Evidence for the Formation of Thermally Unstable Dialkyl Trioxide Molecules using Electron Spin Resonance Spectroscopy

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U.v. photolysis of solutions of di-t-butyl peroxide in oxygenated cyclopropane or dichlorodifluoromethane at low temperatures (*ca.* 140 K and below) produces no detectable concentration of free radicals. On cessation of photolysis a single-line e.s.r. spectrum assigned to the t-butylperoxyl radical begins to appear and reaches a steady intensity within a few minutes. The e.s.r. signal is destroyed immediately upon resuming the photolysis and the cycle can be repeated several times. These observations are explained by the formation of the primary–tertiary dialkyl trioxide, $MeOOOBu^t$, which is thermally unstable even at 140 K. One of the possible modes of scission of the dialkyl trioxide generates the t-butylperoxyl radical, which is stable at these temperatures in the absence of photolysis. It is shown that dialkyl trioxides can also be formed at low temperatures in more reactive solvents, *e.g.* toluene, and that their presence may lead to erroneous measurements of free-radical kinetics.

EVIDENCE for the formation of di-t-butyl polyoxides at low temperature (*ca.* 190 K) by the reaction of t-butyl hydroperoxide with lead tetra-acetate,[1] iodosobenzene, or iodosobenzene diacetate,[2] in solution in methylene chloride, or by the reaction of ozone with solid potassium t-butoxide,[3] has been obtained from the measurement of oxygen evolution as the products were warmed above 190 K. Bartlett and Guaraldi [4] have obtained evidence for the existence of both di-t-butyl trioxide and tetraoxide by e.s.r. studies. A solution of di-t-butyl diperoxycarbonate in methylene chloride was photolysed at 77 K and the concentration of t-butylperoxyl radicals was monitored by e.s.r. From the changes in concentration as the temperature was varied they concluded that below 200 K the tetraoxide was stable and in equilibrium with t-butylperoxyl radicals [reaction (1)]. The di-t-butyl trioxide was stable below 240 K but dissociated above this temperature [reaction (2)].

$$Bu^tOOOOBu^t \rightleftharpoons 2Bu^tOO^{\cdot} \qquad (1)$$

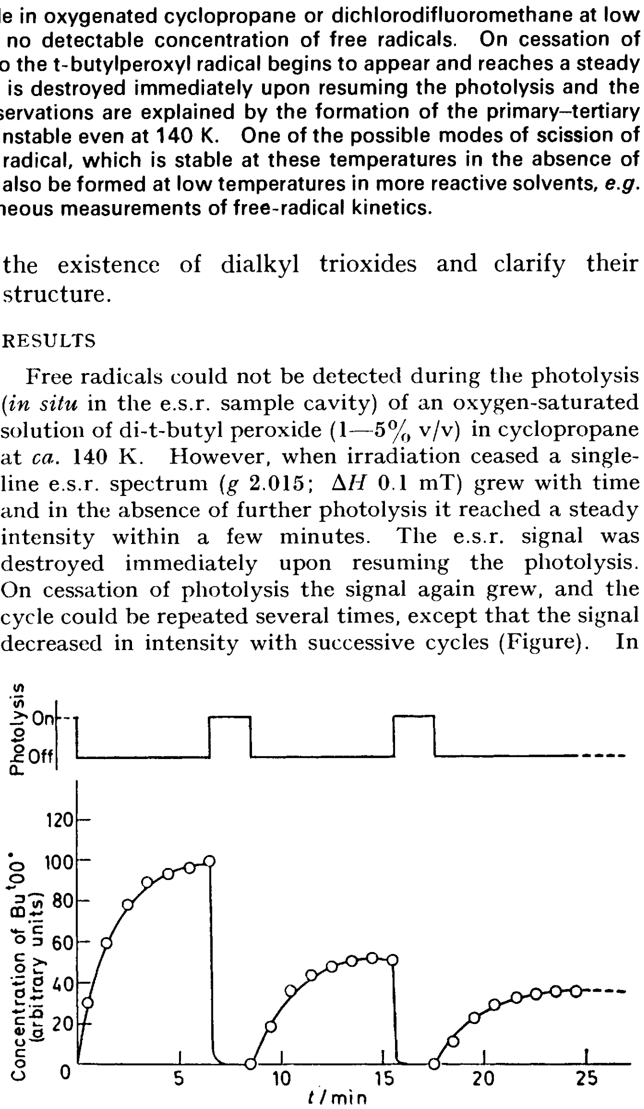
$$Bu^tOOOBu^t \longrightarrow Bu^tOO^{\cdot} + {}^{\cdot}OBu^t \qquad (2)$$

The existence of dialkyl tetraoxides in solution at low temperatures is now well established and thermodynamic data for the equilibrium between a dialkyl tetraoxide and the corresponding alkylperoxyl radicals are available.[5,6] In comparison far less is known about the properties of dialkyl trioxides.

