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ESR spin-trap study of radicals present during the thermolysis of some di-*tert*-alkyl peroxides

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ABSTRACT: The thermolysis mechanism of di-*tert*-butyl and di-*tert*-amyl peroxide was investigated in a variety of solvents employing electron spin resonance in collaboration with the spin-trapping technique. The *tert*-amyloxyl radical was trapped for the first time during the thermolysis of di-*tert*-amyl peroxide. The relative ease of β-scission of the *tert*-amyloxyl radical to give propan-2-one and butan-2-one was established as 32:1 at 382 K. In addition, competition reactions indicate that radicals derived from di-*tert*-butyl peroxide are *ca.* 5.5 times more reactive than those derived from di-*tert*-amyl peroxide towards hydrogen atom abstraction from toluene at 382 K. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: radicals; thermolysis; spin trap; di-*tert*-alkyl peroxides; ESR; β-scission

INTRODUCTION

Virtually all organic peroxides are thermally and photolytically sensitive owing to the weakness of the oxygen–oxygen bond. As a consequence, they act as a popular source of organic radicals and have been widely used as radical initiators in the synthesis of speciality polymers. Their thermal decomposition is influenced both by their structure and by the reaction conditions. A common initiator is di-*tert*-butyl peroxide, which decomposes at a convenient rate thermally above *ca.* 360 K to form the *tert*-butoxyl radical:

$$\mathrm{Me_3CO{-}OCMe_3} \xrightarrow{\Delta \text{ or } h\nu} 2\ \mathrm{Me_3CO^{\bullet}} \qquad (1)$$

tert-Alkoxyl radicals, however, tend to undergo β-scission which, in the case of the *tert*-butoxyl radical, yields the methyl radical:

$$\mathrm{Me_3CO^{\bullet}} \xrightarrow{\beta\text{-scission}} \mathrm{Me^{\bullet}} + \mathrm{Me_2CO} \qquad (2)$$

β-Scission of the *tert*-butoxyl radical is relatively slow. However, in the *tert*-amyloxyl radical the corresponding β-scission reaction is much faster,[1] with the result that a higher proportion of the corresponding alkyl radical is present. Since the ethyl radical is a poorer hydrogen atom abstractor than either methyl or *tert*-butoxyl radicals, hydrogen atom abstraction from a growing polymer chain is less likely.

As far as we are aware, a spin-trap study of the *tert*-amyloxyl radical has not been reported previously despite the considerable commercial importance of di-*tert*-amyl peroxide as an initiator. The aim of our research was, in the first instance, to investigate the possibility of observing the *tert*-amyloxyl radical, employing the spin-trapping technique, although its rapid β-scission reaction results in a much shorter lifetime than, for example, would be the case for the *tert*-butoxyl radical.

Three spin traps, *N*-*tert*-butyl-α-phenylnitrone (PBN), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) and 2,4,6-tri-*tert*-butylnitrosobenzene (TTBNB, sometimes also referred to as BNB) were selected for this study. Employing a family of spin traps presents an opportunity to trap and identify both carbon-centred and oxygen-centred radicals. For example, both PBN and DMPO are relatively efficient spin traps for oxygen-centred radicals compared with carbon-centred radicals, but the nature of the radical forming the adduct influences the N and H_{β} hyperfine splitting constants only to a small extent.[2] Consequently, although both PBN and DMPO can usually distinguish between $R^{\bullet}$, $RO^{\bullet}$ and $ROO^{\bullet}$ radicals, they tend to give little direct information on the nature of an individual radical within each category. In addition, we also employed PBN with both the phenyl and *tert*-butyl groups fully deuterated [*N*-*tert*-d_9-butyl-α-d_5-phenylnitrone (PBN-d_{14})]. The deuterated version of the spin trap tends to disclose more information on the nature of the original radical owing to a dramatic decrease in spectral linewidth. It is also useful in the interpretation of those spectra which comprise more than one adduct.

