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PREPARATION OF SPECIFIC PRIMARY AND SECONDARY ALKYLPEROXYL RADICALS IN SOLUTION FOR E.S.R. INVESTIGATION

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Several secondary and two primary alkylperoxyl radicals $RO_2^{\cdot}$ have recently been identified[1] by e.s.r. spectroscopy following photolysis either of a cooled solution of ditertiary butyl peroxide in the corresponding alkane RH in the presence of oxygen or of the diacyl peroxide RCOOOCOR or hydroperoxide ROOH. The first method is limited in that the specificity of attack of t-butoxyl radicals upon RH is incomplete, and several different secondary C-H bonds in a straight-chain alkane can be attacked to give a radical mixture, and the second approach necessitates the preparation of the diacyl peroxides.

We report here the facile preparation of a variety of both primary and secondary alkylperoxyl radicals as follows. When a deoxygenated 5 mM solution of ceric ammonium nitrate in an alcohol RCH_2OH is photolysed at a low temperature, whilst retaining liquidity, then a clearly resolved e.s.r. spectrum of the radical $R^{\cdot}$ is obtained[2, 3]

$$\mathrm{RCH_2OH} \xrightarrow[\underline{h\nu}]{\mathrm{Ce^{IV}}} \mathrm{R}^{\cdot}$$

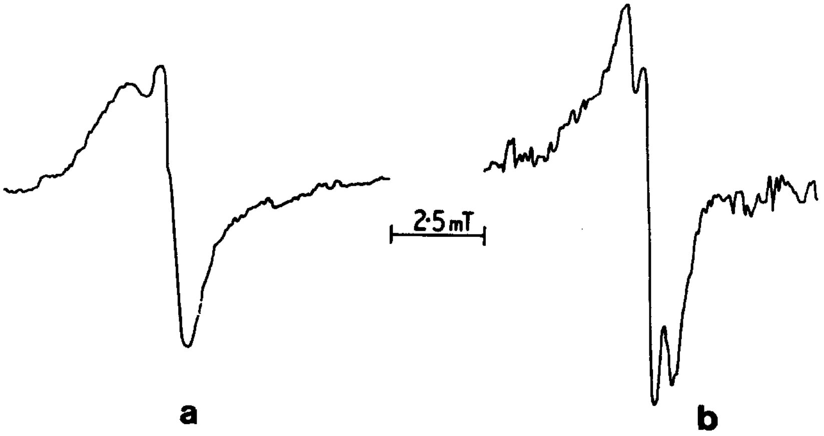
Similarly, when a deoxygenated 2 M solution of a carboxylic acid RCO_2H in methanol containing 5 mM ceric ammonium nitrate is photolysed at a low temperature, then the spectrum of $R^{\cdot}$ is found,

$$\mathrm{RCO_2H} \xrightarrow[\underline{h\nu}]{\mathrm{Ce^{IV}}} \mathrm{R}^{\cdot}$$

If oxygen is NOT removed from both of these types of solution prior to irradiation then the spectrum of $R^{\cdot}$ is, in every case, replaced by a much broader spectrum centred near $\underline{g} = 2.015$ and normally without hyperfine structure but displaying a doublet or triplet feature in certain cases. Clearly the alkyl radical has reacted with oxygen

$$R^{\cdot} \quad + \quad O_2 \quad \rightarrow \quad RO_2^{\cdot}$$

Examples of the spectra obtained are given below as well as a summary of our preliminary data. In some cases, the weakness of the spectra necessitated accumulation in a computer-of-average-transients; usually 50 scans were sufficient to yield a good S/N ratio.



Solution e.s.r. spectra of (a) $CH_3O_2^{\cdot}$ (at 183 K) and (b) $CH_3CH_2CH_2CH_2CH_2O_2^{\cdot}$ obtained by photolysis of solutions of Ce^{IV} in ethanol and methanolic hexanoic acid respectively.

The absence of hyperfine structure in many of the radicals is attributable to the temperatures of the experiments: Bennett and Summers[1] report the doublet feature of the pent-3-ylperoxyl radical, prominent at 160 K and detectable at 190 K, to be obscured by spectral broadening at 220 K.

Certain of the radicals reported here, e.g., $CH_3O_2^{\cdot}$, $n\text{-}C_4H_9O_2^{\cdot}$, are reported for the first time and offer eminently suitable subjects for kinetic e s.r. study by intermittent illumination methods. The successful identification of the corresponding peroxyl radical in each of our experiments conducted hitherto indicates that the procedure described is possibly the most general of those currently available for the preparation of peroxyl radicals.

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Principal Features in the E.S.R. Spectra of Alkylperoxyl Radicals in Solution

Radical	Co-reactant with Ce^{IV}	T(°K)	g-factor	$\underline{a}_H$ (mT)
$CH_3O_2^{\cdot}$	C_2H_5OH	183	2.0134	Unresolved, weak feature emergent to low field of centre of spectrum
	CH_3CO_2H	188	2.0150	Unresolved
$C_2H_5O_2^{\cdot}$	$n\text{-}C_3H_7OH$	143	2.0153	Unresolved
	$n\text{-}C_3H_7OH$	195	2.0153	Unresolved, but emergent
	$C_2H_5CO_2H$	188	2.0140	Unresolved
$n\text{-}C_3H_7O_2^{\cdot}$	$n\text{-}C_4H_9OH$	199	2.0149	Unresolved
$n\text{-}C_4H_9O_2^{\cdot}$	$n\text{-}C_5H_{11}OH$	198	2.0145	Unresolved
$n\text{-}C_5H_{11}O_2^{\cdot}$	$n\text{-}C_5H_{11}CO_2H$	$\sim$200	2.0149	0.53 (triplet)[a]
$PhCH_2CH_2O_2^{\cdot}$	$PhCH_2CH_2CH_2OH$	201	2.0176	Unresolved
$(CH_3)_2CHO_2^{\cdot}$	$(CH_3)_2CHCH_2OH$	213	2.0152	Unresolved
cyclo-$C_6H_{11}O_2^{\cdot}$	cyclo-$C_6H_{11}CO_2H$	203	2.0161	0.62 (doublet)[b]

[a] Reference 1 gives 0.52 mT for $n\text{-}C_3H_7O_2^{\cdot}$

[b] Reference 1 gives 0.50 mT for this radical

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