

[Review Paper]

The Autoxidation of Simple Esters: Towards an Understanding of the Chemistry of Degradation of Polyol Esters Used as Lubricants

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The liquid phase oxidation of a series of neopentyl esters, chosen to model the more complex polyol esters used as lubricants, has been studied in two ways. In one, detailed product analyses, following reaction with oxygen in a closed reactor at elevated temperatures, allows for mechanisms to be proposed. In the second, the esters were reacted with two different alkoxy radicals, the results leading to valuable information about the relative rates of attack on the various C–H bonds. For example, it was found that attack could take readily on both the alkyl and acyl groups in the ester and that the β -acyl C–H bonds are more susceptible to attack than α -C–H bonds.

To support the proposals for the mechanisms, details are given of experiments in which reactions of specific peroxy radicals derived from esters were studied in detail and compared with similar experiments with alkylperoxy radicals. The reactions of peroxy radicals formed from esters are similar to those derived from alkanes and it is possible to use rate constants for reactions of alkylperoxy and related oxygenated radicals to model successfully the reactions of the esterperoxy radicals.

Overall the mechanisms for the autoxidation of the esters can be explained in terms of well-established mechanisms associated with the autoxidation of alkanes, as would be expected from the similarity of the peroxy radical chemistry of the two systems. However, care has to be taken in accounting for the influence of the functional group which has a profound effect on the point of attack in the case of the autoxidation of the esters.

Keywords

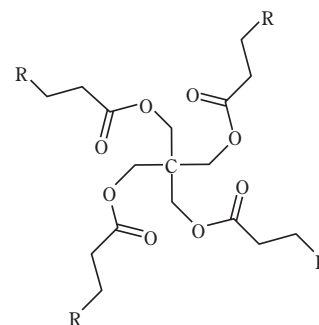
Polyol ester, Neopentyl ester, Lubricant, Autoxidation, Hydroperoxy radical, Alkoxy radical

1. Introduction

Engines are being designed to operate at higher temperatures and thus the thermo-oxidative properties of lubricants must be improved¹⁾. Among the synthetic base fluids which are being used are the polyol esters which have good viscometric, biogradability and lubricity properties and mix well with additives²⁾. The polyol esters account for about one-fifth of the synthetic lubricants produced and the pentaerythrityl esters are amongst the most important³⁾.

Thus in spite of higher costs to those enjoyed by hydrocarbon-based lubricants, they are increasingly in demand, in industrial applications as well as in automotive and aero engines⁴⁾.

The development of the use of esters as lubricants depends, in part, on a thorough understanding of their autoxidation and other chemical mechanisms, the reactions which lead to their eventual degradation in high



Pentaerythrityl ester

performance engines and under other harsh conditions. The autoxidation mechanisms of polyol esters present chemists with a formidable problem for even the mechanisms of the autoxidation of simple aliphatic esters have not been fully elucidated⁵⁾. In this paper, the strategy we adopted to investigate the key features of the autoxidation of polyol esters will first be outlined.

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Table 1 The Peroxyl Radicals Used in These Studies

Peroxyl radical	Formula	Phase	Precursor	References
Methylperoxyl	MeO ₂ •	g	Azomethane	14
Ethylperoxyl	EtO ₂ •	g	Azoethane	12
		l	Azoethane	24
Isopropylperoxyl	Me ₂ CHO ₂ •	g	2,2'-Azoisopropane	10, 11, 13
		l	2,2'-Azoisopropane	6, 7, 8
		l	2,4-Dimethyl-3-pentanone	8
<i>t</i> -Butylperoxyl	Me ₃ CO ₂ •	l	2,2'-Azoisobutane	9
		l	2,2,4,4-Tetramethylpentan-3-one	9
2-Methoxycarbonylprop-2-ylperoxyl (A)		1	<i>trans</i> -2,2'-Dimethyloxycarbonyl-2,2'-azopropane (C)	15
		1	Dimethyl 3-oxo-2,2,4,4-tetramethylpentanedioate	16
2-Acetoxyprop-2-ylperoxyl (B)		1	<i>trans</i> -2,2'-Diacetoxy-2,2'-azopropane (D)	15
		1	2,4-Diacetoxy-2,4-dimethylpentan-3-one	16

2. Strategy Adopted for Studying the Autoxidation of Lubricants

Our first work was concerned with the elementary reactions of simple oxygenated radicals derived from hydrocarbons in solution, particularly the reactions of alkylperoxyl radicals. These are the key to the propagation and termination reactions in autoxidation processes^{6)~9)} and build on earlier work in our laboratories on their reactions in the gas phase^{10)~14)}. Subsequently, the reactions of peroxyl radicals derived from simple esters have been investigated in detail^{15),16)}.

In separate studies, the preferred sites of attack by oxygenated radicals on simple esters have been determined, to ascertain the influence of the ester functional groups on the relative reactivities of C-H bonds along the chain^{17),18)}.

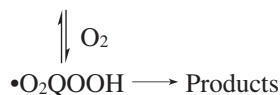
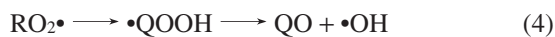
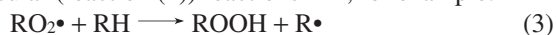
As a third strand, the autoxidation of a series of relatively simple esters has been studied¹⁹⁾ and this is currently being extended to investigations on the autoxidation of some polyol esters²⁰⁾.

3. Self-reactions of Peroxyl Radicals

Peroxyl radicals are important chain carriers in autoxidation processes, being formed by the reaction of alkyl and related radicals and oxygen, for example:



The radicals propagate the chain by intermolecular (reaction (3)) or, in certain circumstances, by intramolecular (reaction (4)) reactions^{21),22)}, for example:



(where QO is a carbonyl compound or an O-heterocycle).

However, other reactions of peroxyl radicals have a significant effect on the rate of oxidation, namely their self-reactions, for they lead to termination as well as propagation steps. It was to these reactions that our studies were directed.

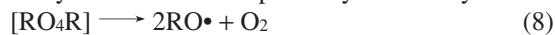
The radicals were generated in two ways, by photolysis of the relevant azo compound and ketone, both in the presence of oxygen (**Table 1**):



It is generally agreed that the self-reactions of peroxyl radicals occur *via* a tetroxide, formed in equilibrium with the peroxyl radicals^{6),7),22),23)}:



Tertiary tetroxides decompose to yield alkoxy radicals:



However, while primary and secondary tetroxides can decompose similarly, they can also decompose by an alternative route, which yields an alcohol and a carbonyl compound, the Russell mechanism²³⁾:



For example, diethyl tetroxide, formed from ethylperoxyl radicals yields ethanol and acetaldehyde^{12),24)}:



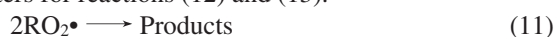
A third, but least important, self-reaction which is also, like the reaction above a termination process, leads to the formation of a peroxide and oxygen.

The self-reactions of peroxyl radicals derived from

methyl¹⁴), ethyl^{12,24}), isopropyl^{6-8,10,11,13}) and *t*-butyl⁹) have been studied (the first two in the gas phase only). Further the self-reactions, in solution, of 2-acetoxyprop-2-ylperoxyl and of 2-methoxycarbonylprop-2-ylperoxyl radicals, ester analogues of the alkylperoxyl radicals studied, have been investigated in detail^{15,16}) (Table 1).

The time-dependent product distributions from the reactions of these systems, under varying conditions of temperature and oxygen concentrations, have been convincingly modelled by computer simulation.

In both the gas and liquid phases, the overall reaction for the self-reactions of alkylperoxyl radicals (reaction (11)) is second order and the temperature has a profound effect on the relative concentrations of products due to the significant difference in the activation parameters for reactions (12) and (13).

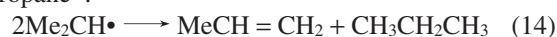


At first sight, there are significant differences in the reactions of alkylperoxyl radicals in the liquid and gas phases. For example, in the photo-oxidation of 2,2'-azopropane in pentane, the principal products, even in the early stages of reactions, when the oxygen concentration is at its maximum, are propane, propene and 2,3-dimethylbutane⁸). The concentrations of the oxygenated products, acetone, isopropanol and isopropyl hydroperoxide, which account for *ca.* 99% of the products in the gas phase¹¹), account for only *ca.* 30% in solution⁸). Furthermore, the hydroperoxide, a major product in the gas phase, is barely detectable in the liquid phase. However, when the radical precursor is changed to the corresponding ketone, 2,4-dimethylpentan-3-one, the product distribution for the liquid and gas phases become more similar, even though the hydroperoxide concentration remains very low in the liquid phase⁸).

Another contrasting feature between the reactions of alkylperoxyl radicals in the two phases is the effect of oxygen concentration. In the gas phase, varying the concentration of oxygen affects the product distribution^{11,12}), whereas in the liquid phase, it has little or no effect^{8,9}).

