Electron Spin Resonance Studies of Photo-Oxidation by Metal Ions in Rigid Media at Low Temperatures

Part 1.—Ce(IV) Photo-Oxidation of Alcohols

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Photolysis of deoxygenated solutions of ceric perchlorate and ceric ammonium nitrate in alcoholic, aqueous alcoholic and water+alcohol+acetonitrile solutions at 77 K by light of wavelength >300 nm leads to formation of radicals derived from the alcohol identified by electron spin resonance (e.s.r.) spectroscopy. Primary alcohols RCH_2OH yield $R\dot{C}HOH$, but secondary alcohols R_2CHOH yield $R\cdot$ in addition to, and sometimes to the exclusion of $R_2\dot{C}OH$. Tertiary alcohols always give an alkyl fragment, e.g. $C_2H_5\cdot$ from tert-amyl alcohol. Allylic alcohols produce the corresponding hydroxyallyl radical and 1,2-diphenylethanol gives a spectrum of benzyl radical, indicating C—C cleavage. The mode of photo-oxidation by Ce(IV) clearly parallels that of the corresponding thermal oxidation.

Aqueous solutions of certain oxidizing inorganic ions, particularly of the one-equivalent type, are reduced by ambient light. The additional presence of ions such as Cl^- or of organic molecules such as alcohols, aldehydes and carboxylic acids, especially oxalate ions, enhances the rate of photoreduction of the metal ion,[1] such a process forming the basis of the ferri-oxalate actinometer. The mechanism of these photo-oxidations is believed to be free radical in character, following charge-transfer-to-metal (CTTM) transitions in the complexes formed by the metal ion,[1] the evidence including (i) the ability of photolyzed solutions to initiate radical polymerization,[2] e.g., that of acrylonitrile by $FeCl_3$ in dimethylformamide,[3] (ii) the production of an optical spectrum attributable to $NO_3\cdot$ on flash photolysis [4] of aqueous acidic Ce(IV) in the presence of NO_3^-, (iii), the characterization by e.s.r. spectroscopy of radicals derived from the ligand following photolysis of frozen solutions of the oxidizing ion complexed with reducing ligands, e.g., the oxalato complex of Fe(III) [5] and various carboxylic acid complexes of Pb(IV).[6] The products of photolysis of carboxylic acids in the presence of Pb(IV) [7] and Ce(IV) [8] have also been shown by Kochi and his collaborators to indicate radical pathways.

We have reported [9] that the primary processes in the photolysis of 1 : 1 complexes of Ce(IV) with tertiary alcohols [10] and aliphatic carboxylic acids can be followed by e.s.r. at 77 K. The present paper sets out the results of a systematic investigation of Ce(IV) photo-oxidation of different types of alcohol by means of this technique.

EXPERIMENTAL

MATERIALS

A.R. ceric ammonium nitrate was used. Solutions of Ce(IV) in $HClO_4$ were prepared as follows; concentrated aqueous ceric ammonium nitrate was treated with 0.880 ammonia until precipitation of ceric oxide ceased; the oxide was separated in a sintered-glass funnel and washed with much distilled water and finally dissolved in 60 % $HClO_4$ (A.R.). Alcohols were of the best grade available commercially, laboratory-grade materials being redistilled or recrystallized. CH_3CN was of spectroscopic quality.

IRRADIATION

Photolyses were carried out in the cavity of a Decca *X*-band spectrometer equipped with a Newport Instruments 7 in. magnet. The lamp was a Hanovia 100 W xenon compact source fitted with a reflector and focusing lens and the output was filtered through a Corning C50.54 clear glass filter transmitting light of $\lambda > 300$ nm. The temperature was maintained either by standing the sample tube in liquid nitrogen in a quartz dewar vessel of 4 mm i.d. or by passing cooled nitrogen gas through the low-temperature cavity supplied by Decca Radar Ltd. The cavity temperature was monitored with a thermocouple.

The sample tube of Spectrosil (3.2 mm o.d.) was joined to a quartz tube (10 mm o.d.) and thence via a graded seal *pq* to a Pyrex tube (fig. 1). 0.5 ml each of solutions of Ce(IV) and alcohol were placed separately in the bulbs *b* which were then placed in the sidearms *s* fitted with Teflon O-rings each backed by an O-ring of Viton A. The upper section was constructed from thick-walled Pyrex to enable the device to withstand considerable torque and a B10 cone provided the connection to a high-vacuum line. The vacuum was maintained by a greaseless stopcock *g*, again based on a Teflon O-ring backed by a Viton A O-ring, constructed initially by Mr. K. Holden of the departmental workshop but supplied latterly by J. Young Ltd. of Acton. The solutions were degassed by a series of freeze-pump-thaw cycles and the stopcock finally closed. Following melting of the solutions (often at ~273 K), mixing was effected by vigorous shaking, whereupon a red or orange colour usually developed, and a portion of the mixed solution immediately shaken into the e.s.r. tube and frozen to 77 K, being then ready for photolysis in the cavity.

