An Electron Spin Resonance Study of Fatty Acids and Esters. Part 2.† Hydrogen Abstraction from Saturated Acids and their Derivatives

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The radicals generated from saturated fatty acids and their derivatives by hydrogen abstraction with photochemically formed t-butoxyl radicals have been investigated. These arise from the various methylene groups in the acids. The relative rates of abstraction from the methylene groups in the α-position, the position adjacent to the terminal methyl, and the remaining chain positions are 2:2:1, respectively, at 290 K, for acids of chain length $>C_6$.

With propanoic acid, butanoic acid, and butanonitrile, hydrogen abstraction at the α-methylene group predominates. With 1-lauroyl-2-myristoyl-3-palmitoyl-*rac*-glycerol, enhanced attack at the position adjacent to the terminal methyl was observed.

Autoxidation of saturated fatty acids and esters is slower than that of their unsaturated counterparts. Stirton *et al.*[1] have reported an 11-fold difference in rate of autoxidation between stearate and oleate. More recently Small *et al.*[2] reported a relative reactivity of 1.65 : 1 for methyl oleate and stearate in their reactions with t-butoxyl radicals.

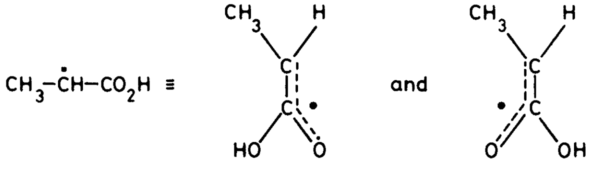
The autoxidation of saturated fatty acids and their methyl esters has been studied at temperatures in the range 150—200 °C [3–7] and under catalysed conditions.[8–11] Not surprisingly, under such conditions, complex mixtures of products have been reported, including carbonyl, hydroxy, and carboxylic compounds.

It has been suggested that the thermal oxidation of saturated fatty acids proceeds with dehydrogenation as the initial step.[4–6] The resulting unsaturated molecules are subsequently autoxidised in accord with the more classical mechanism proposed for methyl oleate.[12]

There has been some controversy about the site of attack. Zvidema [13] postulated that the oxidation of paraffins at 100—200 °C took place predominantly at the β-carbon atom with additional attack on the γ-atom, the primary product of the reaction being the hydroperoxide which then decomposed to yield a β-ketone and water.

Hydrogen abstraction from saturated fatty acids by HO· radicals generated in the Ti–H_2O_2 flow system has been investigated previously by e.s.r. spectroscopy.[14–19] The radiolytic oxidation of fatty acids and their anions has also been studied by e.s.r. techniques.[20,21] We showed recently that hydrogen abstraction from monoenoic and monoynoic fatty acids by t-butoxyl radicals gave rise to e.s.r. spectra in which the main components were due to substituted allyl and propynyl radicals respectively.[22,23] The main radicals were accompanied by minor secondary radicals generated by H-abstraction from chain methylene groups (non-activated) and from the methylene adjacent to the terminal methyl group ($\omega - 1$).

In this paper we report details of an e.s.r. spectral study of a variety of secondary radicals obtained on H-abstraction from saturated acids and various derivatives (including a saturated triacylglycerol) by t-butoxyl radicals. The results provide insight into the regioselectivity of H-abstraction in saturated fatty acids by alkoxyl radicals. These species may play an important part in the autoxidation of fatty acids at elevated temperatures [3–7] and under catalysed conditions.[8–11]



(1) (1a) (1b)

Results

E.s.r. spectra of the fatty acid radicals were obtained by photolysis of degassed solutions of the freshly purified acid or derivative in neat di-t-butyl peroxide in the cavity of the spectrometer. Intense spectra were obtained for most of the samples but the sample lifetime of the higher homologues was short owing to rapid build-up of polymer on the walls of the tube. No radicals were observed by e.s.r. on photolysis of neat acids in the absence of di-t-butyl peroxide.