Modelling experiments show that these differences arise from two effects, both caused by the solvent. First, the relatively small amount of oxygenated products formed when using azo compounds in solution as compared to ketones (and indeed to when the azo compound are used in the gas phase) is due to the effect of solvent in the initial photolytic event. On photolysis, the azo compound yields nitrogen and two alkyl radicals²⁵⁻²⁷). These are produced in a solvent cage and the radicals are subsequently partitioned between cage escape and cage reaction, the latter leading to the formation of hydrocarbons, for example, from 2,2'-azo-

propane⁸):



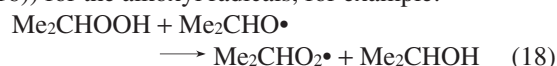
Alternatively, the alkyl radicals escape from the cage, and are rapidly trapped by oxygen to give alkylperoxyl radicals (reaction (2)). However, the photolysis of a ketone leads to a solvent-caged alkyl and acyl radical pair, rather than carbon monoxide and two alkyl radicals. These can undergo recombination, to reform the ketone, or metathesis within the cage⁸) to form propene and isobutanal. Cage escape, again leads to oxygenated products.

Secondly, the major difference in the effect of oxygen pressure on the relative composition of the products from both the liquid phase (whether an azo compound or a ketone is used) and the gas phase systems, and the difference in the yields of hydroperoxides again lies in the role of the solvent, for its concentration is very high compared to that of oxygen. In the liquid phase, both solvent and oxygen compete for the alkoxy radicals, formed from the self-reaction of alkylperoxyl radicals, for example:



(where RH is a solvent or reactant molecule).

Although the rate constant for reaction (16)²⁸) is much larger than that for reaction (17)²⁹), the relative concentrations of solvent to oxygen are such that reaction (17) is the preferred route. In the gas phase, reaction (16) is dominant and this in turn leads to the reaction between alkoxy and hydroperoxyl radicals to form the hydroperoxide¹¹). Nevertheless, at lower oxygen pressures, there is increasing competition between the hydroperoxide (reaction (18)) and oxygen (reaction (16)) for the alkoxy radicals, for example:



This is manifested by considerable changes in the ratio of yields of alcohol and hydroperoxide as the oxygen pressure decreases in the gas phase reaction, something not observed in the liquid phase.

The effect of temperature on product distribution in the gas phase is accounted for by the different activation parameters for the self-reactions of the alkylperoxyl radicals, for the Russell mechanism (reaction (9)) has a lower *A* factor and lower energy of activation than reaction (12)^{11,12,14}). Thus although reaction (9) has a lower activation energy than reaction (12), it will only be relatively faster at low temperatures for the entropic demands for the reaction on going from the reactants to the transition state are much greater than for reaction (12). Consequently, at higher temperatures, reaction (12) becomes dominant. The reaction mechanism must take account of these competing self-reactions of peroxyl radicals for reaction (9) is a termination reaction and reaction (12) propagates radicals.

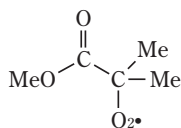
Not only does this apply to the liquid phase but additionally, the changes in solvent viscosity on changing temperature affects the ratio of cage to non-cage reactions^{8),9)}.

The mechanisms of all the liquid and gas phase systems were tested, using a computer modelling program, and satisfactory results were obtained for the variations in product distribution observed as the temperature and oxygen pressure are altered. Further variations observed for the liquid phase system on changing the radical precursors and reactor surfaces, pyrex glass and stainless steel, could be accounted for.

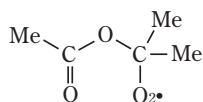
The reactions in the liquid phase were first carried out in a pyrex reactor so that the results could be compared directly with the earlier gas phase experiments. Subsequently, they were repeated in a steel reactor to simulate more nearly conditions experienced in an engine. There were small differences in rate but the relative product distributions were unaltered.

Although the solvent plays a major role in liquid phase reactions in determining the product distribution, the overall chemistry and, in particular, the rate data for the reactions of alkyl, alkoxy and alkylperoxy radicals are remarkably similar in the two phases. This is highly significant for there is a large corpus of available and reliable rate data for these radicals in the gas phase which can be used, with confidence, in the liquid phase.

This proved to be of overriding importance when we investigated in the self-reactions of peroxy radicals derived from esters. Two of these radicals were chosen for detailed study, 2-methoxycarbonylprop-2-ylperoxy (A) and 2-acetoxypent-2-ylperoxy (B), modelling radicals which would be formed by α -acyl and α -alkyl attack on a pentaerythrityl alkanoate, respectively.



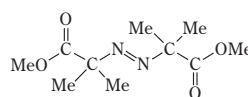
A



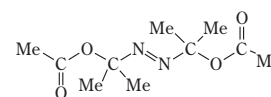
B

Two precursors were used for each radical, the relevant azo compound and ketone (Table 1). There is a remarkable degree of similarity in the behaviour of the precursors on photo-oxidation with those used to generate alkylperoxy radicals. Thus from *trans*-2,2'-dimethoxycarbonyl-2,2'-azopropane (C), the principal products are methyl isobutyrate, methyl methacrylate and dimethyl tetramethylsuccinate, the equivalent of isobutane, isobutene and 2,2,3,3-tetramethylbutane formed in a solvent cage from the photolysis of 2,2'-azoisobutane. The most important oxygenated product from the esterperoxy radical (A) is methyl 2-hydroxyisobutyrate, the equivalent of *t*-butanol formed from *t*-butylperoxy radicals⁹⁾. The proportion of oxygenated: non-oxygenated radicals in the systems

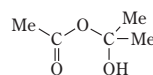
increase on increasing the temperature and decreasing the viscosity of the solvent. Likewise the principal products found on the photo-oxidation of *trans*-2,2'-diacetoxy-2,2'-azopropane (D) are 2-propyl acetate, 2-propenyl acetate and pinacol diacetate and the major, oxygenated products (present in much smaller amounts) are acetone and acetic acid, formed in equimolar concentrations. The oxygenates are accounted for by the self-reaction of the peroxy radicals (B) and the resulting alkoxy radical reacting with a solvent molecule, or direct *via* a Russell-type reaction, to form an unstable hydroxyl species (E) which decomposes to acetone and acetic acid.



C



D



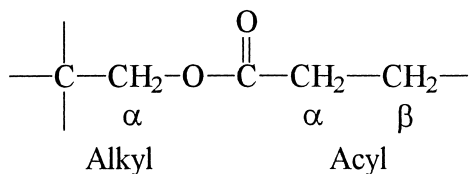
E

When the ketones are used as precursors, the oxygenated species are dominant. The only hydrocarbon-like compounds formed, and then only in very small amounts are methyl isobutyrate from dimethyl 3-oxo-2,2,4,4-tetramethylpentanedioate and isopentyl acetate from 2,4-diacetoxy-2,4-dimethylpentan-3-one. This is a similar result to that obtained on the photo-oxidation of 2,4-dimethyl-3-pentanone⁸⁾ and 2,2,4,4-tetramethylpentan-3-one⁹⁾ where small amounts of propene and isobutene, respectively, were observed, even in presence of large concentrations of oxygen. As discussed earlier in this paper, these compounds are formed within a solvent cage, after initiation, between the acyl and alkyl radicals: a similar process clearly occurs in the more complex ketone systems used in the esterperoxy studies.

The product distributions for the two azo and two ketone systems, leading to esterperoxy radicals were simulated. The rate constants chosen were those for their alkyl analogues and these gave very satisfactory results, thus allowing their use when tackling the mechanism of autoxidation of the complex esters used as lubricants.

4. Preferred Site of Attack by Oxygenated Radicals on Neopentyl Esters

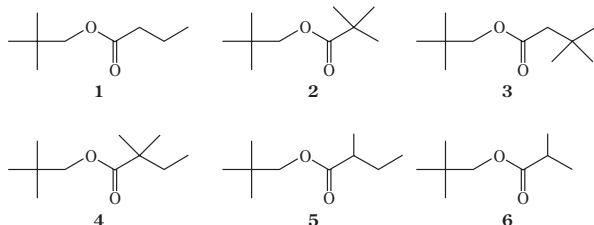
There is no general agreement about the preferred position of initial attack during the autoxidation of esters. For example, Jensen *et al.* found that hydrogen abstraction reactions on pentaerythrityl tetraheptanoate occur on the acyl groups³⁰⁾, particularly at the β and subsequent positions, a result in harmony with the work of Aldrich *et al.* and Sniegowski who also investigated



Scheme 1 Notation to Identify C-H Bonds in Ester

the relative rates of attack on different sites in the ester^{31,32}. Chao *et al.* found that lengthening the chain in pentaerythryl esters from pentanoate to octanoate reduced the induction period significantly³³. Others have reported that attack on the alkyl groups of the ester lubricants is important^{34,35}.

As with the esters of pentaerythritol, earlier studies with simple aliphatic esters are not self-consistent^{5,36-38} in terms of whether the alkyl or acyl sites are more reactive towards oxygenated radicals. In view of these inconsistencies, the relative rate data for the reactions of alkoxy radicals, which play a crucial role in autoxidation processes, with the various C-H sites in an ester molecule were determined, using a range of neopentyl esters as the substrates. Two alkoxy radicals were chosen, *t*-butoxy and cumyloxy and six esters were chosen as substrates, the neopentyl esters of butanoic (1), 2,2-dimethylpropanoic (2), 3,3-dimethylbutanoic (3), 2,2-dimethylbutanoic (4), 2-methylbutanoic (5) and 2-methylpropanoic (6) acids.



