The autoxidation of aliphatic esters. Part 3.[1] The reactions of alkoxyl and methyl radicals, from the thermolysis and photolysis of peroxides, with neopentyl esters

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This paper reports a study of the dimerisation of ester radicals arising from the thermolysis and photolysis of di-*tert*-butyl peroxide (DTBPO) and dicumyl peroxide [DCPO, bis(α,α-dimethylbenzyl) peroxide] in neopentyl butanoate and a selection of structurally related neopentyl esters, in the temperature range 298 to 438 K. The acyl moieties of these esters were chosen to incorporate a variety of structural types to provide mechanistic information about the reactions. At 438 K, the thermolyses of DTBPO and DCPO in neopentyl butanoate give six ester radical dimers (three pairs of diastereoisomers). The two major diastereoisomers *threo*- and *meso*-dineopentyl 2,3-diethylbutanedioate have been prepared and the crystal structure of the *meso* compound determined. Interestingly, the dimer product distribution is independent of the peroxide used. By contrast, at 298 K more than twice as many dimers are observed and the product distributions from the two peroxides are no longer the same. Similar results are also observed for the other neopentyl esters. Evidence is presented to show that the ester radicals arise from hydrogen atom abstraction from the esters by alkoxyl and methyl radicals; the latter being formed by the fragmentation of the alkoxyls. At 438 K the dimer product distributions are determined predominantly by a thermodynamically controlled equilibrium of ester radicals prior to dimerisation. Lowering the temperature leads to the increased importance of kinetic effects in determining the product distribution.

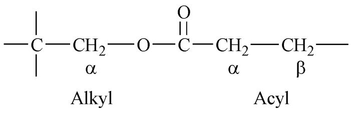
Introduction

Modern automotive engines subject the lubricant to a high degree of stress. Emission control legislation and new engine designs, to meet the demands for improved economy and performance, require the development of new and improved lubricant formulations. Thus, much current research is focused on prolonging the working lifetime of the lubricant. This involves detailed studies on the thermo-oxidative degradation of the base fluid and the use of additives designed to minimise this degradation and thus to prevent deposit formation.[2]

It is generally agreed that lubricants are degraded by radical autoxidation processes and that the primary products react further to give undesirable acidic and polymeric materials.[3] The details of the initial processes are well defined for mineral oil base fluids and, although less thoroughly studied, the same general mechanisms are assumed to occur with synthetic ester lubricants.[1,4]

At York we have embarked on a research programme aimed at understanding the radical oxidation mechanisms of models for pentaerythritol, trimethylolpropane and neopentylglycol ester lubricants. In previous studies we have investigated the selectivity of hydrogen atom abstraction from esters by alkoxyl radicals and the mechanisms of ester autoxidation.[1,5] In this paper we examine the products from the homolysis of peroxides in esters arising from alkoxyl and methyl radicals.

The notation employed to identify the different positions on the ester substrates is the same as that used previously and is illustrated in Scheme 1.



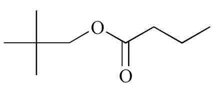
$$-\overset{|}{\underset{|}{C}}-\underset{\alpha}{CH_2}-O-\overset{\overset{O}{||}}{C}-\underset{\alpha}{CH_2}-\underset{\beta}{CH_2}-$$

Scheme 1 Notation used to identify C–H bonds in esters.

Results

The products from the thermolysis and photolysis of di-*tert*-butyl peroxide (DTBPO) and dicumyl‡ peroxide (DCPO) in neopentyl esters 1–4 under nitrogen

The thermolyses and photolyses of DTBPO and DCPO in neopentyl esters **1**–**4**, under nitrogen, have been studied in the temperature range 298–438 K. Analysis by GC shows that the gaseous products are a mixture of methane and ethane and in the liquid phase the peroxides form an alcohol (*tert*-butyl alcohol or 2-phenylpropan-2-ol) and a ketone (acetone or acetophenone) and the esters give some long retention time products.



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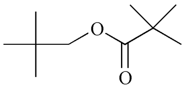

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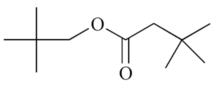

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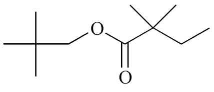

4

Products arising from the peroxide. The yields of methane, ethane, alcohol and ketone from the reactions of both peroxides in each ester at 438 K are reported in Tables 1 and 2. The data show that for all the esters methane is the major gaseous product and, for a given substrate, the yield of methane is significantly higher for reactions using DCPO. The accountabilities of all the reactions were very high with (yields of ketone + alcohol)/2(peroxide consumed) being close to unity and the [yield of methane + 2(yield of ethane)]/(yield of ketone) being >0.80 for almost all the substrates.

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‡ The IUPAC name for cumyl is α,α-dimethylbenzyl.

