hance the 4400-A peak and reduce the 3950-A peak in radiolyzed solutions.

It is notable that the 3950-A peak produced by the γ irradiation of HI–3-MP glass is not affected by the presence of 1.4×10^{-2} mf CCl_4, in contrast to the peak in RI solutions. This appears to mean either that HI is a more efficient electron scavenger than CCl_4 or that the peak observed in the radiolyzed HI solution is due to the neutral species produced in the photolyzed HI solution rather than to a species such as I_2^-.

$G(I_2)$ Yield at Low RI Concentration. Among the observations of interest in this work is the fact that a positive value of $G(I_2)$ ($G = 0.06$) is found for solutions of n-C_4H_9I in 3-MP glass at a concentration as low as 3×10^{-4} mf, whereas, in a liquid alkyl iodide–hydrocarbon solution (C_2H_5I in n-C_5H_{12}), iodine production was not observable at 4.8×10^{-2} mf.[20] One interpretation of this phenomenon is that the butyl iodide exists as clumps of molecules in the glass and that charge or energy or both are efficiently transferred from the 3-MP to these domains of concentrated iodide.

(20) (a) P. R. Geissler and J. E. Willard, *J. Am. Chem. Soc.*, **84**, 4627 (1962); (b) also see G. Westmorland, T. S. Croft, W. C. Blaskey, and R. J. Hanrahan, Division of Physical Chemistry, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, Paper 119.

γ Radiolysis of Oleic Acid[1]

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Abstract: Exposure of oleic acid in the absence of air to Co^{60} γ rays (in agreement with findings in earlier investigations involving other types of ionizing radiation) results in polymerization, *cis–trans* isomerization, decarboxylation, and hydrogenation, in order of decreasing extensiveness. Hydrocarbons resulting from decarboxylation are primarily of chain length C_{17}; others of higher molecular weight are believed to be derived from dimers by secondary reaction. Contrary to conclusions reached in earlier work, the major hydrocarbon is *cis*-8-heptadecene, the "straightforward" decarboxylation product of oleic acid. Decarboxylation, which occurs independently of concurrent events (hydrogenation and isomerization) affecting the center of unsaturation, is believed to be initiated by loss of an electron from the carboxyl group, followed by events in which the hydrogen-bonded association dimers of the acid play an important role. Dimers, apparently largely doubly unsaturated and cross-linked at carbon atoms adjacent to the double bonds, are believed to arise largely *via* coupling of allylic radicals produced both by hydrogen-atom abstraction and by C–H bond homolysis. Higher polymers are produced by secondary reactions.

Except insofar as hydrocarbons, by virtue of their low polarity, may be included in the class, little intensive study has been devoted to the effects of ionizing radiation on lipids, although interest in possible genesis of petroleum *via* interaction of natural radioactivity with lipids of organic matter in sedimentary deposits stimulated investigation of radiolysis of fatty acids (*i.e.*, long straight-chain carboxylic acids) early in the still rather short history of such studies. This research[2] established, for example, that decarboxylation of saturated fatty acids (to yield hydrocarbon RH from acid RCOOH) occurs under these circumstances and that, in addition to carbon dioxide, hydrogen is an important constituent of the mixture of gaseous products; smaller amounts of carbon monoxide and water are also formed.[3] With the possible exception of carbon dioxide, these volatile products arise *via* processes which remain vaguely understood.

Oleic acid (*cis*-9-octadecenoic, the most abundant fatty acid involved in lipids of historic living organisms) was shown[4] to undergo extensive polymerization, hydrogenation (to stearic acid), and decarboxylation to 8-heptadecene, which was, curiously, believed[5] to have the *trans* configuration.[6]

As part of a program[7] designed to enhance understanding of alteration of lipids *in vivo* induced by penetrating radiation, oleic acid has now been exposed to a wide range of doses of γ radiation and detailed analysis of the resulting mixtures used to deduce probable mechanisms of radiolysis of this key substance.

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[1] This paper is based on work performed under Contract AT(04-1)-GEN-12 between the Atomic Energy Commission and the University of California, Los Angeles, Calif.

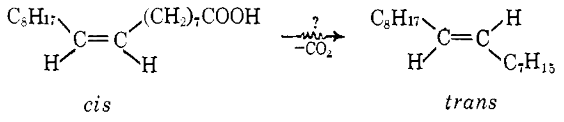
(2) C. W. Sheppard and V. L. Burton, *J. Am. Chem. Soc.*, **68**, 1636 (1946).

(3) W. L. Whitehead, C. Goodman, and I. A. Breger, *J. Chim. Phys.*, **48**, 184 (1951).

(4) V. L. Burton, *J. Am. Chem. Soc.*, **71**, 4117 (1949).

(5) V. L. Burton and I. A. Breger, *Science*, **116**, 477 (1952); identification of *trans*-8-heptadecene was based primarily on an infrared spectrum interpretation which would be regarded today as insufficiently appreciative of the high intensity of the 10.3-μ absorption of *trans* unsaturation and of the location and moderate intensity of the 14.3-μ absorption of *cis*; the significance of absorption at 3.35 μ (*cis*) and at 10.1 and 11.0 μ (terminal or "vinyl" unsaturation) in their spectra was also overlooked.

(6) The obvious implication that *cis–trans* isomerization of the carbon–carbon double bond and decarboxylation are concomitant processes is clearly of fundamental importance from the mechanism standpoint.



(7) See D. R. Howton, *Radiation Res.*, **20**, 161 (1963).

Experimental Section

Irradiation. Two-gram samples of purified oleic acid were sealed in Pyrex ampoules from which air had been displaced with nitrogen and exposed to up to 7.0 × 10^8 rads (4.4 × 10^{22} ev/g) of γ radiation by location inside a cluster of Co^{60} pencils.[8] Dose rates ranged from 11.4 to 7.5 × 10^4 rads/min (Fricke dosimetry). Under conditions of prolonged irradiation, samples experienced sustained temperatures of about 70°.

Fractionation of Irradiated Materials. Using techniques described in detail elsewhere,[7] material was removed from the capsule (within which considerable pressure had developed) and treated with diazomethane, and the product was chromatographed on a solvent-activated silicic acid column. The mixture was applied in *n*-pentane solution, and the chromatogram was developed by application of *n*-pentane–ether mixtures in which the proportion of the latter, more polar component was serially increased, thus eluting constituents of the mixture in order of increasing polarity or silicic acid adsorptivity.

Gas–liquid partition chromatography (glpc) involved the following columns: 40 × 0.25 in. ethylene glycol succinate (column E-I) or silicone gum rubber (S) supported on diatomaceous earth; 72 × 0.25 in. ethylene glycol succinate similarly supported (E-II); and a 100-ft, $^1/_{16}$-in. o.d., 0.02-in. i.d., stainless steel capillary column (C) coated with Apiezon L (Metropolitan-Vickers Electrical Co.). All columns were used in a Wheelco Model 10 chromatograph (Barber-Colman Co.) equipped with an ionization detector. "Preparative scale" runs were made on the Aerograph Master A-100 instrument (Wilkens Instrument and Research, Inc.) using a 5-ft., 0.5-in. i.d. stainless steel column (P) packed with 20% 1,4-butanediol succinate on firebrick and employing thermal conductivity detection. Chromatograms were interpreted quantitatively by peak area measurement, corrected empirically on the basis of glpc behavior of mixtures of known composition.

Infrared spectrophotometry was carried out on a Baird Associates Model B instrument fitted with NaCl optics, using carbon tetrachloride or carbon disulfide as solvents.

Ozonization, used to reveal presence and location of unsaturation, involved application of the technique of Stein and Nicolaides,[9] in which solutions in methylene chloride of materials of interest are treated with ozone at Dry Ice temperature, the ozonides reduced with triphenylphosphine, and the resulting aldehydic products analyzed by glc.

Oleic acid was prepared from olive oil as described by Knight, *et al.*[10] Glpc (column E-I) of the material (as the methyl esters) showed the presence of 1.0% palmitic, 1.7% stearic, and no linoleic acids. The procedure of Stein and Slawson[7,11] and direct high-resolution glc (column C) were used to confirm indications of the less sensitive infrared examination that the material is also free of elaidic acid.

