The thermal decomposition mechanisms of tert-alkyl peroxypivalates studied by the nitroxide radical trapping technique

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Received April 22, 1999

The thermolysis of a series of tert-alkyl peroxypivalates 1 in cumene has been investigated by using the nitroxide radical-trapping technique. tert-Alkoxyl radicals generated from the thermolysis underwent the unimolecular reactions, β-scission, and 1,5-H shift, competing with hydrogen abstraction from cumene. The absolute rate constants for β-scission of tert-alkoxyl radicals, which vary over 4 orders of magnitude, indicate the vastly different behavior of alkoxyl radicals. However, the radical generation efficiencies of 1 varied only slightly, from 53 (R = Me) to 63% (R = Bu), supporting a mechanism involving concerted two-bond scission within the solvent cage to generate the tert-butyl radical, CO₂, and an alkoxyl radical. The thermal decomposition rates of tert-alkyl peroxypivalates 1 were influenced by both inductive and steric effects [Taft–Ingold equation, log(k₉) = (0.97 ± 0.14)Σα* − (0.31 ± 0.04)Σr₂, was obtained].

Introduction

Peroxyl esters are among the most commonly used free radical initiators for the radical polymerization of olefinic compounds such as styrene and (meth)acrylates.1 They are also useful radical sources for kinetic studies in radical chemistry,2 tert-Alkyl peroxypivalates, such as tert-butyl peroxypivalate 1a, are some of the most useful peroxyl esters in polymer manufacturing, and there have been several reports concerning their decomposition mechanisms.3,4 Peroxyl esters 1 thermolyze homolytically via a concerted two-bond scission with no cage return (k₋₁ = 0 in Scheme 1), as demonstrated by the quantitative formation of carbon dioxide and the independence of the decomposition rate on solvent viscosity.5a

The decomposition involves a proportion of cage reaction, in which stable compounds are formed directly from the transition state 2, e.g., isobutylene and tert-butyl alcohol formed by disproportionation and di-tert-butyl ether by radical recombination (eqs 2 and 3 in Scheme 1) for peroxyl 1a,6b However, there has been one report suggesting a transition state 4 involving a concerted “three-bond” scission for the thermolysis of 1 (Scheme 2).4 This decomposition mechanism was based on the product ratio of acetone to the corresponding alcohol RCMe₂OH without any consideration of the production of the alcohol by other reactions.5 It was concluded that the thermolysis rates of 1 were enhanced by both hyperconjugative and inductive stabilizing effects and that steric effects did not contribute to the rate enhancement. Recently, Hendrickson et al. have reported7 that both steric and electronic factors influence the decomposition rate constants of t-alkyl tert-buty1 peroxides 5.

In this study, the thermolysis of a series of tert-alkyl peroxypivalates 1a–g in cumene has been investigated by using the radical trapping technique employing 1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxyl (T), focusing on the detailed behavior of tert-alkoxyl radicals and the decomposition mechanism. The technique was developed by the CSIRO and has been mostly used to investigate initiation mechanisms in free radical polymerization.7 The aminoxyl T reacts with carbon-centered radicals (but not oxygen-centered radicals) at close to diffusion-
controlled rates to produce stable alkoxyamines. In our previous work, we have shown that the thermolysis of tert-alkyl peroxypivalates is not affected by the presence of T and equimolar amounts of tert-butyl and tert-alkoxyl radicals 3 are generated.

Results and Discussion

Thermal Decomposition Products of 1 in the Presence of T. tert-Alkyl peroxypivalates 1a–g were prepared by the reaction of pivaloyl chloride with tert-alkyl hydroperoxides in alkaline solution according to the literature procedure. The thermal decomposition of 1 (0.040 M) in cumene as solvent in the presence of T (0.040 M) was carried out in vacuo at 60 °C for 3.0 h. Alkoxyamines formed by trapping of the radicals resulting from the reactions of the primary radicals with cumene were analyzed by HPLC, HPLC–MS, and NMR.

[Scheme 1]

The tentative structure of 10f is proposed on the basis of the MS and 1H NMR. A tiny amount of an isomer of 10f was also detected. The relative yields of tert-alkoxyamine radical-derived products 7–10 to the yield of tert-butoxamine 6 (taken as 100%) are shown in Table 1, and a postulated reaction mechanism for the decomposition of tert-alkoxy radicals is shown in Scheme 3.

