

# An EPR spin-trap study of the radicals present during the thermolysis of some novel monoperoxycarbonates and peroxydicarbonates

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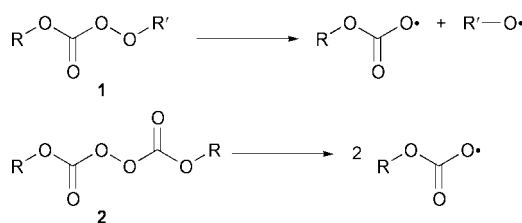
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EPR spin-trapping experiments have been employed to study the radicals present during the thermolysis of two peroxydicarbonates, bis(4-*tert*-butylcyclohexyl) peroxydicarbonate (**3**) and bis(2-ethylhexyl) peroxydicarbonate (**4**), and two monoperoxycarbonates, *OO-tert*-butyl *O*-(2-ethylhexyl) monoperoxycarbonate (**5**) and *OO-tert*-butyl *O*-isopropyl monoperoxycarbonate (**6**). The appropriate alkoxy-carbonyloxy radical is trapped during the thermolysis of each of the four peroxides and the *tert*-butoxyl radical during the thermolysis of **5** and **6**. The trapping of a range of second generation carbon-centred radicals is also reported. Evidence is presented that some of these carbon-centred radicals are formed *via* a 1,5 C to O hydrogen shift whilst others are formed by hydrogen atom abstraction from the parent peroxide.

## Introduction

Although the synthesis of diethyl peroxydicarbonate was first reported by Wieland *et al.* in 1925<sup>1</sup> it was not until 1950 that the synthesis of a range of monoperoxycarbonates (**1**) and peroxydicarbonates (**2**) was first detailed<sup>2</sup> (Scheme 1).



Scheme 1

Peroxydicarbonates are now widely used commercially as initiators for radical polymerisations, especially of vinyl monomers and esters.<sup>3,4</sup> They have proven to be useful initiators at relatively low temperatures, releasing two alkoxy-carbonyloxy radicals upon thermolysis, the nature of the alkyl group having little effect on their 10 hour half-life decomposition temperature.<sup>5</sup>

Although the rate of decarboxylation of alkoxy-carbonyloxy radicals is relatively slow<sup>6-9</sup> these radicals are more reactive towards hydrogen atom abstraction from substrates and addition to monomers than *tert*-butoxyl and other alkoxy radicals due to the inductive electron-withdrawing effect of the RO group. Consequently induced decomposition can occur and has been widely reported.<sup>3-5,8,10,11</sup>

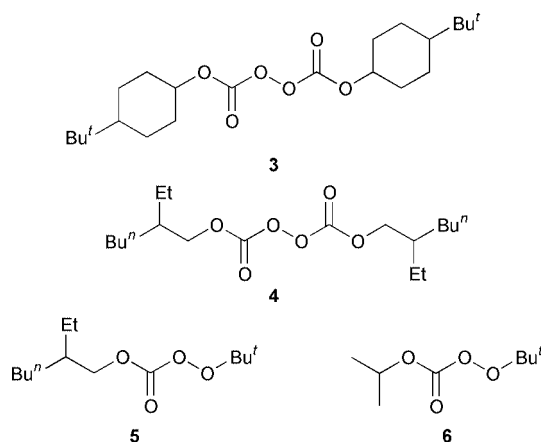
Detailed studies of the species present during the thermolysis of peroxydicarbonates seem rather limited. A thermolysis scheme for diisopropyl peroxydicarbonate was outlined in 1950<sup>2,6</sup> which, based on the nature of the decomposition products, suggested that the primary step was dissociation into alkoxy-carbonyloxy radicals followed either by decarboxylation or hydrogen atom abstraction from the parent peroxide. This conclusion has been supported by Strong<sup>4</sup> and Duynstee *et al.*<sup>11</sup> Similar conclusions have been drawn from product analysis following the decomposition of dicyclohexyl peroxydicarbonate<sup>8</sup> and of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate<sup>12</sup> where

the presence of the corresponding alkoxy-carbonyloxy radical and hydrogen atom abstraction of the  $\alpha$ -hydrogen atom from the cyclohexane ring of the parent peroxide has been invoked.