In an earlier communication [7] we presented evidence from e.s.r. studies for the formation of a crossed dialkyl trioxide $ROOOBu^t$ (R = p- or s-alkyl) during the photolysis of an oxygenated solution of di-t-butyl peroxide in cyclopropane at low temperatures (*ca.* 140 K). In contrast to di-t-butyl trioxide, this crossed trioxide was thermally unstable even at 140 K and dissociated to form t-butylperoxyl radicals. Based on this observation, Howard [8] has described an elegant experiment for the production of the t-butylperoxyl radical ($Bu^{t16}O^{17}O^{\cdot}$) specifically labelled with ^{17}O in the terminal position. The proposed mechanism strongly suggests the formation of a crossed secondary-tertiary dialkyl trioxide. In this paper we present further evidence for the existence of dialkyl trioxides and clarify their structure.

RESULTS

Free radicals could not be detected during the photolysis (*in situ* in the e.s.r. sample cavity) of an oxygen-saturated solution of di-t-butyl peroxide (1—5% v/v) in cyclopropane at *ca.* 140 K. However, when irradiation ceased a single-line e.s.r. spectrum (g 2.015; ΔH 0.1 mT) grew with time and in the absence of further photolysis it reached a steady intensity within a few minutes. The e.s.r. signal was destroyed immediately upon resuming the photolysis. On cessation of photolysis the signal again grew, and the cycle could be repeated several times, except that the signal decreased in intensity with successive cycles (Figure). In further experiments it was found that the maximum signal could be restored to its original intensity by re-oxygenating the solution. Thus the successive reduction of the maximum intensity reached in the absence of photolysis was caused by the depletion of dissolved oxygen in the sample.



Effect of photolysis on the growth and decay of t-butylperoxyl radicals at 140 K in cyclopropane

If, after the signal had reached its maximum in the dark, the temperature of the sample was raised to *ca.* 170 K, then a further increase in intensity occurred On cooling back to *ca.* 140 K the intensity decreased to its original dark value indicating that the radical was in equilibrium with a dimer. A further, but irreversible, increase in the intensity of the signal occurred when the temperature was raised to >240 K. The line width also increased markedly at higher temperatures (*ca.* 1 mT at 240 K).

To ascertain whether the solvent was involved in the reactions leading to the formation of the free-radical species, the experiments were repeated using a non-hydrogenic solvent, dichlorodifluoromethane, m.p. 115 K. When an oxygenated solution of di-t-butyl peroxide (1—5% v/v) in dichlorodifluoromethane was subjected to the same experimental sequence, then exactly the same behaviour was observed as that for cyclopropane.

DISCUSSION

The photolysis of an oxygenated solution of di-t-butyl peroxide in an alkane has been used previously to produce a variety of t-alkylperoxyl radicals and s-alkylperoxyl radicals[9,10] [reactions (3)—(5)]. However cyclopropane has a very high C–H bond strength (422 kJ mol^{-1})[11] and thus it is not surprising that the same method does not yield a detectable concentration of cyclopropylperoxyl radicals. (Indeed because of its low reactivity towards t-butoxyl radicals, cyclopropane has been used extensively as a solvent in many e.s.r. studies.[12,13])

$$\mathrm{Bu^tOOBu^t} \xrightarrow{h\nu} 2\,\mathrm{Bu^tO^{\bullet}} \qquad (3)$$

$$\mathrm{Bu^tO^{\bullet}} + \mathrm{RH} \longrightarrow \mathrm{Bu^tOH} + \mathrm{R^{\bullet}} \qquad (4)$$

$$\mathrm{R^{\bullet}} + \mathrm{O_2} \longrightarrow \mathrm{ROO^{\bullet}} \qquad (5)$$

The spectral parameters (*g* value and line-width) indicate that the e.s.r. spectrum arises from a t-alkylperoxyl radical. The stability at low temperatures and the increase in line-width at higher temperatures support this assignment. The existence of an equilibrium with a dimer in the temperature range 120—170 K is also typical of t-alkylperoxyl radicals.[5,6] On the basis of earlier work[7,8] the radical is identified as the t-butylperoxyl radical. The growth in the spectrum of the t-butylperoxyl radical in the absence of light indicates that the radical is being generated by the thermal decomposition of an unstable non-radical intermediate, which we consider to be a dialkyl trioxide, ROOOBu^t.