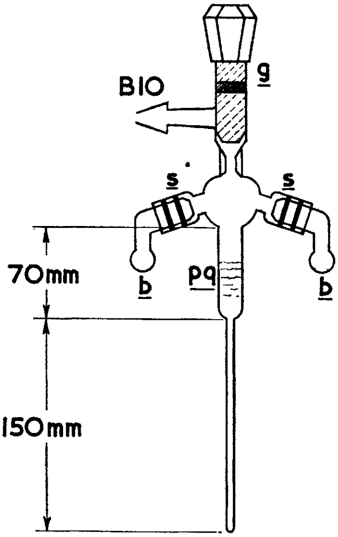


FIG. 1.—Arrangement of sample tube (the B10 cone is normally at right-angles to the plane of the paper).

Solutions were prepared in several different ways of which the following are most generally typical.

METHOD A.—ceric perchlorate (0.1 M) in aqueous 4 M $HClO_4$ and the organic substrate (0.1 or 1.0 M) in water.

METHOD B (used when the substrate was insufficiently water-soluble to give a solution of concentration >0.05 M or if the substrate precipitated during the final cooling state): a quantity of acetonitrile was added as co-solvent.

METHOD C: ceric ammonium nitrate dissolved in neat organic liquid to *ca.* 0.1 M or to saturation (whichever the least concentrated). In this case the solution was placed rapidly in one bulb and degassed in the usual way.

METHOD D: ceric ammonium nitrate (0.1 M) and the organic substrate (1.0 M) in water.

METHOD E: as with method D but with acetonitrile-water (50 % v/v) as solvent for water-insoluble substrates.

RESULTS

NO ADDED SUBSTRATE

Using filtered light ($\lambda > 300$ nm) only weak absorptions appeared on photolysis. 0.1 M Ce(IV) in 4 M $HClO_4$ produced weak H-atom signals which were intensified on removal of the filter. Prolonged irradiation of 60 % $HClO_4$ also produced H-atoms when the full source was used. 1 M aqueous ceric ammonium nitrate gave a very small singlet near $g = 2$ before photolysis, a small signal assigned to $NO_2\cdot$ with filtered light (see below) and a larger $NO_2\cdot$ signal and some H-atom absorption on removal of the filter.

PRIMARY ALIPHATIC ALCOHOLS

METHANOL.—Methods A, C and D all yielded a distorted but reproducible basic 1 : 2 : 1 triplet of average separation 20±2 Oe (fig. 2(*a*), (*b*)); methods C and D produced in addition two wing peaks of average separation 120±2 Oe, the high field peak being of asymmetric character (fig. 2(*b*)). The wing peaks were a feature of all experiments involving ceric ammonium nitrate irrespective of substrate although in a number of cases, e.g., the tertiary alcohols, its intensity was only a few percent of that of the co-existing carbon radical. We attribute the additional spectrum to $NO_2\cdot$ radical. The 1 : 2 : 1 triplet, although distorted compared with spectra obtained with higher aliphatic alcohols, is probably due to $\cdot CH_2OH$, which has been characterized in rigid solution by photolysis [11] and radiolysis [12] methods (a_H 19 Oe) and in solution by oxidation of methanol by the Ti^{3+}/H_2O_2 couple in a continuous-flow system with a reported principal coupling constant of 17.2 Oe.[13]

METHANOL-d^3.—The spectrum obtained by method C and illustrated in fig. 2(*c*) is much narrower than that obtained from methanol and suggests formation of an incompletely-resolved $\cdot CD_2OD$ spectrum. A broad singlet was obtained on radiolysis of solid CD_3OH.[12]

ETHANOL.—Method A produced a basic five-line spectrum of average separation 22.3±0.1 Oe with additional subsidiary peaks due to a minor species (fig. 2(*d*)). Method C also produced this spectrum (a_H 22.1 Oe) together with the $NO_2\cdot$ spectrum (width 116 Oe). The five-line spectrum closely resembles that obtained both on photolyzing ethanol + H_2O_2 mixtures at low temperatures [11] and on radiolysis of ethanol at 77 K [12] (a_H 22 Oe by both methods) and is assigned to $CH_3\dot{C}HOH$.