Propanoic Acid and Anhydride.—The predominant radical observed from photolysis of propanoic acid and di-t-butyl peroxide resulted from hydrogen abstraction α to the carboxy group, *i.e.* radical (1) (the α-radical). Two configurations of the radical in which the O–C–C–C skeleton is planar can be envisaged (1a and b), but only one set of signals was observed over the temperature range 250—305 K. The hyperfine splitting (h.f.s.) constants derived from the double quartet spectrum were unequivocally assigned to specific hydrogen atoms and were in excellent agreement with those previously reported.[14,17,24] Hydrogen abstraction from propanoic anhydride gave rise to two radicals each with a double quartet pattern. The minor radical (*ca.* 25% at 250 K) had h.f.s. constants similar to those of radical (1b) and the major radical (*ca.* 75% at 250 K) had a smaller β-h.f.s. (Table 1).

Butanoic Acid and Derivatives.—Photolysis of a solution of butanoic acid in di-t-butyl peroxide at 250 K gave an intense spectrum with signals arising from radicals (2) and (3) (Table 2). The assignment for the primary radical (4) is tentative since considerable overlap of the lines occurs. However the h.f.s. constants are in excellent agreement with those of structurally related primary radicals.[14,17,24]

$CH_3CH_2\dot{C}HCO_2H$ (2) $CH_3\dot{C}HCH_2CO_2H$ (3) $\cdot CH_2CH_2CH_2CO_2H$ (4)

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† Part 1, ref. 22.

Table 1. E.s.r. parameters [a] for radicals generated from propanoic acid and anhydride at 250 K

Radical	$a(H_\alpha)$	$a(H_\beta)$	Relative conc.
$CH_3\dot{C}HCO_2H$	2.00 (1 H)	2.44 (3 H)	1
$CH_3\text{-}\dot{C}H\text{-}CO_2R$ [b] *cisoid*	1.92 (1 H)	2.28 (3 H)	0.75
$CH_3\dot{C}H\text{-}CO_2R$ [b] *transoid*	1.92 (1 H)	2.48 (3 H)	0.25

[a] All h.f.s. constants checked by computer simulation. [b] R = COEt.

As found for propanoic acid, hydrogen abstraction occurred overwhelmingly α to the carboxy group (>77%). The relative concentration of the primary radical could not be determined accurately, but an upper limit of *ca.* 3% was estimated.

Hydrogen abstraction from butanoic anhydride again occurred predominantly α to the carboxy group and, as with propanoic anhydride, two sets of e.s.r. signals resulting from from two α-radicals were observed. The predominant radical had a smaller β-h.f.s. than the minor one. The ratio of the concentrations of the two radicals showed no significant variation with temperature in the range 250—300 K, and had a mean value of 4.6 ± 0.3 : 1.

The e.s.r. spectrum obtained on photolysis of a solution of butanonitrile and di-t-butyl peroxide showed the presence of radicals (5)—(7). The relative amounts of each radical and their h.f.s. constants are given in Table 2.

$CH_3CH_2\dot{C}HCN$ (5) $CH_3\dot{C}HCH_2CN$ (6) $\cdot CH_2CH_2CH_2CN$ (7)

The e.s.r. spectrum obtained on H-abstraction from methyl butanoate showed a much more complicated pattern than that from the acid. The increased complexity arises from coupling of the hydrogens of the ester group with the unpaired electron (see Table 2). The replacement of the carboxylic OH by OMe has an effect on the relative ease of abstraction of the various hydrogen atoms. The relative amount of the primary radical was increased considerably at the expense of the α-radical, though the latter is still by far the predominant radical formed.

Four distinct radicals were observed on H-abstraction from butyl trifluoroacetate. The spectrum was complicated as a result of a large number of overlapping lines and the relative concentrations were difficult to measure accurately (Table 2). Hydrogen abstraction from butyl acetate gave an e.s.r. spectrum which also showed the presence of four radicals, although again the central region contained a considerable number of overlapping lines. The relative amounts of each of the four radicals are given in Table 2.

Pentanoic Acid and Higher Homologues.—Pentanoic acid can form four radicals (8)—(11). The main radicals observed

$CH_3CH_2CH_2\dot{C}HCO_2H$ (8) $CH_3CH_2\dot{C}HCH_2CO_2H$ (9)

$CH_3\dot{C}HCH_2CH_2CO_2H$ (10) $\cdot CH_2CH_2CH_2CH_2CO_2H$ (11)

in the e.s.r. spectrum were the ω − 1 radical (10) and the α-radical (8). The secondary radical (9) arising from hydrogen abstraction at C-3 was also observed but in an amount difficult to quantify accurately owing to its low relative concentration. The upper limit is estimated as 12%. The primary radicals, resulting from H-abstraction at the terminal CH_3 group could not be detected for this acid or its higher homologues.