Di-*t*-butyl peroxide decomposes to yield *t*-butoxy radicals,



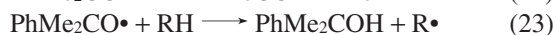
which in turn may fragment,



or react with the substrate, RH:



Similarly the products from dicumyl peroxide include the corresponding ketone and alcohol, acetophenone and 2-phenylpropan-2-ol:



One approach to determining the position of initial attack on the ester is to measure the yields of products from the alkoxy radical. The ratio of yields of the alcohol and ketone, for both peroxide systems, gives the ratio of rate constants for decomposition of the alkoxy radical and the abstraction reaction on the ester by the radical. This assumes that the site of the initial

attack on the ester is fixed and that once formed, the radical cannot rearrange either by an inter- or by an intra-molecular process. The ratio of rate constants k_{21}/k_{20} and k_{23}/k_{22} for each ester were obtained for the six esters 1-6.

For a given temperature, the ratio of rate constants for the *t*-butoxy system is always smaller than that for cumyloxy as would be expected for the latter decomposes at a much faster rate than the former. Nevertheless the ratio of the two ratios at a given temperature is constant. This shows that, assuming the fragmentation rates at a given temperature are independent of the ester substrate, the rate constants k_{21} and k_{23} are similar and that the rate of hydrogen abstraction is effectively independent of the structure of the alkoxy radical. This is particularly important because the values of alkoxy radical abstraction reactions can be estimated in modelling experiments in more complex ester autoxidation systems.

As the fragmentation rates of an alkoxy radical are not affected at a specific temperature by the ester substrate, it is possible to use the ratios k_{21}/k_{20} and k_{23}/k_{22} to compare the overall reactivity of the six esters with alkoxy radicals. In turn, the rate constants k_{21} and k_{23} are a summation of the values for reactions at each individual site on the ester molecule. Thus, for example, k_{21} is given by the relationship

$$k_{21} = ak_{\text{prim-alk}} + bk_{\alpha\text{-alk}} + ck_{\alpha\text{-acyl}} + dk_{\beta\text{-acyl}} + ek_{\gamma\text{-acyl}} + fk_{\text{prim-acyl}}$$

Where $k_{\text{prim-alk}}$, $k_{\alpha\text{-alk}}$, $k_{\alpha\text{-acyl}}$, $k_{\beta\text{-acyl}}$, $k_{\gamma\text{-acyl}}$ and $k_{\text{prim-acyl}}$ are the rate constants for attack on the C-H bonds in different environments and *a-f* refer to the number of hydrogen bonds of each type. The data from the reactions of the alkoxy radicals with esters 1-6 were then used to provide information about the relative ease of hydrogen abstraction from the different sites.

Comparison of the values of k_{21}/k_{20} and k_{23}/k_{22} (Tables 2 and 3) for the reaction of neopentyl 2,2-dimethylpropanoate (2), which only contains primary and α -alkyl secondary hydrogens with the other esters which also contain α - and β -acyl hydrogens, strongly suggest that the α -alkyl hydrogens are susceptible to attack.

Comparison of the results for ester 2 and neopentyl 3,3-dimethylbutanoate (3) shows that the additional α -acyl group does not make a significant difference to the ratio of rate constants, k_{21}/k_{20} and k_{23}/k_{22} , suggesting that the alkoxy radicals attack α -alkyl in preference to α -acyl hydrogens. The data comparing esters 2 and 3 with those from neopentyl 2,2-dimethylbutanoate (4) shows that β -acyl hydrogens are more reactive than the α -acyl hydrogens and those from neopentyl 2-methylbutanoate (5) show that, as expected, a tertiary C-H is most highly susceptible to attack. This qualitative analysis provided a strong basis for attempting to quantify the results. From this and generally accepted

data in the literature, relative rate constants were estimated and tested against the experimental data (Table 4). The estimated rate data for k_{21} and k_{23} for all the esters studied, were then expressed relative to ester 1, are remarkably similar for both alkoxy radicals (reactions (21) and (23)) and also correspond to the experimental results obtained in this study (Tables 2-4).

Small amounts of products with molecular ions with $[m/z = (2 \times \text{mass of ester}) - 2]$ were detected by GC/MS. A gas chromatogram of these products from the thermolysis of di-*t*-butyl peroxide in ester 1 at 438 K is given in Fig. 1. They are labelled A1, A2, B1, B2,

C1 and C2, each pair being diastereoisomers arising from the dimerisation of secondary ester radicals. Importantly only 6 of the 21 possible radical dimers were detected. A1 and A2 were prepared and identified as stereoisomers of dineopentyl 2,3-diethylbutanedioate, *meso*- and (\pm)-*threo*. An almost identical distribution of products was obtained using dicumylperoxide and ester 1. The other neopentyl esters also gave radical dimer products, the distribution of which being independent of the peroxide used.

On lowering the temperature, not only did the relative proportions of these isomers alter but more isomers were detectable. For example, at 298 K, photolysis of a solution of di-*t*-butyl peroxide in ester 1 yielded at

Table 2 The Rate Constants for *t*-Butoxyl Radical Hydrogen Abstraction Relative to Fragmentation in Neopentyl Esters

Ester ^{a)}	$(k_{21}/k_{20}) [10^{-1} \text{ dm}^3 \text{ mol}^{-1}]$			
	408 K	418 K	429 K	438 K
1	2.59 ± 0.30	2.01 ± 0.09	1.75 ± 0.15	1.18 ± 0.05
2	1.64 ± 0.20	1.36 ± 0.35	1.03 ± 0.02	0.91 ± 0.01
3	2.47 ± 0.11	1.50 ± 0.13	1.30 ± 0.05	0.96 ± 0.02
4	2.23 ± 0.30	1.72 ± 0.13	1.43 ± 0.14	1.37 ± 0.11
5	—	2.12 ± 0.19	—	1.58 ± 0.08
6	—	2.22 ± 0.11	—	1.46 ± 0.03

a) Concentration, 5.40 mol dm⁻³

Table 3 The Rate Constants for Cumyloxy Radical Hydrogen Abstraction Relative to Fragmentation in Neopentyl Esters

Ester ^{a)}	$(k_{23}/k_{22}) [10^{-1} \text{ dm}^3 \text{ mol}^{-1}]$		
	298 K ^{b)}	418 K ^{c)}	438 K ^{c)}
1	97.1 ± 10.4	4.03 ± 0.08	3.30 ± 0.15
2	60.6 ± 5.7	3.03 ± 0.17	2.28 ± 0.07
3	75.2 ± 7.7	3.13 ± 0.08	2.57 ± 0.02
4	84.7 ± 12.2	3.42 ± 0.07	2.76 ± 0.06
5	137 ± 21	4.55 ± 0.17	3.47 ± 0.08
6	111 ± 15	3.95 ± 0.17	3.05 ± 0.08

a) Concentration, 5.40 mol dm⁻³. b) Cumyloxy radicals generated by photolysis of dicumyl peroxide. c) Cumyloxy radicals generated by thermolysis of dicumyl peroxide.

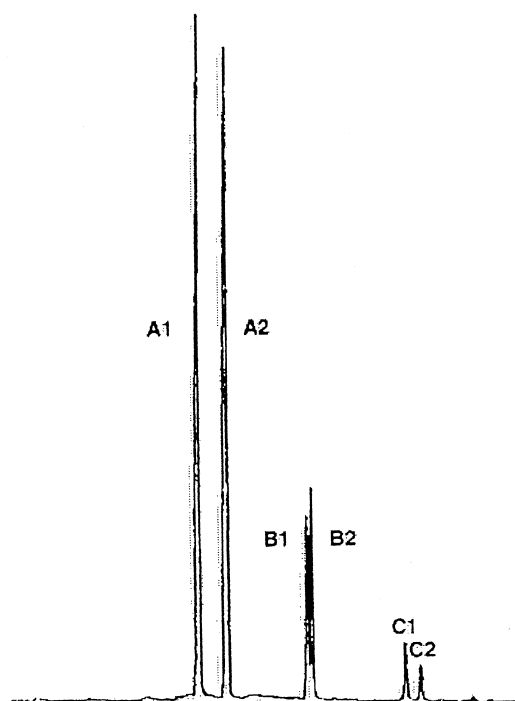


Fig. 1 GC Chromatogram of the Radical Dimers Formed by the Thermolysis of Di-*t*-butyl Peroxide in Neopentyl Butanoate (1) at 438 K

Table 4 Relative Rates of Reaction of Neopentyl Esters with *t*-Butoxyl and Cumyloxy Radicals

Ester	Number of C-H bonds							Experimental relative rates (from Tables 2, 3) [Ester (1) = 100]							Estimated relative rates ^{a)}
	Alkyl		Acyl				<i>t</i> -Butoxyl				Cumyloxy				
	Prim	Sec α	Prim	Sec α	Sec β	T α	408 K	418 K	429 K	438 K	298 K	418 K	438 K		
1	9	2	3	2	2	—	100	100	100	100	100	100	100	100	
2	9	2	9	—	—	—	63	67	59	77	62	75	69	61	
3	9	2	9	2	—	—	95	75	74	81	77	78	78	76	
4	9	2	9	—	2	—	86	86	82	116	87	85	84	91	
5	9	2	6	1	2	1	—	105	—	134	141	113	105	132	
6	9	2	6	1	—	1	—	110	—	124	114	98	92	103	

a) Estimated assuming the relative rates of reaction of alkoxy radicals with C-H bonds in neopentyl esters are prim-alkyl, 1; prim-acyl, 1; sec- α -alkyl, 24; sec- α -acyl, 8; sec- β -acyl, 16; *t*- α -acyl, 40.