TTBNB, on the other hand, preferentially traps carbon-centred radicals with the original radical attacking the nitrogen atom of the nitroso group. Consequently, H_{β} hyperfine splitting now originates from the

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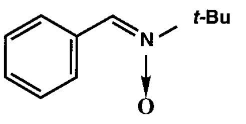
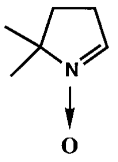
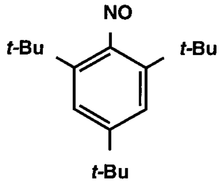


PBN



DMPO



TTBNB

original radical and, hence, the hyperfine structure from TTBNB adducts is far more informative. One problem sometimes observed with TTBNB, however, is that, if the trapped radical is bulky, steric factors often lead to the formation of the anilino adduct by attack at the oxygen atom of the nitroso group.[3] Consequently, the proportion of the anilino to nitroxyl adduct tends to progress: $^{\bullet}CH_3$ (almost entirely nitroxyl) < $^{\bullet}CH_2R$ (mixture) < $^{\bullet}CHR_2$ (mixture) < $^{\bullet}CR_3$ (almost entirely anilino).

Since many of the radicals produced by thermolysis of peroxides are efficient hydrogen atom abstractors, we employed toluene as the main solvent for most of our experiments. The TTBNB benzyl radical adduct acts as a useful reference adduct for the hydrogen atom-abstracting ability of the various radicals present during thermolysis. Where spectral interpretation was hindered by the presence of this adduct, either benzene or chlorobenzene was used as an alternative solvent.

EXPERIMENTAL

Materials

All materials were used as supplied. Di-*tert*-butyl peroxide (purity, as checked by NMR, >99.5%) and di-*tert*-amyl peroxide (purity, as checked by NMR, >99.5%) were supplied by Elf Atochem as liquids. All other chemicals, solvents and spin traps were obtained from Aldrich, except PBN-d_{14}, which was obtained from the OMRF Spin-Trap Source.

Preparation of solutions

The concentration of the spin traps was usually in the range 0.05–0.3 mol l^{-1} and the peroxide generally 0.05–0.15 mol l^{-1}. Before thermolysis all solutions were degassed with nitrogen for 5–10 min and the sample tube was then tightly sealed. A few samples were vacuum degassed, in which case the standard freeze–thaw procedure was employed. All samples for ESR 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 ± 1 K). Spectra were recorded at a modulation amplitude of 0.02 mT with spectrum accumulation over 16 scans.

Thermolysis was undertaken for up to 60 min (varying with the peroxide and the reaction temperature) and spectra were recorded, as required, at various times during this period. It was found convenient to undertake thermolysis for the required period but then to record the spectrum at *ca.* 293 K. This procedure often the enhanced spectral resolution and also prevented further peroxide decomposition during spectral measurement. Improvements in spectral resolution were also sometimes obtained if the solution was further degassed with nitrogen before measurement.

Spectrum simulations were undertaken employing either a program written at Lancaster University (by P.G.M) or PEST WinSim[4] (an NIEHS Public EPR Software Tool). The hyperfine splitting constants obtained from these spectral simulations are considered to be accurate to ±0.005 mT.

RESULTS AND DISCUSSION

The main aim of our investigation of the di-*tert*-alkyl peroxides was to trap, for the first time, the *tert*-amyloxyl radical. Di-*tert*-butyl peroxide was included in our study to establish the correct conditions for trapping of alkoxyl and alkyl radicals during thermolysis.

Experiments employing DMPO as spin trap

Di-*tert*-butyl peroxide decomposes thermally at a convenient rate for ESR study between *ca.* 353 and 383 K. The spectrum in toluene shows a clean 1 : 1 doublet of 1 : 1 doublets of 1 : 1 : 1 triplets with hyperfine parameters clearly assignable to the DMPO adduct of the *tert*-butoxyl radical (Table 1).