PROPAN-1-OL.—Method A produced a poorly-resolved quartet of basic pattern 1 : 3 : 3 : 1 ($a_H \sim 24$ Oe) with an additional central peak. Method C produced initially a spectrum identified as that of ethyl radical ($a^H_{CH_2}$ 19.8, $a^H_{CH_3}$ 26.4 Oe) but an additional spectrum appeared on further photolysis. Method D yielded a mixture of three radicals shown in fig. 2(*e*) consisting of $NO_2\cdot$ and $C_2H_5\cdot$ and a basic five-line spectrum (a_H 22 Oe) which is probably due to $CH_3CH_2\dot{C}HOH$. On standing in the dark at 77 K for 10 min the $C_2H_5\cdot$ signal diminished appreciably; on warming the mixture to ~175 K only the five-line spectrum remained (fig. 2(*f*)). The e.s.r. spectrum obtained on radiolysis of propan-1-ol also exhibits five lines (a_H 21 Oe)[12, 14] and is assigned to $CH_3CH_2\dot{C}HOH$ and similar results are obtained on photolysis of a propan-1-ol glass containing H_2O_2.[11] However, the liquid phase spectrum produced by photolyzing propan-1-ol containing 0.4 % H_2O_2 using an intense source shows six lines with $a^H_{CH(OH)}$ 15.06, $a^H_{CH_2}$ 21.40 Oe.[15]

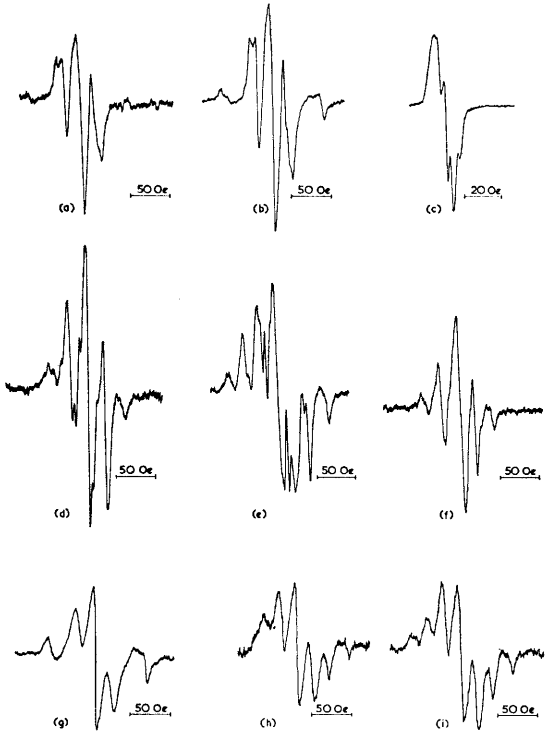


FIG. 2.—E.s.r. spectra obtained during photo-oxidations of primary alcohols by Ce(IV). (*a*) methanol (method A); (*b*) methanol (method D); (*c*) methanol-d[3] (method C); (*d*) ethanol (method A); (*e*) propan-1-ol (method D, 77 K); (*f*) propan-1-ol (method D, warmed to ~175 K); (*g*) 2-methylpropan-1-ol (method C); (*h*) butan-1-ol (method C); (*i*) pentan-1-ol (method C).

2-METHYLPROPAN-1-OL (ISOBUTANOL). Method C gave a 1 : 2 : 1 triplet (a_H 20.2 Oe) together with an $NO_2\cdot$ spectrum of width 120 Oe (fig. 2(*g*)). A similar spectrum was obtained by Alger, Anderson and Webb on radiolysis of isobutanol [12] and Chacaty's similar experiments also produced a basic triplet (a_H 21 ± 1 Oe) with some weak satellite lines.[14] Accordingly it appears that $(CH_3)_2CH\dot{C}HOH$ is formed, a radical characterized in solution by both intense photolysis [15] and Ti^{3+}/H_2O_2 oxidation flow [13] techniques with $a^H_{CH(OH)}$ 14.74, $a^H_{CHMe_2}$ 21.41 Oe.[15]

BUTAN-1-OL.—Method C gave a five-line spectrum of an approximate intensity distribution 1 : 2 : 2 : 2 : 1 (a_H 19 Oe) together with an $NO_2\cdot$ spectrum of width 117 Oe (fig. 2(*h*)), cf. pentan-1-ol. Radiolysis at 77 K of butan-1-ol produces a seven-line spectrum with five central lines of comparable intensity and two weaker outermost lines,[12, 14] but Chacaty [14] noted that warming to 120 K results in a change to a five-line spectrum (a_H 21 ± 1 Oe).[14] The change is attributed to a conversion from $CH_3\dot{C}HCH_2CH_2OH \rightarrow CH_3CH_2CH_2\dot{C}HOH$. Low-temperature H_2O_2 photo-oxidation experiments indicate six or seven lines in a poorly-resolved spectrum[11] with $a_H \sim 20$ Oe. Room temperature H_2O_2 photolysis produces a six-line spectrum of $CH_3CH_2CH_2\dot{C}HOH$ with $a^H_{CH(OH)}$ 15.3, $a^H_{CH_2}$ 20.0 Oe.[15] It seems probable that we are observing the 120 K species of Chacaty, i.e., $CH_3CH_2CH_2\dot{C}HOH$.

PENTAN-1-OL.—Fig. 2(*i*) illustrates the spectrum obtained using method C which can be seen to be almost identical with that found for butan-1-ol. Alger, Anderson and Webb[12] also found a strong similarity between the e.s.r. spectra of butan-1-ol and pentan-1-ol following radiolysis, implying formation of structurally similar radicals $RCH_2CH_2\dot{C}HOH$ (R = Me or Et).