It can be seen from Table 1 that the total yields of alkoxyamines 7–10 were entirely comparable to the yield of 6 in all runs, showing that the thermolysis of 1 generates an equimolar amount of tert-buty1 and tert-alkoxy radicals. A slightly lower yield of alkoxyamine tert-Butyl radicals generated from the thermolysis of 1 were immediately trapped by T to form tert-butoxyamine 6 \( [k_T(\text{Bu}^2) = \text{ca. 9 } \times 10^{8} \text{ M}^{-1} \text{s}^{-1}] \). On the other hand, a variety of products were formed from the reaction of tert-alkoxy radicals. Alkoxyamines 7 and 8 were derived from hydrogen abstraction from cumene by tert-alkoxy radicals (it is unlikely that any of the alkyl radicals are involved in significant H-abstraction from cumene under these reaction conditions, since the rate of trapping is extremely fast). No other cumene-derived products were detected. Phenylalkyl radicals such as 2-phenylpropyl radicals could rearrange via 1,2-phenyl migration; however, this reaction is too slow (\( \leq 10^4 \text{s}^{-1} \)) to compete with trapping under the reaction conditions. Alkoxyamines 9 and 10 were derived from the alkyl radicals formed by \( \beta \)-scission and by rearrangement of tert-alkoxy radicals, respectively. Unfortunately, an insufficient amount of 10f was available for complete characterization by NMR. The tentative structure of 10f is proposed on the basis of the MS and 1H NMR. A tiny amount of an isomer of 10f was also detected. The relative yields of tert-alkoxy radical-derived products 7–10 to the yield of tert-butoxyamine 6 (taken as 100%) are shown in Table 1, and a postulated reaction mechanism for the decomposition of tert-alkoxy radicals is shown in Scheme 3.

reaction rate constant for hydrogen abstraction from tert-alkoxyl radicals (3c, 3d, and 3f) in Cumene at 60°C.

Table 2. Relative Rates of 1,5-Hydrogen Shift versus β-Scission of tert-Alkoxyalkyl Radicals (3c, 3d, and 3f) in Cumene at 60°C

<table>
<thead>
<tr>
<th>tert-alkoxy radical (3)</th>
<th>R in 3</th>
<th>δ-hydrogen</th>
<th>k_{L5H}/k_β(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3c</td>
<td>Pr&lt;i&gt;^n</td>
<td>3 primary</td>
<td>1.3</td>
</tr>
<tr>
<td>3d</td>
<td>Me₂C₂H₂</td>
<td>9 primary</td>
<td>1.2</td>
</tr>
<tr>
<td>3f</td>
<td>c-C₅H₁₁</td>
<td>2 secondary</td>
<td>0.03</td>
</tr>
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</table>

with the literature value of 6.3 M⁻¹ at 60°C in benzene.14 Similarly, the individual reactivities of the α- and β-hydrogens of cumene toward abstraction by 3a were determined. The values, corrected for the statistical factor, were $k_{α-H}/k_β(Me) = 7.7$ and $k_{α-H}/k_β(Me) = 0.060$ M⁻¹ (per C–H bond), respectively, and the relative reactivity of β-H to α-H of cumene was $k_{β-H}/k_{α-H} = 0.008$ (per C–H).15 Thus, the reactivity of the β-H of cumene seems to be very comparable to that of tert-butylnitrobenzene ($k_{β-H}/k_{α-H} = 0.050$ M⁻¹ at 60°C (per C–H bond)).

β-Scission of tert-Alkoxyalkyl Radicals. In contrast to the tert-butyl radical, other tert-alkoxy radicals 3b–g underwent significant β-scission to form alkoxyamines 9b–g as the major reaction pathway (eq 8 in Scheme 3). For 3c and 3d other pathways are equally important (i.e., 1,5-hydrogen shift) as shown in Table 2. The relative rates of β-scission to hydrogen abstraction from cumene, $k_β(R)/k_β(Me)$ for tert-alkoxy radicals 3 were obtained from the ratio of 9(7 + 8). Assuming that $k_β(R)$ for any tert-alkoxy radical has approximately the same value,15 the absolute rate constants for β-scission of tert-alkoxy-

Table 1. Relative Yields of tert-Alkoxy Radical-Derived Products in the Thermolysis of 1 in Cumene in the Presence of T at 60°C