8-Heptadecyne, prepared in 12–15% yield by condensation of 1-nonyne (K & K Laboratories) with *n*-octyl bromide by means of sodamide in liquid ammonia,[12] had bp 146° at 4 mm, $n^{25}D$ 1.4460, mp −13°, and anticipated infrared absorption.

Anal.[13] Calcd for $C_{17}H_{32}$: C, 86.76; H, 13.64. Found: C, 86.26; H, 13.78.

***cis*-8-Heptadecene** was obtained by semi-hydrogenation of 8-heptadecyne in methanol containing an equal weight of quinoline[14] over Lindlar's catalyst[15] at atmospheric pressure and 0°.[16] Material containing about 4% of the *trans* isomer but sensibly free of heptadecane and heptadecyne (by glpc, column E-I) exhibited $n^{20}D$ 1.4469 and mp −37°.

***trans*-8-Heptadecene,** prepared by reduction[17] of the corresponding acetylene with metallic sodium dissolved in liquid ammonia and freed of unchanged acetylenic precursor by preparative glpc (column P), gave samples containing about 1% residual acetylenic contaminant (column E-I), of 100% *trans* configuration (by infrared analysis, on the basis of absorptivity at 10.37 μ of NBS *trans*-3-hexene, sample 529–55), $n^{20}D$ 1.4447[18] and mp −7°.

Anal.[13] Calcd for $C_{17}H_{34}$: C, 85.63; H, 14.37. Found: C, 85.28; H, 14.42.

Tetradecamethylene-1,14-dicarboxaldehyde was prepared by Rosenmund reduction of thapsic (1,14-tetradecamethylenedicarboxylic) acid chloride. Crystallization of the crude product from petroleum ether gave a solid, mp 57–64°, which, from inspection of the carbonyl group stretching frequency peaks of its infrared spectrum, contained about 30% dialdehydes (the presence of anhydrides and/or esters[19] was also indicated), including (as shown by glc analysis) small amounts of lower homologs of the desired product stemming from starting material contaminants. On a diethylene glycol succinate coated column of type E-I at 184°, the ratio of emergence time of the C_{16} dialdehyde to that of dimethyl thapsate was 0.71.

***cis*-1,8-Heptadecadiene** was prepared in quantity sufficient to establish its glc behavior by dehydrobromination of *cis*-1-bromo-8-heptadecene[20] by refluxing with potassium *t*-butoxide in *t*-butyl alcohol; along with other products, the desired diene was obtained in about 8% yield.

Results

During exposure of neat, deaerated oleic acid in glass ampoules to doses of 50 to 700 Mrads of Co^{60} γ radiation, the production of fixed gases (presumably largely hydrogen and carbon dioxide[4]) is evidenced by the development of considerable pressure within the sealed containers. Except for possible increased viscosity of the crude product following delivery of the highest dose employed, no overt indication of extensive high-order polymerization was noted; all samples remained clear and readily soluble in ether. Following treatment of the crude product with diazomethane preparatory to silicic acid chromatography, the material exhibited infrared absorption at about 10.3 μ which increased in specific intensity with dose and is indicative of production of *trans*-olefinic unsaturation.[21]

Silicic Acid Adsorption Chromatography of Products. Elution chromatography of the diazomethane-treated irradiation products on silicic acid columns effects clean separation of material (the "oleate" fraction) having adsorption chromatographic behavior like that derived from the starting material (*i.e.*, like methyl oleate, which is eluted rapidly by 2% ether in pentane but not by pentane alone) from products possessing either diminished (hydrocarbon fraction, eluted readily by pentane) or enhanced (polymer fraction, swept from the column with ether after complete elution of the oleate fraction) adsorptivity. Relative amounts of these fractions obtained in experiments involving various doses of irradiation are summarized in Table I.

Oleate Fraction. This material is expected to consist largely of methyl oleate (from unaltered oleic acid) but should also include, if present, other monocarboxylic esters differing in chain length and/or degree of unsaturation.[22] Indeed, high-resolution glc analyses (see

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(8) The device employed (nominal rating, 10^4 curies) is pictured and briefly described by J. H. Lawrence, B. Marowitz, and B. S. Loeb in "Radioisotopes and Radiation," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 61.

(9) R. A. Stein and N. Nicolaides, *J. Lipid Res.*, **3**, 476 (1962).

(10) H. B. Knight, E. F. Jordan, Jr., E. T. Roe, and D. Swern, *Biochem. Prepn.*, **2**, 100 (1952).

(11) R. A. Stein, *J. Am. Oil Chemists' Soc.*, **38**, 636 (1961).

(12) K. Ahmad and F. M. Strong, *J. Am. Chem. Soc.*, 70, 1699 (1948); W. F. Huber, *ibid.*, 73, 2730 (1951).

(13) Elek Microanalytical Laboratories, Torrance, Calif.

(14) D. T. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, **78**, 2518 (1956).

(15) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(16) S. H. Harper and R. J. D. Smith, *J. Chem. Soc.*, 1512 (1955).

(17) K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216 (1941).

(18) B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, 3156 (1953), report that in the cases of several structurally closely related pairs of olefins, the index of refraction of the *trans* isomer is slightly lower than that of the *cis*, as observed in the present instance.

(19) E. Mosettig and R. Mozingo, *Org. Reactions*, **4**, 363 (1948).

(20) J. C. Nevenzel and D. R. Howton, *J. Org. Chem.*, **22**, 319 (1957).

(21) See H.-P. Pan, S. A. Goldblith, and B. E. Proctor, *J. Am. Oil. Chemists' Soc.*, **35**, 1 (1958).

(22) Silicic acid chromatography carried out under these conditions does not readily distinguish homologs or analogs differing in degree of unsaturation, although higher homologs may be expected to be concentrated in early fractions and unsaturated analogs in late fractions of any elution "peak."

Table I. Silicic Acid Adsorption Chromatographic Fractions[a] from Co^{60} γ Radiolysis of Oleic Acid at Various Doses

Dose, Mrads	Fraction, %		
	Hydrocarbon	Oleate	Polymer
50	0.91	80.9	13.2
100	1.47	68.0	24.2
200	2.29	45.3	42.5
300	2.50	35.2	53.4
420	2.46	27.4	65.7

[a] Weight per cent of total diazomethane-treated product applied to column; together with material of intermediate adsorptivity, recoveries were generally close to quantitative.

Table II) reveal the presence of methyl esters of oleic, stearic, and palmitic acids (constituents of the starting material) and of methyl elaidate, which evidences definitively that simple *cis–trans* isomerization of oleic acid is a significant radiolytic process. No other products of intermediate or shorter chain length or of higher unsaturation are present. At higher doses, quantities of material having glc properties corresponding to those expected for monodecarboxylated dimers of oleic acid (*cf.* "dimer monocarboxylate," Table II) become appreciable.

Table II. Analysis[a] of Oleate Fractions Obtained at Various Doses

	Dose, Mrads				
	50	100	200	300	420
Methyl oleate	90.15	86.3	80.35	74.9	68.1
elaidate	5.01	6.37	8.40	10.28	11.08
stearate	2.58	3.44	5.10	6.75	7.83
palmitate	1.03	1.10	1.37	1.35	1.45
"Dimer monocarboxylate"[b]	0[c,d]	(2.8)[d]	(1.4)[d]	6.3	10.2

[a] Expressed as wt % of total oleate fraction of silicic acid chromatogram. [b] Material of much higher glpc retention time, corresponding to that expected for the monodecarboxylated dimer ester. [c] Inappreciable. [d] Uncertain quantitative significance.

The inertness of saturated acids (as compared with oleic) to radiolysis is evident from the observation that the quantity of palmitic acid in the total irradiated mixture varies little from that initially present as a minor contaminant of the oleic acid used as starting material. In contrast, the small amount of stearic acid present at the start of irradiation increases markedly with dose, since this substance is produced by hydrogenation of oleic acid at a rate exceeding considerably that of its destruction.

Polymer Fraction. Material adsorbed by silicic acid more strongly than methyl oleate was ordinarily removed from the column with ether, without further effort to fractionate it. Rechromatography of selected samples of this sort, employing an extended series of eluting solvent mixtures (see Figure 1) revealed their great complexity, even on the basis of this somewhat limited criterion.[22] The wide spectrum of adsorption chromatographic behavior of such mixtures embraces that of certain types of dimers and trimers of methyl oleate established in earlier studies[7] and exhibits a general shift toward stronger adsorption (presumably reflecting greater structural complexity) with increasing dose.