SECONDARY ALCOHOLS

PROPAN-2-OL.—Method A ([substrate] $\sim$0.1 M) yielded initially the relatively narrow-lined quartet characteristic of $CH_3\cdot$ but a minor radical was also present which increased in size on further photolysis relative to that of $CH_3\cdot$ until both species were in comparable concentration. The radical mixture illustrated in fig. 3(*a*) was analyzed in terms of $CH_3\cdot$ (a_H 23.0 ± 0.2 Oe) and $Me_2\dot{C}OH$ ($a^H_{CH_3}$ 20.0 ± 0.5 Oe) by means of a computer simulation (fig. 3(*b*)).

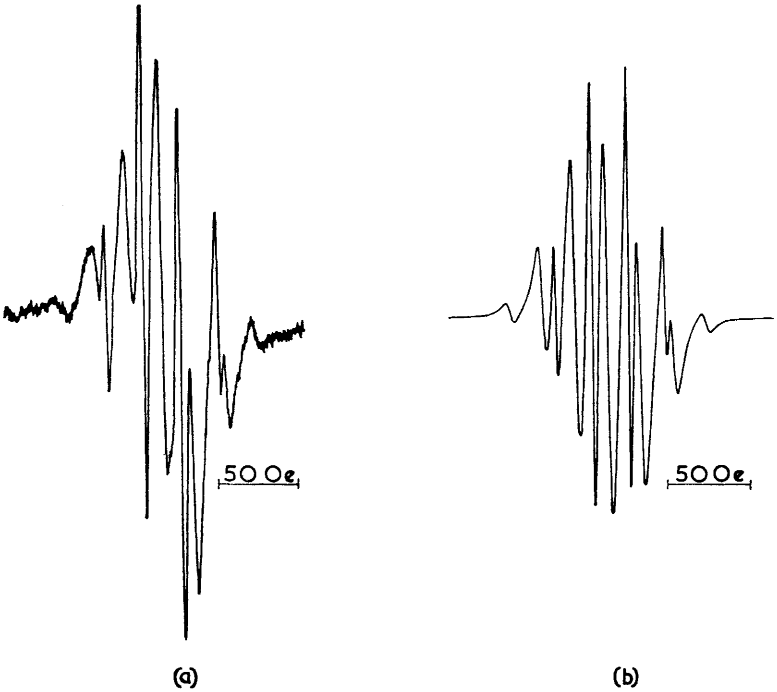


FIG. 3.—E.s.r. spectra obtained during photo-oxidation of propan-2-ol by Ce (IV). (*a*) experimental; (*b*) computer simulation.

Using method C, initial photolysis produced a radical mixture comprising $Me_2\dot{C}OH$, $CH_3\cdot$ and $NO_2\cdot$ but continued photolysis resulted in relative enhancement of $Me_2\dot{C}OH$ and $NO_2\cdot$. Method D yielded only $CH_3\cdot$ and $NO_2\cdot$.

The averaged coupling constant in $Me_2\dot{C}OH$ compares with values of 20 Oe obtained by other low-temperature methods of generation.[11, 12]

BUTAN-2-OL (SEC-BUTANOL).—Method C yielded a mixture of $CH_3\cdot$ (a_H 22.7± 0.5 Oe) and a 1 : 2 : 1 triplet (a_H 33.8 Oe). Method D produced a poor $CH_3\cdot$ spectrum. Photolysis at 77 K of butan-2-ol containing H_2O_2 gave a six-line spectrum [11] and clearly C—C fission has taken place during Ce(IV) photo-oxidation.

PENTAN-3-OL.—Method C yielded $C_2H_5\cdot$ ($a^H_{CH_3}$ 26.8±0.1, $a^H_{CH_2}$ 20.5±0.2 Oe).

CYCLOHEXANOL.—Method C produced a mixture of $NO_2\cdot$ and an eight-line spectrum. Gibson, Symons and Townsend [11] obtained a six-line spectrum on low-temperature photolysis of an H_2O_2 solution (a_H 20 Oe) and we have been able to confirm this result.

TERTIARY ALCOHOLS

TERT-BUTANOL.—Photolysis at 77 K under different conditions led to the immediate production of a 1 : 3 : 3 : 1 quartet with $a_H = 22.7\pm0.3$ Oe identified as $CH_3\cdot$ radical. Method C produced in addition a minor spectrum which intensified on continued photolysis, e.g., for 15 min, to yield a 1 : 2 : 1 triplet of overall width 42 Oe. Warming a photolyzed aqueous ceric ammonium nitrate sample to 180 K resulted in the disappearance of $CH_3\cdot$ and production of a similar 1 : 2 : 1 triplet. Standing a sample prepared by method C and irradiated for only 4 s (to give a " pure " $CH_3\cdot$ spectrum) for a period of 27 h at 77 K also led to the same triplet at the expense of $CH_3\cdot$ (fig. 4), which was again produced by photolysis of ceric ammonium nitrate in neat tert-butanol at 245 K. The triplet presumably originates from a $\cdot CH_2X$ species, the most likely candidate being $\cdot CH_2CMe_2OH$ for which a coupling of 21.3 Oe has been reported [13] in water at 293 K. Photolysis of ceric perchlorate in a solution of tert-butanol in CH_3CN produces, in addition to $CH_3\cdot$, a spectrum attributable to $\cdot CH_2CN$ [16] which often appeared when this co-solvent was utilized.