Mechanism of Dialkyl Trioxide Formation.—The most plausible route for the formation of the dialkyl trioxide during photolysis is by the cross-termination of the t-butoxyl radical, Bu^{t}O$^{\bullet}$, with an alkylperoxyl radical, ROO$^{\bullet}$ [reaction (6)].

$$\mathrm{ROO^{\bullet}} + \mathrm{Bu^tO^{\bullet}} \longrightarrow \mathrm{ROOOBu^t} \qquad (6)$$

The identical behaviour, observed in cyclopropane and dichlorodifluoromethane, shows that the alkyl group, R, is not derived from the solvent. Therefore the substituent must be derived from the di-t-butyl peroxide and a possible source is hydrogen abstraction by the photolytically generated t-butoxyl radicals [*i.e.* R = $(CH_3)_3COOC(CH_3)_2CH_2$–]. However, when the experiments were repeated using [$^2H_{18}$]di-t-butyl peroxide virtually the same behaviour was observed as with the non-deuteriated peroxide. On cessation of photolysis, the spectrum of the t-butylperoxyl radical grew to a comparable intensity. (Note that no observable differences would be expected between the e.s.r. spectra of [$^1H_9$]-Bu^{t}OO$^{\bullet}$ and [$^2H_9$]-Bu^{t}OO$^{\bullet}$). The absence of any observable isotope effect at these low temperatures (*ca.* 140 K) indicates that hydrogen-atom abstraction from di-t-butyl peroxide does not contribute significantly to formation of the dialkyl trixide, ROOOBu^t, and thus to the generation of t-butylperoxyl radicals.

The usual reaction pathway for t-butoxyl radicals in solution is hydrogen abstraction from the solvent [reaction (4)]. However, in the absence of a good hydrogen donor the t-butoxyl radicals can either undergo β-scission to form methyl radicals[14] and acetone [reaction (7)] or add to oxygen to form the t-butyltrioxyl radical[15,16] [reaction (8)].

$$\mathrm{Bu^tO^{\bullet}} \longrightarrow \mathrm{Me^{\bullet}} + \mathrm{Me_2C{=}O} \qquad (7)$$

$$\mathrm{Bu^tO^{\bullet}} + \mathrm{O_2} \rightleftharpoons \mathrm{Bu^tOOO^{\bullet}} \qquad (8)$$

Decomposition of t-butoxyl radicals by β-scission is well established at higher temperatures[14] and it has also been found[17] to occur in a rigid matrix at 77 K. The methyl radicals, formed by β-scission, will react rapidly with oxygen to form methylperoxyl radicals [reaction (9)], which in turn can react with t-butoxyl radicals to give the dialkyl trioxide, MeOOOBu^t [reaction (10)]. This dialkyl trioxide can decompose in two ways, either to regenerate methylperoxyl radicals or to generate t-butylperoxyl radicals [reaction (10)]. The absence of an e.s.r. spectrum of methylperoxyl radicals is not surprising as their self-termination is several orders of magnitude faster than that for t-butylperoxyl radicals.

$$\mathrm{Me^{\bullet}} + \mathrm{O_2} \longrightarrow \mathrm{MeOO^{\bullet}} \qquad (9)$$

$$\mathrm{MeOO^{\bullet}} + \mathrm{Bu^tO^{\bullet}} \rightleftharpoons \mathrm{MeOOOBu^t} \rightleftharpoons \mathrm{MeO^{\bullet}} + \mathrm{Bu^tOO^{\bullet}} \qquad (10)$$

The formation of t-butylperoxyl radicals in the absence of photolysis shows that the crossed dialkyl trioxide, MeOOOBu^t, is thermally unstable even at 140 K. It will also be decomposing during photolysis but then the t-butylperoxyl radicals that are formed will react rapidly with t-butoxyl radicals to form the symmetrical di-t-butyl trioxide [reaction (11)]. This trioxide is thermally stable below 240 K and will not act as a source of radicals at 140 K. However it is unstable above 240 K and the observed increase in intensity of the e.s.r. spectrum around this temperature is attributed to the dissociation of di-t-butyl trioxide.