<table>
<thead>
<tr>
<th>run</th>
<th>tert-alkoxy radicals (3)</th>
<th>R in 3</th>
<th>7</th>
<th>8</th>
<th>9a</th>
<th>9b–g</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a</td>
<td>Me</td>
<td>94.0</td>
<td>4.3</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3a</td>
<td>Me</td>
<td>92.8</td>
<td>4.3</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3b</td>
<td>Et</td>
<td>38.8</td>
<td>1.6</td>
<td>0.9</td>
<td>58.7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3c</td>
<td>Pr&lt;i&gt;^n</td>
<td>22.4</td>
<td>0.8</td>
<td>0.6</td>
<td>32.8</td>
<td>43.3</td>
</tr>
<tr>
<td>5</td>
<td>3d</td>
<td>Me₂C₂H₂</td>
<td>2.7</td>
<td>0.1</td>
<td>0.7</td>
<td>43.1</td>
<td>53.5</td>
</tr>
<tr>
<td>6</td>
<td>3e</td>
<td>Pr&lt;i&gt;^n</td>
<td>4.8</td>
<td>0.2</td>
<td>0.5</td>
<td>94.5</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3f</td>
<td>c-C₅H₁₁</td>
<td>0.6</td>
<td>trace</td>
<td>0.1</td>
<td>96.8</td>
<td>2.5&lt;i&gt;c&lt;/i&gt;</td>
</tr>
<tr>
<td>8</td>
<td>3g</td>
<td>Bu&lt;i&gt;^i</td>
<td>0.2</td>
<td>trace</td>
<td>0.1</td>
<td>99.7</td>
<td></td>
</tr>
</tbody>
</table>

<i>a</i> [T]₀ = 0.040 M, [T]₀ = 0.040 M, reaction time: 3.0 h. <i>b</i> Reaction time: 65 h. <i>c</i> The total yield of two isomers (2.3% + 0.2%).

7 was observed in a longer reaction time (run 2 in Table 1), which might be due to lower stability of 7 under the reaction conditions.12 The major reaction with tert-butyl radicals 3a was hydrogen abstraction from cumene. β-Scission to form methyl radicals was a very minor process. On the other hand, tert-alkoxy radicals 3b–g underwent significant β-scission, generating alkyl radicals to form the corresponding alkoxyamines 9b–g. In addition, alkoxyl radicals 3c, 3d, and 3f underwent intermolecular hydrogen abstraction (1,5-H shift) to form 10c, 10d, and 10f, respectively.

Hydrogen Abstraction from Cumene by tert-Alkoxyalkyl Radicals. Cumene underwent hydrogen abstraction by tert-alkoxy radicals, resulting in alkoxyamines 7 and 8 (eqs 5 and 6 in Scheme 3). The overall reactivity of cumene toward hydrogen abstraction by tert-alkoxy radicals was estimated by using the competing fragmentation reaction to form methyl radicals (eq 7) as a “free radical clock”<sup>13</sup>. From the ratio of the product yield (7 + 8)/9a in run 1 and taking the concentration of cumene as 7.2 M, the value of $k_β/β(Me)$ for tert-alkoxy radicals 3a was calculated to be 8.0 M⁻¹, where $k_β$ is an overall reaction rate constant for hydrogen abstraction from cumene (per molecule). Our value is in good agreement with the literature value of 6.3 M⁻¹ at 60°C in benzene.<sup>14</sup>

(12) The half-life of the analogue alkoxyamine to 7, 1-(2-methyl-2-phenylethoxy)-2,2,6,6-tetramethyl-4-oxopiperidine, has been reported to be ca. 3.6 h at 100°C in degassed tert-butylbenzene (Howard, J. A.; Tait, J. C. J. Org. Chem. 1978, 43, 4279–4283).
(15) Although Walling and Jacknow<sup>16</sup> have obtained a much higher value ($k_{β-H}/k_{α-H} = 0.038$) from the yields of 2-chloro-2-phenylpropane 11 (81.3%) and 1-chloro-2-phenylpropane 12 (18.7%) in the photochlorination of cumene by t-BuOCl at 40°C, it was later shown that the reaction involved a chlorine atom chain,<sup>17</sup> which would lead to a product distribution of 11:12 = ca. 70:30.<sup>18</sup>
(19) The value was calculated from the Arrhenius equation $\ln[A/(\text{H abstraction})/A(\beta-\text{scission})] = -4.22 \text{ M}^{-1} \times E_0(\beta-\text{H abstraction}) - E_0(\beta-\text{scission}) \times 24.7 \text{ kJ mol}^{-1}$. Howard, J. A.; Scialano, J. C. Landolt-Börnstein, New Series, Radial Reaction Rates in Solution; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Part d, pp 107–108.
radicals, \( k_{\beta} (R) \), were estimated from the concentration of cumene (7.2 M) and the reported value of \( k_{\alpha} \) for \( 3a \) (= 8.7 \times 10^{5} \text{ M}^{-1} \text{ s}^{-1})^{21} \). The resulting values of \( k_{\beta} (R) \) increased in the following order: \( 3a \) (1.1 \times 10^{6} \text{ s}^{-1}) < \( 3c \) (8.9 \times 10^{5} \text{ s}^{-1}), \( 3b \) (9.1 \times 10^{5} \text{ s}^{-1}) < \( 3d \) (9.6 \times 10^{5} \text{ s}^{-1}) < \( 3e \) (1.2 \times 10^{6} \text{ s}^{-1}) < \( 3f \) (1.0 \times 10^{6} \text{ s}^{-1}) < \( 3g \) (3.1 \times 10^{5} \text{ s}^{-1}).