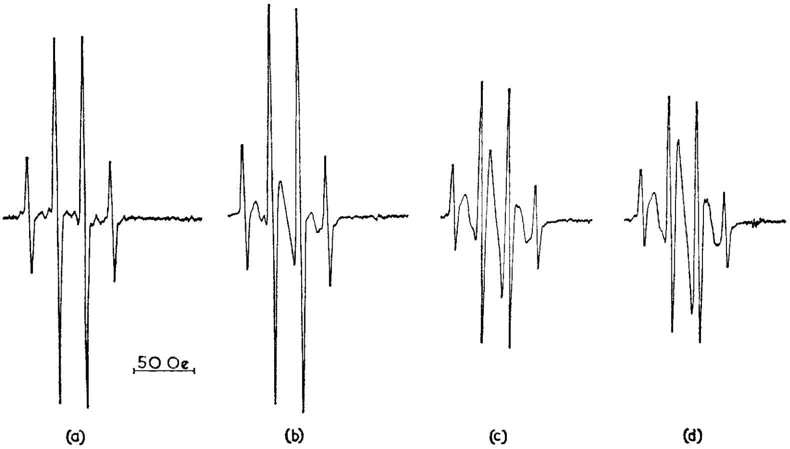


FIG. 4.—Decay in dark of e.s.r. spectrum of methyl radical in tert-butanol at 77 K following photo-oxidation by Ce(IV). (*a*) immediately after 4 s photolysis ; (*b*) 3 h later ; (*c*) 19 h later ; (*d*) 27 h later.

3-ETHYLPENTAN-3-OL.—Investigation by methods A and C yielded the spectrum of $C_2H_5\cdot$ with $a^H_{CH_3}$ 26.5±0.3 Oe, $a^H_{CH_2}$ 21.0±0.3 Oe.

1,1-DIMETHYLPROPAN-1-OL (TERT-AMYL ALCOHOL).—Method C gave an ethyl radical shown in fig. 5(*a*) with $a^H_{CH_3}$ 26.3±0.3, $a^H_{CH_2}$ 20.8±0.3 Oe. Method A unexpectedly gave a 1 : 3 : 3 : 1 quartet with $a_{H(av)}$ 23.3 Oe ; this suggests $CH_3\cdot$

is formed but the peaks were unusually broad and the outermost peaks were partially split into doublets.

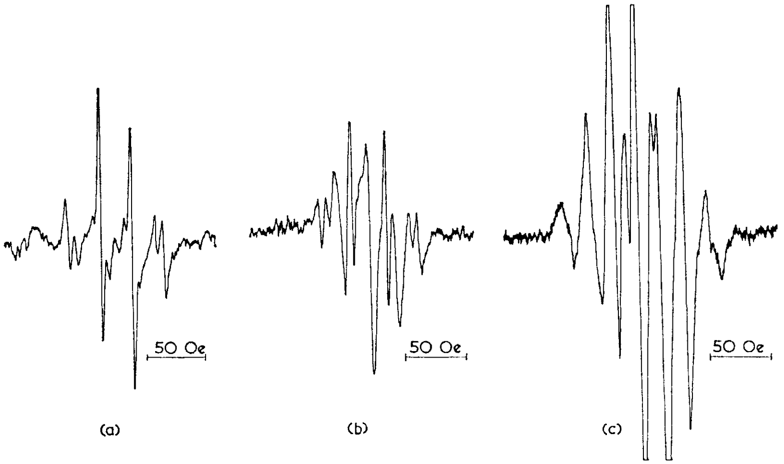


FIG. 5.—E.s.r. spectrum obtained during photo-oxidations of tertiary alcohols by Ce(IV). (*a*) 1,1-dimethylpropan-1-ol; (*b*) 3-methylhexan-3-ol; (*c*) 2,3-dimethylbutan-2-ol.

3-METHYLHEXAN-3-OL.—Method C gave a spectrum consisting of a mixture of $C_2H_5\cdot$, identified by the coupling constant of the two most intense peaks ($a^{H}_{CH_3}$ 27.0±0.3 Oe), and a 1 : 2 : 1 triplet ($a_H \sim 24$ Oe), (fig. 5(*b*)).