$$\mathrm{Bu^tOO^{\bullet}} + \mathrm{Bu^tO^{\bullet}} \longrightarrow \mathrm{Bu^tOOOBu^t} \qquad (11)$$

An alternative route to methyl t-butyl trioxide could be by the reaction of t-butyltrioxyl radicals with methyl radicals [reaction (12)]. The t-butyltrioxyl radical is thought to have been detected during the photolysis of neat di-t-butyl peroxide,[15,16] though we were unable to detect the radical in comparable experiments. Ingold

$$\mathrm{Me^{\bullet}} + \mathrm{Bu^tOOO^{\bullet}} \longrightarrow \mathrm{MeOOOBu^t} \qquad (12)$$

and his co-workers[18] have also been unable to prepare this radical at low temperatures. Thus while this route cannot be excluded it seems unlikely to be a major source of the trioxide.*

Of the other possible species present dialkyl peroxides would be stable at 140 K. As already mentioned di-t-butyl trioxide is also stable below 240 K. At these low temperatures di-t-alkyl tetraoxides are in equilibrium with the corresponding peroxyl radicals.[5,6] But even if a non-equilibrium concentration of the tetraoxide was produced during photolysis, the rate of dissociation to peroxyl radicals[6] would be very fast compared with the observed growth rate, which occurs over a period of several minutes.

We conclude that the results are best interpreted in terms of the formation of the dialkyl trioxide, $MeOOOBu^t$, which is unstable even at *ca.* 140 K. The overall reaction sequence is summarised in the Scheme.

$$\begin{aligned}
Bu^tOOBu^t &\xrightarrow{h\nu} 2Bu^tO^\bullet \\
Bu^tO^\bullet &\longrightarrow Me^\bullet + Me_2C{=}O \\
Me^\bullet + O_2 &\longrightarrow MeOO^\bullet \\
MeOO^\bullet + Bu^tO^\bullet &\rightleftharpoons MeOOOBu^t \rightleftharpoons MeO^\bullet + Bu^tOO^\bullet \\
Bu^tOO^\bullet + Bu^tO^\bullet &\longrightarrow Bu^tOOOBu^t \\
2Bu^tOO^\bullet &\rightleftharpoons Bu^tOOOOBu^t \\
\left.\begin{matrix} MeOO^\bullet \\ MeO^\bullet \end{matrix}\right\} &\longrightarrow \text{Products}
\end{aligned}$$

SCHEME

Thermochemistry.—The conclusion that $MeOOOBu^t$ is thermally unstable, even at very low temperatures, is in marked contrast to the thermal stability of di-t-butyl trioxide below *ca.* 240 K.[4] Perfluorination of the substituents increases the stability still further since bistrifluoromethyl trioxide can be isolated at ambient temperatures.[19,20]

Thermochemical calculations predict[21] that the nature of the alkyl groups should not have a very marked effect on the strength of the OO–O bond. From calculations using the data of Benson,[21] the bond dissociation energy $D(Bu^tOO{-}OMe) = 83.6$ and $D(Bu^tO{-}OOMe) = 87.8$ kJ mol^{-1}. These values are comparable to $D(Bu^tO{-}OOBu^t) = 85.7$ kJ mol^{-1}. Though these calculated values are rather imprecise (the error limits on an absolute basis are ± 25 kJ mol^{-1}) they indicate that there should not be any marked difference in stability between the two dialkyl trioxides, which is in marked contrast to our experimental results. However, in relative terms the calculations suggest that the dialkyl trioxide, Bu^tOOOMe, should dissociate more readily to t-butylperoxyl and methoxyl radicals than to methylperoxyl and t-butoxyl radicals, which accords with the observed build up of t-butylperoxyl radicals on the cessation of photolysis.

At present there does not appear to be a satisfactory explanation for the marked effect of the alkyl group on the stability of the dialkyl trioxides. It is of interest to note that a similar effect has been observed for dialkyl tetraoxides in gas-phase studies.[22] Kinetic measurements show that dimethyl tetraoxide is much less stable than di-t-butyl tetraoxide, whereas thermochemical calculations suggest that their stabilities should be very similar.

Dialkyl Trioxides in Other Systems.—The formation of crossed dialkyl trioxides $ROOOBu^t$ in other systems is indicated by the observation that under certain conditions an e.s.r. signal characteristic of the t-butylperoxyl radical is observed during the photolysis of di-t-butyl peroxide in oxygenated solutions of certain other hydrocarbon solvents.