Table 5 The Temperature Dependence of the Relative Yields of the Ester Radical Dimers from the Thermolysis and the Photolysis of Di-*t*-butyl Peroxide under Nitrogen, in Neopentyl Butanoate **1**

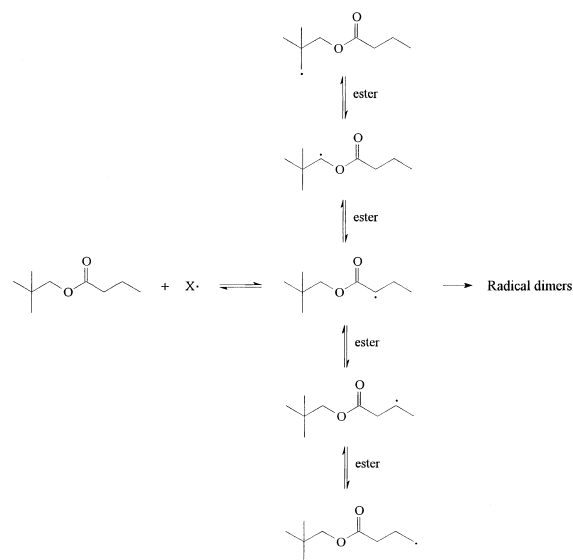
Dimer ^{a)}	Temperature [K]						
	298 ^{b)}	353 ^{b)}	373 ^{b)}	393 ^{b)}	393 ^{c)}	408 ^{c)}	438 ^{c)}
1 (A1)	100	100	100	100	100	100	100
2 (X)	83	53	48	27	24	10	10
3 (A2) ^{d)}	167	161	167	137	125	112	100
4	10	19	20	11	9	4	4
5	10	23	17	5	6	4	4
6	50	31	22	11	9	11	11
7 (B1)	25	50	38	38	24	22	20
8 (B2)	20	53	43	34	29	25	20
9	18	29	28	12	9	8	8
10	22	16	20	7	7	1	1
11 (C1)	23	31	35	18	19	12	19
12 (C2)	23	29	30	11	11	9	18
13	10	19	12	5	8	2	2
14	10	29	12	4	3	3	3

a) Dimer peaks numbered in order of elution from GC column.
 b) Peroxide photolysed. c) Peroxide thermolysed. d) This GC peak is believed to contain the diastereoisomer of dimer **X**.

least 14 radical dimers, including the six observed at 438 K (**Table 5**). The observed selectivity at 438 K at first seemed surprising, given the results from the studies of product distributions at the lower temperature. Diastereoisomers can only be formed from ester **1** by combinations of the three secondary radicals (α - and β -acyl and α -alkyl). The major products **A1** and **A2**, identified as described above, show that under these conditions the α -acyl radical was in considerable excess over the other possible species, and it therefore appeared that the other four isomers were formed by cross-dimerisations of the α -acyl radical with the β -acyl and the α -alkyl radicals.

The products from the reactions of esters **2-4** can be rationalised in a similar way. It should be noted that the ester radicals are not simply produced by reactions between the ester substrate and alkoxy radicals (reactions (21) and (23)). The latter radicals also fragment (reactions (20) and (22)) and to different extents as shown by the formation of methane. This was determined quantitatively and showed that almost all of the methyl radicals can be accounted for as methane and thus abstraction from the parent ester is their most important reaction. As alkoxy and alkyl radicals are electrophilic and nucleophilic, respectively, one would expect their different selectivities for C-H bonds to show up^{38),39)} when comparing the behaviour of esters towards the two different peroxides.

The evidence from the experiments in which *t*-butyl peroxide decomposes in the esters points to the ester radicals which are formed, reacting with the substrate (the parent ester) between their initial formation and dimerisation. These reactions occur many times, at



Scheme 2 Intermolecular Rearrangements of Ester Radicals from Neopentyl Butanoate

438 K so that the products do not reveal the identities of the initial sites of abstraction but rather the thermodynamic equilibrium distribution of ester radicals (**Scheme 2**). As the temperature is lowered, the rate of reaction between the ester radical and ester molecule becomes slower and thus the number of dimers increases. At 298 K, this kinetic effect becomes dominant.

To confirm the existence of this intermolecular rearrangement, we examined the fate of an α -acyl ester radical under the reaction conditions by thermolysing neopentyl 2-bromobutanoate in ester **1** at 438 K. This ester yielded the six isomeric radical dimers in similar proportions to those obtained using the two peroxides.

These experiments allow one to conclude that (i) at high temperatures, ester radicals in the presence of their parent ester rearrange by hydrogen abstraction, (ii) as a result, the dimer product distribution is an unreliable indication of selectivity of attack by radicals on the ester molecule and (iii) where radical equilibration is complete, the most stable ester radical is α to the carbonyl group.

5. The Autoxidation of Aliphatic Esters

Esters **1-5** were chosen for the autoxidation experiments because, as described above, the neopentyl group models the alkyl core of the pentaerythryl esters and the acyl groups allow for comparison of various C-H sites. They were heated to 438 K in a sealed stainless steel autoclave¹⁹⁾ under oxygen before being subjected to detailed analysis for reactants and products. Each product was identified by MS and the spectra checked with those from authentic samples, most of which were

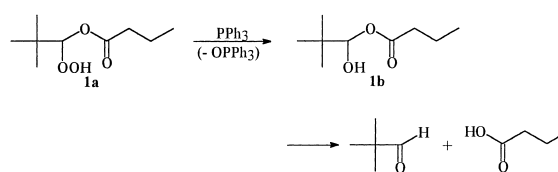
Table 6 The Autoxidation of Neopentyl Butanoate (**1**), 2,2-Dimethylpropanoate (**2**), 3,3-Dimethylbutanoate (**3**), 2,2-Dimethylbutanoate (**4**) and 2-Methylbutanoate (**5**): 1.5 cm³, ester; 5 bar oxygen; 438 K

Substrate	Yields [10 ⁻² mol dm ⁻³]									
	1		2		3		4		5	
	Reaction time [min]	δ [Substrate] ^{a)}	Reaction time [min]	δ [Substrate] ^{a)}	Reaction time [min]	δ [Substrate] ^{a)}	Reaction time [min]	δ [Substrate] ^{a)}	Reaction time [min]	δ [Substrate] ^{a)}
Carbon monoxide	d)	d)	1.73	d)	2.33	d)	d)	d)	5.00	d)
Carbon dioxide	0.09	d)	0.26	d)	0.64	d)	1.10	d)	2.09	d)
Formaldehyde	0.04	d)	0.06	d)	0.05	d)	0.02	d)	0.01	d)
Acetone	0.37	0.38	1.77	1.66	2.89	2.70	3.46	3.29	4.90	4.47
Butanone	— ^{e)}	—	—	—	—	—	0.38	0.42	8.25	8.21
3-Methylbutan-2-one	—	—	—	—	—	—	1.03	1.04	—	—
<i>t</i> -Butyl hydroperoxide	0.08	—	0.09	—	0.12	—	—	—	0.12	—
<i>t</i> -Butanol	0.15	0.24	0.78	0.84	1.69	1.77	—	—	1.84	2.22
<i>t</i> -Butyl formate	0.06	0.06	0.15	0.14	0.27	0.26	—	—	—	—
Neopentanol	0.53	0.52	0.26	0.26	0.76	0.76	—	—	3.37	3.34
Neopentyl formate	0.02	0.02	—	—	0.28	0.28	—	—	0.19	0.19
2,2-Dimethylpropanal	—	0.18	—	—	—	0.08	—	0.15	0.17	1.69
2,2-Dimethylpropanoic acid	0.02	0.03	2.87	3.10	0.38	0.38	0.57	0.63	1.71	1.82
Acetic acid	—	—	—	—	—	—	1.91	1.99	4.44	5.16
Propanoic acid	0.03	0.02	—	—	—	—	—	—	—	—
Butanoic acid	0.24	0.30	—	—	—	—	—	—	d)	d)
2-Methylbutanoic acid	—	—	—	—	—	—	—	—	5.15	5.31
3,3-Dimethylbutanoic acid	—	—	—	—	3.98	4.13	—	—	—	—
2,2-Dimethylbutanoic acid	—	—	—	—	—	—	3.71	3.86	—	—
e	0.12	0.29	0.13	0.17	0.10	0.14	—	—	3.44	4.04
f	0.25	0.09	—	—	0.33	0.31	—	—	3.61	3.61
h	0.28	0.53	—	—	0.18	0.21	0.25	0.29	—	—
i	d)	—	—	—	—	—	0.83	0.80	—	—
l	—	—	—	—	0.32	0.35	—	—	—	—
r	0.01	0.03	0.03	0.07	0.07	0.11	0.15	0.20	—	—
t	0.06	0.10	0.16	0.22	0.27	0.34	0.28	0.43	0.37	0.44
Peroxides ^{f)}	0.87	—	0.47	—	0.82	—	1.14	—	1.13	—

a) Conversion of the substrate: [Substrate]₀ = 5.30 mol dm⁻³ (**1**); 4.59 mol dm⁻³ (**2**); 4.20 mol dm⁻³ (**3**), (**4**); 5.39 mol dm⁻³ (**5**). b) Yield before triphenylphosphine reduction. c) Yield after triphenylphosphine reduction. d) Not determined. e) Not found. f) Total yield of hydroperoxides, peracids and hydrogen peroxide.

