The interplay of electronic, steric and stereoelectronic effects in hydrogen-atom abstraction reactions of SO4−•, revealed by EPR spectroscopy

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Attack by $SO_4^{-\bullet}$ (generated by photolysis and one-electron transfer) on a number of carbohydrates and some model compounds has been followed directly by EPR spectroscopy.

$SO_4^{-\bullet}$ is a reactive, electrophilic species but is more selective (less reactive) than $HO^{\bullet}$. We present evidence for the importance of polar effects and radical stabilisation, especially in determining trends in selectivity. Examples include the preference for C–H abstraction α to a ring oxygen atom in a five-membered ring (*e.g.* THF, sucrose, β-D-fructofuranose) and abstraction of the axial C^1 hydrogen atom from β-D-glucose.
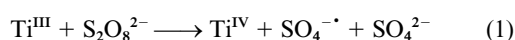
The reaction of $SO_4^{-\bullet}$ with α-D-glucose is selective towards the C^2, C^5 and C^6 positions. This reflects the activating effect of a β-oxygen substituent where the radical orbital can eclipse the β-C–O bond providing a SOMO–σ* interaction which stabilises the developing radical centre. For *myo*-inositol, abstraction is also observed from axial C–H bonds for which the resulting radicals are stabilised by an axial β-OH substituent but, due to the absence of a ring oxygen atom, more rapid abstraction occurs from the equatorial C–H bond.
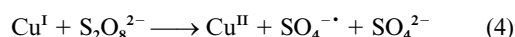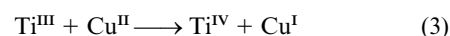
1. Introduction

It is generally accepted that the hydroxyl radical is one of the most reactive species known. Many of its reactions, including examples of hydrogen-atom abstraction, have rate constants approaching the diffusion-controlled limit (*ca.* 10^{10} dm³ mol⁻¹ s⁻¹).[1] Nevertheless, some trends in reactivity (and hence selectivity in reaction) can be discerned:[1] for example hydrogen-abstraction from *tert*-butyl alcohol (6×10^8 dm³ mol⁻¹ s⁻¹, to give $^{\bullet}CH_2CMe_2OH$) is significantly slower than from ethanol (1.9×10^9 dm³ mol⁻¹ s⁻¹, to give $^{\bullet}CHMeOH$ predominantly) but faster than that from ethanoic acid (1.6×10^7 dm³ mol⁻¹ s⁻¹, to give $^{\bullet}CH_2CO_2H$). This is believed to reflect the importance of polar effects and the electrophilic character of the hydroxyl radical (see *e.g.* ref. 2). Steric effects are not generally thought to be important but there are reported examples of the influence of stereoelectronic effects including the apparent preference of attack at the C–H bond adjacent to the ring oxygen in the reaction of furanose sugars (for instance to give **1**

preferentially from β-D-fructofuranose),[3] in contrast to the behaviour with pyranose sugars, for which reaction with the C–H bonds appears to be unselective.[4] This selectivity, which evidently involves optimum overlap between the developing radical centre and the lone pair of electrons on the adjacent oxygen, has also been noted in the reactions of $^tBuO^{\bullet}$ with ethers:[5] the relatively high selectivity for the C–H bond adjacent to oxygen in tetrahydrofuran compared with several other cyclic or acyclic examples is attributed to the relatively small dihedral

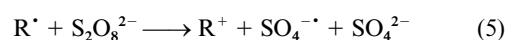angle (θ) between the C–H bonds and the p-type orbital on oxygen (**2**).[6]

The radical anion $SO_4^{-\bullet}$ can be generated by the photolysis[7] or thermolysis[8] of the peroxydisulfate dianion as well as by the one-electron reduction of peroxydisulfate[9] (and in some cases peroxymonosulfate)[10] by low-valent transition metal ions. The use of (catalytic) copper(II) and peroxydisulfate as an oxidant evidently involves similar reactions.[11] We have established conditions under which steady-state concentrations of radicals formed from reactions involving $SO_4^{-\bullet}$ (for example obtained *via* reaction of Ti^{III} and $S_2O_8^{2-}$ in a flow system),[9] can be directly detected by EPR spectroscopy [reactions (1) and (2)],

$$Ti^{III} + S_2O_8^{2-} \longrightarrow Ti^{IV} + SO_4^{-\bullet} + SO_4^{2-} \qquad (1)$$