Monoperoxycarbonates undergo single bond cleavage to release an alkoxy radical and an alkoxy-carbonyloxy radical.<sup>5</sup> The nature of R' in **1** can have a pronounced effect on the activity of these initiators *via* variation in the rate of  $\beta$ -scission of the resulting alkoxy radical but the nature of R has little influence on their 10 hour half-life temperature. These peroxides provide a useful source of *tert*-alkoxy radicals at temperatures below those commonly required for their formation from the corresponding di-*tert*-alkyl peroxide. Unlike peroxydicarbonates, monoperoxycarbonates do not appear to be prone to induced decomposition even at moderate concentrations up to 1 M.<sup>13</sup> Decarboxylation of the corresponding alkoxy-carbonyloxy radical again appears to be slow compared to addition to the alkene.<sup>13,14</sup> The co-generated alkoxy radical will undergo the usual  $\beta$ -scission reactions. In the case of *OO-tert*-hexyl *O*-isopropyl and *OO-tert*-butyl *O*-isopropyl monoperoxycarbonates there is evidence that the alkoxy moiety undergoes a 1,5-H shift reaction.<sup>14</sup>

Although there appears to be no previous EPR study of radicals present during thermolysis there is a report, by Korth *et al.*, of the direct EPR observation of radicals during the photolysis of di-*n*-propyl peroxydicarbonate at 145 K (well below thermolysis temperature) in cyclopropane.<sup>15,16</sup> The singlet observed at  $g$  2.0128 was assigned to the *n*-propoxy-carbonyloxy radical. These workers also reported the presence of a secondary alkyl radical whose formation was attributed to abstraction of the  $\alpha$ -hydrogen atom from the propyl group of the parent peroxide.

In this publication we report the results of our experiments to determine the nature of the radicals present during the thermolysis of two novel peroxydicarbonates and two novel monoperoxycarbonates whose thermolysis mechanisms have, hitherto, received only limited attention. The two peroxydicarbonates have been selected on the basis of their comparatively low temperature thermolysis activity and because the homolytic cleavage of the O–O bond initially produces only alkoxy-carbonyloxy radicals, thus presenting a rare opportunity to explore the spin-trapping of these species. We have selected



bis(4-*tert*-butylcyclohexyl) peroxycarbonate (**3**) and bis(2-ethylhexyl) peroxycarbonate (**4**). The former has been the subject of a product analysis study,<sup>12</sup> as has dicyclohexyl peroxycarbonate.<sup>8</sup> The two monoperoxycarbonates, *OO*-*tert*-butyl *O*-(2-ethylhexyl) monoperoxycarbonate (**5**) and *OO*-*tert*-butyl *O*-isopropyl monoperoxycarbonate (**6**), have been selected as they would be expected to co-generate both an alkoxy moiety and an alkoxy-carbonyloxy moiety by homolytic cleavage of the O–O bond. The latter has been the subject of both a trapping study, employing  $\alpha$ -methylstyrene dimer as a trap,<sup>14</sup> and a product analysis study.<sup>15</sup>

The radicals anticipated during thermolysis, especially the alkoxy-carbonyloxy radicals, present a challenging spin-trap study and in order to meet this challenge we have employed three different spin-traps. There are few reports of the trapping of alkoxy-carbonyloxy radicals<sup>17</sup> and, consequently, we have selected *N*-[<sup>2</sup>H<sub>5</sub>]benzylidene-[<sup>2</sup>H<sub>9</sub>]*tert*-butylamine *N*-oxide (PBN-*d*<sub>14</sub>) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) because of their generally superior ability to trap oxygen-centred radicals compared to carbon-centred radicals.<sup>18</sup> PBN-*d*<sub>14</sub> has been selected as it discloses more information on the nature of the original radical than PBN due to the much smaller spectral linewidth observed in its adducts as a consequence of deuteration.