specially synthesised. **Table 6** gives examples of results from the five esters. A more comprehensive set of results has also been published⁴⁰⁾. The results show product analyses prior to and following treatment with triphenylphosphine which enables the concentrations of hydroperoxides to be determined¹⁹⁾. The total *minimum* yield of each hydroperoxide is given by the sum of the increase in the yield of the corresponding alcohol and that of 2,2-dimethylpropanal following the treatment of the products with triphenylphosphine. Comparison of these yields and the total yield of peroxides (hydroperoxides, peracids and hydrogen peroxide) measured separately^{41),42)} indicates that hydroperoxides are clearly the most dominant peroxide produced.

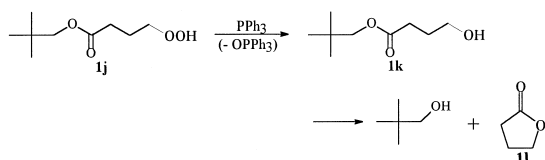
In general, the results suggest that the mechanism of autoxidation bears a very strong resemblance to that of alkanes and that the fates of the radical intermediates and molecular products are similar for the two classes of compound. For example, hydroperoxides are formed early in the reaction and high yields of car-



Scheme 3 The Products Formed on Reaction of the Hydroperoxide, **1a**, with Triphenylphosphine

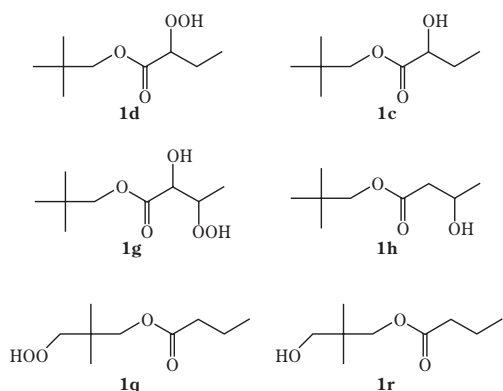
bonyls and acids are obtained subsequently. This finding accords with the results reported earlier in this paper which showed that the esterperoxyl radicals behave similarly to the corresponding alkylperoxyl radicals. The autoxidation of ester **1** will be discussed first and specific points on the other esters will follow.

The hydroperoxides are produced from the parent ester *via* esterperoxyl radicals, which are the main chain carriers early in the reaction (*cf.* reactions (1)-(3)). Five isomeric hydroperoxides are formed in the



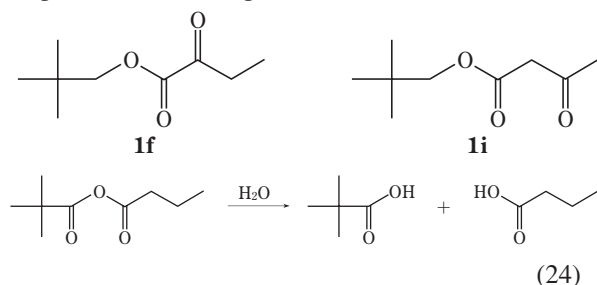
Scheme 4 The Products Formed on Reaction of the Hydroperoxide, **1j**, with Triphenylphosphine

early stages revealing that the autoxidation involves all types of C–H bonds in the ester (**Table 6**). Three secondary (**1a**, **1d**, **1g**) and two primary (**1j**, **1q**) hydroperoxides are produced which on treatment with triphenylphosphine lead to an increase in the yield of 2,2-dimethylpropanal (**Scheme 3**), hydroxyesters, **1e**, **1h**, **1r** and the γ -lactone **1l** (**Scheme 4**).

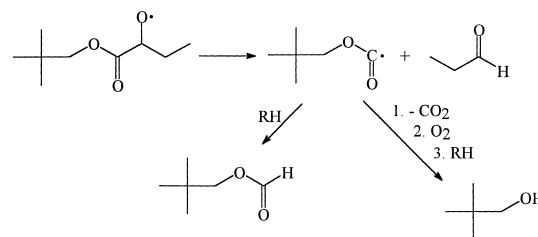


Esterperoxy radicals, as has been discussed earlier in the paper, can combine to form tetroxides (reaction (7)) which then yield alcohols and carbonyl compounds (reaction (9)), and alternatively, alkoxy radicals (reaction (8)). A large array of products will arise, given that there are five different esterperoxy radicals and that these can self- and cross-react. Thus five alcohols are formed, **1b**, **1e**, **1h**, **1k**, **1r**, **1b** and **1k** are not observed since **1b** decomposes readily to 2,2-dimethylpropanal and butanoic acid (**Scheme 3**) and **1k** rapidly cyclises to **1l** (**Scheme 4**).

The alcohols are matched by the corresponding carbonyl compounds. Thus the ketoesters, **1f** and **1i**, correspond to **1e** and **1h**, and the anhydride, **1c**, which corresponds to **1b** decomposes (reaction (24)).



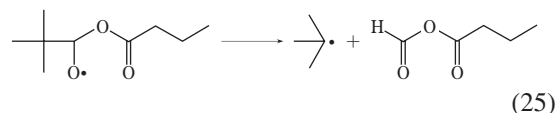
Alkoxy radicals, as discussed above, play a very important role in the autoxidation process and the



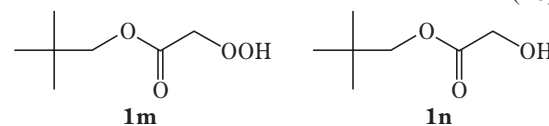
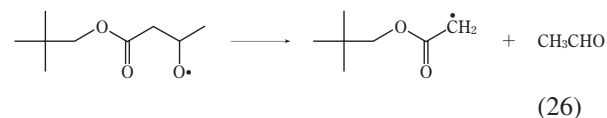
Scheme 5 The Formation of Neopentanol and from the Fragmentation of the α -Acyloxy Radical of **1**

results with *t*-butoxyl and cumyloxyl show that they will attack all the C–H sites of the ester molecule (reaction (21)). They also react with hydroperoxides (reaction (18)), a process that becomes increasingly important as the reaction proceeds. In competition with these reactions, alkoxy radicals undergo β -scission.

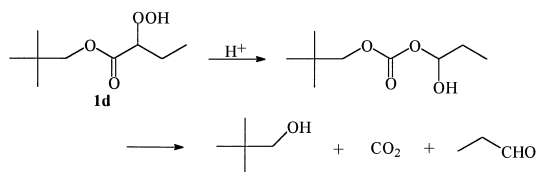
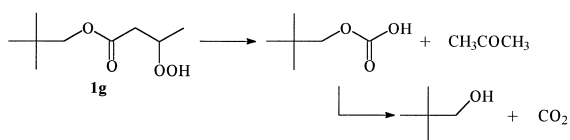
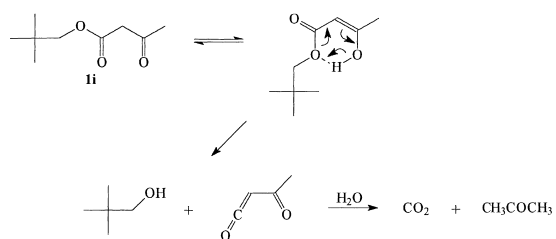
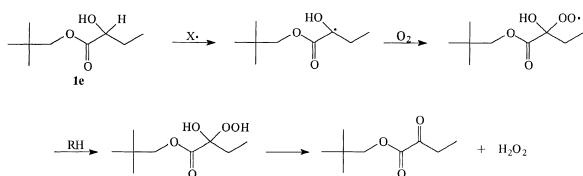
Three types of secondary alkoxy radicals are intermediates in the autoxidation of ester **1**. The α -alkoxy radical preferentially undergoes carbon–carbon bond cleavage to form the *t*-butyl radical and a mixed anhydride (reaction (25))⁴³. The anhydride is hydrolysed by water or reacts with an alcohol to give an ester and a carboxylic acid. This is one of the routes to the product, neopentyl formate.



The major route for the fragmentation of the α -acylalkoxy radical will be to form the neopentylcarbonyl fragment and propanal (**Scheme 5**) and that for the β -acylalkoxy radical [based on the behaviour of simpler alkoxy radicals⁴⁴] is to react to form the resonance stabilised neopentoxycarbonylmethyl radical (reaction (26)), which in turn, leads to **1m** and **1n**, both of which are observed amongst the products.