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Table 1 Product yields (10^{-4} mol) from the thermolysis of DTBPO in neopentyl butanoates **1**–**4** under nitrogen at 438 K

Ester	Acetone	*tert*-Butyl alcohol	Methane	Ethane	Methane/acetone
1	6.2	4.2	6.0	0.16	0.96
2	6.6	3.2	6.2	0.21	0.94
3	6.6	3.4	6.3	0.16	0.95
4	6.0	4.6	5.7	0.12	0.95

Table 2 Product yields (10^{-4} mol) from the thermolysis of DCPO in neopentyl butanoates **1**–**4** under nitrogen at 438 K

Ester	Acetophenone	2-Phenylpropan-2-ol	Methane	Ethane	Methane/acetophenone
1	9.0	1.6	7.6	0.12	0.84
2	6.9	0.8	5.2	0.10	0.86
3	9.5	1.3	7.6	0.15	0.80
4	7.6	1.4	5.9	0.05	0.78

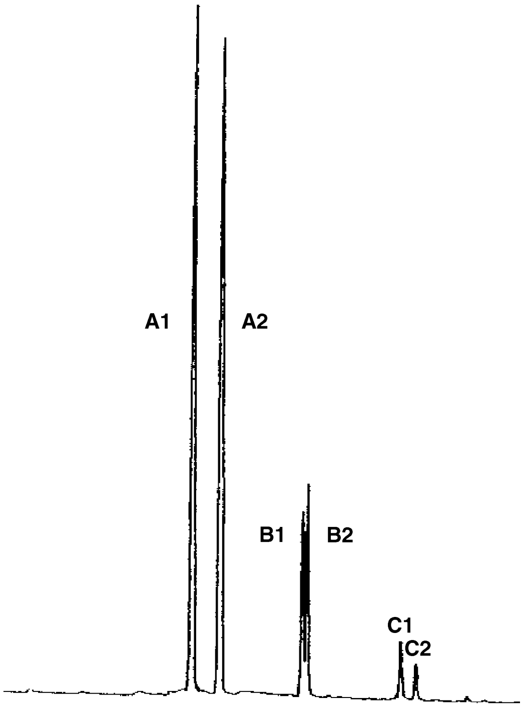


Fig. 1 GC chromatogram of the radical dimers formed by the thermolysis of DTBPO in neopentyl butanoate (**1**) at 438 K.

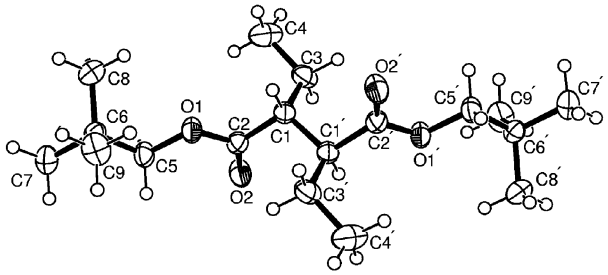
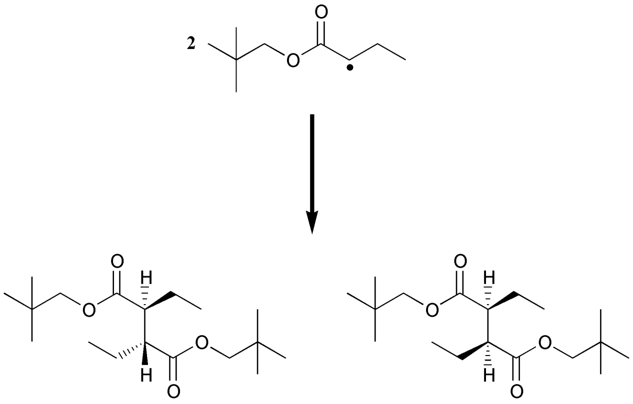


Fig. 2 ORTEP representation of *meso*-dineopentyl 2,3-diethylbutanedioate (50% probability ellipsoids).



meso Dineopentyl
2,3-diethylbutanedioate

One enantiomer of *threo*
dineopentyl 2,3-diethylbutanedioate

Scheme 2 The product diastereoisomers from the self-dimerisation of α-acyl neopentyl butanoate radicals.

Products arising from ester 1 at 438 K. The reaction of DTBPO in ester **1** at 438 K gives six longer retention time products (labelled **A1**, **A2**, **B1**, **B2**, **C1** and **C2** in the chromatogram in Fig. 1, Table 3) each of which by GC-MS has a molecular ion with $m/z = 314$ (see Experimental for mass spectral details). The similarity of the MS fragmentation patterns of **A1** and **A2**, **B1** and **B2**, and **C1** and **C2** indicates that these products are three pairs of diastereoisomers arising from the dimerisation of secondary ester radicals. Column chromatography of the reaction mixture led to the isolation and purification of **A1** which was identified by ^{1}H and ^{13}C NMR spectroscopy as a dineopentyl 2,3-diethylbutanedioate from the self-dimerisation of two α-acyl radicals of ester **1** (Scheme 2).

The identities of **A1** and **A2** were confirmed by their synthesis using the iodine promoted self-coupling of the α-anion of ester **1**.[6] One of the diastereoisomers was obtained as crystals which single crystal X-ray crystallography showed to be the *meso* compound (Fig. 2). By elimination the other, which remained as a liquid, is the racemic mixture of *threo* enantiomers.

GC analysis of the products from the thermolysis of DCPO in ester **1** under nitrogen at 438 K showed the same six radical dimers as were formed from the reaction using DTBPO. Furthermore, the dimer distributions for both peroxides were essentially identical (Fig. 3).

Products arising from the esters 2–4 at 438 K. As noted above for ester **1**, the other neopentyl esters also gave radical dimer products from their reactions with DTBPO or DCPO and, for a given ester, the dimer product distribution was independent of the peroxide used (Table 3). Ester **2** gave four radical dimers (labelled **D1**, **D2**, **E** and **F** in Fig. 4). GC-MS analysis showed that **D1** and **D2** are a pair of diastereoisomers and **E** and **F** are structural isomers. Thermolysis of the peroxides in esters **3** and **4** each gave three diastereoisomeric pairs of radical dimers (Table 3).