It is obvious that the rate constants depend greatly on the nature of the R group in tert-alkyl radicals, varying by 4 orders of magnitude over the series \( 3a - g \). Kochi has mentioned that the rates for \( \beta \)-scission depend on the stability of the leaving alkyl radicals.\(^{22} \) Our value of \( k_{\beta} \) for \( 3a \) was very similar to the literature value of 0.7 \times 10^{6} \text{ s}^{-1} \) at 60 °C.\(^{23} \) However, it seems unlikely that the rate constant for neopentyl radical elimination from \( 3d \) is significantly higher (more than 10 times) than that of n-propyl radical elimination from \( 3c \) and that of ethyl radical elimination from \( 3b \). The elimination rates to produce neopentyl and n-propyl radicals in the \( \beta \)-scission of the alkoxyl radical \( \text{13} \) have been reported to be the same at 0 °C.\(^{24} \)

This contradiction could be caused by the above assumption of the same values of \( k_{\alpha} \). We have previously reported that the lower reactivity of alkoxyl radical \( \text{3d} \) is due to the steric hindrance around the oxygen radical caused by the methyl groups on the \( \gamma \)-carbon as shown in the preferred conformer \( \text{14} \) of \( \text{3d} \).\(^{25} \)

Similarly, if there is significant steric hindrance around the oxygen in other tert-alkoxyl radicals (although with the exception of \( \text{3g} \), it is expected to be less than that in \( \text{3d} \)), the above \( k_{\alpha} \) values become smaller correspondingly.

It is also worth noting that the rate constants for \( \beta \)-scission of \( 3a - g \) are less than the rate constant for diffusion of a radical from a solvent cage (estimated to be of the order of \( 10^{10} \text{ s}^{-1} \)).\(^{30,25} \) Therefore, it is unlikely that \( \beta \)-scission occurs via the transition state \( 4 \) in the solvent cage as shown in Scheme 2. Further evidence against the transition state \( 4 \) is provided by radical efficiencies (see the following text).

1,5-Hydrogen Shift of tert-Alkoxyl Radicals. tert-Alkoxyl radicals \( \text{3c, 3d, and 3f} \) underwent the alternative unimolecular reaction, a 1,5-H shift, in addition to...
of the cage reaction (100 - f)%, for 1a in cumene was estimated to be ca. 50%.\textsuperscript{30,31,32}

It is noteworthy that the efficiency does not change very much by changing the alkyl group R in 1 despite the very different behavior of these alkoxyl radicals. Kiefer et al.\textsuperscript{26} and Leffler\textsuperscript{27} have studied radical efficiency and mentioned that in a concerted decomposition, more intervening molecular fragments between the caged radicals cause higher radical generation efficiency because the reaction of caged radicals is hindered by such molecules, thus allowing more of the radicals to escape.

The value of f for di-tert-butyl monoperoxyxalate 15, which decomposed via a concerted two-bond scission and in which the caged radicals are separated by one CO\textsubscript{2} molecule, was reported to be ca. 0.50.\textsuperscript{30} By contrast, the decomposition of di-tert-butyl peroxyxalate 16, which forms two intervening molecules of CO\textsubscript{2}, resulted in 93–99% radical efficiency.\textsuperscript{26,29} Thus, in the thermal decomposition of peroxyxalates 1, the transition state 4 (which would result in two intervening molecules) can probably be excluded; i.e., the extent of C–R bond cleavage is not advanced in the transition state. The small but significant increase of f for 1d and 1g compared to the tert-butyl analogue 1a might be attributed to the correspondingly longer distance between radical pairs (tert-butyl and tert-alkoxyl radicals) caused by steric repulsion, i.e., radical combination should be slightly less for 1d and 1g.

