# Electron Spin Resonance Detection of Aliphatic Radicals during Photo-oxidations by $Ce^{IV}$

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*Summary* Oxidation of tertiary alcohols and carboxylic acids by $Ce^{IV}$ during u.v. irradiation of $Ce^{IV}$–substrate complexes in an aqueous perchloric acid medium at 77°K leads to the formation of trapped alkyl radicals detected by e.s.r.

DIRECT e.s.r. spectroscopic characterisation of radical intermediates in the oxidation of organic species by one-equivalent oxidants has hitherto been restricted to cases where (i) the intermediate is sufficiently stable to persist for a time ($\gg$ 10 msec.) enabling its detection in a flow system and (ii) the oxidation is sufficiently rapid for a reasonable (*ca.* $10^{-5}$M) concentration of radicals to be built up during the transit time from mixing-point to detector. Both of these stringent conditions are met, for example, in the cerium(IV) sulphate oxidation of phenol *via* phenoxyl radical.[1]

We report the detection by e.s.r. of alkyl radicals generated during the photodecomposition of charge-transfer complexes between $CeOH^{3+}$ ion and two tertiary alcohols and several aliphatic carboxylic acids in deoxygenated acidic ($HClO_4$) aqueous or aqueous acetonitrile media at 77°K. The oxidant and reductant are brought into the requisite proximity through charge-transfer interaction before the solution is frozen. The electron-transfer process is induced photolytically and the resulting radicals, being immobilised, are unable to reduce a second $Ce^{IV}$ species, which is their customary fate in liquid solution.

*Alkyl radicals detected during photo-oxidations by* $Ce^{IV}$

| Substrate | Radical | Coupling constant (oe) |
|---|---|---|
| t-Butyl alcohol .. .. | Methyl | 22·8 |
| 3-Ethylpentan-3-ol .. | Ethyl | $a^{H}_{CH_3}$ : 26·2; $a^{H}_{CH_2}$ : 20·9 |
| Acetic acid .. .. | Methyl | 22·8 |
| Propionic acid .. .. | Ethyl | $a^{H}_{CH_3}$ : 26·9; $a^{H}_{CH_2}$ : 21·0 |
| Isobutyric acid .. .. | Isopropyl | $a^{H}_{CH_3} \triangleq a^{H}_{CH}$ : 24·4 |
| Pivalic acid .. .. | t-Butyl | 21·7 |

When an aqueous or aqueous acetonitrile solution ($[HClO_4] = 4{\cdot}0$M, $[Ce^{IV}] = [\text{substrate}] = 0{\cdot}1$M) is photolysed in a Pyrex Dewar vessel in the cavity of an e.s.r. spectrometer with light from a Hanovia 100 w xenon compact source fitted with a reflector and a focussing lens, then unambiguous spectra are obtained of alkyl radicals (Table and Figure).

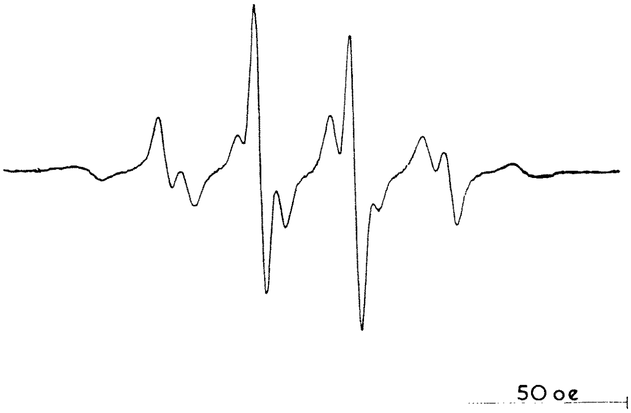
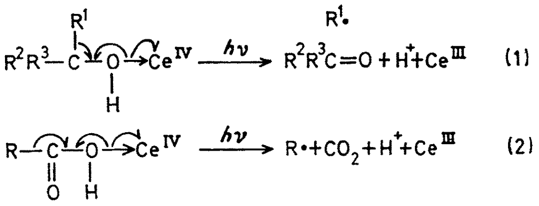


FIGURE. *E.s.r. spectrum of ethyl radical generated during photolysis of an aqueous acidic solution of* $Ce^{IV}$ *and propionic acid at* 77°K.

We conclude that these photo-oxidations proceed by the following concerted mechanisms:



$$R^2R^3\overset{R^1}{C}-\underset{H}{O}\rightarrow Ce^{IV} \xrightarrow{h\nu} R^2R^3C{=}O + \overset{R^1\cdot}{} + H^+ + Ce^{III} \quad (1)$$

$$R-\underset{O}{\overset{}{C}}(=O)-\underset{H}{O}\rightarrow Ce^{IV} \xrightarrow{h\nu} R\cdot + CO_2 + H^+ + Ce^{III} \quad (2)$$

These mechanisms are supported by the absence of spectra attributable to radicals of the type $R^1R^2R^3C{-}O\cdot$ or $RCO_2\cdot$. Route (1) is identical with that suggested by Hoare and Waters[2] for the thermal oxidation by $Co^{III}$ of tertiary alcohols and route (2) with that suggested both for $Co^{III}$ [3] and $Ce^{IV}$ [4] thermal oxidations of carboxylic acids and for the analogous photo-oxidation[4] by $Ce^{IV}$.

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