The infrared absorbing properties of these polymer fractions (see Table III) resembles those of methyl oleate itself closely except in two important respects: (1) reduced specific intensity of ester carbonyl absorption, presumably due to presence of decarboxylated oleate moieties; and (2) strong, relatively dose-independent *trans*-unsaturation absorption at a wavelength ($10.32\ \mu$) significantly shorter than normal—a phenomen known[7] to be attributable to branching at carbon atoms adjacent to the double bond.[23] Taken together, these observations are consistent with the belief that the polymer fractions are composed of substances built up from oleate and heptadecene units (but retaining at least two carbomethoxy groups), to some extent hydrogenated, and cross-linked (at least in part) at sites adjacent to that of unsaturation.

Table III. *trans* Unsaturation and Carboxyl-Group Content of Polymers Obtained at Various Doses

	Dose, Mrads				
	50	100	200	300	420
% *trans*[a]	20.1	20.8	23.2	20.6	20.7
% ester[b]	86.7	85.2	80.1	72.2	72.2

[a] Calculated as per cent by weight of methyl elaidate moieties on the basis of specific intensity of absorption at 10.30–10.32 μ, using the extinction coefficient of methyl elaidate at 10.37 μ. [b] Residual carboxyl-group content, calculated as per cent by weight of methyl oleate moieties, based on the specific intensity of ester-carbonyl infrared absorption, employing methyl oleate as standard.

Methanolysis of the leading 16% portion (in which dimers would be expected to be concentrated) of the polymer fraction of a 200-Mrad-dose product yielded equivalent amounts of methyl oleate (and elaidate) and hydroxystearate (probably equal quantities of the 9 and 10 isomers), indicative of the presence in the entire polymer fraction at this dose of about 5% by weight of ester-cross-linked material; the remainder, as anticipated for C–C-linked dimers, is unaltered by such treatment (see Figure 1).

Hydrocarbon Fraction. Weakly absorbed material eluted by pentane from activated silicic acid is identified as the decarboxylation product (*i.e.*, hydrocarbon) by virtue of this property, together with infrared absorption evidence of the absence of functionality other than carbon–carbon unsaturation. Glc analysis of such material (see Table IV) shows it to consist principally of C_{15}–C_{17} components ("monomeric" hydrocarbons), but that material of about double this molecular weight ("dimeric") is also present in appreciable quantity. These two groups of substances are easily separated by distillation, following which it is found that both exhibit very similar infrared absorption, disclosing characteristics attributable to the presence of *cis* (predominantly), *trans*, and terminal unsaturation. The more volatile ("monomeric") hydrocarbon mixture[24] has physical properties (in addition to its infrared

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(23) Careful infrared spectrophotometry failed to reveal the presence of any α,α,β-trisubstituted ethylenic unsaturation, indicative of branching *at* the double bond site in these polymers; this structural feature is known to give rise to distinctive absorption bands, albeit of low intensity; see N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 1540 (1947).

(24) The total silicic acid chromatographically isolated hydrocarbon fraction is expected to contain *all* hydrocarbons formed during the irradiation, regardless of unsaturation or chain length;[22] products isolated in earlier studies[4,5] by distillation techniques are therefore expected to differ from those presently described in that the latter include the much less volatile di- and (if present) higher order polymeric hydrocarbons.

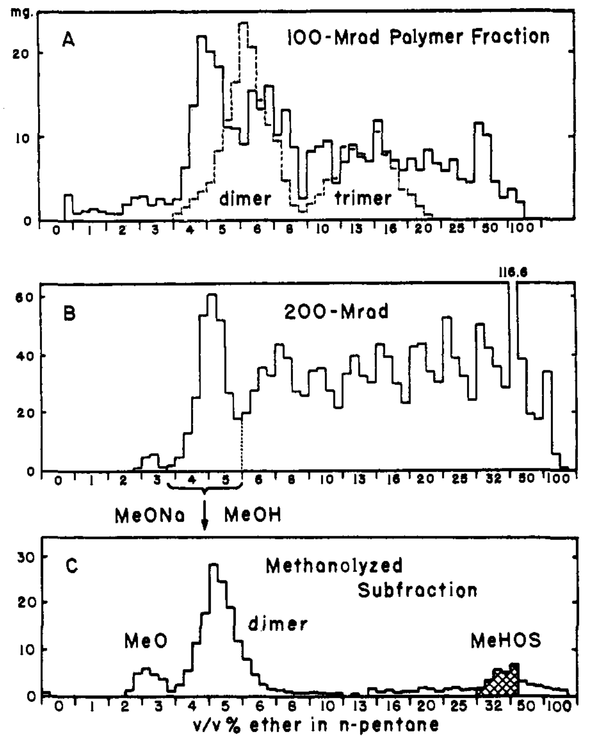

Figure 1. Silicic acid chromatograms of polymer fractions from 100- and 200-Mrad experiments (A and B, respectively) and of the sodium methoxide catalyzed methanolysis product (C) of an early portion of the 200-Mrad product. The chromatographic behavior under essentially identical conditions (except for use of 17 and 21% solvent mixtures instead of 16 and 20%) of dimers and trimers of (methyl) oleate obtained in earlier studies[7] is shown superimposed (broken trace) on the 100-Mrad product chromatogram. Following methanolysis of the leading 16% portion of the 200-Mrad polymers, about 75% of the product showed unaltered chromatographic behavior; 21.3 mg now behaved like methyl oleate (or elaidate), and 23.6 mg like methyl 9- (and 10-) hydroxystearate.[7] Also in agreement with the latter identification, material eluted by 32 and 50% solvent mixtures (shaded histograms) was crystalline at room temperature.

spectrum) in good agreement with those reported by Burton and Breger.[5,25]

Table IV. Composition (wt %) of Hydrocarbons[a] Formed by Co^{60} γ Radiolysis of Oleic Acid at Various Doses

	Dose, Mrads				
	50	100	200	300	420
cis-8-Heptadecene	78.3	74.0	69.4	63.0	61.0
trans-8-Heptadecene	6.2	7.5	9.3	10.9	10.7
Heptadecane	2.4	2.8	3.9	5.7	8.6
Pentadecane	1.2	1.6	1.6	1.7	2.0
1,8-Heptadecadienes	5.5	3.9	2.6	2.1	1.8
Hexadecene	2.4	2.2	1.0	0.7	0.5
"Dimeric"	4.1	8.1	12.2	15.8	15.3

[a] Identification of all components (except "dimeric") based on glpc behavior of authentic substances under the same conditions (column C).

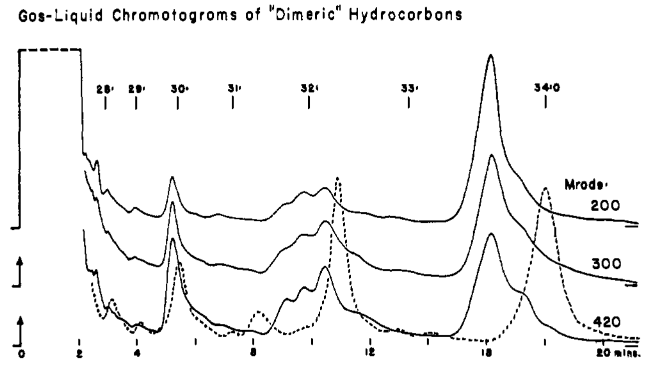

Figure 2. Glc of "dimeric" hydrocarbons from 200-, 300-, and 420-Mrad experiments on a nonpolar column (S, at about 225°) before (full tracings) and (for material from the 420-Mrad run) after (dashed tracings) catalytic hydrogenation. For clarity, the base lines of the three primary chromatograms have been displaced vertically as indicated by the solvent-front-emergence markers (arrows) at right, and the curves normalized to make heights of the C_{30} peaks proportional to the weight percentage of these components of the mixtures; the hydrogenated-product curve is normalized to equalize the area of the resulting 34:0 peak with that of the C_{34} group from which it derives. Points of emergence (maximal) of straight-chain saturated hydrocarbons (based on the behavior of authentic standards under the same conditions) are indicated by marks above, *n*-tetratriacontane being designated 34:0, etc.; conclusions regarding certain features of the structures of the "dimeric" hydrocarbons (see text) indicate that under conditions employed here, their glc behavior is independent of branching, although clearly influenced by unsaturation.