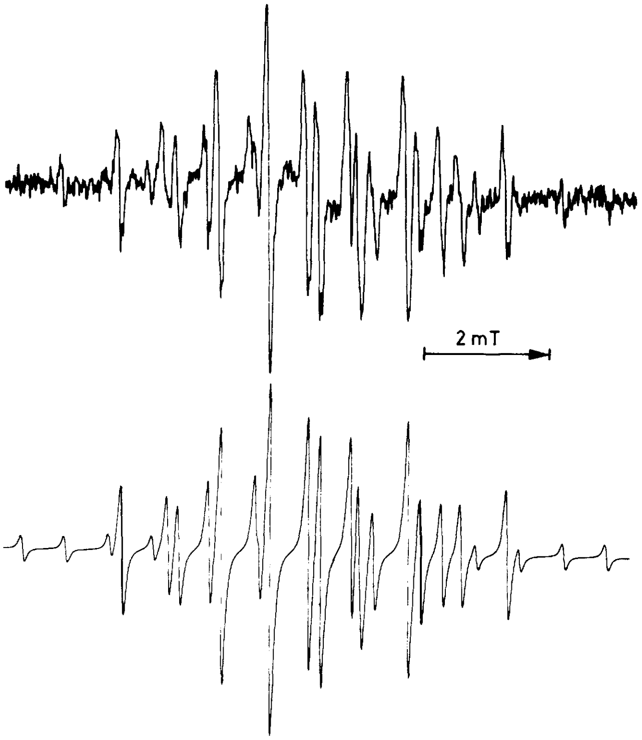


Figure 1. E.s.r. spectrum (9.4 GHz) of radicals obtained by H-abstraction from n-hexanoic acid by $Bu^tO\cdot$ radicals: upper trace, experimental spectrum; lower trace, computer simulation

Hydrogen abstraction from hexanoic acid gave rise to an e.s.r. spectrum in which the ω − 1 radical, the α-radical, and other secondary radicals were clearly observed (Figure 1). The two radicals resulting from hydrogen abstraction from C-3 and C-4 were spectroscopically equivalent, inductive and electric field effects producing no observable difference in spin density distribution at these sites. The relative amounts of each of the radicals observed and their respective h.f.s. constants are reported in Table 3. Small triplet γ-h.f.s. constants were resolvable in the spectra of the secondary radicals derived from pentanoic and hexanoic acids, but could not be resolved for higher homologues.

For heptanoic acid the h.f.s. constants of the three observable radicals in the spectrum were similar to those obtained from the spectra of pentanoic and hexanoic acids. The splitting pattern for the ω − 1 radical in the spectra from C_5 and higher acids was different from that of the similar radical from butanoic acid and its derivatives. In the longer chain acids the hydrogen atoms of the terminal methyl group have the same h.f.s. as the hydrogens of the ω − 2 methylene group. In the ω − 1 radicals from butanoic acid the h.f.s. constants of the ω − 2 methylene group are perturbed (reduced) because this position is also α to the carboxy group, *i.e.* the change results from the head group effect at C-2.

The e.s.r. spectra obtained on hydrogen abstraction from the C_8—C_{18} homologues were very similar to each other, containing three sets of signals resulting from hydrogen abstraction at C(α), C(ω − 1), and the remaining secondary methylenes. Minor differences in h.f.s. of the secondary methylenes (some of which are in the vicinity of the head groups) were not resolved and hence the signal from these

Table 2. E.s.r. parameters for radicals derived from butanoic acid and its derivatives [a]