2,3-DIMETHYLBUTAN-2-OL.—Whilst method A gave only a poorly resolved spectrum, method C gave a nine-line spectrum shown in fig. 5(*c*) of overall width 120 Oe. This is due to a mixture of radicals of which one displays a basic seven-line spectrum of binomial character (a_H 20 Oe) and which cannot therefore be $Me_2\dot{C}H$, known to exhibit an eight-line spectrum with a_H 26.4 Oe.[17]

ALLYLIC ALCOHOLS

ALLYL ALCOHOL.—Methods A, C and D all resulted in production of a four-line spectrum of total width 44.3 Oe (fig. 6(*a*)) and identical in appearance and width with that reported by Maas and Volman using H_2O_2 photo-oxidation at 125 K [18]

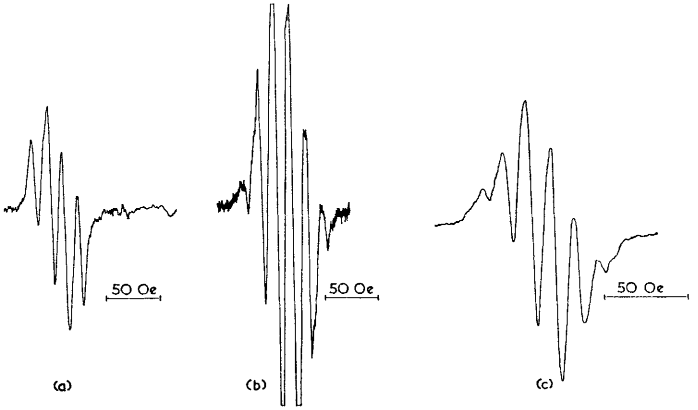


FIG. 6.—E.s.r. spectra obtained during photo-oxidations of allylic alcohols by Ce(IV). (*a*) allyl alcohol; (*b*) but-2-en-1-ol (193 K); (*c*) but-3-en-2-ol (130 K).

and by other groups using a similar technique.[19, 20] It is assigned to the allyl-type radical $CH_2{=}CH{-}\dot{C}HOH$.

BUT-2-EN-1-OL (CROTYL ALCOHOL).—Method A ([substrate] ~ 1 M) produced a broad spectrum at 77 K showing only traces of structure, but subsequent warming to 193 K yielded a six-line spectrum shown in fig. 6(*b*) of total width 77 ± 1 Oe (a_H 15.4 Oe). This is identical with the spectrum obtained by photo-oxidation of crotyl alcohol by H_2O_2 and measured at 122 K [18] (total width 75 Oe) and is assigned to $CH_3{-}CH{=}CH{-}\dot{C}HOH$.

BUT-3-EN-2-OL.—Method C gave a partly-resolved six-line spectrum at 77 K but subsequent warming to 130 K resulted in improved resolution illustrated in fig. 6(*c*) and an overall width of 71 Oe was obtained, i.e., $a_{H(\text{average})}$ equals 14.3 Oe. Again, an identical spectrum of 70 Oe width was obtained on low-temperature oxidation by $\cdot OH$.[18]

BENZYLIC ALCOHOLS

BENZYL ALCOHOL.—Method C produced only $NO_2\cdot$ after 8 min of photolysis. However, by shaking benzyl alcohol with ceric perchlorate solution, removing the organic layer, degassing and photolyzing that at 77 K, a spectrum consisting of a large singlet of width 50 Oe and three smaller peaks on either side was obtained which could not be analyzed. It did not appear to be the spectrum expected of $C_6H_5\dot{C}HOH$.[21]

1,2-DIPHENYLETHANOL.—Method E produced the spectrum shown in fig. 7(*a*) which was analyzed by computer simulation as due to benzyl radical (fig. 7(*b*)) with the coupling constants, a_{CH_2} 16.5, $a_{H(4)} = a_{H(2,6)}$ 5.5 Oe. These compared with values of a_{CH_2} 16.4, $a_{H(4)}$ 6.19, $a_{H(2,6)}$ 5.17 Oe reported for a solution spectrum [21] and with identical values obtained from a solid-state spectrum.[22]

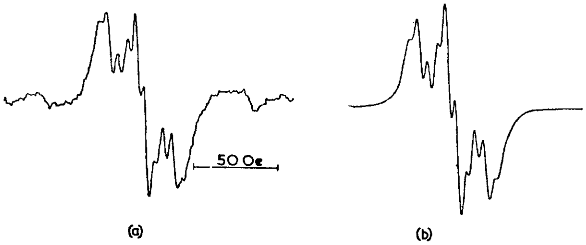


FIG. 7.—E.s.r. spectrum of benzyl radical obtained during photo-oxidation of 1,2-diphenylethanol by Ce(IV). (*a*) experimental; (*b*) computer simulation.

1,1-DIPHENYLETHANOL.—Method E produced a spectrum of $\cdot CH_2CN$. Photolysis of ceric ammonium nitrate in CH_3CN for a comparable period gave no signal and we ascribe the appearance of $\cdot CH_2CN$ to attack of phenyl radical upon CH_3CN.