Employing di-*tert*-amyl peroxide, in the temperature range 353–381 K, the spectra consist of a mixture of two adducts. The first has slightly different parameters to those assigned to the *tert*-butoxyl adduct above (Table 1). We are confident that these parameters can be assigned to the *tert*-amyloxyl adduct of DMPO. The second adduct decays almost instantaneously at room temperature and contributes only *ca.* 2% to the total spectrum intensity (for parameters, see Table 1). By

Table 1. Hyperfine splitting constants for the ESR spectra of the DMPO adducts observed during the thermolysis of di-*tert*-alkyl peroxides, recorded at room temperature, together with literature data

Radical	Solvent	a(N) (mT)	$a(H_\beta)$ (mT)	$a(H_\gamma)$ (mT)	Ref.
$Me_3CO^\bullet$	Toluene	1.312	0.759	0.194	5
	Toluene	1.308	0.744	0.168	6
	Toluene	1.308	0.745	0.185	This work[a]
	Benzene	1.317	0.781	0.179	This work[a]
	Chlorobenzene	1.323	0.838	0.169	This work[a]
$Me_2(Et)CO^\bullet$	Toluene	1.313	0.746	0.186	This work[b]
	Benzene	1.318	0.744	0.184	This work[b]
	Chlorobenzene	1.298	0.690	0.167	This work[b]
$Et^\bullet$	Benzene	1.420	2.049		7
	Benzene	1.514	2.014		This work[b]
	Toluene	1.411	2.054		This work[b]
	Chlorobenzene[c]	1.435	1.995		This work[b]

[a] Employing di-*tert*-butyl peroxide.
[b] Employing di-*tert*-amyl peroxide.
[c] At 373 K.

comparison with the literature data in Table 1, we assign this contribution to the ethyl radical adduct of DMPO. Similar results were obtained from experiments in benzene and chlorobenzene.

Experiments employing PBN and PBN-d_{14} as spin traps

All of these experiments gave mixtures of adducts. The spectrum obtained following the thermolysis of di-*tert*-butyl peroxide in toluene with PBN as spin trap consists of a mixture of at least three significant adducts assigned to those of the *tert*-butoxyl, methyl and benzyl radicals. Their hyperfine parameters are summarized in Table 2. The benzyl radical arises by hydrogen atom abstraction by the *tert*-butoxyl radical from toluene. In order to eliminate this latter adduct, the experiment was repeated in benzene and chlorobenzene when, surprisingly, mixtures of three adducts were again obtained in both solvents. Two of these adducts are those of the *tert*-butoxyl and methyl radicals [Fig. 1(a); for hyperfine parameters, see Table 2]; the former is assigned by comparison with the parameters obtained for the *tert*-amyloxyl adduct (see below), but the nature of the third adduct remains unassigned. Its hyperfine parameters suggest the possibility of an oxygen-centred radical yet experiments in thoroughly vacuum degassed or oxygen-saturated solutions changed the proportions of the three adducts only slightly. This seems to eliminate the possibility of the conversion of $Me^\bullet$ to $MeO^\bullet$ within the solution. Also, the parameters are not consistent with PBN peroxyl radical adducts, which tend to have lower a(N) (*ca.* 1.30–1.35 mT) and lower $a(H_\beta)$ (*ca.* 0.10–0.15 mT) values.[9,13]

A further possibility is the formation of the 2-methylallyloxyl radical via hydrogen atom abstraction from the parent peroxide (Scheme 1). Unfortunately, the hyperfine parameters of the 2-methylallyloxyl radical adduct of PBN are unknown. If this is a major reaction pathway then both of the $^\bullet CH_2R$ radicals formed in this