Radical	$a(H_\alpha)$	$a(H_\beta)$		Relative [b] conc.
$\mathrm{CH_3CH_2\dot{C}HCO_2H}$	1.97 (1 H)	2.28 (2 H)		0.77
$\mathrm{CH_3\dot{C}HCH_2CO_2H}$	2.20 (1 H)	2.44 (3 H)	2.20 (2 H)	0.23
$\mathrm{CH_3CH_2\dot{C}HCO_2R}$ [c] *cisoid*	1.92 (1 H)	2.19 (2 H)		0.55
$\mathrm{CH_3CH_2\dot{C}HCO_2R}$ [c] *transoid*	1.92 (1 H)	2.34 (2 H)		0.12
$\mathrm{CH_3\dot{C}HCH_2CO_2R}$ [c]	2.20 (1 H)	2.20 (2 H)	2.46 (3 H)	0.28
$\mathrm{{}^{\bullet}CH_2CH_2CH_2CO_2R}$ [c]	2.20 (1 H)	2.58 (2 H)		0.04
$\mathrm{CH_3CH_2\dot{C}HCO_2Me}$ [d]	2.00 (1 H)	2.38 (2 H)		0.46
$\mathrm{CH_3\dot{C}HCH_2CO_2Me}$	2.23 (1 H)	2.23 (2 H)	2.51 (3 H)	0.31
$\mathrm{{}^{\bullet}CH_2CH_2CH_2CO_2Me}$	2.20 (1 H)	2.58 (2 H)		0.23
$\mathrm{CH_3CH_2\dot{C}HCN}$ [e]	1.93 (1 H)	2.38 (2 H)		>0.91
$\mathrm{CH_3\dot{C}HCH_2CN}$	2.30 (1 H)	2.30 (2 H)	2.50 (3 H)	<0.06
$\mathrm{{}^{\bullet}CH_2CH_2CH_2CN}$	2.20 (2 H)	2.60 (2 H)		<0.03
$\mathrm{CH_3CH_2CH_2\dot{C}HOCOCF_3}$	2.10 (1 H)	2.50 (2 H)		<0.1
$\mathrm{CH_3CH_2\dot{C}HCH_2OCOCF_3}$	2.20 (1 H)	2.50 (4 H)		*ca.* 0.3
$\mathrm{CH_3\dot{C}HCH_2CH_2OCOCF_3}$	2.30 (1 H)	2.50 (3 H)	2.30 (2 H)	*ca.* 0.6
$\mathrm{{}^{\bullet}CH_2CH_2CH_2CH_2OCOCF_3}$	2.13 (2 H)	2.60 (2 H)		*ca.* 0.1
$\mathrm{CH_3CH_2CH_2\dot{C}HOCOCH_3}$	2.12 (1 H)	2.61 (2 H)		0.19
$\mathrm{CH_3CH_2\dot{C}HCH_2OCOCH_3}$	2.12 (1 H)	2.40 (4 H)		0.25
$\mathrm{CH_3\dot{C}HCH_2CH_2OCOCH_3}$	2.30 (1 H)	2.50 (3 H)	2.30 (2 H)	0.41
$\mathrm{{}^{\bullet}CH_2CH_2CH_2CH_2OCOCH_3}$	2.13 (2 H)	2.60 (2H)		0.15

[a] All h.f.s. constants checked by computer simulations; the accuracy of measurement is *ca.* ±0.05 mT in most cases. [b] At 290 K. [c] R = PrCO. [d] Also $a(3\ H_\gamma) = 0.14$ mT. [e] Also $a(N) = 0.34$ mT.

Table 3. E.s.r. parameters [a] for radicals generated from pentanoic, hexanoic, and heptanoic acids

Radical	$a(H_\alpha)$	$a(H_\beta)$	$a(H_\gamma)$	Relative conc.
$\mathrm{CH_3CH_2CH_2\dot{C}HCO_2H}$	1.96 (1 H)	2.22 (2 H)	0.05 (2 H)	0.41
$\mathrm{CH_3CH_2\dot{C}HCH_2CO_2H}$	2.13 (1 H)	2.50 (4 H)		0.12
$\mathrm{CH_3\dot{C}HCH_2CH_2CO_2H}$	2.12	2.42 (5 H)		0.47
$\mathrm{CH_3CH_2CH_2CH_2\dot{C}HCO_2H}$	1.96 (1 H)	2.22 (2 H)	0.10 (2 H)	0.42
$\mathrm{CH_3CH_2CH_2\dot{C}HCH_2CO_2H}$	2.13 (1 H)	2.50 (4 H)		0.19
$\mathrm{CH_3CH_2\dot{C}HCH_2CH_2CO_2H}$				
$\mathrm{CH_3\dot{C}HCH_2CH_2CH_2CO_2H}$	2.12 (1 H)	2.42 (5 H)		0.40
$\mathrm{CH_3CH_2CH_2CH_2CH_2\dot{C}HCO_2H}$	1.96 (1 H)	2.22 (2 H)		0.28
$\mathrm{CH_3CH_2CH_2CH_2\dot{C}HCH_2CO_2H}$	2.13 (1 H)	2.49 (4 H)		0.44
$\mathrm{CH_3CH_2CH_2\dot{C}HCH_2CH_2CO_2H}$				
$\mathrm{CH_3CH_2\dot{C}HCH_2CH_2CH_2CO_2H}$				
$\mathrm{CH_3\dot{C}HCH_2CH_2CH_2CH_2CO_2H}$	2.12 (1 H)	2.42 (5 H)		0.29