A comparison of data in Tables II and IV shows the compositions of the oleate and monomeric hydrocarbon fractions to be closely parallel (except for minor terminally unsaturated and fragmented components of the latter), indicating that decarboxylation and alteration of the remote unsaturation center (hydrogenation and *cis–trans* isomerization) occur independently.

Ozonization of the monomeric hydrocarbon mixture (from a 420-Mrad run) yields *n*-oct- and -nonaldehydes essentially exclusively and in the same ratio given by authentic *cis*-8-heptadecene, showing that positional isomerization does not accompany *cis–trans* configurational alteration of the original center of unsaturation.

Glpc examination of the "dimeric" hydrocarbons before and after catalytic hydrogenation (see Figure 2) reveals the presence of four classes of components, the chromatographic behavior of which is consistent with their identification as (1) C_{34} hydrocarbons having two, one, and no double bonds, relative amounts of the more saturated components increasing, as expected, with increasing radiation dose, but all converted by catalytic hydrogenation to tetratriacontane(s) (34:0, probably branched; see Discussion); (2) a group of substances evidently also differing only in degree of unsaturation, being catalytically hydrogenated to a single substance (except possibly for differences in branching) of glc behavior similar to but definitely not identical with that of *n*-ditriacontane (32:0); (3) a smaller and apparently less complex group, principally monounsaturated, hydrogenated to a product having glc behavior indistinguishable from that of *n*-triacontane (30:0); and (4) a complex mixture of substances of intermediate chain length (principal component C_{26}). The absence of substances of odd chain length (*e.g.*, C_{31} and C_{33}) is curious. The variation of the relative amounts of these groups of substances with radiation dose is summarized in Table V. From these data, together with information gained from the chromatograms shown in Figure 2, two important inferences may

(25) "Monomeric" hydrocarbon from a 420-Mrad-dose experiment had bp 150° at 2–3 mm, 120° at 0.2 mm; mp about −11 to −6°; and n^{20}D 1.4458. Burton and Breger[5] give bp 297–298°, mp −12.5 to −11°, and n^{20}D 1.4472 for material of similar history produced from oleic acid by exposure to about 1000 Mrads of 14-Mev deuterons. (The value of n^{20}D 1.472 in their Table I is a misprint. The correct figure is plotted in their Figure 1.)

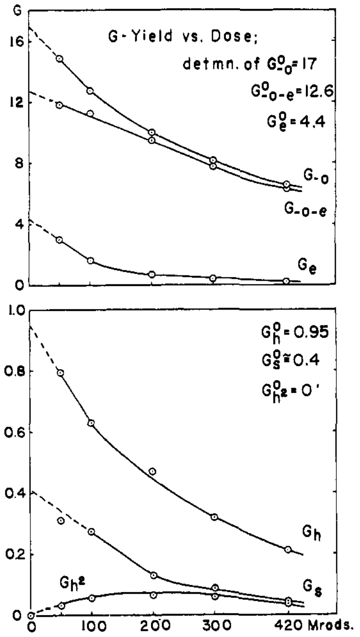

Figure 3. G yields of conversion of oleic acid to various products per 100 ev of energy absorbed: G_{-o} = total alteration of oleic acid; G_{-o-e} = molecules of oleic acid converted to substances other than elaidic acid, based on the glc determination of recovered oleate and of elaidate produced; G_h = yields of "monomeric" hydrocarbons obtained, calculated on heptadecene basis; G_{h^2} = yields of "dimeric" hydrocarbons (monomer units) based on the amount of material not recovered as "monomeric" components on glc with *n*-heptadecane as internal standard; G_s = yields of stearic acid based on glc analysis of oleate fractions, corrected for quantity of stearic initially present as impurity in oleic acid used as starting material. G^0 = yields at start of irradiation (zero conversion) by extrapolation.

be drawn: first, that at low dose the higher hydrocarbons consist essentially entirely of C_{34} dienes; and second, that the C_{32} and C_{30} (and possibly C_{26}) products, present in nearly constant ratio over a broad range of dosage but in negligible quantity initially, are formed from the C_{34} material by independent (as opposed to successive) secondary reactions.

Table V. Relative Amounts[a] of Higher Hydrocarbons Formed by Co^{60} γ Radiolysis of Oleic Acid at Various Doses

Dose, Mrads	C_{34}	C_{32}	C_{30}	C_{26}
200	1.00	0.27	0.11	...
300	1.00	0.54	0.24	...
420	1.00	0.84	0.42	0.56

[a] On the basis of the major group (C_{34}) taken as unity.

Ozonization of the dimeric hydrocarbon concentrate from a 420-Mrad run yields a complex mixture of mono- and dialdehydes, the quantities[26] and structures of which (see Table VI) are consistent with their origin in a family of dienes (probably branched) of general formula $CH_3(CH_2)_nCH{=}CH(C_mH_{2m})CH{=}CH(CH_2)_{n'}CH_3$.

Table VI. Ozonization Products of "Dimeric" Hydrocarbons Formed by 420-Mrad Co^{60} γ Radiolysis of Oleic Acid

$CH_3(CH_2)_nCHO$		$OHC(C_mH_{2m})CHO$	
n	Mole %	*m*	Mole %
		11	1
		12	1
8	2.0	13	21.7
7	68.5	14	58.15
6	26.1	15	15.9
5	3.6	16	3

Both the mono- and dialdehydes formed in the largest amount are those expected to arise from a C_{34} diene (in accord with glc behavior of the major component of the dimeric hydrocarbon mixture) formed by union of two heptadecenyl radicals: $CH_3(CH_2)_7CH{=}CHC_{14}H_{28}CH{=}CH(CH_2)_7CH_3$; some double-bond migration has apparently occurred, although not to any very great extent beyond those next adjacent to the original position. Absence of lower homologous dialdehydes ($m <$ 13) suggests that the C_{26}–C_{32} substances (representing about 65% of the 420-Mrad-run dimeric hydrocarbon mixture employed as starting material; see Table V) represent consequences of loss of carbon from regions other than that between the centers of unsaturation.

G yields of oleic acid altered and of hydrocarbons, stearic acid, and elaidic acid formed (see Figure 3) are of interest from several points of view. These changes (per unit energy absorbed by the mixture) decrease, as expected, as products accumulate and, themselves interacting with an increasing share of the total absorbed energy, undergo further change. Data in Tables I and II, for example, show that oleic acid comprises less than 20% of the mixture after 420 Mrads of irradiation have been absorbed. Such high conversions, dictated by the primary objective of obtaining isolable quantities of identifiable products, are, of course, inextricably associated with the involvement of considerable secondary reaction. G yields at high dose thus represent net changes in amounts of various components of the radiolysis mixture resulting from interplay of a very considerable number of different reactions. In order to gain some insight into the relative importance of primary radiolytic events, G yields obtaining at the initiation of irradiation were estimated by extrapolating plots of G yield *vs.* dose back to zero dose (see Figure 3).[27]

The magnitude of the zero-dose alteration of oleic acid (G^0_{-o} = 17, or about 12.6 exclusive of conversion to elaidic acid) reveals that several molecules of the substrate are involved in change of one kind or another per ionization and/or excitation event, in accord with the observation that the major product is polymeric (G^0_{poly} $\sim$ 11 oleate units).

The *cis–trans* isomerization of oleic to elaidic acid is also of considerable quantitative importance; the observed G^0_e = 4.4[28] is probably minimally indicative of the extensiveness of the process leading to this change, inas-

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(26) Correction for quantities of oct- and nonaldehydes produced from residual monomeric hydrocarbons in this distillation residue was effected by taking advantage of the known composition of the latter and the fact that heptadecane present in it is, of course, unaffected by reaction with ozone; identity of the dialdehydes is based on direct comparison of glc behavior (evidently uninfluenced under conditions employed by branching) with that of authentic tetradecamethylene-1,14-dicarboxaldehyde and adventitious close homologs.

(27) The accuracy of the resulting zero-dose yields (G^0) is of necessity rather severely limited in consequence of most critical analyses (of mixtures obtained at lowest doses) being also most imprecise; estimation of the net production of stearic acid after absorption of 50 Mrads, for example, is based on the difference of two small numbers.