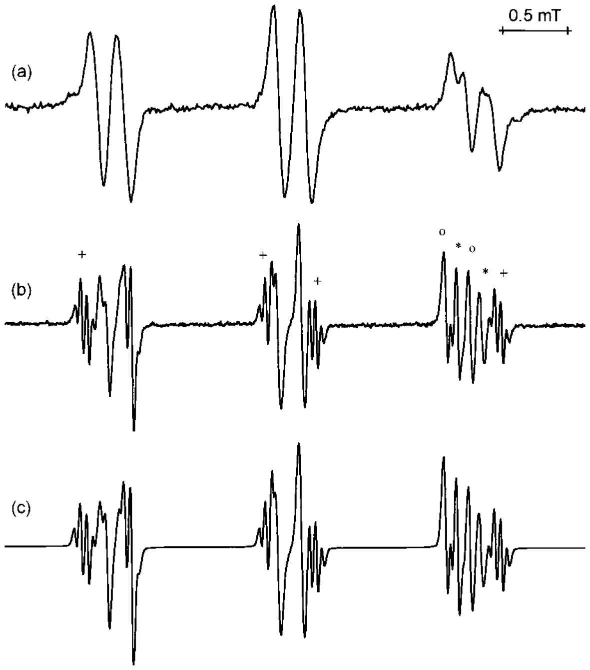


Figure 1. The ESR spectra, recorded at room temperature, following (a) the thermolysis of di-*tert*-butyl peroxide (0.200 mol dm^{-3}) for 17 min at 353 K in the presence of PBN (0.100 mol dm^{-3}) and (b) the thermolysis of di-*tert*-butyl peroxide (0.200 mol dm^{-3}) for 15 min at 353 K in the presence of PBN-d_{14} (0.010 mol dm^{-3}), both in benzene a solvent. Where they do not overlap with lines from other adducts, + indicates lines arising from the methyl adduct, o lines arising of the *tert*-butoxyl adduct and * lines arising from the unassigned adduct. (c) A computer simulation of (b); percentages as given in the text and hyperfine parameters as given in Table 2.

Table 2. Hyperfine splitting constants for the ESR spectra of the PBN and PBN-d_{14} adducts observed during the thermolysis of di-*tert*-alkyl peroxides, recorded at room temperature, together with literature data

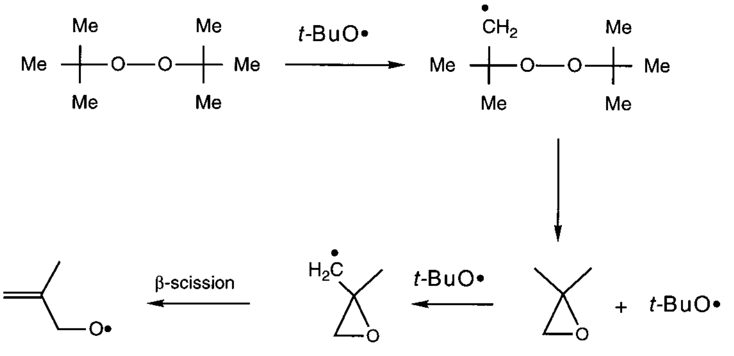
Spin trap	Radical	Solvent	a(N) (mT)	$a(H_\beta)$ (mT)	$a(H_\gamma)$ (mT)	Ref.
PBN	$Me_3CO^\bullet$	Benzene	1.422	0.195		8
		Benzene	1.411	0.183		9
		Benzene	1.363	0.195		This work[a]
		Toluene	1.362	0.172		10
		Toluene	1.370	0.190		This work[a]
		Chlorobenzene[c]	1.366	0.198		This work[a]
	$Me_2(Et)CO^\bullet$	Toluene	1.368	0.192		This work[b]
		Benzene	1.375	0.208		This work[b]
		Chlorobenzene	1.374	0.205		This work[b]
	$Me^\bullet$	Toluene	1.494	0.363	0.047 (3H)[d]	11
		Toluene	1.480	0.355		This work[a]
		Benzene	1.491	0.357		This work[a]
		Chlorobenzene[c]	1.490	0.352		This work[a]
	$Et^\bullet$	Toluene	1.458	0.322	0.049 (2H)[d]	11
		Toluene	1.460	0.335		This work[b]
		Benzene	1.460	0.330		This work[b]
		Chlorobenzene	1.465	0.328		This work[b]
	Benzyl	Toluene	1.443	0.250		12
		Toluene	1.455	0.240		This work[a]
	Unassigned	Benzene	1.440	0.183		This work[a]
		Chlorobenzene[c]	1.448	0.208		This work[a]
PBN-d_{14}	$Me_3CO^\bullet$	Benzene	1.367	0.194		This work[a]
	$Me_2(Et)CO^\bullet$	Benzene	1.376	0.194		This work[b]
	$Me^\bullet$	Benzene	1.490	0.355	0.048 (3H)	This work[a]
	$Et^\bullet$	Benzene	1.462	0.334	0.043 (2H)	This work[b]
	Unassigned	Benzene	1.437	0.182		This work[a]

