# Photolysis of Di-t-butyl Peroxide Under Acid Conditions

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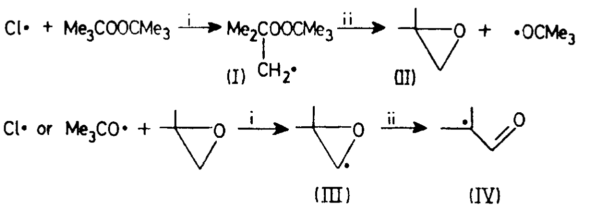
*Summary* Photolysis of di-t-butyl peroxide in the presence of trifluoroacetic acid gives a species which can fragment to give a methyl radical, or can add to an alkene; this species is tentatively identified as the t-butyl alcohol radical cation, $\mathrm{Bu^t\overset{\cdot+}{O}H}$.

THE photolysis of di-t-butyl peroxide under neutral conditions has been investigated very thoroughly. We now report an e.s.r. study of the photolysis under acid conditions, which shows that the course of the reactions which are involved can be dramatically altered.

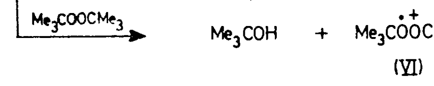
$$\mathrm{Me_3COOCMe_3 \xrightarrow{h\nu} Me_3CO\cdot \xrightarrow{RH} Me_3COH + R\cdot} \qquad (1)$$

$$\mathrm{Me_3CO\cdot + HCl \longrightarrow Me_3COH + Cl\cdot} \qquad (2)$$


(3)
(4)

Photolysis in a neutral medium such as an alkane gives initially t-butoxyl radicals. In a weakly interacting environment the unpaired electron in these radicals possesses appreciable unquenched orbital angular momentum, and their e.s.r. spectra have not been detected in fluid solution; the radicals which are observed are those (R·) resulting from hydrogen abstraction from the alkane (RH) (equation 1).[1]

If hydrogen chloride is present, the spectrum of the ketoalkyl radical (IV) is observed instead.



$$\mathrm{Me_3CO\cdot + HOCOCF_3 \longrightarrow \underset{(V)}{Me_3C\overset{\cdot+}{O}H}\ \overset{-}{O}COCF_3} \qquad (5)$$

$$\mathrm{\underset{(V)}{Me_3C\overset{\cdot+}{O}H} \longrightarrow Me\cdot + Me_2C{=}\overset{+}{O}H} \qquad (6)$$

$$\mathrm{\xrightarrow{RH} Me_3C\overset{+}{O}H_2 + R\cdot} \qquad (7)$$

$$\mathrm{\xrightarrow{R_2C=CR_2} Me_3C\underset{H}{\overset{+}{O}}CR_2CR_2\cdot} \qquad (8)$$

$$\mathrm{\xrightarrow{Me_3COOCMe_3} Me_3COH + \underset{(VI)}{Me_3C\overset{\cdot+}{O}OCMe_3}} \qquad (9)$$

SCHEME

The course which the reaction takes appears now to be determined by the interaction of t-butoxyl radicals with the hydrogen chloride to give chlorine atoms (equation 2),[2,3] which yield in turn the $\beta$-peroxyalkyl radical (I) (regenerating the HCl and leading to a catalytic cycle), the oxiran (II), the oxiranyl radical (III) and the ketoalkyl radical (IV).† The radicals (I),[4] (III),[5] and (IV)[5] have been generated by independent routes, and the isolated reactions 3(ii) and 4(ii) (which is subject to acid catalysis) were confirmed.

Quite different results are obtained if di-t-butyl peroxide is photolysed in cyclopropane in the presence of trifluoro-

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† Benson has reported that the thermolysis of di-t-butyl peroxide in the presence of hydrogen chloride in the gas phase gives 2,2-dimethyloxiran together with a trace of isobutyraldehyde (ref. 3).

acetic acid. At low temperature, a strong singlet is observed, $g = 2{\cdot}0091$ (independent of acid concentration), line width *ca.* 2·0 G; at higher temperature, this is replaced by the spectrum of the methyl radical. If a more reactive alkane or an alkene is added to the system, these spectra are suppressed, and only the spectra of the radicals resulting from hydrogen abstraction from the alkane or from addition to the alkene are observed. The principal results, together with related experiments with t-butyl t-pentyl peroxide, di-t-pentyl peroxide, and t-butyl peroxyacetate are summarised in the Table.

TABLE. The photolysis of organic peroxides in the presence of trifluoroacetic acid.