The hydroperoxides decompose by homolytic and heterolytic cleavage of the O–O bond, under the reaction conditions. Radical pathways yield alkoxy radicals which react as described above. A major non-radical decomposition pathway involves the elimination of water: primary and secondary hydroperoxides yield aldehydes and ketones, respectively. The 2-hydroperoxyester, **1d**, rearranges and decomposes (**Scheme 6**) to yield propanal and carbon dioxide (**Table 6**) while the 3-hydroperoxyester, **1g**, gives neopentanol, acetone

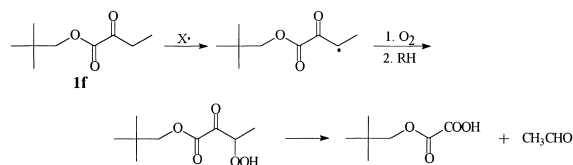
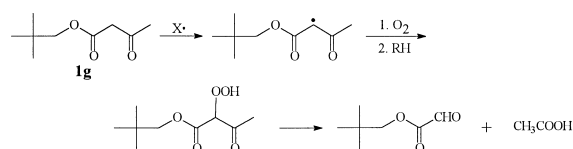
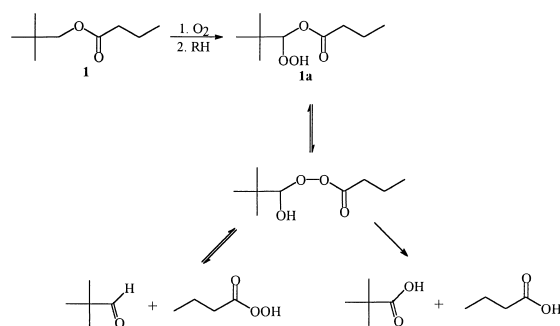
Scheme 6 The Non-radical Decomposition of 2-Hydroperoxyester, **1d**Scheme 7 The Non-radical Decomposition of 3-Hydroperoxyester, **1g**Scheme 8 The Thermolysis of the β -Ketoester, **1i**Scheme 9 The Proposed Mechanism for the Autoxidation of Neopentyl 2-Hydroxybutanoate, **1e**

and carbon dioxide (**Scheme 7**) (**Table 6**).

The yields of hydroperoxides increase in the early stages of reaction and then decrease, as the reaction between the hydroperoxide and alkoxy radicals becomes more important (reaction (18))¹⁰⁻¹².

The hydroxy- and keto-esters, for example **1e** and **1f**, are formed in comparable and significant amounts (**Table 6**). However, **1h** appears to be formed in larger amounts than neopentyl 3-oxobutanoate, **1i**, and it was shown that the latter decomposes, readily, probably *via* its enol tautomer, to neopentanol, carbon dioxide and acetone (**Scheme 8**).

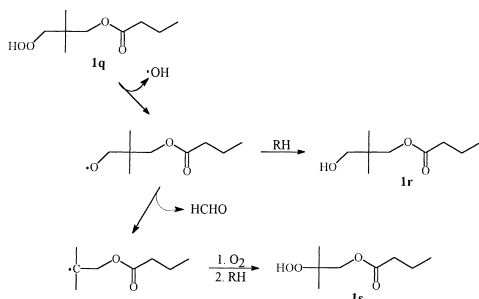
It is likely that the keto- and hydroxy-ester products will be oxidised faster than the substrate esters¹⁹ and that the hydroxyesters will be oxidised in a similar way to alcohols (**Scheme 9**). Similarly, 2- and 3-keto-

Scheme 10 The Proposed Mechanism for the Autoxidation of Neopentyl 2-Oxobutanoate, **1f**Scheme 11 The Proposed Mechanism for the Autoxidation of Neopentyl 3-Oxobutanoate, **1g**Scheme 12 An Oxidative Mechanism for the Formation of Butanoic Acid from Neopentyl Butanoate, **1**

esters, **1f** and **1i**, will be autoxidised *via* the established routes for those of ketones (**Schemes 10** and **11**)^{45,46}.

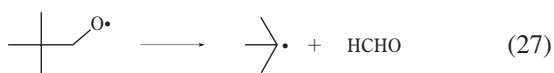
The two major products, butanoic acid and neopentanol could be formed by hydrolysis of **1** but independent experiments with water and water with the proportions of acids formed during the reaction, under nitrogen, show that the alcohol and acid are formed by an oxidative pathway. Butanoic acid is likely to be formed *via* **Scheme 12**, a route suggested for the formation of acetic acid in the autoxidation of pentyl acetate^{47,48} and carboxylic acids from polyol esters^{34,49}. Another route to butanoic acid also involves α -alkyl oxidation *via* the decomposition of **1b** the α -hydroxyalkyl ester, discussed earlier (**Scheme 3**).

The formation of neopentanol can be accounted for in a several ways. Non-radical pathways have been described (**Schemes 6** and **7**). Other non-radical routes include the lactonisation of **1k** (**Scheme 4**) and the decomposition of **1i** (**Scheme 8**). Radical pathways to neopentanol are also possible, for example from the fragmentation of the ester α -acyloxy radical

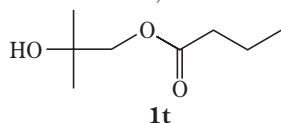


Scheme 13 Decomposition Mechanism of 3-Hydroperoxy-2,2-dimethylpropyl Butanoate, **1q**

which yields the alkoxy carbonyl radical, which in turn, decarboxylates to the neopentyl radical, by the mechanism proposed by Itoh *et al.*⁵⁰. The neopentyl radical is then oxidised to the alcohol (**Scheme 5**). The alkoxy carbonyl radical will be sufficiently long lived to abstract a hydrogen atom to form another observed product, neopentyl formate. However, this mechanism will not be a dominant one, as the neopentoxyl radical fragments readily to the *t*-butyl radical and formaldehyde (reaction (27))⁵¹.



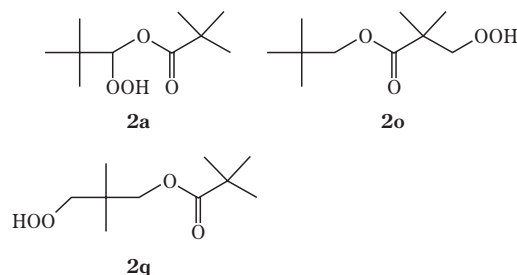
Initial attack on the primary C–H bonds has not yet been discussed. Although they are stronger than the secondary C–H bonds, they are nevertheless more numerous. The hydroperoxide, **1j**, is observed the concentration of the lactone, **1l**, which is produced from the alcohol, **1k**, builds up during the reaction. The hydroperoxide, **1q**, and the alcohol, **1r**, are also formed. Further the reactions of **1q** lead to the removal of one carbon atom from the tertiary centre to form eventually the hydroperoxide, **1s** (**Scheme 13**). **1s**, in turn, forms the alcohol, **1t**.



Two other major products from the autoxidation of **1** are acetone and *t*-butanol. The main source is the *t*-butyl radical and there are three potential routes to its formation, the radical oxidation and decarbonylation of 2,2-dimethylpropanal⁵², the fragmentation of the α -alkylalkoxy radical [from α -alkyl oxidation (reaction (25))] and from the fragmentation of the neopentoxyl radical (reaction (27))⁵¹. All these are derived from the neopentyl group of the ester. The *t*-butyl radicals oxidise rapidly to *t*-butoxyl which can fragment to acetone or abstract a hydrogen atom from hydroperoxides or the ester substrate to yield *t*-butanol.

The autoxidations of esters **2**, **3** and **4** were studied because it is then possible to compare the effect of

changes in the acyl moieties systematically. In general, corresponding products were obtained to those found from ester **1**. For example, **2** yields three hydroperoxides **2a**, **2o** and **2q**. Similar results were obtained from esters **3** and **4**. Further a corresponding range of alcohols and ketones were observed (**Table 1**) and the corresponding aldehydes from primary attack are not seen due to their enhanced susceptibility to oxidation compared to many of the other products.



Using the rate of consumption of the ester as a crude measure of the order of reactivity of the esters towards autoxidation, the order is **1** > **4** > **3** > **2**⁴⁰. In spite of blocking all the secondary sites on the acid moiety, the rate of oxidation of **2** is only reduced by a factor of 2-4 compared to esters **3** and **4**, suggesting that α -alkyl attack is very important and/or significant reaction occurs at the primary C–H bonds. Further the blocking of the β -acyl secondary carbon, as in **3**, has a greater effect on the rate of oxidation than blocking the α -acyl positions. This agrees with the evidence from the study of alkoxy radicals on the esters described above (**Table 4**).

All four esters **1-4** give similar products in spite of altering the structure of the acyl group. Not surprisingly, the products formed from the alkyl group, for example, the parent acid, are similar (**Scheme 12**). Blocking either the α - or the β -acyl position does not prevent acyl group oxidation processes leading to neopentanol, in agreement with the multiple routes to this product (**Schemes 5-8**). On closer examination, it is clear that the yield of neopentanol from **2** is particularly low. This is readily rationalised in terms of the blocking of the α -acyl positions and the only routes are *via* oxidation of the less reactive β -acyl primary C–H bonds (**Schemes 7** and **8**).