[a] Employing di-*tert*-butyl peroxide.
[b] Employing di-*tert*-amyl peroxide.
[c] At 362 K.
[d] Observed by ENDOR.

scheme would need to be short-lived as no $^\bullet CH_2R$ TTBNB adducts are observed (see below). Also, the parent molecule is present in only low concentrations so significant yields of the 2-methylallyloxyl radical are not expected. There is also a possibility of reaction with solvent molecules.

When the latter experiment was repeated (in benzene) employing PBN-d_{14}, the much enhanced resolution clearly reveals the mixture of three adducts [Fig. 1(b)]. These adducts again include methyl (32%), but with the 3Hγ coupling now evident (for hyperfine parameters, see Table 2). One of the remaining adducts has been assigned to that of the *tert*-butoxyl radical (27%) with the other (41%) attributed to the unassigned radical.

The spectra obtained during the thermolysis of di-*tert*-amyl peroxide in either toluene, benzene or chlorobenzene are time dependent. During the early stages of thermolysis the hyperfine parameters are consistent



Scheme 1

with those expected for the *tert*-amyloxyl adduct of PBN (see Table 2 for parameters). However, during later stages of thermolysis the Et$^{\bullet}$ adduct dominates (see Table 2 for parameters).

The spectra obtained during the thermolysis of di-*tert*-amyl peroxide, in benzene employing PBN-d_{14} as spin trap show only two adducts. One of these is that of ethyl, the major species in the early stages of the reaction, with the $2\mathrm{H}_{\gamma}$ coupling now evident (for hyperfine parameters, see Table 2). The remaining adduct has been assigned to that of the *tert*-amyloxyl radical (see Table 2 for parameters).

The proportion of Et$^{\bullet}$ radical adduct in experiments involving di-*tert*-amyl peroxide exceeds that of Me$^{\bullet}$ radical adduct in experiments involving di-*tert*-butyl peroxide. This is in accord with the much faster β-scission [Eqn (2)] in the alkoxyl radical derived from the former. No significant benzyl radical adduct concentration is observed in experiments with di-*tert*-amyl peroxide in toluene, which is in accord not only with the faster β-scission reaction but the poorer hydrogen atom-abstracting ability of Et$^{\bullet}$ compared with both $\mathrm{Me_3CO}^{\bullet}$ and Me$^{\bullet}$.

Experiments employing TTBNB as spin trap

Experiments employing TTBNB as spin trap during the thermolysis of the di-*tert*-alkyl peroxides in toluene allow the benzyl adduct, formed by hydrogen atom abstraction, to act in a competitive reaction with respect to the β-scission of the corresponding *tert*-alkoxyl radical.