[a] All h.f.s. constants checked by computer simulation; the accuracy of measurement is *ca.* ±0.05 mT in most cases.

radicals was an envelope of all the slightly different signals. This manifested itself in a larger linewidth for the secondary radicals and the line shape deviated from purely Lorentzian to Gaussian. The following h.f.s. constants were essentially the same for the radicals derived from each acid: α-radical, $a(H_\alpha)$ 1.96, $a(2H_\beta)$ 2.24 mT; secondary radical $a(H_\alpha)$ 2.10, $a(4H_\beta)$ 2.40 mT; ω − 1 radical, $a(H_\alpha)$ 2.12, $a(5H_\beta)$ 2.42 mT. Minor increases in $a(H_\beta)$ were observed for octanoic and nonanoic secondary radicals.

Figure 2 shows the variation of the relative concentrations of the three observable radicals with increasing chain length of the aliphatic acid. The steady increase in the relative concentration of secondary radical with concomitant decrease in concentration of the α and ω − 1 radicals with increasing carbon number is virtually as expected on a purely statistical basis. The series of relative rates of hydrogen abstraction shown in Table 4 were obtained by correction of each radical concentration for the number of contributing hydrogen atoms.

Triacylglycerols.—An e.s.r. spectrum, which contained the signals of radicals derived by hydrogen abstraction at the α-site, ω − 1 site, and the remaining secondary sites was obtained on photolysis of mixtures of di-t-butyl peroxide and 1-lauroyl-2-myristoyl-3-palmitoyl-*rac*-glycerol at 300 K. The spectrum was similar to that obtained on hydrogen abstraction from the long-chain saturated acids. However, estimates of the relative concentrations of each type of radical indicated an increased amount of ω − 1 radical as compared with the other secondary radicals (Figure 3).

Long-chain Cyclopropane, Epoxy, and Trimethylsilyloxy Fatty Acid Esters.—Hydrogen abstraction from cyclopropane (12), epoxy (13), and 12-trimethylsilyloxy (14) derivatives of methyl stearate gave e.s.r. spectra which were indistinguishable from the spectrum obtained from methyl stearate in each case. This suggests that the new sites for hydrogen abstraction introduced by the functional groups are not significantly activated with respect to the other possible sites of attack.

Discussion

The observation of (1) as the predominant radical formed on hydrogen abstraction from propanoic acid by t-butoxyl

Table 4. Relative rates of hydrogen abstraction from saturated fatty acids at 290 K by t-butoxyl radicals [a]

	k_{rel}			
Acid	α [b]	s [c]	ω − 1 [d]	p [e]
C_3	1.0			<0.2
C_4	3.4		1.0	*ca.* 0.2
C_5	3.4	1.0	3.9	<0.2
C_6	4.5	1.0	4.2	<0.2
C_7	1.9	1.0	2.0	<0.2
C_8	2.6	1.0	1.8	<0.2
C_9	3.4	1.0	1.8	<0.2
C_{10}	1.8	1.0	2.2	<0.2
C_{11}	1.8	1.0	1.3	<0.2
C_{14}	1.6	1.0	2.0	<0.2
C_{16}	1.6	1.0	2.4	<0.2
C_{18}	1.1	1.0	2.6	<0.2

[a] Relative rates on a per hydrogen atom basis. [b] Abstraction from the methylene α to the carboxylate group. [c] Abstraction from chain methylene groups. [d] Abstraction from the ω − 1 methylene group. [e] Abstraction from the terminal methyl group.