Effect of temperature on the radical dimer distributions from the thermolyses and photolyses of DTBPO and DCPO in esters 1–4

A solution of DTBPO in ester **1** was photolysed at 298 K using

Table 3 The relative peak areas of the ester radical dimers from the thermolysis of DTBPO and DCPO in esters **1**–**4**, under nitrogen at 438 K

Ester	Peroxide	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
1	DTBPO	100	100	20	20	20	20
1	DCPO	100	100	20	20	20	20
2	DTBPO	80	90	85	100		
2	DCPO	80	100	85	95		
3	DTBPO	40	100	35	95	20	10
3	DCPO	50	100	50	100	20	20
4	DTBPO	50	100	55	90	35	45
4	DCPO	45	100	50	90	50	60

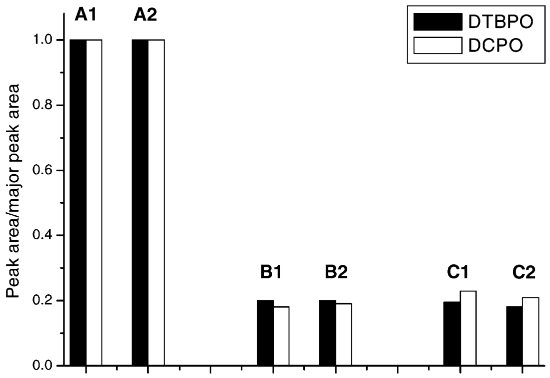


Fig. 3 The distribution of radical dimers from the thermolysis of DTBPO and DCPO in neopentyl butanoate (**1**) at 438 K.

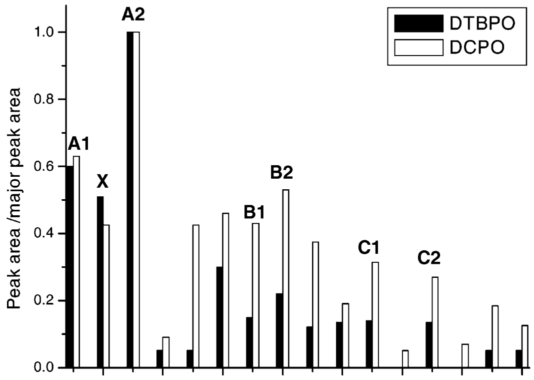


Fig. 5 The distribution of radical dimers from the photolysis of DTBPO and DCPO in neopentyl butanoate (**1**) at 298 K.

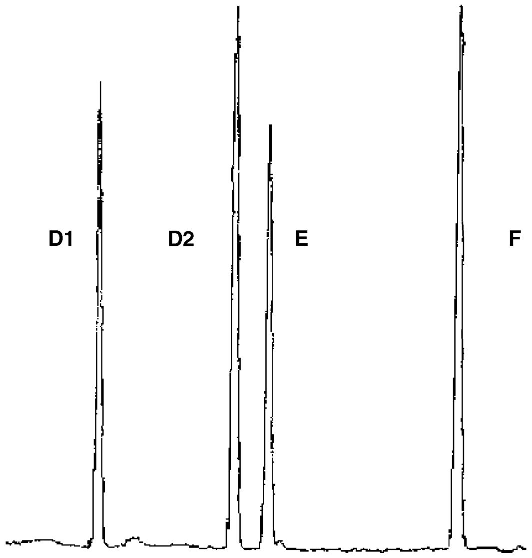


Fig. 4 GC chromatogram of the radical dimers formed by the thermolysis of DTBPO in neopentyl 2,2-dimethylpropanoate (**2**) at 438 K.

a xenon arc light source ($\lambda > 300$ nm). The peaks from at least fourteen radical dimers were observed by GC and GC-MS, including the six observed in the reaction at 438 K (Fig. 5); GC-MS analysis showed that most of these are present as pairs of diastereoisomers. Significantly more of **A2** than **A1** appears to be formed at 298 K. For esters **3** and **4** the number of radical dimers also increased, from 6 to 9 and from 6 to 15 respectively, when the reactions were carried out at 298 K. In contrast, for ester **2** the number of radical dimers formed at 298 K was the same as that obtained at 438 K.

Similar results were generally obtained with DCPO to those from DTBPO. In both systems, the number of radical dimers formed from ester **2** was independent of reaction temperature whereas esters **1**, **3** and **4** yielded many more radical dimers at 298 K compared to their reactions at 438 K. However, there are clear distinctions between the reactions of the two peroxides with the latter group of esters, at 298 K. DCPO gives more products (esters **1**, **3** and **4** gave 14, 9 and 15 GC peaks with DTBPO and 17, 12 and 17 respectively with DCPO) and a different product distribution to DTBPO (see for example Fig. 5).

The reaction of DTBPO in ester **1** was also examined at the following temperatures: between 298 and 438 K; 353, 373 and 393 K (photolysis) and 393 and 408 K (thermolysis). All the radical dimers were detectable up to 408 K, although their distributions changed with temperature (Table 4). One of the most significant differences is in the proportions of the α-acyl dimers **A1** and **A2**. The reaction at 393 K was duplicated, using thermolysis as the source of radicals in one experiment and photolysis (with a small proportion of thermolysis) in the other. The distribution of radical dimers from the two experiments is almost identical (Table 4).

The thermolysis of neopentyl 2-bromobutanoate in neopentyl butanoate (1) at 438 K

Solutions of neopentyl 2-bromobutanoate in ester **1** were heated under nitrogen at 438 K. GC analysis showed that the mixtures, which had changed from colourless to light brown, contained the radical dimers of **1** (Fig. 6) and that the distribution of dimer products was almost identical to those from the thermolyses of DTBPO and DCPO in ester **1** at 438 K.