Thermolysis of di-*tert*-butyl peroxide after 5 min, at 382 K, gives a spectrum consisting of a mixture of two nitroxyl adducts derived from carbon-centred radicals [Fig. 2(a)] and an anilino adduct. The nitroxyl adducts are those of the methyl radical, derived via β-scission of *tert*-butoxyl, and the expected benzyl radical, obtained by hydrogen atom abstraction from the solvent (for hyperfine parameters, see Table 3). Occasionally, small amounts of the *tert*-butoxyl radical adduct were observed in these experiments (for parameters, see Table 3). The anilino adduct has parameters [$a(\mathrm{N}) = 1.168$, $a(2\mathrm{H}) = 0.230$ and $a(2\mathrm{H}_m) = 0.176$ mT at room temperature and $a(\mathrm{N}) = 1.161$, $a(2\mathrm{H}) = 0.220$ and $a(2\mathrm{H}_m) = 0.170$ mT at 382 K] consistent with those expected for the benzyl radical adduct. The proportion of methyl to total benzyl obtained by spectral simulation [Fig. 2(b)] is *ca.* 1 : 6 at 382 K.

Although literature data are not available for the rate constant for hydrogen atom abstraction from toluene and for the β-scission of *t*-BuO$^{\bullet}$ at our reaction temperature, the data that are available[16,17] indicate that the two reactions should be very competitive.

At the same temperature, and with the same rate of radical production, thermolysis of di-*tert*-amyl peroxide in the presence of TTBNB after 5 min gives a mixture of three nitroxyl adducts, derived from carbon-centred radicals, and an anilino adduct. The nitroxyl adducts can be readily identified as those derived from the ethyl radical, derived via β-scission of *tert*-amyloxyl, the benzyl radical obtained by hydrogen atom abstraction from the solvent and, perhaps surprisingly, the methyl radical (but only *ca.* 1%) [Fig. 2(c); for hyperfine parameters, see Table 3]. The anilino adduct has parameters [$a(\mathrm{N}) = 1.177$, $a(2\mathrm{H}) = 0.237$ and $a(2\mathrm{H}_m) = 0.184$ mT at room temperature and $a(\mathrm{N}) = 1.179$, $a(2\mathrm{H}) = 0.225$ and $a(2\mathrm{H}_m) = 0.182$ mT at 382 K] which, although similar to those of the benzyl adduct, are

Table 3. Hyperfine splitting constants (determined at room temperature except where noted) for nitroxyl TTBNB adducts observed during the thermolysis of di-*tert*-alkyl peroxides, together with literature data

Radical	Solvent	$a(\mathrm{N})$ (mT)	$a(\mathrm{H}_{\beta})$ (mT)	$a(2\mathrm{H}_m)$ (mT)	Ref.
Me$^{\bullet}$	Benzene	1.303	1.233 (3H)	0.081	14
	Toluene	1.291	1.225 (3H)	0.078	This work[a,b]
	Toluene[c]	1.303	1.210 (3H)	0.075	This work[a,b]
	Chlorobenzene	1.303	1.240 (3H)	0.082	This work[a]
	Chlorobenzene[c]	1.311	1.220 (3H)	0.080	This work[a,b]
t-BuO$^{\bullet}$	*tert*-Butyl acetate	2.460		0.090	15
	Toluene[c]	2.410		0.090	This work[a]
Benzyl	Benzene	1.362	1.475 (2H)	0.083	14
	Toluene	1.360	1.475 (2H)	0.083	This work[a,b]
	Toluene[c]	1.363	1.394 (2H)	0.074	This work[a,b]
Et$^{\bullet}$	Benzene	1.346	1.799 (2H)	0.083	14
	Toluene	1.340	1.787 (2H)	0.077	This work[b]
	Toluene[c]	1.344	1.705 (2H)	0.079	This work[b]
	Chlorobenzene	1.340	1.810 (2H)	0.078	This work[b]
	Chlorobenzene[c]	1.354	1.718 (2H)	0.080	This work[b]

[a] Employing di-*tert*-butyl peroxide.
[b] Employing di-*tert*-amyl peroxide.
[c] At 382 K.