In order to preferentially trap the carbon-centred radicals expected *via*  $\beta$ -scission of the alkoxy moiety and 1,5-H shift reactions, and also any radicals formed following hydrogen atom abstraction from the parent peroxide, we have employed 2,4,6-tri-*tert*-butylnitrosobenzene (TTBNB, sometimes also referred to as BNB) as a spin-trap. This spin-trap can give both aminoxyl and anilino adducts, the latter by attack at the oxygen atom of the nitroso group.<sup>19–21</sup> Unfortunately, anilino adducts tend to have broader lines (and more similar hyperfine parameters) than aminoxyl adducts and, therefore, although the number of interacting  $\beta$ -protons indicate whether the original radical was a primary, secondary or tertiary C-centred species, it is difficult to obtain information on the exact structure of the original radical within each category.

## Experimental

### Materials

Peroxide **5** (purity > 99%, as checked by NMR) was used as supplied as a liquid and peroxides **4** and **6** as 75% solutions in isododecane, by Elf-Atochem GmbH. Peroxide **3** (purity > 99%, as checked by NMR) was used as supplied as a liquid by Akzo Nobel Chemicals Ltd. All other chemicals, solvents and spin-traps were obtained from Aldrich, except PBN-*d*<sub>14</sub> which was obtained from the OMRF Spin-trap Source.

### Preparation of solutions

The concentration of the spin-traps was usually in the range 0.04–0.15 mol dm<sup>-3</sup> and the peroxides in the range 0.09–0.25

mol dm<sup>-3</sup>. Before thermolysis all solutions were degassed with nitrogen, for between 5 and 10 minutes, and the sample tube then tightly sealed. All samples for EPR study were prepared in 4 mm internal diameter quartz tubes.

### Spectroscopic measurements

All spectra were recorded on a Bruker EMX X-band spectrometer operating with 100 kHz magnetic field modulation. Thermolysis was undertaken employing the Bruker B-VT1000 variable temperature control system (accurate to  $\pm 1$  K). Spectra were recorded with a modulation amplitude in the range 0.01 and 0.02 mT with spectrum accumulation over 4 to 16 scans.

Thermolysis was undertaken *in situ* for a period of up to 60 minutes (varying with the peroxide and the reaction temperature) and spectra were recorded, as required, at various times during this period. In most cases spectra were recorded at room temperature following thermolysis at elevated temperature.

Spectral simulations were undertaken employing *PEST WinSim*<sup>22</sup> (a NIEHS Public EPR Software Tool). The percentage contribution of each adduct to the total spectrum integrated area has been calculated for each simulation. The hyperfine splitting constants obtained from these spectral simulations are considered accurate to  $\pm 0.005$  mT.

## Results and discussion

As peroxides **4** and **6** were supplied as a 75% solution in commercial isododecane, it was important to establish that any adducts of radicals derived by hydrogen atom abstraction from this diluent did not interfere with our experiments. We undertook this precaution in the same way as described in a previous publication.<sup>23</sup> No isododecane derived radical adducts were observed in any of the experiments described below indicating the presence of isododecane as the manufacturer's diluent does not interfere with our experiments.

### Peroxycarbonates

We describe first the results of our experiments involving the thermolysis of **3** and **4** as these peroxycarbonates would be expected to produce, initially, two identical alkoxy-carbonyloxy moieties and no alkoxy moiety.

**Bis(4-*tert*-butylcyclohexyl) peroxycarbonate (3).** Thermolysis of **3** was undertaken in benzene in the presence of PBN-*d*<sub>14</sub> over the temperature range 300–353 K. The resulting spectra consisted of a single adduct with hyperfine parameters [*a*(N) 1.328 and *a*(H) 0.171 mT at 300 K] typical of an oxygen-centred adduct.<sup>20,23–25</sup> These parameters are similar to those reported for the PBN cyclohexyloxy-carbonyloxy radical adduct<sup>17</sup> (see Table 1) and, in view of the reported slow decarboxylation of alkoxy-carbonyloxy radicals, we provisionally assigned these parameters to the PBN-*d*<sub>14</sub> adduct of the (4-*tert*-butylcyclohexyloxy)carbonyloxy radical (**7**) (see Scheme 2).