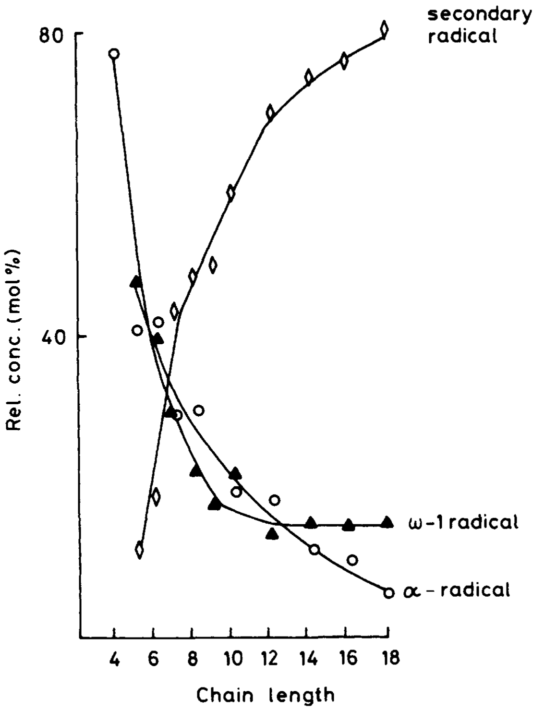


Figure 2. Plot of the relative concentrations (mol %) of the α, ω − 1, and secondary radicals derived from n-alkanoic acids as a function of chain length at 290 K

radicals contrasts with the observations for other abstracting radicals. Taniguchi *et al.*,[17] using a flow technique to measure the relative ease of abstraction of the various types of hydrogen atoms by hydroxyl radicals, generated by an H_2O_2–Ti^{4+} system, found that hydrogen abstraction occurred preferentially at the terminal methyl group (*ca.* 70%). Hewgill *et al.*,[14] also using hydroxyl radicals in an aqueous system, observed hydrogen abstraction at the methyl group (50%) in acid solution, but in basic solution hydrogen abstraction occurred preferentially at the α-site for the anion although the preference was small.

The radical (1) has also been observed in the product of halogen abstraction from α-halogenopropanoic acid.[24,25] An MINDO/3 semiempirical calculation on the two possible isomeric α-radicals [*cisoid* (1a) and *transoid* (1b)] indicated that the *transoid* configuration is marginally lower in energy than the *cisoid* configuration, as would be expected. The barrier to rotation about the C(1)–C(2) bond for conversion of *cis*- into *trans*-isomers was computed to be 6.7 kJ mol^{-1}. This value is probably an underestimate because MINDO/3, despite predicting barriers to rotation about double bonds with reliability, often underestimates barriers to rotation about delocalised bonds.[26] Nonetheless the relative stabilities are generally well reproduced by MINDO/3, which supports the intuitive expectation that the ground-state rotamer population of the delocalised radical should be predominantly *transoid*.

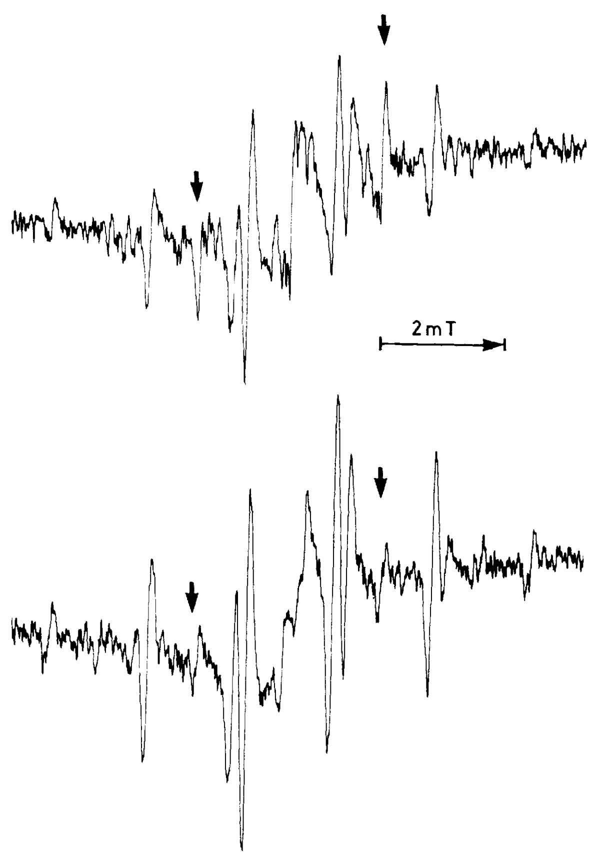
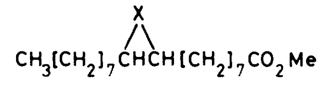
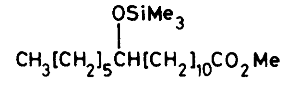