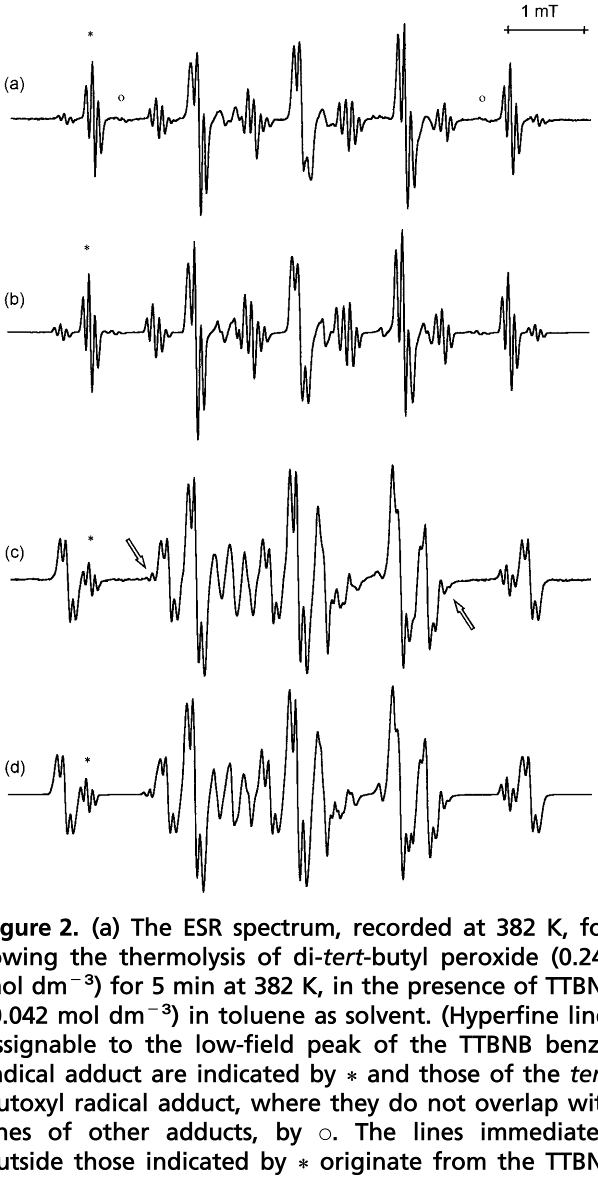


Figure 2. (a) The ESR spectrum, recorded at 382 K, following the thermolysis of di-*tert*-butyl peroxide (0.241 mol dm^{-3}) for 5 min at 382 K, in the presence of TTBNB (0.042 mol dm^{-3}) in toluene as solvent. (Hyperfine lines assignable to the low-field peak of the TTBNB benzyl radical adduct are indicated by $*$ and those of the *tert*-butoxyl radical adduct, where they do not overlap with lines of other adducts, by $\circ$. The lines immediately outside those indicated by $*$ originate from the TTBNB methyl radical adduct.) (b) A computer simulation of (a), TTBNB benzyl radical adduct 60%, TTBNB methyl radical adduct 14%, TTBNB *tert*-butoxyl adduct 1% and the TTBNB benzylanilino adduct 25%; hyperfine parameters as given in Table 3. (c) The ESR spectrum, recorded at 382 K, following the thermolysis of di-*tert*-amyl peroxide (0.120 mol dm^{-3}) for 5 min at 382 K in the presence of TTBNB (0.042 mol dm^{-3}) in toluene as solvent. (The low-field peak of the TTBNB benzyl radical adduct is indicated by $*$, the lines immediately outside it originate from the TTBNB ethyl radical adduct and arrows indicate the lines arising from the methyl adduct where they do not overlap with lines from other adducts.) (d) A computer simulation of (c), TTBNB benzyl radical adduct 7%, TTBNB ethyl radical adduct 67%, TTBNB ethylanilino adduct 25% and TTBNB methyl adduct 1%; hyperfine parameters as given in Table 3.