Discussion

The peroxides used in this study have been thermolysed and photolysed to give alkoxyl radicals [reaction (1)] and these in turn react further in two competing processes: fragmentation [reaction (2)] and hydrogen atom abstraction [reaction (3)]. Reaction (2) is more significant with DCPO than DTBPO[7] and for both peroxides it becomes increasingly important as the temperature is increased.[1]

The reactions of the methyl radicals

The methyl radicals abstract hydrogen atoms from the ester to give methane [reaction (4)] and are involved in a number of other radical–radical reactions [reactions (5)–(7)]. From the

Table 4 The temperature dependence of the relative yields of the ester radical dimers from the thermolysis and the photolysis of DTBPO under nitrogen, in neopentyl butanoate **1**

	Temperature/K						
Dimer[a]	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	
3 (**A2**)[d]	167	161	167	137	125	112	100
4	10	19	20	11	9	4	
5	10	23	17	5	6	4	
6	50	31	22	11	9	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	
10	22	16	20	7	7	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	
14	10	29	12	4	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**.

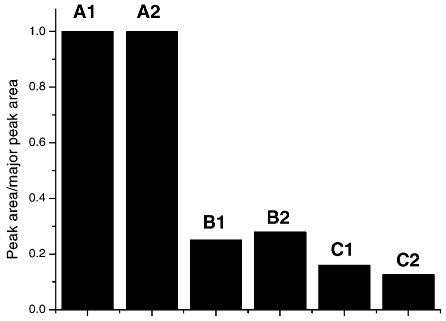


Fig. 6 The distribution of radical dimers from the thermolysis of neopentyl 2-bromobutanoate in neopentyl butanoate (**1**) at 438 K.

$$R'(CH_3)_2CO\text{–}OC(CH_3)_2R' \rightarrow 2R'(CH_3)_2CO^{\bullet} \quad (1)$$

$$R'(CH_3)_2CO^{\bullet} \rightarrow R'COCH_3 + CH_3^{\bullet} \quad (2)$$

$$R'(CH_3)_2CO^{\bullet} + RH \rightarrow R'(CH_3)_2COH + R^{\bullet} \quad (3)$$

$$CH_3^{\bullet} + RH \rightarrow CH_4 + R^{\bullet} \quad (4)$$

$$CH_3^{\bullet} + R^{\bullet} \rightarrow CH_4 + R(-H) \quad (5)$$

$$CH_3^{\bullet} + R^{\bullet} \rightarrow CH_3R \quad (6)$$

$$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow CH_3CH_3 \quad (7)$$

$$[RH = \text{ester and } R^{\bullet} = (\text{ester} - H)^{\bullet}]$$

methane : ketone ratios in Tables 1 and 2, it is clear that 80–90% of the methyl radicals are consumed in reactions (4) and (5) rather than in reactions (6) and (7). Since the rate constants for the radical–radical reactions are very large compared with the expected value for hydrogen abstraction by methyl,[8] this indicates that the concentration of the radicals in the reactions must be very low and $k_4[\text{ester}] \gg k_5[(\text{ester} - H)^{\bullet}]$, $k_6[(\text{ester} - H)^{\bullet}]$ and $k_7[Me^{\bullet}]$. The high methane to ethane ratios confirm this conclusion. It is likely that the methyl radicals unaccounted for as either methane or ethane are involved in reactions (5) and (6) to give methylated and unsaturated neopentyl esters. However, although some of these products could be detected by GC-MS, it was not possible to separate them from the ester substrates, making it impossible to quantify them in this study.

Ester radical dimerisation at 438 K

The ester radicals are consumed in disproportionation and dimerisation processes [reactions (8) and (9)].

$$R^{\bullet} + R^{\bullet} \rightarrow RH + R(-H) \quad (8)$$

$$R^{\bullet} + R^{\bullet} \rightarrow R\text{–}R \quad (9)$$

Product analyses of the thermolyses of the peroxides in ester **1** at 438 K reveal three key results: (i) only 6 of a possible 21 ester radical dimers (excluding enantiomers) are detected; (ii) the six dimers that are observed are formed as three pairs of diastereoisomers; (iii) the reactions with two peroxides give essentially identical dimer distributions. These points are discussed in detail below.

Diastereoisomers can only be formed from ester **1** by combinations of the three secondary radicals (α- and β-acyl and α-alkyl). The preferential hydrogen abstraction by the alkoxyl and methyl radicals from secondary C–H bonds can be accounted for in terms of the relative bond dissociation energies of primary and secondary C–H bonds.[9] However, the observed selectivity of the radical dimerisation was unexpected since only half of the possible 6 diastereoisomer pairs was detected. The major products, **A1** and **A2** (~80%) have been identified as α-acyl–α-acyl dimers, *meso*- and (±)-*threo*-dineopentyl 2,3-diethylbutanedioate (Scheme 2), indicating that the α-acyl radical is the major ester radical in the reaction system. It follows that **B1** and **B2**, and **C1** and **C2** are formed by cross-dimerisations of the α-acyl radical with the β-acyl and the α-alkyl radicals.