In order to obtain further evidence for this assignment the experiment was repeated in the presence of DMPO. Again a spectrum consisting of a single adduct was obtained [see Fig. 1(a)]. The *a*(N) and *a*(H <sub>$\beta$</sub> ) parameters (1.226 and 0.988 mT respectively) are of particular interest. These parameters are significantly different from those of the adduct of the cyclohexyloxy radical [*a*(N) 1.269 and *a*(H <sub>$\beta$</sub> ) 0.565 mT in cyclohexane, see Table 2],<sup>26</sup> and presumably, therefore, of the adduct of the 4-*tert*-butylcyclohexyloxy radical, which is the alternative oxygen centred adduct that could be present following decarboxylation of radical **7**. In particular, the *a*(H <sub>$\beta$</sub> ) value observed in our experiment (0.988 mT) is higher than expected for DMPO adducts of alkoxy radicals.<sup>27</sup> There are two additional interesting features. First, the comparatively small *a*(N) value is in line with that predicted on the basis of  $\sigma_1$  substituent

**Table 1** Hyperfine splitting constants for the EPR spectra of the various PBN-*d*<sub>14</sub> adducts observed during the thermolysis of **3**, **4**, **5** and **6**, together with literature data for C<sub>6</sub>H<sub>11</sub>OC(O)O<sup>•</sup>

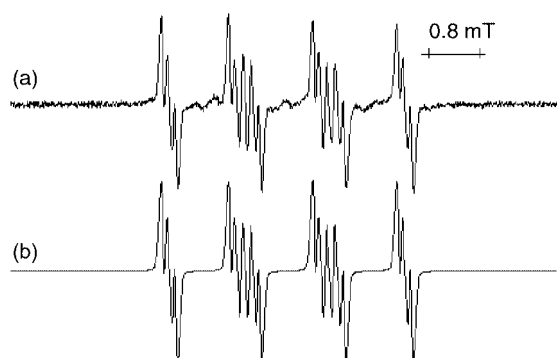
Radical	Solvent	<i>a</i> (N)/mT	<i>h</i> (H <sub>β</sub> )/mT	<i>a</i> (H <sub>γ</sub> )/mT	Peroxide
Adducts of oxygen-centred radicals					
C <sub>6</sub> H <sub>11</sub> OC(O)O <sup>•</sup>	CCl <sub>4</sub>	1.29	0.18		Ref. 17 <sup>a</sup>
<b>7</b>	Benzene	1.328	0.171		<b>3</b> <sup>b</sup>
<b>8</b>	Benzene	1.325	0.173		<b>4</b> <sup>b</sup>
	Benzene	1.327	0.190		<b>5</b> <sup>c</sup>
<b>9</b>	Benzene	1.328	0.180		<b>6</b> <sup>d</sup>
Bu <sup>t</sup> O <sup>•</sup>	Benzene	1.368	0.209		<b>6</b> <sup>d</sup>
Unassigned	Benzene	1.440	0.195		<b>5</b> <sup>c</sup>
	Benzene	1.438	0.194		<b>6</b> <sup>d</sup>
Adducts of carbon-centred radicals					
Me <sup>•</sup>	Benzene	1.490	0.357	0.49 (3H)	<b>5</b> <sup>c</sup>

<sup>a</sup> Data obtained employing PBN as spin-trap at 293 K. <sup>b</sup> Recorded at 300 K. <sup>c</sup> Recorded at 353 K. <sup>d</sup> Recorded at 333 K.

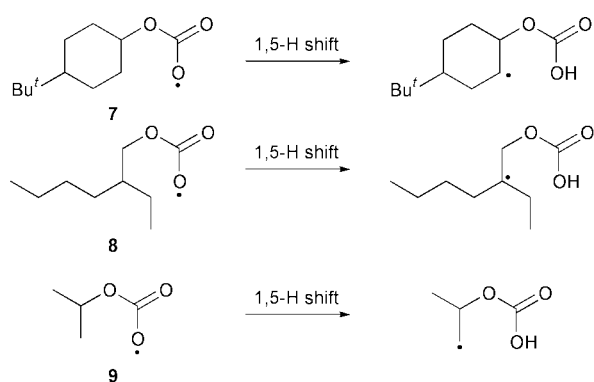
**Table 2** Hyperfine splitting constants for the EPR spectra of the various DMPO adducts observed during the thermolysis of **3**, **4**, **5** and **6**, recorded at 353 K