(28) P. C. Kaufman, *J. Phys. Chem.*, 67, 1671 (1963), reports $G \sim 4$ for *cis–trans* isomerization of liquid 2-butenes at 23° and 40 Mrads of Co^{60} γ radiation.

much as a sizable fraction of the transition state involved presumably results in regeneration of oleic acid.

Decarboxylation ($G^0_{\mathrm{h}} = 1$)[29] and hydrogenation ($G^0_{\mathrm{s}} = 0.4$) are comparatively minor eventualities.

Comparison of decay in quantities of elaidic and of oleic acids present in the mixtures per unit energy absorbed suggests that rate constants pertaining to involvement of the two geometric isomers in various subsequent reactions (such as polymerization and/or hydrogenation) are greater for elaidic than for oleic acid.[31]

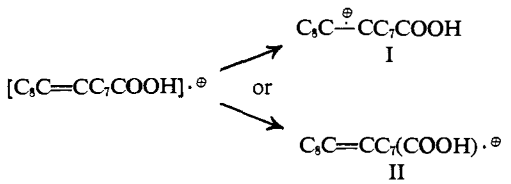
Extrapolation of the plot of yields of "dimeric" hydrocarbons ($G_{\mathrm{h_2}}$) to zero at zero dose is in accord with the view that these substances probably arise *via* a rather extensive series of secondary reactions.

Discussion

Absorption of the 1.1-Mev Co^{60} γ rays by systems such as that represented by liquid oleic acid leads, *via* the Compton process, to production of primary electrons of about half this energy which give rise, in turn, to numerous secondary electrons, most of which retain kinetic energies of less than 100 ev.[32] Depending on the amount of energy transfered to the individual molecule of oleic acid and on the manner in which this excitation energy is partitioned within the molecule, there are produced a variety of highly reactive intermediates leading ultimately to the observed products. On the basis of the nature and yields of these, and in consideration of conclusions reached in a wide assortment of earlier studies by others, intermediates resulting from *ionization* or covalent-bond *homolysis* and those involved in direct *cis–trans isomerization* (elaidinization) appear to deserve to be regarded most seriously.

$$\underset{\text{oleic acid}}{\mathrm{C_8C{=}CC_7COOH}} \rightsquigarrow [\mathrm{C_8C{=}CC_7COOH}]^* \longrightarrow \begin{cases} [\mathrm{C_8C{=}CC_7COOH}]\cdot^{\oplus} + \mathrm{e}^{\ominus} & \text{ionization} \\ \mathrm{C_{7(8)}C\overset{\cdots}{-}\dot{C}\overset{\cdots}{-}CC_{7(6)}COOH} + \mathrm{H}\cdot & \text{homolysis} \\ \text{elaidic acid} & \text{isomerization} \end{cases}$$

Primary Events. Ionization. Although the electron ejected in the ionization of a complex molecule may be usefully envisaged as coming initially from a molecular orbital,[33,34] much evidence suggests that the resulting electron deficiency or "hole" is very quickly (in times shorter than those of interatomic vibrations) and efficiently localized in certain groups, of which the center of unsaturation and the carboxyl group of oleic acid are representative.



$$[\mathrm{C_8C{=}CC_7COOH}]\cdot^{\oplus} \begin{array}{l} \nearrow \quad \underset{\mathrm{I}}{\mathrm{C_8C\overset{\oplus}{\dot{-}}CC_7COOH}} \\ \text{or} \\ \searrow \quad \underset{\mathrm{II}}{\mathrm{C_8C{=}CC_7(COOH)}\cdot^{\oplus}} \end{array}$$

Inasmuch as further chemical change leading to stable products would be expected to ensue electron-hole localization, support for the correctness of these views should consist of evidence for suppression of reaction in the saturated regions of the oleic acid molecule and for important involvement of intermediates of types I and II. As discussed in detail by Williams,[35] ionization of saturated hydrocarbons initiates three reactions characterizing the radiation chemistry of such substances: fragmentation, dehydrogenation, and cross linking (polymerization). Although the structures of polymers produced by irradiation of oleic acid are not known in detail sufficient to exclude occurrence of saturated-group cross linking, other modes are clearly involved importantly. The observation that fragmentation rarely occurs lacks force it might otherwise have in this connection because of the probability that fragmentation is minimal for other reasons. Evidence that dehydrogenation does not occur appreciably is, however, both abundant and unequivocal. Wagner and his colleagues[28,36] and others[37] have provided extensive experimental support for the participation of intermediates of type I in the radiation chemistry of olefins (where suppression of fragmentation, dehydrogenation, and cross linking at sites other than that of the double bond is again clearly evidenced), and Williams[38] has discussed the probable importance and chemistry of type-II intermediates. Evidence for involvement of intermediates of types I and II in the γ radiolysis of oleic acid is considered in sequel.

Homolysis. Amounts of energy transferred to molecules of oleic acid during γ irradiation may easily be adequate to bring about the homolytic dissociation of any of its covalent bonds, the strengths of which are, at most, equivalent to about half the energy required for ionization of the substance. Fragmentation arising *via* homolytic splitting of carbon–carbon bonds is suppressed in the radiolysis of material in condensed phases, where the proximity of neighboring molecules greatly reduces the probability of escape of the fragments and facilitates dissipation of energy released on recombination. On the other hand, the expectation that the fugacity of hydrogen atoms will be very much greater than that of alkyl radicals leads to the expectation that C–H bond homolysis might be an important primary event in the γ radiolysis of liquid oleic acid.[39]

It will be assumed in further discussion that the probability of homolytic scission of the assortment of distinguishable types of covalent hydrogen bonds in

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(29) Although direct quantitative comparison is hampered by the rather strong dose dependence of $G_{\mathrm{CO_2}}$ (*cf.* G_{h}, Figure 3) and by uncertain dosimetry in earlier investigations, it is nonetheless clearly evident that decarboxylation of oleic acid is considerably less extensive per unit dose than is that of saturated fatty acids;[3,4,30] definitive experiments carried out in this laboratory (to be published) have demonstrated, for example, that under otherwise identical conditions (involving 100 Mrads of γ radiation), the yield of hydrocarbon from stearic is about 14 times that from oleic acid.

(30) R. H. Johnsen, *J. Phys. Chem.*, **63**, 2041 (1959).

(31) Information bearing on the relative reactivities of *cis* and *trans* olefins in such reactions is conflicting: see P. E. M. Allen, H. W. Melville, and J. C. Robb, *Proc. Roy. Soc.* (London), **A218**, 311 (1953); and K. R. Jennings and R. J. Cvetanović, *J. Chem. Phys.*, **35**, 1233 (1961).

(32) L. Kevan and W. F. Libby, *Advan. Photochem.*, **2**, 185 (1964).

(33) G. G. Hall and J. Leonard-Jones, *Proc. Roy. Soc.* (London), **A202**, 155 (1950).

(34) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

(35) T. F. Williams, *Trans. Faraday Soc.*, **57**, 755 (1961).

(36) P. C. Chang, N. C. Yang, and C. D. Wagner, *J. Am. Chem. Soc.*, **81**, 2060 (1959); C. D. Wagner, *Tetrahedron*, **14**, 164 (1961).

(37) E. Collinson, F. S. Dainton, and D. C. Walker, *Trans. Faraday Soc.*, **57**, 1744 (1961); P. B. Ayscough, A. P. McCann, C. Thompson, and D. C. Walker, *ibid.*, **57**, 1487 (1961).

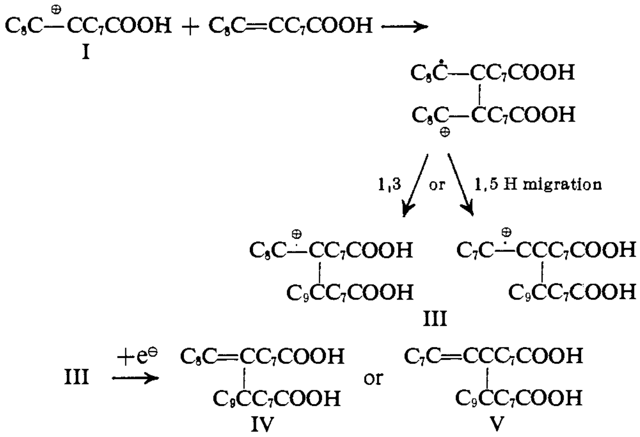
(38) T. F. Williams, *Nature*, **194**, 348 (1962).