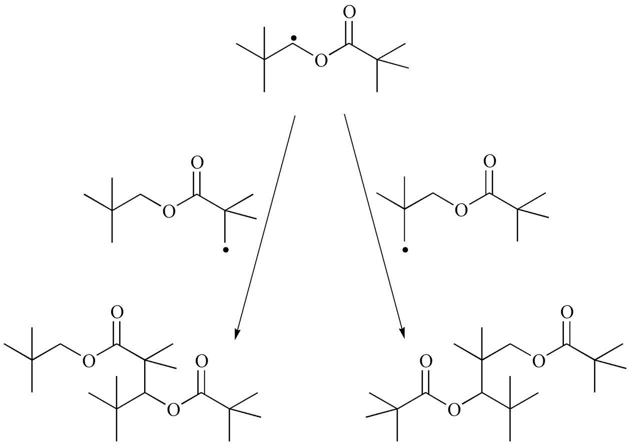
The reactions of the other neopentyl esters, **2**–**4**, with DTBPO and DCPO at 438 K show similar trends to those of ester **1**. Thus, the dimerisations are relatively selective and for a given ester both peroxides give the same dimer product distribution. Ester **2** has only one secondary carbon and, as expected, gives one pair of diastereoisomers (**D1** and **D2**) from the self-reaction of the α-alkyl radical. The other two dimers detected (**E** and **F**) are not diastereoisomers and must arise from the cross-dimerisation of this radical with the two primary ester radicals (Scheme 3). Esters **3** and **4**, each with two secondary carbon atoms, give the expected three diastereoisomeric pairs of radical dimers.

If *tert*-butoxyl and cumyloxyl were the only radicals involved in abstracting hydrogen atoms from the esters then, even though the alkoxyl radicals are different, it would perhaps not be surprising that the radical dimer distributions from the reactions are so similar. However, it is clear that methyl radicals play a significant role in these reactions and, from the methane yields, that virtually all of them react by hydrogen atom abstraction from the ester. Indeed, there are several reports in the literature of methyl radicals abstracting the α-acyl hydrogen atoms from methyl esters to give the corresponding α-acyl–α-acyl dimers.[10] With larger alkyl groups, hydrogen abstraction from the alkyl portion is also observed.[11] Furthermore, methyl and alkoxyl radicals, on electronic grounds, would not be expected to have the same selectivity for hydrogen atom abstraction: alkoxyls are electrophilic whereas methyl is nucleophilic.[12] Thus, since the two peroxides produce distinctly different ratios of alkoxyl and methyl radicals, with DCPO giving a much higher proportion of methyl radicals, the reactions of the two peroxides would be expected to give different dimer distributions.

The above conclusions assume that when the abstracting radicals remove a hydrogen atom, the resulting ester radicals react either by dimerisation or by disproportionation and that the position of the initial hydrogen abstraction is locked in the dimer products. Thus, the carbon atoms involved in the new C–C bond correspond to the sites of hydrogen abstraction. However, we argue that once an ester radical is produced it should also be able to abstract a hydrogen atom from the ester, which is present in a very large excess as both substrate and solvent. Assuming this happens several times before two radicals dimerise, the products would not reveal the identities of the initial sites of hydrogen abstraction but rather the thermodynamic equilibrium distribution of ester radicals (Scheme 4). Consequently, it is not surprising that for a given ester both peroxides give essentially the same dimer product distribution. To explore this hypothesis in more detail, the temperature of the reaction was lowered from 438 to 298 K.

Ester radical dimerisation at 298 K

Lowering the reaction temperature to 298 K resulted in a significant increase in the number of radical dimers from the reaction of ester **1** with DTBPO. This supports the suggestion that the reaction at 438 K is thermodynamically rather than kinetically controlled, since lowering the temperature of a reaction that is kinetically controlled would be expected to reduce rather than increase the number of products obtained. We believe that at 298 K kinetic effects are important and that the ratio of intermolecular radical scrambling to dimerisation and disproportionation has decreased [reactions (8) and (9)]. Thus, the product analysis of reactions at 298 K should give more information about the initial sites of hydrogen abstraction, although it is still likely that ester radical hydrogen abstraction is occurring.



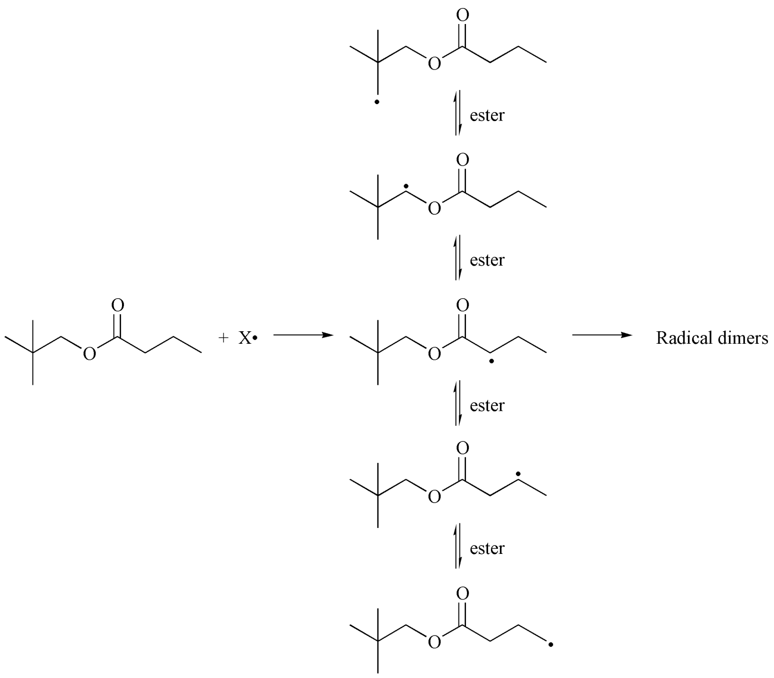
Scheme 3 Cross-dimerisation of α-alkyl and primary radicals of neopentyl 2,2-dimethylpropanoate.