Radical	Solvent	<i>a</i> (N)/mT	<i>a</i> (H <sub>β</sub> )/mT	<i>a</i> (H <sub>other</sub> )/mT	Peroxide
<b>7</b>	Benzene	1.226	0.988	0.121; 0.075	<b>3</b> <sup>a</sup>
<b>8</b>	Benzene	1.223	0.984	0.122; 0.075	<b>4</b> <sup>a</sup>
	Benzene	1.224	0.984	0.121; 0.070	<b>5</b>
Bu <sup>t</sup> O <sup>•</sup>	Benzene	1.331	0.794	0.172 (1H <sub>γ</sub> )	<b>5</b>
	Benzene	1.331	0.795	0.171 (1H <sub>γ</sub> )	<b>6</b>
<b>9</b>	Benzene	1.244	0.998	0.147; 0.070	<b>6</b>

<sup>a</sup> Recorded at 300 K.



**Fig. 1** (a) The EPR spectrum, recorded at 293 K during the thermolysis of **3** (0.2 mol dm<sup>-3</sup>), in the presence of DMPO (0.02 mol dm<sup>-3</sup>) in benzene, together with (b) its computer simulation.



**Scheme 2**

constants<sup>28–30</sup> for DMPO alkoxy-carbonyloxy radical adducts in benzene. Secondly, the spectrum exhibits coupling to two non-equivalent protons, presumably those at the 3- and 4-positions. These additional couplings are not usually observed in adducts of alkoxy radicals but coupling to the

3-position proton is sometimes observed in the adducts of acyloxy radicals.<sup>27</sup> Consequently, we assign the adducts observed with both PBN-*d*<sub>14</sub> and DMPO to those of the (4-*tert*-butylcyclohexyloxy)carbonyloxy radical.

In order to examine any carbon-centred adducts present thermolysis was also undertaken, at 353 K in benzene, in the presence of TTBNB. The resulting spectrum consisted of a mixture of three adducts. Two of these were aminoxyl (11%) and anilino (74%) adducts of a secondary carbon-centred radical and the other an anilino adduct (15%) of a tertiary carbon-centred radical. The hyperfine parameters of these various adducts are summarised in Table 3 and the nature of the carbon-centred radicals responsible for forming these adducts is discussed further below.

**Bis(2-ethylhexyl) peroxydicarbonate (4).** Thermolysis of **4** was undertaken in benzene in the presence of PBN-*d*<sub>14</sub> over the temperature range 300–313 K; the resulting spectra, again, consisting of a single adduct with hyperfine parameters typical of an oxygen-centred adduct (see Table 1).<sup>20,23–25</sup> The hyperfine parameters of this adduct are virtually the same as those observed during the thermolysis of **3** in the presence of PBN-*d*<sub>14</sub> and are assigned to the adduct of the (2-ethylhexyloxy)-carbonyloxy radical (**8**).

The experiment was repeated in benzene over the temperature range 300–333 K in the presence of DMPO. Again a spectrum consisting of a single adduct was obtained with the same characteristic parameters as those obtained during the thermolysis of **3**. We assign these parameters to the DMPO adduct of radical **8**.

In order to examine any carbon-centred adducts present, thermolysis of **4** was also undertaken, over the temperature range 300–353 K in benzene, in the presence of TTBNB. The resulting spectrum again consisted of a mixture of three adducts. Two of these were aminoxyl (14%) and anilino (35%) adducts of a secondary carbon-centred radical and the other an anilino adduct (51%) of a tertiary carbon-centred radical. The hyperfine parameters of these various adducts are

**Table 3** Hyperfine splitting constants for the EPR spectra of the various TTBNB adducts of carbon-centred radicals observed during the thermolysis of **3**, **4**, **5** and **6**, recorded at 353 K