Two of the key products in the autoxidation of **1** are the hydroperoxyesters, **1d** and **1g**. Based on the work of Jensen *et al.*⁵³, we propose that **1g** subsequently decomposes to neopentanol, acetone and carbon dioxide (**Scheme 7**). Blocking the β -acyl position unfortunately does not block the formation of these products since they can come from other routes. Support for Jensen's mechanism comes from the oxidation of **4** which, by reaction *via* **4g** gives large concentrations of 3-methylbutan-2-one.

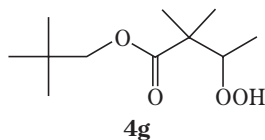
Table 7 Comparison of Yields of Products, Relative to Butanoic Acid and 2-Methylbutanoic Acid, from the Autoxidation of Neopentyl Butanoate (**1**) and 2-Methylbutanoate (**5**), Respectively: 1.5 cm³, ester; 5 bar oxygen; 438 K

Substrate Reaction time [min]	Relative yields					
	1		5		Ratio changes ^{a)}	
	90		60		A ^{b)}	B ^{c)}
Products	A ^{b)}	B ^{c)}	A ^{b)}	B ^{c)}	A ^{b)}	B ^{c)}
Carbon monoxide	0.58	d)	0.77	d)	+0.33	—
Carbon dioxide	0.18	d)	0.43	d)	+1.39	—
Formaldehyde	0.01	d)	0.00	d)	-1.00	—
Acetone	0.81	0.73	0.95	0.84	+0.17	+0.15
Butanone	d)	d)	1.60	1.50	—	—
<i>t</i> -Butyl hydroperoxide	0.07	0.00	0.02	0.00	-0.71	—
<i>t</i> -Butanol	0.42	0.46	0.36	0.42	-0.14	-0.09
<i>t</i> -Butyl formate	0.07	0.07	0.00	0.00	-1.00	-1.00
Neopentanol	0.54	0.51	0.65	0.63	+0.20	+0.24
Neopentyl formate	0.05	0.05	0.02	0.04	-0.60	-0.20
2,2-Dimethylpropanal	0.00	0.13	0.23	0.32	—	+1.46
2,2-Dimethylpropanoic acid	0.15	0.15	0.33	0.34	+1.20	+1.27
Acetic acid	0.37	0.35	0.86	0.97	+1.32	+1.77
Butanoic acid	1.00	1.00	e)	e)	f)	f)
2-Methylbutanoic acid	e)	e)	1.00	1.00	f)	f)
e	0.12	0.17	0.67	0.76	+4.58	+3.47
f	0.21	0.16	0.70	0.68	+2.33	+3.25
t	0.09	0.13	0.07	0.08	-0.22	-0.39

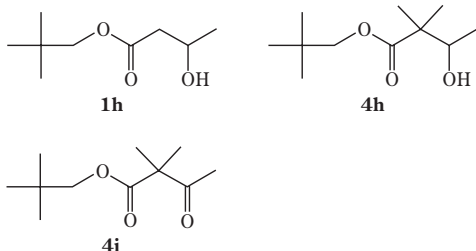
a) [(Relative yield from the autoxidation of **5**) – (Relative yield from the autoxidation of **1**)] / (Relative yield from the autoxidation of **1**).

b) Yield before triphenylphosphine reduction. c) Yield after triphenylphosphine reduction. d) Not determined. e) Not applicable.

f) Reactions of **1** and **5** standardised to the yields of butanoic acid and 2-methylbutanoic acid respectively.



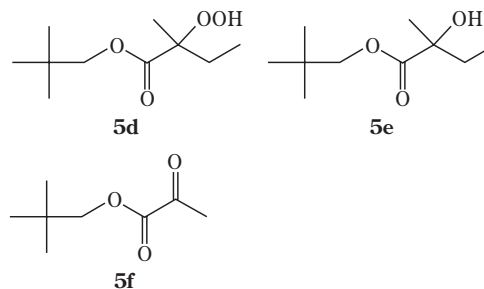
β -Ketoesters corresponding to **1i** cannot be obtained from **2** and **3**, but, **4i** is obtained from **4**, indeed in higher yield than for **1i** from **1**, for **4i** is unable to enolise and is consequently stable to decarboxylation⁵⁴⁾ (Scheme 8). Thus **4i** dominates over **4h**, whereas **1h** is in excess over **1i**. The relative stabilities of **1i** and **4i** was confirmed with separate experiments¹⁹⁾.



The mechanisms proposed for the autoxidation of esters **1-4** were tested by carrying out parallel experiments with neopentyl 2-methylbutanoate (**5**). The autoxidation was significantly faster than that of ester **1**, the most reactive towards autoxidation of the four esters previously studied, as would be expected from the presence of the tertiary C–H bond.

Again, as expected, the major products are **5d**, **5e**

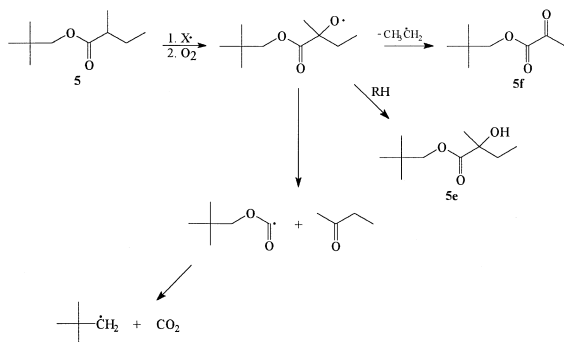
and **5f** from attack at the tertiary C–H position. Attack at the α -alkyl site is still very important to judge from the high yield of 2-methylbutanoic acid (Table 6). This agrees with the results obtained from the reactions of alkoxy radicals with these esters¹⁷⁾.



Assuming that the parent acid comes from the oxidation of the alkyl group, it is possible to compare the relative rates of product formation from **1** and **5** (Table 7). The most significant differences are in the increased rate of formation, from **5**, of carbon dioxide, the 2-hydroxyester (**5e**), the 2-ketoester (**5f**), acetic acid and 2,2-dimethylpropanoic acid. The increased rates of formation of carbon dioxide, **5e** and **5f** are expected from the increases selectivity for the tertiary α -acyl-alkoxy radical (Scheme 14).

6. Summary

In this paper, we have discussed several different



Scheme 14 Products Arising from the Oxidation of the α -Acyl Position of Neopentyl 2-Methylpropanoate, **5**

methods of determining the chemical pathways occurring in the early stages of ester autoxidation. The esters chosen have different structures in the acyl group. The same alkyl group was chosen, neopentyl, that imitates that found in the polyol esters that are used as lubricants.

Detailed studies of the reactions of oxygenated radicals derived from esters, in particular, esterperoxy radicals, show that they have very similar chemistry to the well-characterised reactions of oxygenated radicals derived from alkanes. Thus it is no surprise to find that the results for the autoxidation of the neopentyl esters are explicable in terms of reaction mechanisms that are associated with the autoxidation of alkanes.

The similarities and differences in the behaviour of the five esters towards autoxidation can be explained in terms of the relative reactivities of the various C-H bonds in the esters as determined from our experiments between esters and alkoxy radicals. In particular, there is attack on both the alkyl and the acyl groups, and primary C-H bonds play their part. Further, the β -acyl C-H bonds appear to be more susceptible to attack than the α -acyl C-H bonds. Thus, with the two main threads of evidence, namely the similarity in general behaviour, on autoxidation, of alkanes and aliphatic esters, and the clearer guidelines on selectivity of attack by oxygenated radicals on esters, it is now possible to gain detailed information on the mechanism of the autoxidation of polyol esters used as lubricants.