Figure 3. Top: e.s.r. spectrum obtained on photolysis of a solution of 1-lauroyl-2-myristoyl-3-palmitoyl-*rac*-glycerol in di-t-butyl peroxide at 300 K; bottom: e.s.r. spectrum obtained from palmitic acid (C_{16}) under similar conditions. Arrows indicate prominent lines from the ω − 1 radicals



(12) X = CH_2 (13) X = O

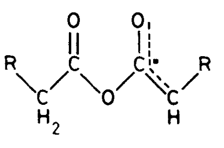


$CH_3[CH_2]_5CH(OSiMe_3)[CH_2]_{10}CO_2Me$

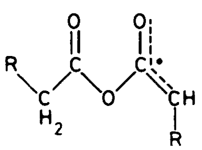
(14)

For hydrogen abstraction from propanoic and butanoic anhydrides two sets of signals were observed, differing only in their β-h.f.s. The two radicals may well be *cisoid* (15a) and *transoid* (15b) conformers.

The minor radical has been identified as the *transoid* isomer on the basis of its β-h.f.s. being the same as that for the α-radical from the parent acids, which we believe to be *transoid*. The major radical therefore from the anhydrides is the *cisoid*



(15a)



(15b)

isomer. We tentatively interpret the reduction in the amount of the *transoid* radical (in comparison with parent acids) in terms of an increase in conformational preference of the anhydride for the extended zig-zag conformation. This would parallel an inference from n.m.r. data by Butcher and Wilson[27] for propanal, a reasonable analogy, in which the *cis*-rotamer is approximately 4 kJ mol^{-1} more stable than the *trans*-form with a barrier to rotation of 10 kJ mol^{-1}. Further support for the assignment comes from the relative magnitudes of the β-h.f.s. constants, which are in accord with those for *cis*- and *trans*-methylallyl radicals.[28]

Our results for the carboxylic acids, anhydrides, esters, and one nitrile show that t-butoxyl radicals abstract hydrogen slightly more rapidly from the $\omega - 1$ and α-methylene groups than from other chain positions (see Tables 1—4). The relative rates of hydrogen abstraction, on a per hydrogen atom basis ($k_{\rm rel}$), are independent of chain length for the $\omega - 1$ hydrogen atoms, within experimental error. The $k_{\rm rel}$ values for the α-hydrogen atoms show a decrease with increasing chain length, but the variation is scarcely above experimental error. As would be expected, acids of chain length below C_6 do not fit this pattern well, presumably because the hydrogen atoms β to the end groups also experience a significant substituent effect. If results from the shorter chain compounds are omitted the following average relative rates for $Bu^tO^\cdot$ radicals at 290 K can be derived:

Site	α	s	$\omega - 1$	p
$k_{\rm rel}$	2.0	1.0	2.0	*ca.* 0.2

where s and p stand for abstraction from other secondary methylenes and from primary methyl groups, respectively.

Halogen atoms[29] and hydroxyl radicals[14-17] also abstract more readily from the $\omega - 1$ site but, in contrast to t-butoxyl radicals, less readily from α-sites in carboxylic acids. However, activation at the α-site in carboxylate anions towards hydroxyl radical attack has been observed,[14] with hydroxyl radicals generated in the $TiCl_3$–H_2O_2 system. Hewgill *et al.*[16] demonstrated that carboxylic acids can co-ordinate to titanium *via* the carboxy group, thus altering the nature of the substituent effects in this system. Some differences in the regioselectivity of hydroxyl radicals generated from $TiCl_3$–H_2O_2 as compared with those generated by radiolysis have been ascribed to preferential reaction of product radicals with either metal ions or H_2O_2.[30-33] Thus the hydroxyl radical results may not be directly comparable with the t-butoxyl radical behaviour.