Radical	Solvent	$a(N)/\text{mT}$	$a(H_\beta)/\text{mT}$	$a(2H_m)/\text{mT}$	Peroxide
$\text{CH}_3\cdot$ Aminoxyl	Benzene	1.299	1.221 (3H)	0.077	<b>5</b>
	Chlorobenzene	1.311	1.219 (3H)	0.079	<b>6<sup>a</sup></b>
$\text{CH}_2\text{R}\cdot$ Aminoxyl	Benzene	1.372	1.778 (2H)	0.076	<b>5</b>
	Chlorobenzene	1.365	1.680 (2H)	0.072	<b>6<sup>a</sup></b>
$\text{CH}_2\text{R}\cdot$ Anilino	Chlorobenzene	1.016	0.212 (2H)	0.175	<b>6<sup>a</sup></b>
	Benzene	1.395	2.317 (1H)	0.080	<b>3</b>
$\text{CHR}_2\cdot$ Aminoxyl	Benzene	1.390	2.102 (1H)	0.080	<b>4</b>
	Benzene	1.353	2.123 (1H)	0.078	<b>5</b>
	Benzene	1.107	0.160 (1H)	0.180	<b>3</b>
$\text{CHR}_2\cdot$ Anilino	Benzene	1.070	0.181 (1H)	0.143	<b>4</b>
	Benzene	1.077	0.150 (1H)	0.185	<b>5</b>
	Benzene	1.006		0.180	<b>3</b>
$\text{CR}_3\cdot$ Anilino	Benzene	1.005		0.192	<b>4</b>
	Benzene	1.007		0.190	<b>5</b>
	Benzene	1.002		0.195	<b>6<sup>a</sup></b>
	Chlorobenzene	1.002		0.195	<b>6<sup>a</sup></b>

<sup>a</sup> Recorded at 383 K.

again summarised in Table 3 and the nature of the carbon-centred radicals responsible for forming these adducts is discussed further below.

### Monoperoxy carbonates

#### *OO-tert-Butyl O-(2-ethylhexyl) monoperoxy carbonate (5).*

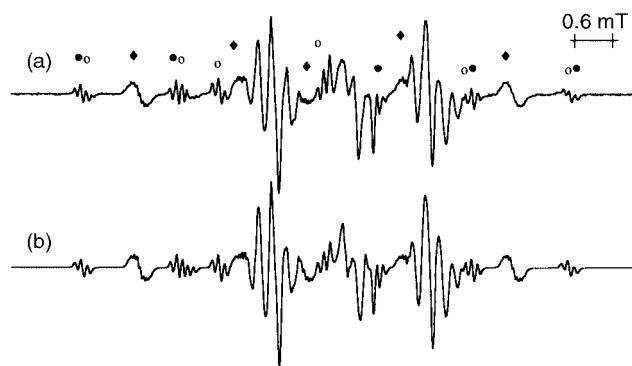
Thermolysis of **5** was undertaken in benzene in the presence of PBN- $d_{14}$  at 353 K; the resulting spectra consisted of a mixture of three adducts. The major adduct (56%) was that of radical **8** observed during the thermolysis of **4**. One of the remaining adducts was that of the methyl radical, formed *via*  $\beta$ -scission of the *tert*-butoxyl radical.<sup>20,23,25</sup> The remaining adduct was that of the “unassigned” adduct always observed in our experiments which releases the *tert*-butoxyl radical during peroxide thermolysis when employing either PBN or PBN- $d_{14}$  as a spin-trap.<sup>20,23,25</sup> Although there was no clear evidence for the adduct of the *tert*-butoxyl radical, its hyperfine parameters are such that its hyperfine lines would significantly overlap with those of other adducts. It is not possible, therefore, to categorically confirm the presence of this adduct. For hyperfine parameters of the adducts which have been clearly established see Table 1.

When the experiment was repeated at 353 K employing DMPO as the spin-trap the major adduct (83%) observed was that of the *tert*-butoxyl radical along with the adduct (17%) of radical **8** observed during the thermolysis of **4**. For the hyperfine parameters of these adducts see Table 2.

