation is of the *trans*-type; practically unchanged with respect to pure oleic acid is the intensity of the carboxy-group at 5·74 μm suggesting the presence of one carboxylic group for every C_{18} unit. The degree of unsaturation, measured by the hydrogen uptake, was found to be *ca.* 65% that of pure oleic acid. These observations point to the oligomers being dimers of oleic acid and stearic acid units, partially cross-linked at carbon atoms adjacent to *trans*-unsaturation. According to what was stated in the e.s.r. section, the post-irradiation allylic radical coupling should contribute *ca.* 40% of doubly unsaturated dimers having the expected structure. In order to account for the observed degree of unsaturation it might be suggested that the remaining 60% of the dimers contain no more than a single double bond per molecule. The formation of monounsaturated dimers with structures consistent with the i.r. properties might be based on reactions initiated by the molecular ion (A) according to a mechanism originally suggested by Wagner[17,18] for olefins. This mechanism involves the addition of (A) at the double bond of an adjacent molecule followed by internal hydride-ion transfer and charge neutralization (Scheme 1). An alternative path for (A) might be the intermolecular hydrogen abstraction from the allylic methylene group leading, after charge neutralization, to pairs of adjacent allylic and alkyl radicals which may recombine during the irradiation (Scheme 2). This mechanism may be favoured in the crystalline lattice of oleic acid because the reaction distance for the hydrogen abstraction is *ca.* 2 Å shorter than for the double-bond addition.



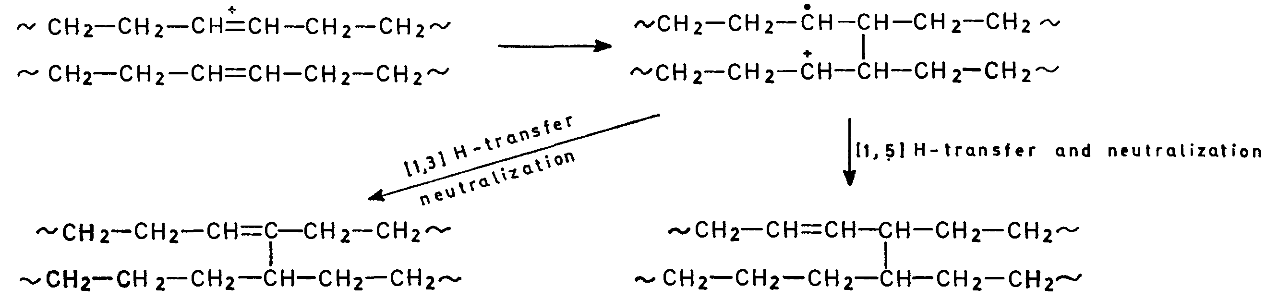
$$\mathrm{Me[CH_2]_7{\cdot}CH{=}CH[CH_2]_7{\cdot}CO_2H} \rightarrow \mathrm{Me{\cdot}[CH_2]_7{\cdot}\overset{+}{C}H{=}CH[CH_2]_7{\cdot}CO_2H}\ (A) + e^- \quad\text{or}\quad \mathrm{Me{\cdot}[CH_2]_7{\cdot}CH{=}CH[CH_2]_7{\cdot}\overset{\times}{C}(=O)OH}\ (B) + e^- \qquad (10)$$



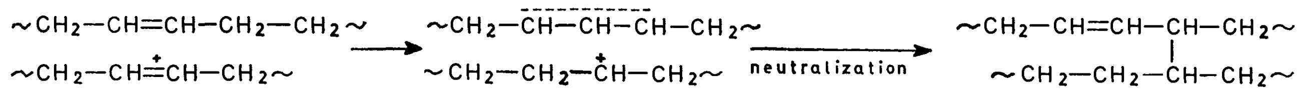
$$\sim\mathrm{CH_2{-}CH_2{-}\overset{\times}{C}(=O)OH} + \sim\mathrm{CH_2{-}CH_2{-}C(=O)OH} \xrightarrow[\text{transfer}]{\text{H}^+\text{ or H}} \sim\mathrm{CH_2{-}CH_2{-}CO_2^{\bullet}} + \sim\mathrm{CH_2{-}CH_2{-}C(\overset{+}{O}H)OH}\ (\mathrm{VII}) \qquad (11)$$

$$\sim\mathrm{CH_2{-}CH_2{-}CO_2^{\bullet}} \longrightarrow \sim\mathrm{CH_2{-}CH_2^{\bullet}} + \mathrm{CO_2} \qquad (12)$$

$$\sim\mathrm{CH_2{-}CH_2^{\bullet}} + \sim\mathrm{CH_2{-}CH_2{-}CO_2H} \longrightarrow \text{Heptadecene} + (\mathrm{VI}) \qquad (13)$$



SCHEME 1



SCHEME 2

The monocarboxylic acid fraction. Besides unchanged oleic acid, the main constituents of this fraction are stearic acid, a compound tentatively identified as an octadecadienoic acid (on the basis of its retention time which is identical to that of linolenic acid), and monocarboxylic acids with chain lengths greater or less than $C_{17}{\cdot}CO_2H$ (Tables 3 and 4); further the i.r. spectrum shows the *trans*-unsaturation band at 10·35 μm. No

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[17] P. Chang, N. C. Yang, and C. D. Wagner, *J. Amer. Chem. Soc.*, 1959, **81**, 2060.