DISCUSSION

The photochemistry of complexes of one-equivalent oxidizing metal ions is dominated by CTTM processes especially with light of wavelength < 400 nm, and this must be particularly so for Ce(IV) which is strongly oxidizing in $HClO_4$ and HNO_3 media (E° being $+1.70$ and $+1.61$ V respectively for the Ce(IV)/Ce(III) couple) [23] and which has an inert-gas electronic configuration, being free, therefore, of complicating photosubstitution processes, induced by ligand field transitions.[1] Photolysis of complexes with simple ligands, such as NO_3^-, results in simple electron abstraction from the ligand to give a small inorganic free radical like $NO_3\cdot$ identifiable by optical and e.s.r. spectroscopy in fluid [4] or frozen solution.[24] An alternative mode of formation of $NO_3\cdot$ and also $HSO_4\cdot$ (or $SO_4^-\cdot$) has been suggested to be preliminary oxidation of ligand water [25];

$$Ce^{4+}\,aq \xrightarrow{h\nu} Ce^{3+} + H^+ + \cdot OH,$$

followed by attack of ·OH upon free anion;

$$\cdot OH + NO_3^- \rightarrow OH^- + NO_3\cdot$$

$$\cdot OH + HSO_4 \rightarrow OH^- + HSO_4\cdot$$

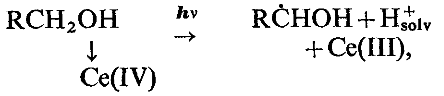
This remains controversial, however,[24] and the intermediacy of ·OH is ruled out in those of our experiments involving solutions of ceric ammonium nitrate in neat organic liquid. Addition of molecules such as alcohols to solutions of ceric perchlorate and ceric ammonium nitrate shifts the absorption to the visible and increases the extinction respectively, imparting a red or orange-red colour, which corresponds to the CTTM band of the resulting complex, usually of 1 : 1 stoichiometry with a formation constant in the range 0.5 to 10 l. mol^{-1}.[26] By restricting the irradiation wavelength to $\lambda > 300$ nm we are partially confining excitation to these CT transitions, and the transitions within the normal aquo species, $CeOH^{3+}$, or its polymeric forms, in $HClO_4$ are less involved. Ceric ammonium nitrate does show appreciable absorption from a CT band (λ_{max} 290 nm) in the region we are utilizing, and the appearance of radicals derived from the nitrate ligand in the absence of organic substrate indicates some degree of photo-oxidation; however, the increased extinction of the alcohol-containing solutions implies preferential absorption of light by the organic complexes. The behaviour, generally closely parallel, of the Ce(IV) perchlorate and nitrate solutions containing alcohols, is reasonable indication that the nitrate ligands do not greatly affect the photochemistry, although the ubiquitous wing peaks of *ca.* 117 Oe separation in most, if not all, experiments involving the nitrate could be adduced as evidence for electron transfer to Ce(IV) from NO_3^- operating in parallel with that from organic ligand.

The assignment of these wing peaks to $NO_2\cdot$ rests on the following evidence: (i) The particularly intense spectrum obtained from benzyl alcohol by method C could be analyzed by the method described by Kneubühl [27] as follows, $g_1 = 2.006$, $g_2 = 2.002$, $g_3 = 1.995$ (all ± 0.001), $a_1^N = 48.9$ Oe, $a_2^N = 64.5$ Oe, $a_3^N = 43.2$ Oe (all ± 0.5 Oe). These values are similar to those reported by Ayscough and Collins [28] for $NO_2\cdot$ in an alkaline glass at 77 K following photolysis of $Fe(CN)_6^{4-}$ ions in the presence of 0.5 M NO_3^- ions.

(ii) The spectrum of $NO_3\cdot$, the principal alternative radical expected, is much narrower, having an axially symmetrical g tensor and no hyperfine splitting, with $g_{\parallel} = 2.0041 \pm 0.0003$ and $g_{\perp} = 2.0207 \pm 0.0003$.[24] This species was produced in a " soft " lattice of HNO_3 and $HClO_4$ at 88 K by 320-420 nm irradiation of 10^{-2} M ceric ammonium nitrate. Continued photolysis in this wavelength range did not result in any transformation of $NO_3\cdot$ into $NO_2\cdot$, indicating that $NO_2\cdot$ produced in our experiments is not a product of secondary photolysis of $NO_3\cdot$ (which *is* photolyzed by light of $\lambda > 490$ nm to give diamagnetic products).[24]

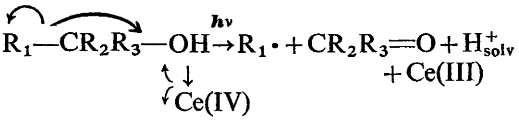
The origin of the $NO_2\cdot$ signal is problematical. We obtained a strong signal from a solution of ceric ammonium nitrate in benzyl alcohol even when a filter transmitting only beyond 360 nm was employed, conditions normally giving rise to only $NO_3\cdot$ in acid glasses.[24] It seems possible that a small fraction of the organic radicals produced are able to reduce neighbouring NO_3^- ions to $NO_2\cdot$ and OH^-.