In order to examine any carbon-centred adducts present the thermolysis of **5** was also undertaken at 353 K in benzene, in the presence of TTBNB. The resulting spectrum was complex (see Fig. 2) but could be interpreted as a mixture of five adducts. One of these was the TTBNB aminoxyl adduct of the methyl radical (5%). Of the remaining adducts two were the aminoxyl (24%) and anilino (47%) adducts of a secondary carbon-centred radical and another anilino adduct (18%) of a tertiary carbon-centred radical. The fifth adduct was an aminoxyl adduct of a primary carbon-centred radical (6%). The hyperfine parameters of these various adducts are summarised in Table 3 and the nature of the radicals responsible for forming them is discussed further below.

#### *OO-tert-Butyl O-isopropyl monoperoxy carbonate (6).*

Thermolysis of **6** in benzene in the presence of PBN- $d_{14}$  over the temperature range 333–353 K resulted in spectra consisting of a mixture of three adducts. The major adduct (53%) had parameters again consistent with an alkoxy-carbonyloxy radical adduct and is assigned to that of the (isopropoxy)carbonyloxy radical (**9**). The remaining adducts were those of the *tert*-butoxyl radical (30%) along with the “unassigned” adduct



**Fig. 2** (a) The EPR spectrum, recorded at 353 K after 15 minutes thermolysis of **5** ( $1.6 \text{ mol dm}^{-3}$ ) in the presence of TTBNB ( $0.05 \text{ mol dm}^{-3}$ ) in benzene. (b) A computer simulation of (a), methylaminoxyl adduct (5%),  $\cdot\text{CH}_2\text{R}$  aminoxyl adduct (6%),  $\cdot\text{CHR}_2$  aminoxyl adduct (24%),  $\cdot\text{CHR}_2$  anilino adduct (47%) and  $\cdot\text{CR}_3$  anilino adduct (18%) (hyperfine parameters are summarised in Table 3). Where the main groups of hyperfine lines of an adduct do not overlap too severely  $\bullet$ ,  $\circ$  and  $\blacklozenge$  indicate groups of lines due to the methyl,  $\cdot\text{CH}_2\text{R}$  and  $\cdot\text{CHR}_2$  aminoxyl adducts respectively. The lines arising from the anilino adducts dominate the centre of the spectrum.

(17%). The hyperfine parameters of these various adducts are summarised in Table 1.

When the experiment was repeated at 353 K, in benzene, employing DMPO as the spin-trap the major adduct observed (81%) was that of the *tert*-butoxyl radical along with an adduct (19%) with parameters appropriate for an alkoxy-carbonyloxy radical which is assigned to that of radical **9**. The hyperfine parameters of the adducts are summarised in Table 2.

Finally the experiment was repeated in benzene at 353 K in the presence of TTBNB in order to examine any carbon-centred adducts present during thermolysis of **6**. As only a weak spectrum was obtained at this temperature the thermolysis temperature was raised to 383 K (employing chlorobenzene as solvent so as to access this higher temperature). The resulting spectrum consisted of a mixture of four adducts. One of these was the TTBNB aminoxyl adduct of the methyl radical (63%). Two further adducts were those of the aminoxyl (8%) and anilino (23%) adducts of a primary carbon-centred radical and another anilino adduct (6%) of a tertiary carbon-centred radical. No adducts of secondary carbon-centred radicals were observed in this experiment. The hyperfine parameters of these various adducts are again summarised in Table 3 and the nature of the carbon-centred radicals responsible for forming these adducts is discussed further below.

## The nature of the carbon-centred radicals trapped by TTBNB

We examine, first, the possible origins of the carbon-centred adducts observed during the thermolysis of **3** and **4** as the thermolysis of these two peroxides will not be affected by the presence and reactions of the *tert*-butoxyl radical (and the methyl radical derived from *tert*-butoxyl by  $\beta$ -scission).