Neopentyl esters **3** and **4** behave like ester **1** in their reaction with DTBPO giving a greater number of products at 298 than at 438 K. In contrast, however, the number of radical dimers from ester **2** is independent of temperature. This, we believe, is associated with their structures: esters **1**, **3** and **4** have two or more secondary carbon atoms whereas ester **2** has only one (α-alkyl). It is likely that for the latter substrate, the ester radical that predominates is the same whether the reaction is favoured by kinetic or by thermodynamic factors.

The results above support those from our previous studies on the autoxidation of neopentyl esters **1**–**4** where all the primary and secondary C–H bonds were found to be susceptible to oxidation.[1,5] However, on closer examination, the dominance of dimer products from the α-acyl radical of ester **1** at all temperatures in this study seems contrary to the selectivity observed in the autoxidation of this ester where the β-acyl and α-alkyl C–H bonds were found to be more reactive. This suggests that, under autoxidative conditions, the ester radicals are rapidly trapped by oxygen before they have an opportunity to undergo the intermolecular radical scrambling.

The reaction of ester **1** with DCPO at 298 K gives more radical dimer products and in a different distribution to that obtained with DTBPO. The main differences in the two product distributions can be attributed to the methyl radical. At 298 K, fragmentation of *tert*-butoxyl [reaction (2)] is unimportant and the alkoxyl radical is the only abstracting radical with the latter peroxide, whereas with DCPO both cumyloxyl and methyl are involved.

The effect of temperature on the reaction of ester **1** with DTBPO was explored further between 298 and 438 K. This reveals that all the products observed at 298 K were detectable up to 408 K suggesting that thermodynamic control of the products may only be complete at 438 K. This study also confirmed that the method of generating the alkoxyl radicals (thermolysis *versus* photolysis) has no effect on the product



Scheme 4 Intermolecular rearrangement of ester radicals from neopentyl butanoate.

ratios. Thus, at 393 K the dimer distribution from ester **1** is similar whether the reaction is initiated thermally or photochemically.

The three pairs of diastereoisomers at 438 K, detected from ester **1**, are major products at all the temperatures investigated. However, whereas the ratios of **B1** : **B2** and **C1** : **C2** are approximately 1.0 at all the temperatures, the **A1** : **A2** ratio decreases from 1.0 at 438 K to 0.6 at 298 K. This could arise from a change in the diastereoselectivity in the dimerisation process, however, we believe it is due to the co-elution of **A2** with the diastereoisomer of the radical dimer which elutes between **A1** and **A2** (**X** in Fig. 5). In agreement with this conclusion the yield of **A2** at all temperatures studied is approximately equal to the sum of the yields of **A1** and **X**.

Thermolysis of neopentyl 2-bromobutanoate in neopentyl butanoate

To confirm the existence of the intermolecular rearrangement of the ester radicals we examined the fate of a specific ester radical under the reaction conditions. For this purpose we chose the thermolysis of neopentyl 2-bromobutanoate in neopentyl butanoate at 438 K. This gave not only the two α-acyl–α-acyl dimers, **A1** and **A2**, expected from the self-combination of the α-acyl radicals but also dimers **B1**, **B2**, **C1** and **C2**. Furthermore, in agreement with the thermodynamic control of the intermolecular rearrangement at 438 K, the distribution of dimers is the effectively same as that obtained from the reactions with DTBPO and DCPO at this temperature.

Conclusions

(1) Ester radicals, generated from the thermolysis or photolysis of peroxides in esters, rearrange by hydrogen atom abstraction from the ester. (2) As a consequence of this radical scrambling, the ester radical dimer product distributions do not provide reliable data to calculate the selectivity of hydrogen abstraction by alkoxyl and methyl radicals. (3) The high temperature studies with ester **1**, where the radical equilibration is complete, show that the most stable radical is α to the carbonyl group.

Experimental

Instrumentation

GC analyses were carried out on a Pye Unicam GCD gas chromatograph fitted with a flame ionisation detector. The gas samples were separated with a glass column packed with silica gel (80–120 mesh) and for the liquid samples a Carbowax 20M capillary column (30 m length, 0.25 mm id, 0.25 µm film thickness) was employed. Data collection used a Trio Trivector integrator. GC mass spectra were obtained with a VG Autospec S Series A027 mass spectrometer linked to a Hewlett Packard 5890 Series 2 gas chromatograph. The spectra were analysed using a VAX3100 Workstation.

^{1}H and ^{13}C NMR spectra were recorded using JEOL 270 and Bruker MSL 300 spectrometers with tetramethylsilane as the internal standard.

The X-ray crystal structure was obtained using an automated Rigaku AFC6S diffractometer, ω–2θ scan mode, with graphite-monochromated Mo-Kα radiation, μ(Mo-Kα) = 0.07 mm^{-1}, ω scan width = 1.21 + tan θ, ω scan speed 1° min^{-1}. The unit cell was indexed by least mean squares refinement on diffractometer angles for 20 automatically centred reflections, λ = 0.71069 Å. The structure was solved by direct methods with SHELXS86[13] and expanded using Fourier techniques with DIRDIF.[14] Full matrix least squares refinements on F^2 with SHELXL97[15] with all non-hydrogen atoms anisotropic and hydrogens refined using a rigid model.

Apparatus and methods

The thermolyses were carried out in a stainless steel autoclave (inside volume 4.87 cm^3) which has been described in previous papers.[1,5] The autoclave, containing a 0.5 mol dm^{-3} solution of the peroxide in the ester (1 cm^3), was evacuated and flushed with nitrogen several times before finally being repressurised to 1 bar with nitrogen and placed in an aluminium block which was heated to the reaction temperature. After the required reaction time, the autoclave was cooled with ice, connected to a vacuum line and the gas from the reaction was shared into a sample loop for GC analysis. The autoclave was then opened and the liquid products also analysed by GC.