(39) Definitive evidence for the strong dominance of C–H over C–C bond homolysis during high-energy electron irradiation of unbranched liquid hydrocarbons is provided by the elegant electron spin resonance studies of R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

oleic acid is inversely related to their strengths, which may be ranked as follows: $-CH_2CH{=}CH-$ (in the methylene group) > $-CH_2COOH$ (methylene) > other $-CH_2-$ > CH_3- > $-CH{=}CH-$ and $-COOH$. These relationships will be taken to hold as well for abstraction of hydrogen from various sites on the oleic acid molecule by thermal hydrogen atoms or free radicals. An important conclusion stemming from these premises is that every C–H bond homolysis, including others less favorable than those involving methylene groups adjacent to the center of unsaturation, may result ultimately, *via* hydrogen atom abstraction and intermolecular transfer, in the production of up to two resonance-stabilized allylic radicals; realization of such an eventuality should be limited primarily by alternative addition of hydrogen atoms to olefinic centers or (much less probably) by radical–radical (or –hydrogen atom) encounter.

Mechanism of Polymerization. Wagner and his colleagues have shown that radiation-induced polymerization of olefins involves two competing processes: one initiated by ionization of the olefin to a molecular cationic radical of type I (see above), which reacts avidly with intact olefinic molecules in a short chain sequence presumably limited in extent by the imminence of charge neutralization, and another involving allylic radical coupling. The ion-radical mechanism is strongly dominant in radiolysis of terminal olefins,[36,37] but less so in the case of the 2-butenes,[28] which are (as α,β-disubstituted ethylenes) more closely analogous to oleic acid.

As applied to the substance of interest, the course of the Wagner ion-radical polymerization may be represented as[40]



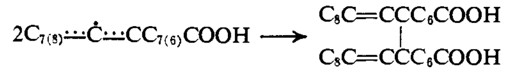
$$\underset{\mathrm{I}}{\mathrm{C_8C\overset{\oplus}{-}CC_7COOH}} + \mathrm{C_8C{=}CC_7COOH} \longrightarrow \begin{array}{l}\mathrm{C_8\dot{C}{-}CC_7COOH}\\ \qquad\quad|\\ \mathrm{C_8\underset{\oplus}{C}{-}CC_7COOH}\end{array}$$

$$\xrightarrow{\text{1,3 or 1,5 H migration}} \underset{\mathrm{III}}{\begin{array}{l}\mathrm{C_8C\overset{\oplus}{\dot{-}}CC_7COOH}\\ \qquad\quad|\\ \quad\mathrm{C_9CC_7COOH}\end{array} \quad \begin{array}{l}\mathrm{C_7C\overset{\oplus}{\dot{-}}CCC_7COOH}\\ \qquad\qquad|\\ \qquad\mathrm{C_9CC_7COOH}\end{array}}$$

$$\mathrm{III} \xrightarrow{+e^{\ominus}} \underset{\mathrm{IV}}{\begin{array}{l}\mathrm{C_8C{=}CC_7COOH}\\ \qquad\quad|\\ \quad\mathrm{C_9CC_7COOH}\end{array}} \quad \text{or} \quad \underset{\mathrm{V}}{\begin{array}{l}\mathrm{C_7C{=}CCC_7COOH}\\ \qquad\qquad|\\ \qquad\mathrm{C_9CC_7COOH}\end{array}}$$

Anticipating the attempt to rationalize the polymerization of oleic acid induced by γ irradiation, it is emphasized here that this process may lead to either vinylic or allylic branching (cross linking at or adjacent to the double bond; see IV and V, respectively), but that the resulting polymers will in any case retain *no more than a single double bond per polymer molecule.*

It has already been pointed out that γ irradiation of oleic acid should also result in formation of allylic radicals *via* C–H-bond homolysis and a variety of hydrogen-atom abstraction processes. In consequence of their resonance stabilization, such intermediates would be expected to attain relatively high steady-state concentrations, favoring eventual reaction by coupling[41] with a second radical of the same type to give *doubly unsaturated dimers.*[42,44]



$$\mathrm{2C_{7(8)}\cdots\dot{C}\cdots CC_{7(6)}COOH} \longrightarrow \begin{array}{l}\mathrm{C_8C{=}CCC_6COOH}\\ \qquad\qquad|\\ \mathrm{C_8C{=}CCC_6COOH}\end{array}$$

VI

(Inasmuch as this process lacks the chain-reaction features of the Wagner ion-radical mechanism, it cannot lead directly to higher polymers; the dimers are, however, capable of growth by secondary reactions, since they contain particularly labile hydrogen situated on trisubstituted carbon adjacent to centers of unsaturation.)

Since both processes yield polymers of very similar basic structure cross-linked at the carbon adjacent to the double bond (giving rise to the infrared *trans*-peak shift observed in the polymer fraction of the oleic acid irradiation products), evaluation of the relative involvement of the two must depend on the determination of whether dimers produced early in the radiolysis are singly or doubly unsaturated. The clearest evidence bearing on this point is provided by observations concerning production and properties of the C_{34} hydrocarbon, believed to arise *via* decarboxylation of oleic acid dimers of type VI. Glpc (see Figure 2) and ozonization studies (production of long-chain dialdehydes) demonstrate that, prior to modification by further secondary reactions, the "dimeric" hydrocarbon consists largely (if not entirely) of doubly unsaturated C_{34} material, and thus that radiolysis-induced polymerization of oleic acid proceeds mainly by allylic-radical coupling rather than by the Wagner ion-radical mechanism.

Mechanism of *cis–trans* Isomerization. As the present investigation and that of Kaufman[28] have shown, *cis–trans* isomerization of α,β-disubstituted ethylenic substances during γ irradiation is a high-yield process. At first blush, the ionized species of oleic acid in which the electron hole is localized at the double-bond site (type I) might appear to be a likely candidate for the role of an intermediate leading to the observed rearrangement. However, the three-electron carbon–carbon bond involved here probably retains considerable rigidity,[45] for which Holroyd and Klein[43] have provided experimental evidence. Charge neutralization of such cationic radicals leads with high probability, however (as do also direct subionization excitation processes occur-

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(40) It will be appreciated that although a single example has been pictured in the diagram above, the virtual symmetry of the center of unsaturation in the oleic acid molecule leads to the expectation that cross linking in such polymers will involve the ninth and tenth carbon atoms of the oleic acid units with equal probability and that residual unsaturation will occupy positions 8, 9, and 10, with the quantitative relationship of 9 to 8 = 10 being determined by the unknown comparative likelihood of 1,3- and 1,5-hydrogen migration.

(41) Disproportionation of interacting allyl radicals is negligible: F. P. Lossing, K. U. Ingold, and J. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

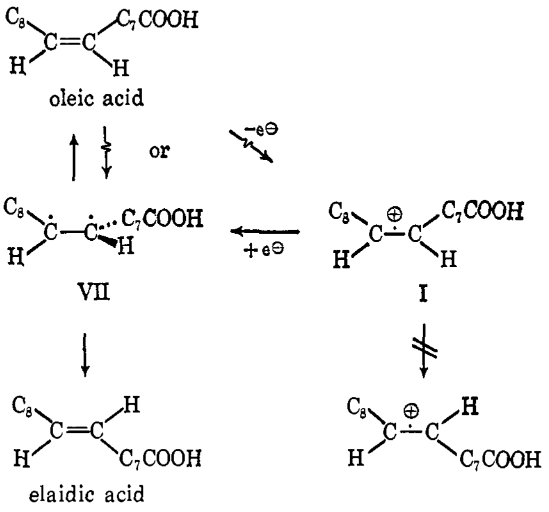
(42) The pictured example of a diallyl dimer is but one of several, the exact structure of which will reflect the equal probability of loss of hydrogen from C-8 or -11, the geometric configurational rigidity of the resulting allylic radical,[43] the possibility of reaction occurring at either end of the radical triad, and the fact that elaidinization may occur either prior to or following coupling; unsaturation in such dimers will thus be located in positions and relative amounts 9 ≠ 8 = 10 of the oleic acid units, and cross links at carbons 9 = 10 ≠ 8 = 11.