[18] C. D. Wagner, *Tetrahedron*, 1961, **14**, 164.

attempt was made to identify other products which might have been eluted from the silicic acid column together with monocarboxylic acids. Stearic acid may be formed *via* reactions (14) and (15) which seem to be consistent with the e.s.r. observations. The *trans*-unsaturation band suggests that oleic acid may undergo *cis–trans*-isomerization during the irradiation. This process is likely to involve a large amount of molecular motion since it is expected to proceed *via* a rotation about the C–C bond; it is surprising therefore that it can take place in a crystalline matrix at *ca.* 90 °C below the m.p. It cannot be excluded however that *trans*-unsaturation arises directly from the radiolytic dehydrogenation of hydrocarbon chains so that the original *cis*-double bonds are not involved; further the recombination of hydrogen atoms with allylic radicals may play some role in the overall process. The monocarboxylic acids with chain lengths greater or less than $C_{17}{\cdot}CO_2H$ are likely to be counterparts of hydrocarbons with molecular weights larger or smaller than that of heptadecene. Accordingly, the radiolytic yields of these products are approximately equal (Table 4). The low radiolytic yields of these products must be a consequence of cage effects as well as of the tendency of electron holes to migrate toward the carboxy-groups and the double bonds.

$$H^{\bullet} + \sim CH_2{-}CH{=}CH{-}CH_2\sim \longrightarrow \sim CH_2{-}CH_2{-}\dot{C}H{-}CH_2\sim \qquad (14)$$

$$\sim CH_2{-}CH_2{-}\dot{C}H{-}CH_2\sim + \sim CH_2{-}CH{=}CH{-}CH_2{-}CH_2\sim \longrightarrow \text{stearic acid} + \sim CH_2{-}\overline{\dot{C}H{-}\dot{C}H{-}\dot{C}H}{-}CH_2\sim \qquad (15)$$

TABLE 4

Composition of the monocarboxylic acid fraction from γ-radiolysis of oleic acid in the solid state (−78 °C) and in the liquid state (+35 °C)

Monocarboxylic acids	Relative yields [% (w/w)] Solid state 56·3 Mrad	116 Mrad	226 Mrad	Liquid state 56 Mrad	111 Mrad	227 Mrad
Octadecenoic acids [a]	99·30	98·28	97·25	97·20	96·69	94·69
Octadecanoic acid (stearic acid)	0·60	1·28	2·09	0·79	1·18	2·82
Octadecadienoic acid	0·08	0·30	0·35	0·04	0·11	0·16
Acid with chain length > or < $C_{17}{\cdot}CO_2H$	0·02	0·14	0·31	1·97	2·02	2·33

[a] Unchanged oleic acid and elaidic acid.

Comparison with the Liquid-state Radiolysis.—The liquid-state radiolysis at +35 °C results in a more extensive decomposition of oleic acid, *ca.* 15% of the initial amount being transformed with a γ-dose of 56 Mrad (Table 1). Further there are other important differences concerning the distribution (Tables 3 and 4) and chemical characteristics of the products which can be summarized as follows: (*a*) the oligomers have a carboxy-content appreciably lower than that of pure oleic acid and a different degree of unsaturation.[3] Their absorption chromatographic behaviour on silicic acid shows a greater molecular complexity; (*b*) the carbon dioxide yield exceeds that of C_{17} hydrocarbons by almost a factor of 3 ($G_{CO_2} = 1{\cdot}70$; $\Sigma G_{C_{17}} = 0{\cdot}65$); (*c*) monocarboxylic acids and hydrocarbons with chain lengths greater or less than $C_{17}CO_2H$ and C_{17} respectively are formed with yields much larger than in the solid state (Table 4) and their i.r. bands at 10·35 μm are definitely stronger revealing a greater concentration of *trans*-unsaturation. Part of these differences can be accounted for by considering that the restrictions on any kind of molecular motion are certainly more severe in a crystalline lattice than in the liquid state. Thus in the liquid state, heptadecenyl radicals arising from C–CO_2H bond rupture may contribute decarboxylated units to the oligomer fraction by recombining with other radicals during the irradiation. This may explain the lower carbonyl content of the oligomer as well as the excess of CO_2; in the solid state, on the contrary, the radicals can only abstract hydrogen atoms from adjacent molecules yielding heptadecene and carboxylated radicals. In the solid state cage effects may be responsible for the lower yields of products whose formation requires C–C bond ruptures followed by the separation of large fragments (carboxylic acids greater or less than $C_{17}CO_2H$, hydrocarbons greater or less than C_{17}, CO_2) or extensive molecular rearrangements (*trans*-unsaturation). Apparently unaffected by the rigidity of the crystalline matrix are the hydrogenations, as indicated by the liquid- and solid-state yields of stearic acid and heptadecane, which are approximately equal (Table 4); this is not surprising however since, as already pointed out, the hydrogenation probably requires the least amount of molecular motion and involves the diffusion through the lattice of hydrogen atoms. The different chemical characteristics of the oligomers arising from the solid- and liquid-state radiolysis suggests that the mechanism of 'polymerization' is influenced by the phase state and temperature. According to Hotown and Wu the liquid-state polymerization proceeds mainly *via* allylic radical coupling.[3] On the contrary, in the solid state this mechanism cannot account for more than 40% of the overall 'polymer' and therefore other mechanisms, presumably ionic, are involved. Several factors might be considered in order to justify this difference; among them are the stabilization of the molecular ions by the crystalline matrix and the low temperature, the decrease of the overall radical yield as a consequence of cage effects, and the influence of the lattice geometry.

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