The contrast between activation at the α-site for $Bu^tO^\cdot$ and $CH_3^\cdot$ radicals on the one hand and deactivation for $Cl^\cdot$ and $Br^\cdot$ atoms on the other deserves comment. Tedder has discussed in detail the factors which control the rates of hydrogen abstraction from aliphatic compounds.[34] There is no significant difference in the strengths of the bonds being formed, *viz.* 431, 439, and 423 kJ mol^{-1} for HCl, $HOBu^t$ and HCH_3, respectively. Thus, the difference can probably be ascribed to polar forces in the transition state. For the halogen atoms the product molecule HX is highly polar and this leads to a repulsive electrostatic effect with the carboxylate group for α-attack. The product molecules $HOBu^t$ and CH_4, formed when t-butoxyl or methyl radicals abstract hydrogen, are much less polar, and therefore the electrostatic repulsion is minor. In the absence of this polar repulsion the resonance stabilization of the incipient α-radical makes attack at the α-site energetically favourable. The activation of the $\omega - 1$ hydrogen atoms is usually attributed to a hyperconjugative effect of the terminal methyl group.

The relative rates of H-abstraction from the triacylglycerol on a per hydrogen atom basis, $k_{\rm rel}$, were as follows:

Site	α	s	$\omega - 1$
$k_{\rm rel}$ at 290 K	2.1	1.0	9.0

This indicates that the α-sites are activated to about the same extent as in the saturated acids, but a significantly increased reactivity is shown at the $\omega - 1$ positions. We tentatively attribute this to increased steric hindrance to H-abstraction by the $Bu^tO^\cdot$ radicals from methylene groups towards the carboxy end of each chain in the triacylglycerol. This would lead to *apparent* activation of the more exposed $\omega - 1$ methylenes.

The present results indicate that hydrogen abstraction from saturated carboxylic acids by t-butoxyl radicals is a fairly random process, with only slight activation at the α and $\omega - 1$ positions. This contrasts with the situation for polyunsaturated carboxylic acids where hydrogen abstraction occurs predominantly from the doubly allylic methylene groups.[22,23]

Experimental

Saturated fatty acids, obtained commercially, were the best grades available. Liquids were redistilled before use. Solid acids (C_{10} upwards) were crystallised from light petroleum (b.p. 40—60 °C). The purity of the acids (in excess of 99.0%) was checked before use by capillary g.l.c.

Methyl esters were prepared by acid-catalysed esterification by standard procedures. After distillation or crystallisation they were analytically pure by capillary g.l.c. and t.l.c. (where applicable).

Propanoic and butanoic anhydride, butanonitrile, and n-butyl acetate, were commercially available and were distilled prior to use.

Butyl Trifluoroacetate.—A mixture of butan-1-ol (37 g, 0.5 mol), trifluoroacetic acid (114 g, 1.0 mol), and concentrated sulphuric acid (1 ml) was refluxed for 16 h. Water was added (200 ml) and the upper layer was then washed with distilled water (50 ml) and with saturated sodium hydrogen carbonate solution (2 × 25 ml). The crude ester was dried over anhydrous sodium sulphate, filtered, and fractionally distilled to give pure *butyl trifluoroacetate* (77.5 g, 78%), b.p. 121—123 °C at 18.5 Torr; δ_H 4.32 (2 H, t, *J* 6.4 Hz, CH_2O), 1.66 (2 H, sextet, *J* 6.4 Hz, $CH_3CH_2CH_2$), 1.33 (2 H, quintet, *J* 6.4 Hz, CH_2-CH_2CH_2), and 0.90 (3 H, t, *J* 6.8 Hz, CH_3); δ_C 67.88 (C-1), 30.2 (C-2), 18.67 (C-3), and 13.30 (C-4); *m*/*z* 141 (16, M^+ − Et), 99 (4), 69 (31, CF_3^+), 57 (34, $C_4H_9^+$), 56 (100, $C_4H_8^+$), 44 (26, CO_2), 43 (44, $C_3H_7^+$), 41 (80, $C_3H_5^+$), 32 (70), and 31 (37 CF^+).

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