(43) R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **69**, 194 (1965).

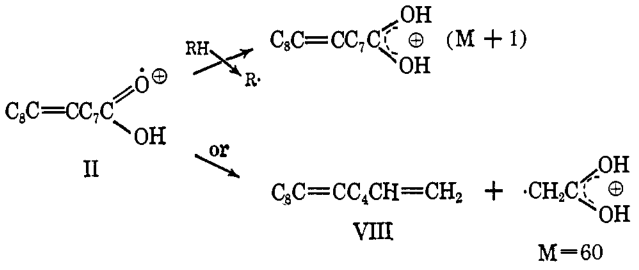
(44) C–H bond energy considerations suggest that analogous incorporation of $C_8C{=}CC_6\dot{C}HCOOH$ units into polymers should not be extensive here, although such radicals may be importantly involved in radiolytic polymerization of *saturated* fatty acids.

(45) R. B. Cundall and P. A. Griffiths, *Discussions Faraday Soc.*, **36**, 111 (1963).

ring in such systems[46]), to the triplet state (VII) invoked as well in photosensitized[47] and indirect radiation-induced[45] *cis–trans* isomerizations.[48]

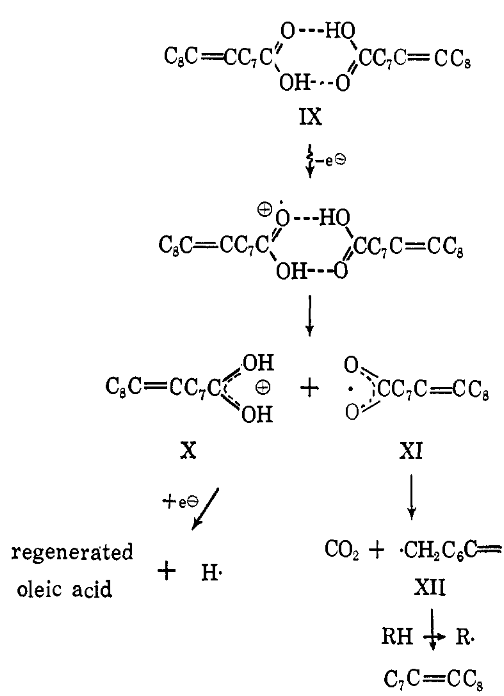


Mechanism of Decarboxylation. Following Williams' provocative discussion[38] of the nature and chemistry of intermediates of type II, the electron deficiency here is considered to be resident to a quantitatively important extent on the doubly bound oxygen atom of the carboxyl group. Mass spectrometry of carboxylic acids[49] provides evidence for the belief that the electron octet of such oxygen atoms is restored with high probability by hydrogen atom abstraction, which may take place either intermolecularly (giving rise to the small but characteristic M + 1 mass spectrum peak) or intramolecularly to give a two-carbon poorer, terminally unsaturated hydrocarbon (VIII) and a charged fragment responsible for the abundant peak of mass 60.



The intramolecular process would, however, be expected to play a much less important role in the liquid than in the low-pressure gas state employed in mass spectrometry because of the greatly reduced likelihood of assumption of a conformation placing the electron-deficient oxygen atom close to the γ-methylene group of the hydrocarbon chain, especially since the mobility of the carboxyl end of the molecule is further restricted by strong hydrogen-bond association between pairs of such molecules. This reasoning is supported by the observation that the "monomeric" hydrocarbon mixture is free of the C_{16} diene (VIII) which would be diagnostic of the involvement of such a process.

However, the carboxyl–carboxyl associative dimeric condition of the liquid fatty acid (IX) provides a particularly attractive possibility for intermolecular hydrogen-atom transfer to the electron-deficient oxygen atom, since the requisite new O–H bond is already partially formed. The following mechanism leading to formation of the principal monomeric hydrocarbon is therefore proposed.[50]



The envisioned hydrogen-atom transfer yields the conjugate acid (X) of otherwise unaltered oleic acid and an oleyloxy radical (XI). In the absence of competitively basic substances, X would appear to have no destiny (aside from proton transfer to another carboxyl group) except eventual encounter with a thermalized electron, regenerating unaltered oleic acid and releasing a hydrogen atom to the milieu.[51] In contrast, XI, as is well known to be typical of such radicals,[52] would very rapidly lose carbon dioxide to yield a primary alkyl radical (XII), abstraction by which of a hydrogen atom from another molecule in its vicinity would be a highly probable event, giving finally the observed end product, 8-heptadecene ($C_7C{=}CC_8$). As pointed out earlier, transfer of a hydrogen atom to XII from any part of a second oleic acid molecule except the methyl or carboxyl groups should be favorably exothermic, with the weakened C–H bonds of "activated" methylene groups adjacent to the olefinic center (giving an allylic radical) being especially vulnerable from this standpoint.[53]

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(46) J. L. Magee in "Comparative Effects of Radiation," M. Burton, J. S. Kirby-Smith, and J. L. Magee, Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p 130.

(47) A. C. Testa, *J. Org. Chem.*, **29**, 2461 (1964).

(48) Involvement of triplet states in such isomerizations is discussed in detail by Y. Hatano, S. Shida, and S. Sato, *Bull. Chem. Soc. Japan*, **37**, 1854 (1964); and by R. A. Caldwell, D. G. Whitten, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 2659 (1966).

(49) K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 252.

(50) For clarity the electron-deficiency localization on the carbonyl oxygen of the carboxyl group and the ensuing hydrogen-atom transfer have been depicted as discrete steps involving an intermediate in which the hydrogen bond of interest, by virtue of the reversal of polarity of the oxygen atom, would, of course, be severely weakened; in operation the two steps would have to be regarded as taking place in a closely concerted manner.

(51) T. F. Williams, *Quart. Rev.* (London), **17**, 118 (1963).

(52) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 493.

(53) Molin and co-workers[54] have interpreted electron spin resonance spectra of a number of saturated straight-chain dicarboxylic acids irradiated with fast electrons in terms of formation of primary alkyl (and acyl) radicals (observed at −130°), which apparently abstract hydrogen

n-Heptadecane would be formed in the same way from stearic acid both present initially and being produced by hydrogenation of oleic acid, while the palmitic acid contaminant would yield the observed *n*-pentadecane. The enhancement in the amount of the saturated hydrocarbon relative to that of the heptadecenes (compare the ratio 1:8.3 after a dose of 420 Mrads with the 1:56 ratio of stearic to oleic acid in the starting material) is attributable not only to hydrogenation of the olefins (including oleic acid itself) but also to the wide disparity in radiosensitivity of the two types of hydrocarbon. The inertness of saturated hydrocarbons in such systems to radiolytic alteration (judged by inappreciable occurrence of otherwise characteristic dehydrogenation and fragmentation reactions) is also indicated in the present study by results of ozonolysis of the monomeric hydrocarbon mixture.

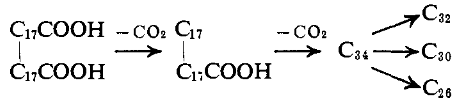
An interesting feature of this mechanism, attributing an important role to the structure of the carboxylic acid association "dimer," is that the member of the pair which undergoes decarboxylation is not that with which the actual triggering ionization event is identified.

The over-all stoichiometry of the reaction is also of interest since, in contrast to the "molecular reaction" $RCOOH \rightarrow RH + CO_2$ (against which, in the case of acetic acid radiolysis, Burr[55] has provided convincing evidence) and in consequence of the temporal and spacial isolation of the individual events involved, *three* molecules of the fatty acid are consumed in the process of creating one of (monomeric) hydrocarbon, the other two being converted (*via* hydrogen-atom transfer processes discussed in greater detail elsewhere) to true fatty acid dimer of the diallyl type.[56]

$$3RCOOH \rightsquigarrow RH + CO_2 + H_2 + \text{dimer}$$

Further application of certain of Williams' deliberations[38] to the problems at hand suggests routes to minor products (including the observed terminally unsaturated 1,8-heptadecadienes) *via* alternative unimolecular modes of reaction of electron-deficient carboxyl-group intermediates.