| Reactants | Temp./°C | Radicals observed |
|---|---|---|
| $\mathrm{Me_3COOCMe_3, CF_3CO_2H, c\text{–}C_3H_6}$[a] | −120 to −80<br>> −80 | Singlet $g$ 2·0091<br>$\mathrm{CH_3{\cdot}}$ |
| $\mathrm{Me_3COOCMe_3, Me_3CO_2H, CF_3CO_2H, c\text{–}C_3H_6}$ | −100 | $\mathrm{Me_3COO{\cdot}}$ $g$ 2·015; singlet $g$ 2·0091 |
| $\mathrm{Me_3COOCMe_2Et, CF_3CO_2H, c\text{–}C_3H_6}$ | −130<br>> −95 | $\mathrm{C_2H_5{\cdot}}$<br>$\mathrm{CH_3{\cdot}}$ ; $\mathrm{C_2H_5{\cdot}}$ |
| $\mathrm{EtMe_2COOCMe_2Et, CF_3CO_2H, c\text{–}C_3H_6}$ | −130 to −65 | $\mathrm{C_2H_5{\cdot}}$[b] |
| $\mathrm{Me_3COOCMe_3, CF_3CO_2H, MeCH_2Me}$ | −100 to −70 | $\mathrm{Me\dot{C}HMe}$ |
| $\mathrm{Me_3COOCMe_3, CH_2{=}CH_2}$ | −75 | $\mathrm{Me_3COCH_2CH_2{\cdot}}$[c] |
| $\mathrm{Me_3COOCMe_3, CF_3CO_2H, CH_2{=}CH_2}$ | −105 to −60 | $\mathrm{Me_3C\overset{+}{O}(H)CH_2CH_2{\cdot}}$[d] |
| $\mathrm{Me_3COOCMe_3, CF_3CO_2D, CH_2{=}CH_2}$ | −105 to −60 | $\mathrm{Me_3C\overset{+}{O}(D)CH_2CH_2{\cdot}}$[d] |
| $\mathrm{Me_3COOC(O)Me, CF_3CO_2H, CH_2{=}CH_2}$ | −100 to −90 | $\mathrm{Me_3C\overset{+}{O}(H)CH_2CH_2{\cdot}}$[d]; $\mathrm{CH_3{\cdot}}$ |
| $\mathrm{Me_3COOCMe_2Et, CF_3CO_2H, CH_2{=}CH_2}$ | −108 to −74 | $\mathrm{Me_3C\overset{+}{O}(H)CH_2CH_2{\cdot}}$[d]; $\mathrm{C_2H_5{\cdot}}$[e] |
| $\mathrm{EtMe_2COOCMe_2Et, CF_3CO_2H, CH_2{=}CH_2}$ | −118 to −67 | $\mathrm{C_2H_5{\cdot}}$ |
| $\mathrm{Me_3COOCMe_3, CH_2{=}CHMe}$ | −110 to −60 | $\mathrm{CH_2{=}CHCH_2{\cdot}}$ |
| $\mathrm{Me_3COOCMe_3, CF_3CO_2H, CH_2{=}CHMe}$ | −140 to −75 | $\mathrm{Me_3C\overset{+}{O}(H)CH_2\dot{C}HMe}$[f] |

[a] $\mathrm{c\text{–}C_3H_6}$ = cyclopropane. [b] In the absence of acid the spectrum of the ethyl radical was much weaker, and was barely detectable below −90 °C. [c] Rather weak spectrum, $a(\mathrm{H}\alpha)$ 22·0 (2H), and $a(\mathrm{H}\beta)$ 33·2 (2H) G at −60 °C; it is commonly believed that the spectrum of the adduct cannot be detected under these conditions. For the same radical obtained by abstraction of bromine from $\beta$-bromoethyl t-butyl ether, Elson, Mao, and Kochi (ref. 7) report $a$ $(\mathrm{H}\alpha)$ 22·04, and $a$ $(\mathrm{H}\beta)$ 35·06 G at −114 °C. [d] $a(\mathrm{H}\alpha)$ 22·0 (2H), $a(\mathrm{H}\beta)$ 28·8 (2H), and $a$ 0·2 ($\not<$7H) G at −90 °C. [e] Relative concentrations *ca.* 1 : 1 . [f] $a(\mathrm{H}\alpha)$ 21·9 (1H), $a(\mathrm{H}\beta)$ 20·0 (2H), and $a(\mathrm{Me})$ 25·0 (3H) G at −104 °C. No spectrum of the allyl radical could be detected.

We propose that these observations may be interpreted on the basis of the reactions in the Scheme.‡

The acid now transfers a proton rather than a hydrogen atom to the t-butoxyl radical to give the alcohol radical cation (V) (equation 5). Above about −80 °C, this undergoes $\beta$-scission to give a methyl radical (equation 6); this reaction is similar to that with the Lewis acid $\mathrm{SnCl_4}$, which we have described previously.[6] The t-pentyl alcohol radical cation loses an ethyl radical more readily and is therefore less easily trapped (by, for example, an alkene). The radical cation (V) can abstract hydrogen from an alkane (*e.g.* propane) (equation 7) but (in contrast to the t-butoxyl radical)[7] with an alkene such as propene it preferentially adds to the double bond (equation 8); addition is more rapid than abstraction of hydrogen, probably because the radical cation $\overset{\cdot+}{\mathrm{Bu^tOH}}$ is more electrophilic than the radical $\mathrm{Bu^tO{\cdot}}$.

The nature of the species giving rise to the singlet is uncertain, but we suggest that it may be the dialkyl peroxide radical cation (VI)[8] which is formed by electron transfer from the peroxide to the radical cation (V);§ (VI) probably undergoes fragmentation at higher temperatures to yield methyl radicals.

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‡ Isolated ionic species presumably have no independent existence under our conditions: the detailed natures of the cation–trifluoroacetate systems are not known, and may involve ion-pair or hydrogen bonding interactions.

§ Adiabatic ionisation potentials are $\mathrm{Bu^tOH}$ 9·78 and $\mathrm{Bu^t{}_2O_2}$ 8·35 eV (see ref. 9).

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