For the isolation of ester dimer **A1**, a larger scale reaction was carried out. A solution of DTBPO (0.1 mol dm^{-3}) in neopentyl butanoate (10 cm^3) was thoroughly purged with argon and then heated at 438 K under argon. After 2 h the solution was cooled and the volatile products were removed under vacuum. The residue which contained the radical dimers **A1**, **A2**, **B1**, **B2**, **C1** and **C2** was purified by flash chromatography (silica gel with dichloromethane) to give **A1**; δ_H (CDCl$_3$) 0.89 (6H, t), 0.96 (18H, s), 1.60 (4H, m), 2.62 (2H, m), 3.78 (4H, s); δ_C (CDCl$_3$) 11.7 ($-CH_2\mathit{C}H_3$), 24.3 ($-\mathit{C}H_2CH_3$), 26.6 [$(\mathit{C}H_3)_3C$], 31.2 [$(CH_3)_3\mathit{C}$], 50.0 ($-O_2CH_2$), 74.0 ($-\mathit{C}H_2O_2C$), 174.5 ($-O_2\mathit{C}CH_2$); MS(CI) *m*/*z* 315 (MH$^+$).

The photolyses were carried out in a cylindrical stainless steel cell (id 10 mm, length 20 mm) fitted at each end with Pyrex optical windows.[16] Three stainless steel side-arms were connected to the cell, one was sealed with a Viton septum and the others were connected *via* glass-to-metal joints to greaseless 'Rotaflo' taps. The temperature of the cell was controlled by placing it in a thermostatted aluminium jacket, heated by a Jencons (230 V, 320 W) heating band. The heating was monitored by a thermocouple connected to an electroserve temperature control unit. The light source used was a 300 W, high intensity xenon arc lamp fitted with a light guide (Laser Lines Ltd.). The reactions used 0.5 mol dm^{-3} solutions of the peroxide in the ester (5 cm^3) and were thoroughly deoxygenated with nitrogen before photolysis.

Materials

All materials were commercially available and used as purchased unless otherwise stated. Tetrahydrofuran (THF) was dried over sodium under a nitrogen atmosphere using benzophenone as an indicator.

The neopentyl ester substrates were prepared as reported previously.[5] Dineopentyl 2,3-diethylbutanedioate was prepared by adding neopentyl butanoate (0.01 mol) in dry THF (2 cm^3) to a stirred solution of lithium diisopropylamide (0.01 mol) in dry THF (10 cm^3) under nitrogen at 195 K. After 10 min, iodine (0.005 mol) in dry THF was added and the mixture was allowed to warm to room temperature. After a further 20 min stirring the reaction was quenched with an aqueous solution of ammonium chloride and extracted with light petroleum (40–60 °C). The organic solution was washed with an aqueous solution of sodium chloride, dried, concentrated under vacuum and purified using column chromatography (silica gel with dichloromethane as eluant) to give a 19.5% yield of a mixture of *meso*- and (±)-*threo*-dineopentyl 2,3-diethylbutanedioate; δ_H (CDCl$_3$) 0.89 (6H, t), 0.96 (18H, s), 1.60 (4H, m), 2.62 (2H, m), 3.82 (4H, s); δ_C (CDCl$_3$) 11.7 ($-CH_2\mathit{C}H_3$), 24.3 ($-\mathit{C}H_2CH_3$), 26.4 [$(\mathit{C}H_3)_3C$], 31.2 [$(CH_3)_3\mathit{C}$], 49.9 ($-O_2C\mathit{C}H_2$), 73.9 ($-\mathit{C}H_2O_2C$), 174.4 ($-O_2\mathit{C}CH_2$); MS(EI) *m*/*z* 299 (25%), 227 (80), 157 (88), 71 (100), 55 (27), 43 (57); MS(CI) *m*/*z* 332 (MNH$_4^+$), 315 (MH$^+$).

When the purified mixture of diastereoisomers was left to stand, crystals of the *meso* compound were obtained. Crystal data§ for *meso*-dineopentyl 2,3-diethylbutanedioate $C_{18}H_{34}O_4$,

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§ CCDC reference number 162741. See http://www.rsc.org/suppdata/p2/b1/b103555j/ for crystallographic files in .cif or other electronic format.

$M = 314.46$, monoclinic, $a = 8.359(5)$, $b = 13.505(4)$, $c = 9.538(4)$ Å, $\beta = 111.74(3)°$, $V = 1000.1(8)$ Å^3, $T = 150$ K, space group $P2_1/a$, $Z = 2$, μ(Mo-Kα) = 0.072 mm^{-1}, 1841 reflections measured, 1750 unique ($R_{int} = 0.012$). Final $R1$, $wR2$ on all data (1750 reflections) 0.0725, 0.1209. $R1$, $wR2$ on $[I_o > 2\sigma(I_o)]$ (1216 reflections) 0.0400, 0.1047.