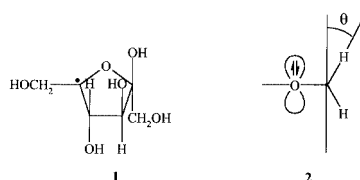$$SO_4^{-\bullet} + RH \longrightarrow HSO_4^{-} + R^{\bullet} \qquad (2)$$

and have shown that the addition of low concentrations of Cu^{II} can enhance the rate of generation of $SO_4^{-\bullet}$ (and the intensity of the spectra) *via* reactions (3) and (4).[11] As we shall reiterate

$$Ti^{III} + Cu^{II} \longrightarrow Ti^{IV} + Cu^{I} \qquad (3)$$

$$Cu^{I} + S_2O_8^{2-} \longrightarrow Cu^{II} + SO_4^{-\bullet} + SO_4^{2-} \qquad (4)$$

below, conditions can be established under which there is no effective contribution to subsequent radical destruction from either oxidation by $S_2O_8^{2-}$ [reaction (5)] or reaction with Cu^{II} or

$$R^{\bullet} + S_2O_8^{2-} \longrightarrow R^{+} + SO_4^{-\bullet} + SO_4^{2-} \qquad (5)$$

Cu^{I} [NB Cu^{I} reduction of non-conjugated radicals, reaction (6), can be extremely rapid].[12]

$$R^{\bullet} + Cu^{I} \xrightarrow{H^{+}} RH + Cu^{II} \qquad (6)$$

A selection of rate constants have been reported for the overall reaction of $SO_4^{-\cdot}$, generated photolytically, with a series of alcohols, ethers and alkenes.[7,13–15] It has been established that C–H abstraction occurs *via* direct attack rather than by electron transfer followed by proton loss. The results show that the reactivity of $SO_4^{-\cdot}$ is somewhat lower than that of $HO^{\cdot}$ (with rate constants in the range 8.4×10^5–1.4×10^9 dm³ mol⁻¹ s⁻¹); its increased reactivity with a range of C–H bonds adjacent to oxygen has been largely attributed to the radical-stabilising effect of the α-oxygen [*i.e.* lower bond dissociation energy (BDE) of the C–H bonds].

We aimed to utilise EPR spectroscopy to determine the relative reactivities of $SO_4^{-\cdot}$ at different sites within a wide range of compounds *via* direct observation of the first-formed radicals. We might expect $SO_4^{-\cdot}$ to show enhanced selectivity compared with $HO^{\cdot}$, with greater influence from polar and stereoelectronic effects, and perhaps greater sensitivity to steric effects. In view of the continued interest in $SO_4^{-\cdot}$ as an inexpensive water-soluble oxidant (*cf.* for example its use to prepare carbohydrate-derived co-polymers with alkenes),[16] we set out to explore its reactivity with cyclic and acyclic model compounds as well as a series of carbohydrates chosen so as to probe the polar, steric and stereoelectronic effects in radical attack.