assigned to the ethyl adduct. The proportion of total ethyl to total benzyl obtained by spectral simulation [Fig. 2(d)] is *ca.* 14:1 at 382 K. This change in the alkyl to benzyl adduct ratio between the *tert*-butoxyl and *tert*-amyloxyl radicals is again consistent with a much faster β-scission reaction in the case of the latter and with the poorer hydrogen atom-abstracting ability of Et$^•$ compared with both Me$_3$CO$^•$ and Me$^•$.

The observation of the methyl radical adduct of TTBNB during the thermolysis of di-*tert*-amyl peroxide is interesting. We propose that it arises from the alternative β-scission of the *tert*-amyloxyl radical to give butan-2-one. The thermolysis was repeated in chlorobenzene, under the same experimental conditions as above, in order to eliminate the benzyl adduct [Fig. 3(a)], when the proportion of methyl adduct to total ethyl adduct was established, by spectrum simulation, to be 1:49. Hence it is possible to estimate the rates of the two competitive β-scission reactions from our experiments. We compared the efficiency of trapping of the methyl radical (via thermolysis of di-*tert*-butyl peroxide) and the ethyl radical (via thermolysis of di-*tert*-amyl peroxide) by TTBNB in chlorobenzene. By adjusting the peroxide concentrations so that the flow of radicals into the system at 382 K is identical, double integration of the spectrum gives the relative efficiency of trapping of these two radicals after 5 min of thermolysis. Our experiments indicate that the efficiency of trapping of ethyl to methyl by TTBNB is *ca.* 3:1. Allowing for the fact that two β-scissions lead to butan-2-one but only one to propan-2-one, we obtain a value of 1:32 for the relative β-scission loss of methyl compared with that of ethyl. This value is in remarkable agreement with that obtained by Suyama *et al.*[18] (1:33) by product yield, determined by GLC and/or GC–MS, following thermolysis.

Experiments under identical conditions also indicate that the radicals derived from di-*tert*-butyl peroxide

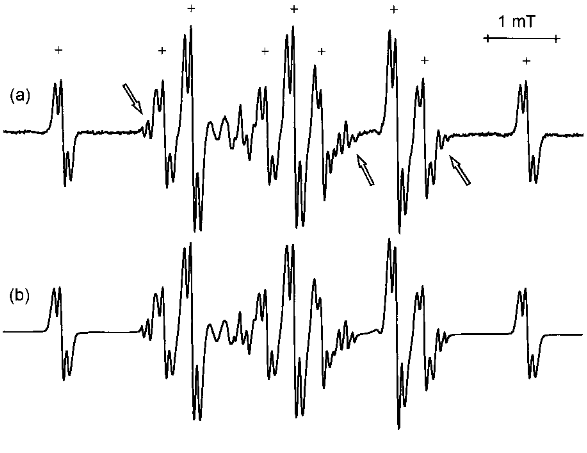


Figure 3. (a) The ESR spectrum, recorded at 382 K, following the thermolysis of di-*tert*-amyl peroxide (0.103 mol dm^{-3}) for 5 min at 382 K in the presence of TTBNB (0.0347 mol dm^{-3}) in chlorobenzene as solvent. (Hyperfine lines assignable to the TTBNB nitroxyl ethyl radical adduct are indicated by $+$ and those of the methyl radical adduct, where they do not overlap with lines of other adducts, by an arrow. (b) A computer simulation of (a), TTBNB nitroxylethyl radical adduct 82%, TTBNB anilinoethyl adduct 16% and the TTBNB methyl adduct 2%; hyperfine parameters as given in Table 3.

abstract hydrogen atoms from toluene *ca.* 5.5 times more efficiently than those derived from di-*tert*-amyl peroxide at 382 K.

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