**Decomposition Mechanism of tert-Alkyl Peroxyxalates in Cumene.** The decomposition rate constants and the activation parameters of the series of 1 [six electron-donating alkyl substituents studied above, one weaker electron-donating (R = PhCH\textsubscript{2}) and one electron-withdrawing substituent (R = Ph)] in cumene are summarized in Table 4. It can be seen from Figure 3 that a linear free energy relationship was observed in a plot of $\Delta S^\ddagger$ versus $\Delta H^\ddagger$, which suggests that the fragmentation mechanism does not change across the series.\textsuperscript{34} The

<table>
<thead>
<tr>
<th>1</th>
<th>R</th>
<th>T (°C)</th>
<th>$k_d \times 10^6$ (s\textsuperscript{-1})</th>
<th>$\Delta H^\ddagger$ (kJ mol\textsuperscript{-1})</th>
<th>$\Delta S^\ddagger$ (J mol\textsuperscript{-1} K\textsuperscript{-1})</th>
<th>$\text{rel } k_d$</th>
<th>$\Sigma \alpha^+$</th>
<th>$\Sigma \Sigma_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Me</td>
<td>60</td>
<td>2.95</td>
<td>118.3 ± 1.1</td>
<td>22.7 ± 6.7</td>
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<td>-2.10</td>
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<tr>
<td>1b</td>
<td>Et</td>
<td>60</td>
<td>3.51</td>
<td>114.9 ± 1.2</td>
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<td>Pr\textsuperscript{e}</td>
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<td>3.37</td>
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<td>18.0 ± 4.8</td>
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<td>1g</td>
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<td>24.4 ± 2.7</td>
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<td>65</td>
<td>10.32</td>
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<td>22.5 ± 1.3</td>
<td>= 3.50</td>
<td>+0.025</td>
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\textsuperscript{a}[1b] = 0.05 M. See ref 4 for 1a–e.h and ref 30 for 1. \textsuperscript{b} The relative thermolysis rate at 60 °C. \textsuperscript{c} The sum of the substituent constant of $\alpha^+$, 6,11,32 \textsuperscript{d} Hancock's corrected steric constant calculated by eq 8 in ref 33. \textsuperscript{e} Extrapolated.
Thermal Decomposition Mechanisms of tert-Alkyl Peroxypivalates

Thermalysis rates of peroxypivalates 1 increased in the order 1a < 1c < 1b < 1e < 1f < 1h < 1g < 1i. The fact that peroxyester 1i decomposes 3.5 times faster than 1a can be explained by a polarized transition state. However, it is clear from Figure 4 that the Taft equation does not fully explain the rate acceleration of all the peroxides. A small deviation of 1h (R = PhCH2) from a linear line passing through the points of 1a and 1i indicates that the resonance effects on the alkyl group stabilities are not important, which can be understood by little possibility of the transition states as mentioned above.

It is worthy of note that the values of ΔH* and ΔS* for two peroxyesters with bulky alkyl groups [R = Me2CCH2 (1d) and Bu (1g)] are lower than those of others. The trend in ΔH* and ΔS* has been explained in terms of frozen bond rotations in the transition state. That is, in the concerted two-bond scission of peroxyesters, both of the σ bonds to the CO2 moiety need to be approximately antiperiplanar, which results in the loss of rotational freedom in the carbonyl to oxygen bond and, hence, in a lower entropy (Figure 5).

It is very important to note that in the antiperiplanar conformer the steric repulsion between oxygen in carbonyl group and RCMe2 groups becomes significant due to the reduced distance between carbonyl oxygen and oxygen in alkoxy groups and may cause the loss of rotational freedom in an additional bond. We suggest that the lower values of ΔS* for peroxyesters are a result of the correspondingly restricted O–O bond rotation caused by the steric hindrance around the oxygen in alkoxy groups as mentioned above. This may indicate that the steric factors control the thermalysis rates of 1. Hancock's corrected steric constants (ΔE‡) separate the hyperconjugation effect from Taft's steric substituent constant (E). The plots of the logarithm of the thermalysis constants of peroxyesters with electron-donating alkyl substituents 1a–1g versus E‡ of R(CH3)2C

Figure 4. Taft plot for the thermalysis of tert-alkyl peroxyesters in cumene.

Figure 5. Antiperiplanar conformer of 1.