2. Results and discussion

Our study generally involved an approach in which an aqueous solution of the substrate (in excess, typically 0.1 mol dm⁻³) is mixed, using a three-way flow-system with Ti^{III} [1×10^{-3} mol dm⁻³, as $Ti_2(SO_4)_3$], peroxydisulfate anion (8×10^{-3} mol dm⁻³, as $Na_2S_2O_8$) and Cu^{II} (3.5×10^{-5} mol dm⁻³, as $CuSO_4 \cdot 5H_2O$) shortly (*ca.* 30 ms) before passing through the cavity of an EPR spectrometer (pH *ca.* 2.5, at room temperature); all concentrations (here and elsewhere in this paper) are those after mixing. The reactions which occur are believed to be (3), (4), and (2), leading to a typical steady state concentration of [R$^{\cdot}$] in the cavity of *ca.* 3×10^{-6} mol dm⁻³ as determined by comparison with the integrated intensity of the spectrum of $^{\cdot}CH_2OH$ generated in the reaction of $HO^{\cdot}$ and methanol under identical conditions.[17] Relative steady-state concentrations were obtained by double integration. Experiments were also carried out at higher concentrations of $S_2O_8^{2-}$ (up to 2×10^{-2} mol dm⁻³) and reduced concentrations of Cu^{II} (down to 1×10^{-5} mol dm⁻³). Additional experiments involved the direct UV-photolysis ($\lambda > 250$ nm) of slowly flowing aqueous solutions of substrates (typically 0.1 mol dm⁻³) in the presence of $S_2O_8^{2-}$ (0.1 mol dm⁻³), a method which tends to give somewhat weaker signals from the appropriate radicals: the same radicals were detected in both sets of experiments.

a) Model compounds: alcohols and ethers

Reaction of $SO_4^{-\cdot}$ with ethanol and propan-2-ol gave relatively intense spectra showing signals attributable solely to the appropriate oxygen-conjugated radicals (α-radicals) (see Fig. 1 a,b and Table 1: hyperfine splittings of these radicals[18] will not be repeated here). Even at low concentrations of Cu^{II} there was no trace of the β-radicals ($^{\cdot}CH_2CH_2OH$, $^{\cdot}CH_2CHMeOH$) which are formed in significant, though minor, amounts with $HO^{\cdot}$.[19] Related alcohols and ethers behaved similarly (*e.g.* diethyl ether and diisopropyl ether, see Table 1). Tetrahydrofuran showed a strong signal from the α-conjugated radical (Fig. 1c) with a trace of an open-chain radical, $^{\cdot}CH_2CH_2CH_2OCH=O$, formed from one-electron reduction of THF hydroperoxide (formed *via* autoxidation of the THF);[20] in contrast $HO^{\cdot}$ gives both the α- and β-radicals, although the α-radical is the major product. Exclusive attack by $SO_4^{-\cdot}$ at the C–H bond adjacent to oxygen (>95%) is believed to reflect the operation of a polar effect, whereby there is a stabilising contribution to the transition state for hydrogen-abstraction (Scheme 1 below). In contrast, the −I effect of the oxygen

Table 1 Radicals observed from the reactions of $SO_4^{-\cdot}$ with some alcohols and ethers

Substrate	Radicals observed
CH_3CH_2OH	$CH_3\dot{C}HOH$
$CH_3CH(OH)CH_3$	$CH_3\dot{C}(OH)CH_3$
$CH_3–C(CH_3)_2OH$	$\dot{C}H_2–C(CH_3)_2OH$
$CH_3CH_2–O–CH_2CH_3$	$CH_3\dot{C}H–O–CH_2CH_3$
$H(CH_3)_2C–O–C(CH_3)_2H$	$H(CH_3)_2C–O–\dot{C}(CH_3)_2$