Evidence for the formation of a dialkyl trioxide in oxygenated hydrocarbon solvents has come from a study[8] similar to this work using $^{17}O_2$. A solution of di-t-butyl peroxide in $[^2H_{10}]$cyclopentane saturated with $^{17}O_2$ was photolysed at 183 K. When the solution was warmed in the dark to room temperature an e.s.r. spectrum was observed that could be assigned to the t-butylperoxyl radical specifically labelled with ^{17}O at the terminal oxygen atom. The detailed mechanism, presented by Howard,[8] is similar to that proposed for the formation of the t-butylperoxyl radical in toluene (see below).

We have observed that photolysis of di-t-butyl peroxide in oxygenated toluene below 190 K initially gives the e.s.r. spectrum of the benzylperoxyl radical [g 2.015, a(2H) 0.54 mT]. However, with continued photolysis the spectrum of the t-butylperoxyl radical rapidly becomes dominant. We suggest that this is indicative of the formation and subsequent decomposition of the dialkyl trioxide, $PhCH_2OOOBu^t$ [reactions (13)—(15)].

$$Bu^tO^\bullet + PhCH_3 \longrightarrow Bu^tOH + PhCH_2^\bullet \qquad (13)$$

$$PhCH_2^\bullet + O_2 \longrightarrow PhCH_2OO^\bullet \qquad (14)$$

$$PhCH_2OO^\bullet + Bu^tO^\bullet \rightleftharpoons PhCH_2OOOBu^t \rightleftharpoons PhCH_2O^\bullet + Bu^tOO^\bullet \qquad (15)$$

The observation of the t-butylperoxyl radical during photolysis results from the fact that the main route for the removal of the t-butylperoxyl radical in non-reactive solvents [reaction (11)] is virtually removed, because of the increased reactivity of the solvent towards hydrogen atom abstraction by t-butoxyl radicals [reaction (13)].

Clearly in any particular system the formation of a dialkyl trioxide will depend on the competition between the solvent and alkylperoxyl radicals for the t-butoxyl radical [reactions (4) and (6)]. Low reactivity with the solvent RH favours the formation of a dialkyl trioxide, whereas a high reactivity will lead to negligible production of the dialkyl trioxide.

Dialkyl trioxides will not be expected to play any

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*A referee has suggested an alternative route for forming the t-butylperoxyl radical, namely:

$$\begin{aligned}
Bu^tO^\bullet + O_2 &\rightleftharpoons Bu^tOOO^\bullet \\
Bu^tOOO^\bullet + Bu^tO^\bullet &\longrightarrow Bu^tOOOOBu^t \\
Bu^tOOOOBu^t &\xrightleftharpoons{\text{slow}} 2Bu^tOO^\bullet
\end{aligned}$$

However we consider that this route is unlikely to contribute for the reasons outlined in this and the following paragraphs.

significant part in the oxidation of alkanes above 273 K. However, under certain conditions at lower temperatures it is possible for dialkyl trioxides to be formed. In these circumstances the partial conversion of one type of alkylperoxyl radical into a different type could occur and lead to erroneous results, for instance in the measurement of the rate constant for the mutual termination at low temperatures. In fact this situation has arisen in our own studies on the benzylperoxyl radical and also in an attempt [23] to measure the rate constant of the mutual termination reaction for neopentylperoxyl radicals, $(CH_3)_3CCH_2OO^{\bullet}$, prepared by the photolysis of di-t-butyl peroxide in a solution containing neopentane. In a subsequent paper we will discuss the influence of dialkyl trioxides on the measured rate constants for the self-reaction of secondary alkylperoxyl radicals at low temperatures.

EXPERIMENTAL

Di-t-butyl peroxide was obtained from Koch–Light and was purified by fractional distillation. Before use it was passed through a column of activated silica gel. $[^2H_{18}]$Di-t-butyl peroxide was prepared by a standard literature method [24] from $[^2H_9]$-t-butyl alcohol (Merck, Sharp and Dohme), and mass spectral analysis showed that the product contained >96% deuterium. All other materials were commercially available samples used without further purification.

The e.s.r. measurements were made with a Varian Century E-line spectrometer. A standard Varian variable-temperature accessory was used to regulate the sample temperature, which was measured with a copper–constantan thermocouple. The light source was a 200-W high-pressure mercury lamp (Osram HBO 200) and the unfiltered output was focussed using two fused silica lenses (50 mm diam.; condenser lens, *f* 70 mm, and secondary lens, *f* 140 mm).[25]

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