2-Bromobutanoic acid was prepared by heating a mixture of butanoic acid (20 mmol), bromine (20 mmol), chlorosulfonic acid (0.5 cm^3) in dichloroethane (50 cm^3) at 85 °C. After 2 h the unreacted bromine and dichloroethane were removed under vacuum and the residue was esterified with neopentanol and a small amount of concentrated sulfuric acid in toluene. The water was removed azeotropically with a Dean–Stark apparatus. After the reaction, the toluene was washed with an aqueous solution of sodium hydrogen carbonate, dried (MgSO$_4$), concentrated under vacuum and purified by flash chromatography on silica gel, using dichloromethane as the eluant, to give neopentyl 2-bromobutanoate in 55% yield; δ_H(CDCl$_3$) 1.15 (9H, s), 1.26 (3H, t), 2.35 (2H, m), 3.75 (2H, s), 4.28 (1H, t); δ_C (CDCl$_3$) 11.83 (–CH$_2$*C*H$_3$), 26.25 [(*C*H$_3$)$_3$C–], 28.35 (–*C*H$_2$CH$_3$), 31.53 [(CH$_3$)$_3$*C*–], 47.87 (–*C*HBrCH$_2$CH$_3$), 74.85 (–*C*H$_2$O$_2$C), 169.69 (–O$_2$*C*CHBr); MS(EI), *m*/*z* 223 (5%), 221 (5), 183 (85), 181 (85), 151 (73), 149 (73), 123 (75), 121 (75), 62 (100), 57 (98); MS(CI) *m*/*z* 256, 254 (MNH$_4^+$).

Mass spectral data for dimers from reactions of esters at 438 K

Ester **1** gave six dimers: MS(EI) *m*/*z* (relative intensities) **A1**: 314 (M$^+$, 0.03%), 227 (6), 157 (81), 129 (12), 88 (21), 87 (20), 71 (100), 57 (17), 55 (28), 43 (57), 41 (22); **A2**: 314 (M$^+$, 0.03%), 227 (7), 157 (85), 129 (10), 88 (12), 87 (10), 71 (100), 57 (17), 55 (29), 43 (65), 41 (23); **B1**: 314 (M$^+$, 1.0%), 227 (11), 157 (100), 129 (17), 128 (16), 88 (9), 87 (12), 71 (60), 57 (16), 55 (23), 43 (46), 41 (23); **B2**: 314 (M$^+$, 1%), 227 (12), 157 (100), 129 (22), 128 (16), 88 (11), 87 (12), 71 (63), 57 (17), 55 (22), 43 (45), 41 (22); **C1**: 314 (M$^+$, 3.5%), 227 (36), 198 (12), 157 (65), 129 (44), 111 (20), 71 (100), 57 (30), 55 (33), 43 (67), 41 (35); **C2**: 314 (M$^+$, 3.5%), 227 (36), 198 (12), 157 (65), 129 (45), 111 (20), 71 (100), 57 (30), 55 (33), 43 (68), 41 (35).

Ester **2** gave four dimers: MS(EI) *m*/*z* (relative intensities) **D1**: 327 (M$^+$ − Me, 1.0%), 285 (5), 201 (6), 199 (4), 184 (4), 171 (4), 85 (54), 57 (100), 41 (14); **D2**: 327 (M$^+$ − Me, 1%), 285 (5), 201 (6), 199 (4), 184 (4), 171 (4), 85 (53), 57 (100), 41 (14); **E**: 327 (M$^+$ − Me, 0.5%), 139 (9), 125 (6), 99 (52), 85 (30), 83 (19), 69 (18), 57 (100), 41 (17); **F**: 327 (M$^+$ − Me, 2%), 285 (7), 171 (43), 125 (19), 113 (47), 85 (30), 71 (15), 70 (12), 69 (12), 57 (100), 43 (14), 41 (21).

Ester **3** gave six dimers: MS(EI) *m*/*z* (relative intensities), in order of GC elution dimer 1: 355 (M$^+$ − Me, 0.03%), 185 (11), 129 (9), 99 (100), 71 (14), 57 (46), 43 (12); dimer 2: 355 (M$^+$ − Me, 0.03%), 185 (11), 129 (9), 99 (100), 71 (14), 57 (47), 43 (12); dimer 3: 355 (M$^+$ − Me, 0.04%), 167 (18), 129 (10), 99 (100), 71 (17), 57 (50), 43 (12); dimer 4: 355 (M$^+$ − Me, 0.04%), 167 (18), 129 (10), 99 (100), 71 (16), 57 (49), 43 (12); dimer 5: 355 (M$^+$ − Me, 0.2%), 313 (5), 100 (8), 99 (100), 83 (7), 71 (9), 57 (47), 43 (8.0), 41 (6); dimer 6: 355 (M$^+$ − Me, 0.3%), 313 (3), 100 (8), 99 (100), 83 (7), 71 (9), 57 (46), 43 (7), 41 (7).

Ester **4** gave six dimers: MS(EI) *m*/*z* (relative intensities), in order of GC elution dimer 1: 355 (M$^+$ − Me, 1.6%), 185 (33), 139 (14), 127 (19), 99 (34), 83 (22), 71 (100), 69 (30), 57 (27), 43 (48), 41 (23); dimer 2: 355 (M$^+$ − Me, 1.6%), 185 (33), 139 (14), 127 (19), 99 (3), 83 (23), 71 (100), 69 (30), 57 (27), 43 (48), 41 (23); dimer 3: 355 (M$^+$ − Me, 0.7%), 185 (39), 145 (10), 127 (32), 99 (22), 83 (16), 71 (100), 57 (18), 55 (13), 43 (38), 41 (17); dimer 4: 355 (M$^+$ − Me, 0.9%), 185 (35), 145 (10), 127 (32), 99 (20), 83 (17), 71 (100), 57 (18), 55 (12), 43 (38), 41 (17); dimer 5: 355 (M$^+$ − Me, 0.2%), 215 (7), 99 (30), 72 (6), 71 (100), 57 (8), 55 (5), 43 (25), 41 (9.0); dimer 6: 355 (M$^+$ − Me, 0.3%), 215 (5), 99 (45), 72 (7), 71 (100), 57 (11), 55 (7.0), 43 (33), 41 (12).

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