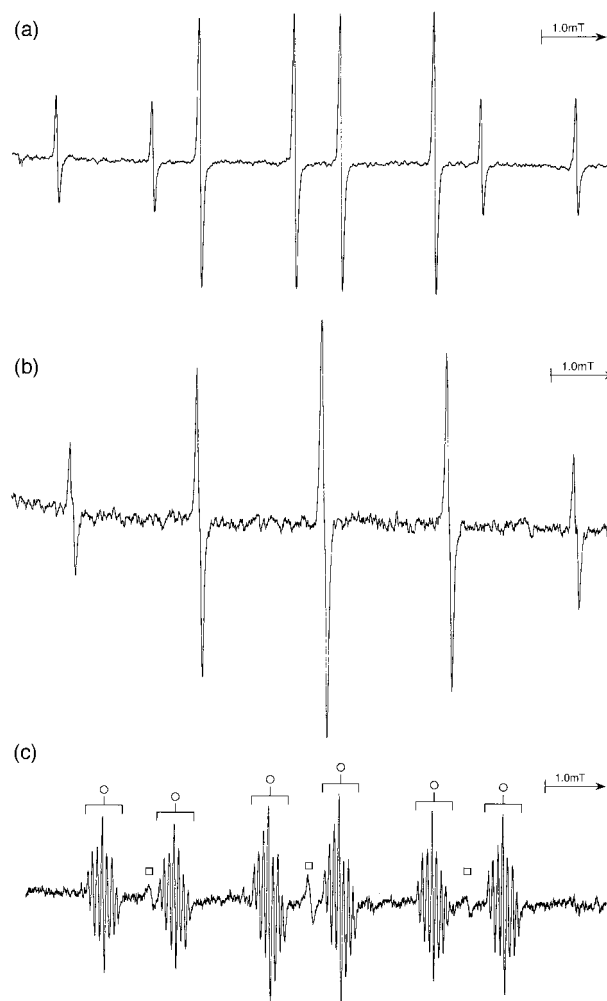**Fig. 1** EPR spectra observed for the reaction between $SO_4^{-\cdot}$ and the following compounds at pH *ca.* 2.5: (a) ethanol (0.7 mol dm⁻³); (b) propan-2-ol (0.3 mol dm⁻³), NB the full width of the spectrum is not shown; (c) tetrahydrofuran (0.15 mol dm⁻³), ○ signals due to the α-radical, □ signals due to $^{\cdot}CH_2CH_2CH_2OCH=O$.

would be expected to deactivate the β-C–H bonds to attack, which may account for the lack of observation of these species. We expect this to be a particularly marked effect for THF and related compounds for which there is excellent overlap between
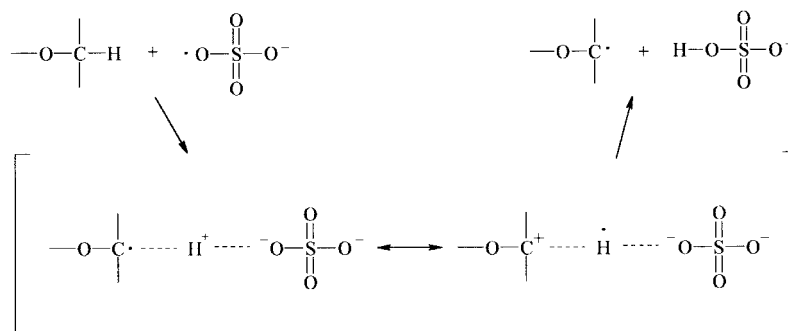
Scheme 1

the developing radical centre and the p-orbital containing the lone pair of electrons of the ring oxygen (**2**) (*cf.* ref. 5). Especially of note are the very strong signals observed from 1,3-dioxolane, whose overall reactivity and the predominance of the di-conjugated species reflect the extra stabilisation (and polar effects) of two α-oxygen atoms.

The extension of this study to some carbohydrates of well-defined structure allowed us to explore the reactivity of individual C–H bonds with established geometries and to investigate whether axial or equatorial hydrogen-atom abstraction is preferred, as well as to compare the effect of conjugation to an endo- or exocyclic oxygen. In particular we aimed to rationalise the apparent contrast between the claim for more rapid hydrogen abstraction from an equatorial position adjacent to a hydroxy group by excited state benzophenone (in *cis*- and *trans*-4-*tert*-butylcyclohexanol, **3** and **4**)[21] and the
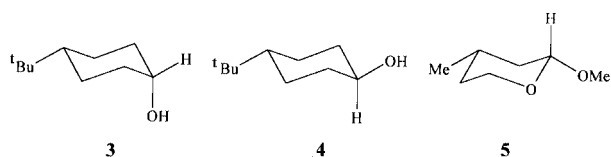
evidence that an axial C–H bond is more rapidly abstracted by benzophenone from *cis*-2-methoxy-4-methyltetrahydropyran (**5**) (as indicated) than the equivalent equatorial hydrogen atom from the *trans*-isomer.[22]