As indicated earlier, the "dimer" hydrocarbons are apparently produced by double decarboxylation of oleic acid dimers. Changes in the composition of this fraction with dose suggest that the initially formed C_{34} diene is modified subsequently by fragmentation (and hydrogenation) reactions.

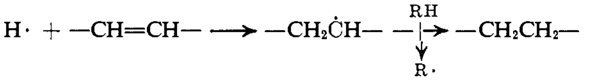


$$\begin{array}{l}C_{17}COOH\\ |\\ C_{17}COOH\end{array} \xrightarrow{-CO_2} \begin{array}{l}C_{17}\\ |\\ C_{17}COOH\end{array} \xrightarrow{-CO_2} C_{34} \rightarrow \begin{cases}C_{32}\\ C_{30}\\ C_{26}\end{cases}$$

The intermediate monodecarboxylated dimer is present (as expected) in the silicic acid chromatographic "oleate" fraction and in quantity (relative to that of "dimeric" hydrocarbon) in accord with the postulated sequence of events. Interestingly, the carbon content of the C_{26} group of hydrocarbons (including lesser amounts of both lower and higher homologs) is just that expected to remain following fragmentation at branching points of polymeric precursors cross-linked at or near the original site of unsaturation.[42]

Mechanism of Hydrogenation. Conversion of oleic to stearic acid and of doubly unsaturated C_{34} "dimeric" hydrocarbons to more saturated derivatives in the course of γ irradiation of liquid oleic acid evidences occurrence of the over-all reaction $-CH=CH- \rightarrow -CH_2CH_2-$ under such conditions, albeit a comparatively minor eventuality (*cf.* $G_s{}^0 = 0.4$). Consideration of what are believed to be the most important primary radiolytic events suggests that double-bond hydrogenation may involve either of two alternative courses.

Hydrogen atoms, produced principally by C–H-bond homolysis but also by charge neutralization of carboxonium and carbonium ions,[38] may react with the oleic acid molecule either by abstraction or addition; the latter process, strongly favored by negligible activation energy (see, for example, Hardwick's[57] demonstration that hydrogen atoms react over 100 times as rapidly by addition to 2-hexene as by abstraction), should lead most probably to eventual hydrogenation of the recipient of olefinic center.[58]



$$H\cdot + \text{—CH=CH—} \longrightarrow \text{—CH}_2\dot{\text{C}}\text{H—} \xrightarrow[R\cdot]{RH} \text{—CH}_2\text{CH}_2\text{—}$$

For reasons advanced above, the culminating hydrogen-atom transfer reaction would be expected to add another unit (R·) to the pool of allylic radicals.

Wagner, *et al.*,[36] have pointed out that molecular cationic radicals of type I derived from olefinic substances by ionization may, *via* intermolecular hydrogen transfer, also result in saturation of the original double bond by initiating processes in which (as was also pointed out to be the case in decarboxylation) up to two allylic radicals may nominally be produced per molecule of oleic converted to stearic acid. Demonstration of the presence of some 9- (or 10-) oleyloxystearate in the polymer fraction may evidence formation of secondary carbonium ions (intermediates in the Wagner olefin hydrogenation mechanism), although alternative rationalization of such products is readily imaginable.

Direct *vs.* Indirect Effects. It is now possible, on the basis of observations made in the present study, together with those of the earlier investigation[7] of the effects of γ irradiation on dilute aqueous solutions of potassium oleate, to compare changes in oleic acid induced by direct radiolysis with those mediated by products of radiolysis of water. Interestingly, the major eventuality in both cases is the formation of polymers of closely similar if not identical constitution (although direct radiolysis apparently leads to products of somewhat higher average order of polymerization) *via* coupling of allylic radical intermediates. Hydrogenation and hydration (in the sense that formation of oleyl-

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from the methylene group adjacent to the carboxyl moiety, giving radicals of type $-\dot{C}HCOOH$ (observed at 20°) as expected in absence of the presumably more labile methylene groups adjacent to olefinic unsaturation.

(54) Yu. N. Molin, I. I. Chkheidze, N. Ya. Buben, and V. V. Voevodskii, *Zh. Strukt. Khim.*, **2**, 293 (1961); *Chem. Abstr.*, **56**, 6809*h* (1962).

(55) J. G. Burr, *J. Phys. Chem.*, **61**, 1481 (1957).

(56) It should be pointed out that decarboxylation initiated by O–H-bond homolysis (assuming escape of the hydrogen atom prior to loss of carbon dioxide from the acyloxy radical) would result in the same over-all stoichiometry: $RCOOH \rightsquigarrow H\cdot + RCOO\cdot \rightarrow CO_2 + R\cdot$; although the present study does not discern the subtle distinction between these two possibilities, the homolysis involved in initiating the alternative process is believed to be one of relatively low probability.

(57) T. J. Hardwick, *J. Phys. Chem.*, **64**, 1623 (1960).

(58) On the basis of reduction in yield of molecular hydrogen caused by presence of small amounts of added carboxylic acids in hexane during high-energy electron irradiation, Hardwick[57] has concluded that hydrogen atoms may add with considerable facility to the carboxyl group; many observations by others, however, contraindicate the importance of such reaction, and there are alternative explanations for the effect.

oxystearic acid exemplifies this) of the center of unsaturation also occur in both systems. On the other hand, however, elaidinization and decarboxylation appear to be uniquely characteristic of direct γ radiolysis, and it may therefore prove possible on the basis of these distinctive features (particularly the former, since decarboxylatable free fatty acids occur rarely in living organisms) to evaluate the relative quantitative importance of direct and indirect effects of ionizing radiation on lipids *in vivo*.

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The Effect of Including Non-Nearest Neighbor β Terms in Pariser–Parr–Pople Type Self-Consistent Molecular Orbital Calculations on π-Electron Systems

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Abstract: A systematic study of the effect of inclusion of all β_{ij} terms in semiempirical π-electron calculations has been made. The two principal effects are the occurrence of charge separation in alternate hydrocarbons similar to that obtained when using orthogonalized orbitals, and a change in the spacing of higher energy levels in polyenes.

Most calculations which use the Pariser and Parr[1] and Pople[2] self-consistent molecular orbital (SCMO) approach take as a basic assumption that all non-nearest neighbor β terms may be neglected. Fischer-Hjalmars pointed out the necessity of including non-nearest neighbor β terms in Hückel-type calculations in order for the approximations employed to be consistent.[3] The purpose of this report is to examine critically the effect of inclusion of all β terms in the secular determinant for molecules in the polyene–polyacene series. The properties examined will be charge distribution, spectral transitions, and ionization potentials. While some work has been done including non-nearest neighbor β terms, such as Hoffman's[4] extended Hückel theory (which is not a self-consistent field method), Allinger's[5] configuration interaction work, and Orloff and Fitts' modified Hückel scheme,[6] no one has yet done a systematic survey on the effect of this inclusion.

Method

The calculations were performed on either an IBM 1620 digital computer with disk pack or an IBM 7040. The program is written in Fortran and is constructed so as to give the operator many variations in operations with only minor changes in the input parameters. One of the basic sets of information needed is the geometry of the molecule in question. The bond lengths and bond angles for the compounds studied were obtained from the Chemical Society tables.[7] The geometries of the higher polyenes were assumed to be similar to hexatriene with the same bond-length alternation. All internuclear separations are automatically calculated by the program.

The valence-state data for carbon was from the work of Hinze and Jaffé.[8] These values are -11.16 ev for the valence-state ionization potential and 0.03 ev for the electron affinity. These yield a semiempirical value[1] of 11.13 ev for the one-center, two-electron repulsion integral.

Two approximations were tried for evaluating the two-center repulsion integrals. These were a Pariser and Parr[1] type parabolic interpolation, at distances less than 5 A with a $1/r$ dependence at greater distances, and the Mataga[9] formula (eq 1, in au).

$$\gamma_{ij} = \cfrac{1}{R_{ij} + \cfrac{2}{\gamma_{ii} + \gamma_{jj}}} \qquad (1)$$

The use of the Mataga approximation has given better spectral agreement than the Pariser and Parr approximation; therefore, they were used for the reported results.

One of the main difficulties encountered in the inclusion of all β terms is that of finding a suitable function to express the more distant interactions correctly. After testing several approximations, including methods where β was proportional to overlap and methods where it was a simple exponential, it was decided to use a function of the form of eq 2. In this equation, S is the

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