It appears to be widely agreed that decarboxylation of alkoxy-carbonyloxy radicals is relatively slow.<sup>6-9,13,14</sup> Indeed, the unimolecular decay of the *n*-propoxycarbonyloxy radical in cyclohexane has been reported to occur almost entirely by intramolecular hydrogen atom abstraction.<sup>31</sup> Intramolecular hydrogen atom abstraction, therefore, presents one route for the formation of carbon-centred radicals. An alternative route is, of course, hydrogen atom abstraction from the parent peroxide by radicals present in the system, primarily the alkoxy-carbonyloxy radicals (this reaction is believed to be responsible for the observed induced decomposition).<sup>3-5,8,10-12</sup> It is important to appreciate when employing TTBNB as a spin-trap, that whilst it is easy to distinguish between the adducts of primary, secondary and tertiary carbon-centred radicals the EPR spectra do not indicate the exact nature of the individual radicals within each category. That is, it is not possible to say with certainty, from the hyperfine parameters alone, that the original radical was formed by abstraction from the parent peroxide or *via* an intramolecular hydrogen atom shift.

We deal, first, with the possible radicals derived from alkoxy-carbonyloxy radicals *via* intramolecular C to O 1,*x*-hydrogen shifts. 1,5 C to O hydrogen shifts are extremely widespread,<sup>32,33</sup> and Scheme 2 summarises the carbon-centred radicals that might be expected in our experiments following such shifts. The (4-*tert*-butylcyclohexyl)oxycarbonyloxy radical (**7**) and the (2-ethylhexyl)oxycarbonyloxy radical (**8**) would form secondary and tertiary carbon-centred radicals respectively. In view of the widespread occurrence of these reactions in radical chemistry we believe that 1,5-hydrogen shifts are a significant source of the adducts observed in our experiments.

In contrast to 1,5 shifts, 1,2-, 1,3- and 1,4- shifts are virtually unknown, although Walling and Padwa report that there is evidence for a 1,6 shift in some 1,1-dimethylalkoxy radicals.<sup>34</sup>

Since the tertiary carbon-centred radical trapped when employing **3** (and, possibly, the secondary carbon-centred radical trapped when employing **4**) would correspond to a 1,4 shift, we are forced to the conclusion that these radicals result from hydrogen atom abstraction from the parent peroxides. It is unlikely that they could be formed following hydrogen atom abstraction by alkoxy-carbonyloxy radicals from any reaction products as our experiments were undertaken during the very early stages of thermolysis when the concentration of reaction products would be very low. Preferential abstraction of the hydrogen atom from the C-H bond adjacent to oxygen is a familiar feature in radical chemistry and has been noted in reactions involving attack by the *tert*-butoxyl and hydroxyl radicals and by the sulfate radical anion.<sup>35,36</sup>

It is informative to compare the results obtained during the thermolysis of **4** with those obtained during the thermolysis of **5**. In these two experiments the same alkoxy-carbonyloxy radical is expected from both peroxides but in the latter case will be accompanied by the *tert*-butoxyl radical (and possibly also the methyl radical formed *via*  $\beta$ -scission of the *tert*-butoxyl radical).

A very significant change in the proportions of the adducts of the secondary and tertiary radicals (from 49 and 51% during the thermolysis of **4** to 71 and 18% during the thermolysis of **5** respectively) is observed. Since the same alkoxy-carbonyloxy radical (**8**) is present in both systems these changes must result from intermolecular hydrogen abstraction reactions of the *tert*-butoxyl (and/or the methyl radical) from the parent peroxide. Note that the methyl radical adduct (5%) and an adduct of a primary carbon-centred radical (6%) are also observed during the thermolysis of **5**. The methyl radical adduct arises from the

*tert*-butoxyl radical by  $\beta$ -scission. The primary carbon-centred radical must arise from abstraction of a methyl proton from the parent peroxide, whilst the changes in proportions of secondary and tertiary radicals present must result from intermolecular hydrogen atom abstraction of methylene and methine protons.

The proportions of adducts observed during the thermolysis of **6** are also interesting. The significant increase in the proportion of the methyl radical adduct indicates that the *tert*-butoxyl radical undergoes  $\beta$ -scission rather than abstraction in this system. In the case of this peroxide the results are more difficult to interpret as intermolecular hydrogen atom abstraction from the methyl group would result in an adduct whose EPR parameters would be indistinguishable from those of the adduct formed following a 1,5-H shift (see Scheme 2).

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