b) α-D-Glucose and related compounds

In contrast with its reaction with HO• (from which all radicals formed by C–H abstraction are observed in relatively unselective fashion),[4] α-D-glucose reacts with $SO_4^{-•}$ to give a spectrum dominated by signals due to the C^1-, C^2-, C^5- and C^6-radicals (**6–9**, Table 2), the major signals being from the C^2- (**7**) and C^6-radicals (**9**) and the carbonyl conjugated species **10** formed *via* the rapid acid-catalysed rearrangement of the C^2-species (see Table 2 and Fig. 2a): there was little or no evidence for the C^3- or C^4-derived species. It is perhaps not surprising that reaction at C^6 occurs readily (it is sterically and statistically favoured). We hypothesize at this stage that the dominance of **7** reflects the stabilising interaction (SOMO–σ*) between the unpaired electron at C^2 and the (eclipsing) β-OH bond (see **11**)

which makes a contribution to the stabilisation of the transition state; we believe there is a similar interaction involving the β-C–O bond in the C^6-derived radical **9** (the hyperfine splitting of the β-hydrogen reflecting the appropriate stabilised, eclipsed con-
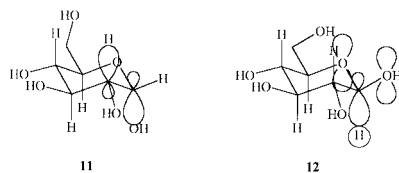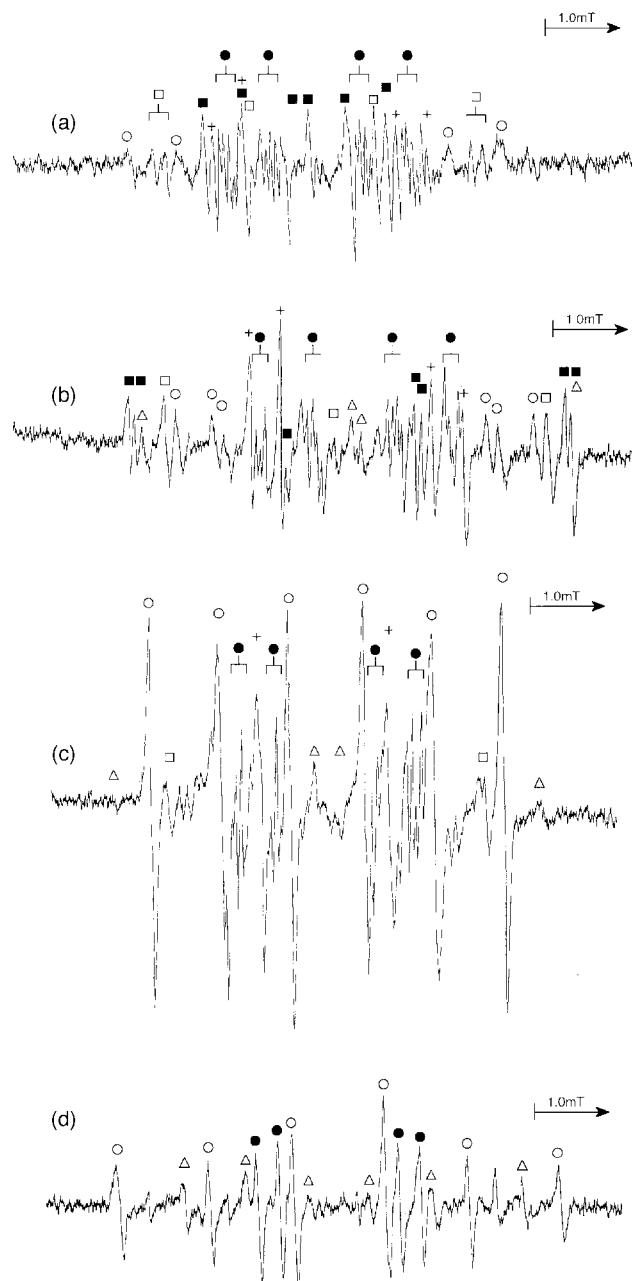