The photo-oxidation of the simplest primary alcohols $\mathrm{RCH_2OH}$ can be expressed by eqn (1):



$$\underset{\substack{\downarrow\\ \mathrm{Ce(IV)}}}{\mathrm{RCH_2OH}} \xrightarrow{h\nu} \mathrm{R\dot{C}HOH + H^+_{solv} + Ce(III)}, \qquad (1)$$

the corresponding hydroxyalkyl radical being found with methanol, ethanol, propan-1-ol, 2-methylpropan-1-ol, butan-1-ol and pentan-1-ol. This mode is also found with propan-2-ol but in additional some C—C cleavage takes place to give $\mathrm{CH_3\cdot}$. Cleavage is also apparent with butan-2-ol and pentan-3-ol and is the normal mode of photo-oxidation of tertiary alcohols by Ce(IV). The extremely prompt appearance of $\mathrm{CH_3\cdot}$ from tert-butanol, e.g., suggests a concerted mode of cleavage (2)



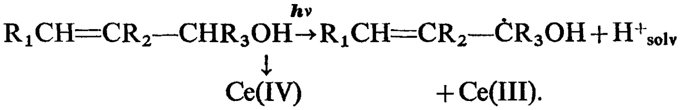
$$\mathrm{R_1{-}CR_2R_3{-}}\underset{\substack{\downarrow\\ \mathrm{Ce(IV)}}}{\mathrm{OH}} \xrightarrow{h\nu} \mathrm{R_1\cdot + CR_2R_3{=}O + H^+_{solv} + Ce(III)} \qquad (2)$$

rather than intermediate formation of $\mathrm{R_1R_2R_3C{-}O\cdot}$ for which we find no e.s.r. signal. The primary production of alkyl radicals during photo-oxidation of tertiary alcohols and some secondary alcohols by Ce(IV) contrasts with the behaviour of $\mathrm{OH\cdot}$ which oxidizes alcohols by hydrogen-abstraction [11, 13, 15] in both matrices and solution:

$$\mathrm{CH_3{-}CMe_2{-}OH + OH\cdot \rightarrow \cdot CH_2{-}CMe_2OH + H_2O.}$$

This rules out intermediacy of $\mathrm{OH\cdot}$ in photo-oxidation in perchlorate matrices.

Allylic alcohols produce the corresponding hydroxyallyl radical by a process analogous to (1),



$$\mathrm{R_1CH{=}CR_2{-}}\underset{\substack{\downarrow\\ \mathrm{Ce(IV)}}}{\mathrm{CHR_3OH}} \xrightarrow{h\nu} \mathrm{R_1CH{=}CR_2{-}\dot{C}R_3OH + H^+_{solv} + Ce(III).}$$

Here a close similarity exists between oxidation by $\mathrm{OH\cdot}$ and photo-oxidation by Ce(IV).

The course of photo-oxidation of alcohols by Ce(IV) has much in common with that of thermal oxidation by the same oxidant. Both reactions proceed through a 1 : 1 complex between oxidant and substrate and involve either attack on the C—H bond of the $\mathrm{CHOH^-}$ group (for primary and secondary alcohols) or fragmentation of an alkyl group to yield a ketone (for tertiary alcohols).[29] C—C cleavage is also a feature of secondary alcohol photo-oxidation, e.g., of pentan-3-ol, and cleavage has been reported during the thermal oxidation of this substrate by the highly oxidizing $\mathrm{CoOH^{2+}}$ ion.[30] A further analogy between thermal and photochemical oxidation by Ce(IV) is instanced by 1,2-diphenylethanol which undergoes thermal oxidation according to a scheme,[31]

$$\mathrm{C_6H_5CH_2CH(C_6H_5)OH \xrightarrow{Ce(IV)} C_6H_5CH_2\cdot + C_6H_5CHO + H^+ + Ce(III).}$$

Fig. 7 illustrates the spectrum of benzyl radical produced by an identical fragmentation in the Ce(IV) photo-oxidation.

1,1-Diphenylethanol might be expected to break down on photo-oxidation to a phenyl radical which, even at 77 K, is sufficiently reactive to attack hydrogen-containing molecules of the matrix [32] and accordingly we attribute our observed spectrum of $\mathrm{\cdot CH_2CN}$ to such a secondary reaction.

Secondary reactions are evident in other of our examples. The $CH_3\cdot$ produced from tert-butanol slowly attacks the alcohol matrix to produce $\cdot CH_2CMe_2OH$ as indicated in fig. 4.

From these experimental results it is clear that the technique described affords a useful insight into the primary processes in photo-oxidation. Use of Ce(IV) as the perchlorate or nitrate enables a more comprehensive picture to be gained of the various mechanisms of oxidation than the similar experiments on oxidative decarboxylation of carboxylic acid complexes of Pb(IV).[6] The high reactivity of Ce(IV) towards certain polyfunctional organic ligands can be overcome by using the milder U(VI) species as oxidant.

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