Figure 6. Correlation between relative rate constants for the thermalysis of 1 and Hancock corrected steric constants (ΔE‡).

Figure 7. Correlation of log(rel k0) with 0.97Σσ* – 0.31ΔE‡.

Thermalysis rates of peroxypivalates 1 increased in the order 1a < 1c < 1b < 1e < 1f < 1h < 1g < 1i. The fact that peroxyester 1i decomposes 3.5 times faster than 1a can be explained by a polarized transition state. However, it is clear from Figure 4 that the Taft equation does not fully explain the rate acceleration of all the peroxides. A small deviation of 1h (R = PhCH2) from a linear line passing through the points of 1a and 1i indicates that the resonance effects on the alkyl group stabilities are not important, which can be understood by little possibility of the transition states as mentioned above.

It is worthy of note that the values of ΔH* and ΔS* for two peroxyesters with bulky alkyl groups [R = Me2CCH2 (1d) and Bu (1g)] are lower than those of others. The trend in ΔH* and ΔS* has been explained in terms of frozen bond rotations in the transition state. That is, in the concerted two-bond scission of peroxyesters, both of the σ bonds to the CO2 moiety need to be approximately antiperiplanar, which results in the loss of rotational freedom in the carbonyl to oxygen bond and, hence, in a lower entropy (Figure 5).

It is very important to note that in the antiperiplanar conformer the steric repulsion between oxygen in carbonyl group and RCMe2 groups becomes significant due to the reduced distance between carbonyl oxygen and oxygen in alkoxy groups and may cause the loss of rotational freedom in an additional bond. We suggest that the lower values of ΔS* for peroxyesters are a result of the correspondingly restricted O–O bond rotation caused by the steric hindrance around the oxygen in alkoxy groups as mentioned above. This may indicate that the steric factors control the thermalysis rates of 1. Hancock's corrected steric constants (ΔE‡) separate the hyperconjugation effect from Taft's steric substituent constant (E). The plots of the logarithm of the thermalysis constants of peroxyesters with electron-donating alkyl substituents 1a–1g versus E‡ of R(CH3)2C


groups as shown in Figure 6 give a good correlation with a slope of $-0.29$ ($r = 0.968$). These results indicate that steric effects are a major contributor to the rate acceleration for 1. Utilization of the Taft–Ingold equation [log $(\text{rel} \, k_d) = \rho \cdot \Delta \sigma + \delta \Delta \Sigma$, $c$] gives $\rho = 0.97 \pm 0.14$ and $\delta = -0.31 \pm 0.04$ ($r = 0.974$) for the thermolysis of peroxyesters 1 (Figure 7). The positive value of $\rho$ shows that an electron-withdrawing substituent $R$ in the tert-alkyl group accelerates the decomposition. Thus, the thermolysis rate of tert-alkyl peroxyprivalates 1 are influenced by both polar (i.e., electronic) and steric effects, although a previous report has excluded any contribution from steric effects to the rate enhancement.6

Conclusions

In this study, the reactions of tert-alkyl radicals and the thermolysis mechanism of 1 were studied by the nitroxide trapping technique. The absolute rate constants for $\beta$-scission of tert-alkyl radicals, which vary over 4 orders of magnitude, indicate the vastly different behavior of alkoxyl radicals. However, even 1,1,2,2-tetramethylpropoxy radicals 3g are relatively stable in the solvent cage, with a $k_d$ less than the rate constant for diffusion from the cage. The radical generation efficiencies of a series of peroxyesters 1 varied slightly, from 53 ($R = Me$) to 63% ($R = Bu^i$). These values are not sufficiently high to support the notion that $\beta$-scission occurs in the solvent cage. Moreover, for $R$ groups such as $R = MeOCH_2$ or Pr$^n$, the major reaction observed is a 1,5-H shift, not $\beta$-fragmentation. Thus, the data presented here support a homolysis mechanism involving concerted two-bond scission within a solvent cage (Scheme 1), not three-bond $\beta$-scission (Scheme 2), as has been suggested previously. This work has clearly shown that the thermolysis rates of a series of tert-alkyl peroxyprivalates 1 correlate with $\rho \cdot \Delta \sigma + \delta \Delta \Sigma$, which indicates that the thermolysis rates are accelerated by an electron-withdrawing substituent in the tert-alkyl group, i.e., both inductive effects and steric effects are important in the thermolysis reaction. Among the tert-alkyl peroxyprivalates 1 studied here, 1d ($R = MeOCH_2$) and 1g ($R = Bu^i$) showed the highest decomposition rates and radical generation efficiencies, mainly as a result of steric effects.