Fig. 2 EPR spectra observed for the reaction between $SO_4^{-•}$ and the following compounds at pH *ca.* 2.5: (a) α-D-glucose (0.017 mol dm^{-3}), + (**6**), □ (**7**), ○ (**8**), ● (**9**), ■ (**10**); (b) β-D-glucose (0.017 mol dm^{-3}), + (**6**), □ (**13**), △ (**14**), ○ (**15**), ● (**16**), ■ (**17**); (c) sucrose (0.017 mol dm^{-3}), □ (**18**), △ (**19**), ● (**20**), + (**21**), ○ (**22**); (d) D-fructose (0.033 mol dm^{-3}), △ (**1**), ○ (**23**), ● (**24**).

formation), and similarly for the C^5-derived radical **8**. Previous studies involving related model compounds such as ethylene glycol have established that such radicals with +M α- and −I β-

Table 2 Structures of radicals observed from the reaction of $SO_4^{-\bullet}$ with some simple carbohydrates

Radical no.	Structure	a (α-H)	a (β-H)	a (other)	Radical no.	Structure	a (α-H)	a (β-H)	a (other)
α-D-Glucose									
6	(structure)		2.450(1)	0.260(1) 0.165(1)	**19**	(structure)		3.100(1) 2.820(1)	0.045(2)
7	(structure)		1.130(1) 2.970(1)	0.160(1)	**20**	(structure)	1.850(1)	0.585(1)	0.140(1) 0.125(1) 0.075(1)
8	(structure)		3.330(1) 0.990(1) 0.710(1)		**21**	(structure)	1.770(1)		
9	(structure)	1.840(1)	0.626(1)	0.140(1) 0.125(1) 0.075(1)	**22**	(structure)		2.950(1) 0.965(1) 0.940(1)	0.050(2)
10	(structure)	1.373(1)		0.533(1) 0.510(1) 0.020(1)	**D-Fructose**				
					1	(structure)		2.587(1) 0.880(2)	
β-D-Glucose									
13	(structure)		2.260(1) 2.850(1)		**23**	(structure)		2.427(2) 1.267(1)	
14	(structure)		2.800(1) 2.930(1)						
15	(structure)		0.653(1) 0.510(1) 3.680(1)	0.053(1)	**24**	(structure)	2.000(1)	0.293(1)	
16	(structure)	1.840(1)	0.773(1)	0.120(1) 0.067(1)	**myo-Inositol**				
17	(structure)	2.030(1)	3.840(1)	0.08(1)	**26**	(structure)		3.005(2)	0.030(1)
Sucrose					**27**	(structure)			
18	(structure)		3.100(1) 1.270(1)	0.050(2)	**28**	(structure)		3.315(1) 0.625(1)	0.130(1) 0.105(1) 0.075(1) 0.033(1)

substituents exist in locked and stabilised conformations;[23] we also note that such an interaction will render the radicals resistant to oxidation.[24] The C^1-radical benefits from conjugation to two α-oxygen atoms (see above).

By comparison, the spectrum from β-D-glucose (Fig. 2b) provides evidence for much greater extent of attack at C^1, to give **6**, and less at C^2, to give **13**. For **6** we believe that susceptibility of the axial C–H bond towards H-abstraction is accelerated by development of overlap with the lone pair of electrons in a p-orbital on the ring oxygen (*cf.* **12**: see also ref.

22); with **13** the equatorial β-OH group cannot provide such assistance.