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References

- 1) See, for example, Taylor, R. I., Coy, R. C., *Proc. Inst. Mech. Eng. Part J*, **214**, 1 (2000).
- 2) Brown, M., Fotheringham, J. D., Hoyes, T. J., Mortier, R. M., Orszulik, S. T., Randles, S. J., Stroud, P. M., "Chemistry and Technology of Lubricants," eds. by Mortier, R. M., Orszulik, S. T., Blackie A and P, London (1997).
- 3) Morse, P. M., *Chem. Eng. News*, 7th September, 1998.
- 4) Como, D. J., *Lubricants World*, **1999**, October, 16.
- 5) See, for example, Bakunin, V. N., Parenago, O. P., *J. Synth. Lubr.*, **9**, 3073 (1992).
- 6) Bennett, J. E., Brunton, G., Lindsay Smith, J. R., Salmon, T. M. F., Waddington, D. J., *J. Chem. Soc., Faraday Trans. 1*, **83**, 2421 (1987).
- 7) Bennett, J. E., Brunton, G., Lindsay Smith, J. R., Salmon, T. M. F., Waddington, D. J., *J. Chem. Soc., Faraday Trans. 1*, **83**, 2433 (1987).
- 8) Costello, A. R., Lindsay Smith, J. R., Waddington, D. J., *Int. J. Chem. Kinet.*, **28**, 201 (1996).
- 9) Costello, A. R., Lindsay Smith, J. R., Stark, M. S., Waddington, D. J., *J. Chem. Soc., Faraday Trans.*, **92**, 3497 (1996).
- 10) Kirsch, L. J., Parkes, D. A., Waddington, D. J., Woolley, A., *J. Chem. Soc., Faraday Trans 1*, **75**, 2678 (1979).
- 11) Cowley, L. T., Waddington, D. J., Woolley, A., *J. Chem. Soc., Faraday Trans. 1*, **78**, 2535 (1982).
- 12) Anastasi, C., Waddington, D. J., Woolley, A., *J. Chem. Soc., Faraday Trans. 1*, **79**, 505 (1983).
- 13) Kirsch, L. J., Parkes, D. A., Waddington, D. J., Woolley, A., *J. Chem. Soc., Faraday Trans. 1*, **74**, 2293 (1978).
- 14) Anastasi, C., Couzens, P. J., Waddington, D. J., Brown, M. J., Smith, D. B., 10th Int. Symp. of Gas Kinetics, Swansea, 1998, Abstract B 19.
- 15) Lindsay Smith, J. R., Simmonds, M., Waddington, D. J., to be published.
- 16) Appleton, A. J., Lindsay Smith, J. R., Waddington, D. J., to be published.
- 17) Lindsay Smith, J. R., Nagatomi, E., Stead, A., Waddington, D. J., Beviere, S., *J. Chem. Soc., Perkin Trans. 2*, **2000**, 1193.
- 18) Lindsay Smith, J. R., Nagatomi, E., Stead, A., Waddington, D. J., *J. Chem. Soc., Perkin Trans. 2*, **2001**, 1527.
- 19) Lindsay Smith, J. R., Nagatomi, E., Waddington, D. J., *J. Chem. Soc., Perkin Trans. 2*, **2000**, 2248.
- 20) Lindsay Smith, J. R., Pritchard, E. D., Stark, M. S., Waddington, D. J., presentation at Additives2001, Oxford, 2001.
- 21) Rust, F. F., *J. Am. Chem. Soc.*, **79**, 4000 (1957).
- 22) Van Sickle, D. E., Mill, T., Mayo, F. R., Richardson, H., Gould, C. W., *J. Org. Chem.*, **38**, 4435 (1973).
- 23) Russell, G. A., *J. Am. Chem. Soc.*, **79**, 3871 (1957).
- 24) Patwardhan, P. M., M. Sc. Thesis, University of York, York, UK, unpublished, 1986.
- 25) Abram, I. I., Milne, G. S., Solomon, B. S., Steel, C., *J. Am. Chem. Soc.*, **91**, 7220 (1969).
- 26) Nishimura, N., Takeda, K., Furumatsu, Y., *Aust. J. Chem.*, **42**, 823 (1989).
- 27) Tanner, D. D., Samal, P. W., Rua, T. C-S., Henriquez, R., *J. Am. Chem. Soc.*, **101**, 1168 (1979); Tanner, D. D., Rahimi, P. M., *J. Am. Chem. Soc.*, **104**, 225 (1982).
- 28) See, for example, Balla, R. J., Nelson, H. H., McDonald, J. R., *Chem. Phys.*, **99**, 4520 (1985).
- 29) See, for example, Paul, H., Small Jr., R. D., Scaiano, J. C., *J. Am. Chem. Soc.*, **100**, 4520 (1978); Wong, S. K., *Int. J. Chem. Kinet.*, **13**, 413 (1981).
- 30) Jensen, R. K., Korcek, S., Zinbo, M., *J. Synth. Lubr.*, **1**, 91 (1984).
- 31) Aldrich, H. S., Cayce, J. M., Edwards, K. E., Gschwender, L., Ingold, K. U., Paulson, R. L., Snyder, C., STLE Congress, Las Vegas, 1999.
- 32) Sniegowski, P., *ASLE Trans.*, **20**, 282 (1977).
- 33) Chao, T. S., Kjonaas, M., DeJovine, J., *Ind. Eng. Chem., Prod. Res. Dev.*, **22**, 357 (1983).
- 34) Martem'yanov, V. S., Kukovitskii, M. M., *Neftekhimiya*, **18**, 539 (1978).
- 35) Martem'yanov, V. S., Khlebnikov, V. L., Marafutdfinova, Z. O.,

- Dokl. Akad. Nauk.*, **276**, 1416 (1984).
- 36) Novozhilova, M. K., Potekhin, V. M., Proskuryakov, V. A., Tarasenkova, E. P., *Zh. Prikl. Khim.*, **43**, 2313 (1970).
- 37) Bennett, J. E., Gilbert, B. C., Lawrence, S., Whitwood, A. C., Holmes, A. J., *J. Chem. Soc., Perkin Trans. 2*, **1996**, 1789; Baum, S., Gilbert, B. C., Gillespie, H., Lawrence, S. L., Whitwood, personal communication.
- 38) Huang, R. L., Goh, S. H., Ong, S. H., "The Chemistry of Free Radicals," Edward Arnold, London (1974); Tedder, J. M., Walton, J. C., *Tetrahedron*, **38**, 313 (1982); Perkins, M. J., "Radical Chemistry," Horwood, New York (1994).
- 39) Zytowski, T., Fischer, H., *J. Am. Chem. Soc.*, **119**, 12869 (1997).
- 40) Lindsay Smith, J. R., Nagatomi, E., Waddington, D. J., supplementary data, <http://www.rsc.org/suppdata/p2/b0boo4589f/>.
- 41) Mair, R. D., Graupner, A. J., *Anal. Chem.*, **36**, 194 (1964).
- 42) Bannerjee, D. K., Buke, C. C., *Anal. Chem.*, **36**, 792 (1964).
- 43) Fossey, J., Lefort, D., Sorba, J., "Free Radicals in Organic Chemistry," Wiley, New York (1995), p. 150.
- 44) See, for example, Fossey, J., Lefort, D., Sorba, J., "Free Radicals in Organic Chemistry," Wiley, New York (1995), p. 68.
- 45) Denisov, E. T., Mitskevich, N. I., Agabekov, V. E., "Liquid-Phase Oxidation of Oxygen Containing Compounds," Consultants Bureau, New York (1977).
- 46) Mill, T., Hendry, D. G., "Comprehensive Chemical Kinetics," ed. by Bamford, C. H., Tipper, C. F. H., Vol. 16, Liquid-phase oxidation, Elsevier, New York (1980).
- 47) Novozhilova, M. K., Potekhin, V. N., Drabkin, A. E., *Zh. Prikl. Khim.*, **43**, 2312 (1970).
- 48) Novozhilova, M. K., Potekhin, V. N., Drabkin, A. E., *Kim. I. Khim. Tekhol.*, **15**, 761 (1972).
- 49) Bogomdnii, G. M., Mirantsova, N. A., Pintegova, N. N., Freiden, B. G., *Zh. Prikl. Khim.*, **56**, 267 (1983).
- 50) Itoh, J., Sakaki, T., Ishii, Y., *J. Chem. Soc. Jpn. Ind. Chem. Sect.*, **68**, 2400 (1965).
- 51) Lightfoot, P. D., Roussel, P., Veyret, B., Lesclaux, R., *J. Chem. Soc., Faraday Trans.*, **86**, 2927 (1990).
- 52) Cairns, G. T., Waddington, D. J., Proceedings of the Deuxieme Symposium Europeen sur la Combustion, Poitiers, **1**, 97 (1976).
- 53) Jensen, R. K., Korcek, Zimbo, M., Johnson, M. D., *Int. J. Chem. Kinet.*, **22**, 1095 (1990).
- 54) Krapcho, A. P., *Synthesis*, **1982**, 805; Krapcho, A. P., *Synthesis*, **1982**, 893.

要 旨

エステル自動酸化反応: ポリオールエステル系潤滑油の酸化劣化反応機構の解明に向けて

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潤滑油として使用される複雑な構造をしたポリオールエステルのモデル化合物として選ばれた一連のネオペンチルエステルの液相酸化反応が二通りの方法により研究された。まず、密閉系の反応器中、高温で自動酸化反応を行い、そこから得られた生成物を詳細に分析することにより酸化反応機構を提案した。次いで、これらのエステルを2種の異なるアルコキシルラジカルと反応させ、その結果から様々な炭素-水素結合のアルコキシルラジカルに対する相対反応性に関する有益な情報を得た。たとえば、アルコキシルラジカルによる水素引き抜き反応はネオペンチルエステルのアルキル基側とアシル基側の両方で即座に起こり、 β -アシル位の方が α -アシル位よりも反応性が高いことがわかった。

提案したネオペンチルエステルの酸化反応機構を検証するために、エステル由来のペルオキシルラジカルの反応に関して詳

細な研究を行い、アルキルペルオキシルラジカルとの比較を行った。エステル由来のペルオキシルラジカルの反応はアルカン由来のペルオキシルラジカルの反応と同様であり、エステルペルオキシルラジカルの反応を解明する際には、アルキルペルオキシルラジカルや関連する酸素含有ラジカルの反応速度係数が適用可能であることがわかった。

全般的に、ネオペンチルエステルの自動酸化反応機構は、現在までにはほぼ解明されているアルカンの自動酸化反応機構により説明可能であり、両方の系におけるペルオキシルラジカルの化学的類似性から予想可能であった。しかしながら、ネオペンチルエステルの自動酸化反応においては、水素引き抜き反応が起こる部位に対して多大な効果を持つ極性基の影響については考慮が必要である。