Experimental Section

Materials. Cumene was washed with concentrated $H_2SO_4$ and water, dried over anhydrous $Na_2SO_4$, distilled at atmospheric pressure, and stored in a refrigerator ($-20\, ^°C$). Tert-Alkyl peroxyprivalates 1 were prepared by the literature procedure. 3-Phenylbutyryl chloride was obtained from the chlorination of 3-phenylbutyric acid by thionyl chloride. Spectroscopic data of 3-phenylbutyryl chloride: $\delta_{400}$ (CDCl$_3$) 1.39, (d, 3H, Me), 2.8 (s, 2H, C=CH), 4.7 (m, 2H, ArH); $\delta_{125}$ (CDCl$_3$) 1.84 (CH$_2$); 126.7, 127.7 (C-2, C-4), 128.8 (C-3), 144.0 (C-1), 172.4 (C=O).

Preparation of Di(3-Phenylbutyryl) Peroxide. 3-Phenylbutyryl chloride (9.13 g, 0.05 mol) in toluene (15 mL) was added dropwise over a period of 25 min with stirring at 0–5 °C to a mixture of 30% hydrogen peroxide (3.40 g, 0.03 mol) and 15% KOH (20.57 g, 0.05 mol). Stirring was continued for 30 min at 0–5 °C, and then toluene was added to the mixture. The organic layer was washed with water and dried over anhydrous $Na_2SO_4$ and MgSO$_4$. After the evaporation of the solvent under vacuum, a product of 6.1 g was obtained. The purity was determined by iodometric titration using isopropanol alcohol and acetic acid as the solvent and saturated sodium iodide as the source of iodide. The purity and yield of the hydperoxide were 98.8% and 74.0%, respectively. The structure was consistent with its NMR: $\delta_{123}$ (CDCl$_3$) 1.42, (d, 6H, 2 x CH$_3$), 7.02–7.32 (m, 4H, 2 x CH$_2$), 3.3–3.5 (m, 2H, 2 x CH$_2$); $\delta_{122}$ (CDCl$_3$) 1.51 (CH$_3$), 36.5 (CH$_2$), 38.6 (CH$_3$), 126.7, 126.9 (C-2, C-4), 128.8 (C-3), 144.8 (C-1), 167.9 (C=O). The half-lives of the analogous peroxides, 3-phenylpropionyl peroxide and 3-methyl-3-phenylbutyryl peroxide, were reported to be ca. 28 h at 55.8 °C and ca. 30 h at 55.0 °C, respectively.8

General Method. The general procedure for carrying out the radical trapping experiments and for the quantitative analysis of the reaction products has been described previously.7,9 The products of the trapping experiments were in each case isolated by preparative HPLC and characterized by spectroscopic methods.

Kinetic Experiment. The thermolysis of 1 (0.055 M), which was carried out in degassed cumene at several temperatures (40–70 °C), was measured by monitoring its disappearance by iodometric titration and was found to satisfy first-order kinetics at all of the temperatures. The decomposition rate constants and the activation parameters at 60 °C were calculated from Arrhenius plots.

Trapping Experiments. In a typical experiment, a solution of 1 (0.040 M) and T (0.040 M) in cumene was degassed by three successive freezing–pump–thaw cycles to 10$^{-4}$ mmHg. The reaction vessel was then sealed under vacuum and heated at 60 ± 0.1 °C for 3.0 h. The majority (ca. 90%) of excess cumene was then removed under reduced pressure prior to analysis by reversed-phase HPLC with methanol/water mixtures as the eluent.

Radical Generation Efficiency. A solution of 1 (0.050 M) and excess T (0.110 M) in cumene was degassed. The reaction vessel was then sealed under vacuum and heated at 60 °C for 6 h ( 10 half-lives of T). The majority (ca. 90%) of excess cumene was removed under reduced pressure, which was followed by the analysis of the residue by HPLC. Several runs were carried out for each peroxyester, and the values of $f$ were determined from the average yield of tert-butoxyamine 6 based on peroxyester consumed. A blank experiment was carried out in order to test the stability of 6. Thermolysis of 6 (0.050 M) in cumene in the presence of T (0.050 M) indicated no significant decomposition of 6 after 6.5 h at 60 °C.

Products and New Compounds. The HPLC-separated products were identified by electrospray mass spectrometry. Products 6, 7, 9, and 10 (except for 10f) were also identified by co-chromatography with authentic samples.7,9–11

The new compound 8 was isolated by preparative HPLC and characterized by NMR. An authentic sample of alkoxylamine 8 was prepared by the thermolysis of di(3-phenylbutyryl) peroxide in the presence of T in benzene. Thus, a solution of di(3-phenylbutyryl) peroxide (97.9 mg, 0.30 mmol) and T (95.1 mg, 0.50 mmol) in benzene (6 mL) was degassed and heated at 60 °C for 89 h. After evaporation of the solvent under vacuum, alkoxylamine 8 was isolated from the residue by preparative HPLC.

The tentative structure of 10f was proposed by means of the MS and $^1$H NMR, and it is the most likely on the basis of the other products observed in the reaction of other tert-alkyl radicals 3c and 3d. However, the $^1$H NMR spectrum of alkoxylamine 10f was complex, and an insufficient amount of 10f was available for complete characterization by NMR, which usually requires proton decoupling experiments, DEPT, and

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COSY relay experiments to confirm assignments. The four strong methyl signals of the isoindoline moiety had chemical shifts that overlapped those of the cyclohexyl ring protons, so that determination of coupling constants and connectivity were difficult. Another isomer of 10f was detected by HPLC and HPLC−MS, but in lower yield (0.2%) than 10f (2.3%). It ran slightly faster on HPLC (90% methanol/water mixture as eluent).

Spectroscopic data for new compounds and some known compounds are listed below [ring CH3 refers to methyl substituents on the isoindole and primed carbon numbers refer to the monosubstituted phenyl ring (for 7 and 8) or the cyclohexyl ring (for 9f)].

2-(1-Methyl-1-phenylethoxy)-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole 7: δH(CD3OD) 26.3, 29.2 and 30.6 [4 ring CH3 and 2 (CH3)2CO], 67.0 (C-1, C-3), 80.3 [(CH3)2CON], 122.6 (C-4, C-7), 127.4 (C-2’), 127.9 (C-4’), 128.2 (C-5, C-6), 128.8 (C-3’), 146.6 (C-3a, C-7a), 149.5 (C-1).

2-(2-Phenylpropoxy)-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole 8: δH(CDCl3) 1.43, 1.44 and 1.48 [3 br s, 15H, 4 x ring CH3 and 2 x (CH3)2CO], 3.05−3.15 [m, 1H, (CH3)2CH], 4.0−4.2 [m, 2H, CH2ON], 7.10−7.15 (m, 2H, ArH), 7.22−7.32 (m, 2H, ArH), 7.34−7.40 (m, 5H ArH); δC(CDCl3) 18.7 (CH3CH), 24−31 (br hump, 4 x ring CH3), 39.8 (CH3CH), 67.3 (C-1, C-3), 83.3 (CH2ON), 121.5 (C-4, C-7), 126.3 (C-2’, C-4’), 127.2 (C-5, C-6), 128.3 (C-3’), 144.9 (C-1’), 145.4 (C-3a, C-7a); m/z 332 (M + Na)+, 310 (M + H)+.

2-Cyclohexyloxy-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole 9f: δH(CDCl3) 1.1−2.2 (m, 2H, aliphatic H), 3.72 (m, 1H, CHON), 7.05−7.15 (m, 2H, ArH), 7.20−7.28 (m, 2H, ArH); δC(CDCl3) 24.6 (C-3’), 25.3 and 30.5 (2 br s, 4 x ring CH3), 67.4 (C-1, C-3), 81.8 (CHON), 121.6 (C-4, C-7), 127.1 (C-5, C-6), 145.5 (C-3a, C-7a); m/z 296 (M + Na)+, 274 (M + H)+.

2-cis-[3-(1-Hydroxy-1-methylethyl)cyclohexyloxy]-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole 10f: δH(CD3OD) 1.1 and 1.26 [2 s, 2 x CH3, (CH3)2COH], 1.35 and 1.51 (2 br s, 2 x CH2 and CH (cyclohexyl) and OH), 0.8−2.4 [m, 10H, 4 x CH2 and CH (cyclohexyl) and OH], 3.95−4.15 (m, 1H, CHON), 7.04−7.15 (m, 2H, ArH), 7.18−7.30 (m, 2H, ArH); m/z 354 (M + Na)+, 332 (M + H)+.

Acknowledgment. We thank Ms. Catherine Rowen for carrying out preliminary investigations. Financial assistance from NOF Corp., Griffith University, and the Australian Research Council is also acknowledged.

J O990680S