Weaker signals in the spectrum obtained for β-D-glucose were also observed from radicals obtained by abstraction of C^3–H (**14**) as well as C^5–H (**15**) and C^6–H (**16**) (see Table 2): signals were also observed for **17**, which is formed by elimination of water from **6**. At this stage we draw attention to the relatively low signal intensity from the C^5-derived species in the spectra from α- and β-D-glucose: this is to some extent unexpected given the potentially stabilising (and hence activating) effect of
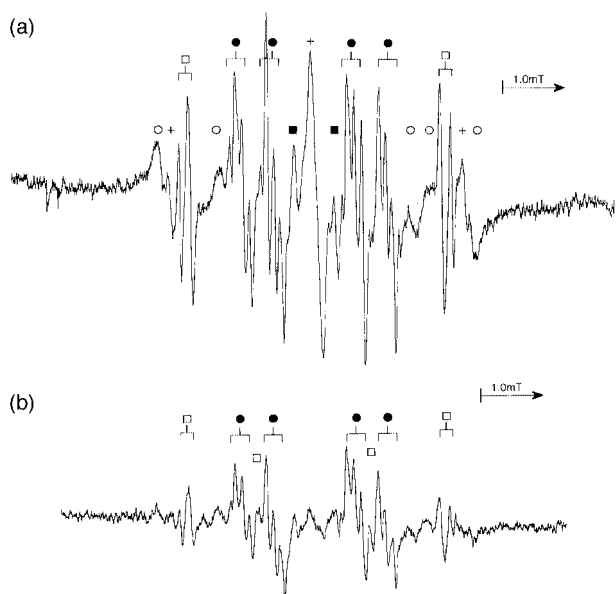
Fig. 3 EPR spectra observed for the reaction of starch (water soluble, 1%) at pH *ca.* 2.5 with: (a) HO$^\bullet$, $\square$ C^2, $\triangle$ C^3, + C^4, $\bigcirc$ C^5, $\bullet$ C^6; (b) SO$_4^{-\bullet}$, $\square$ C^2, $\bullet$ C^6.

the α-oxygen in the ring and the eclipsing β-OH group at C^6. We presume that the β-C^6–OH group does not fully exert its effect in the transition state (unlike C^1–O in the α-D-glucosyl radical shown in **11** and the two α-oxygens in **12**) because the appropriate conformation is not adopted until the radical is fully formed. This is also true for the C^6-radicals formed from α- and β-D-glucose.

The results for methyl α-D-glucopyranoside show a close similarity to those for α-D-glucose itself (with, in addition, attack at the methoxy group to give a spectrum with a_{2H} 1.800 mT and $a_{\gamma H}$ 0.140 mT): signals were also detected for abstraction at C^2 (main), C^3 (trace), C^4 (trace) and especially C^6 (see above).

Sucrose gave the spectrum shown in Fig. 2c (attributed to **18**–**22**), having some notable contrasts between the pattern of attack at the five- and six-membered rings (see Table 2). Thus the relatively intense signal due to **22**, obtained by abstraction from the C^5 atom of the furanose ring, mirrors to some extent the behaviour of HO$^\bullet$ which demonstrates an observable selectivity:[25] very effective overlap of the developing unpaired electron (in the transition state) with the lone pair of electrons on the furanose oxygen evidently activates the C–H towards abstraction. Attack at C^6–H is again noted. In the six-membered ring attack occurs at the C^2 and C^3 as well as at the hydroxymethyl group.

Studies of fructose, carried out under conditions in which mutarotation has been observed to occur (thus with a sample in which the β-D-pyranose form is present as approximately 70% and the β-D-furanose form is approximately 23% and the remaining 7% is various α forms)[26] also illustrate the prevalence of the C^5 β-D-furanose radical **1**, with some attack at C^5 and C^6 in the pyranose form (to give **23** and **24**).

The studies were extended to include a water-soluble form of starch, consisting of approximately eight 1,4-α-linked glucose molecules. As expected the hydroxyl radical gave an EPR spectrum (Fig. 3a) indicating a non-selective reaction, with hyperfine splitting constants similar to those observed for the equivalent radicals from α-D-glucose.[4] The somewhat broadened nature of the signals in the spectrum presumably reflects the size of the radicals formed (*i.e.* slower tumbling), and/or overlap of signals due to closely similar spectra from radicals of a given type (C$_1$ *etc.*) at different points in the chain. The reaction of starch with SO$_4^{-\bullet}$
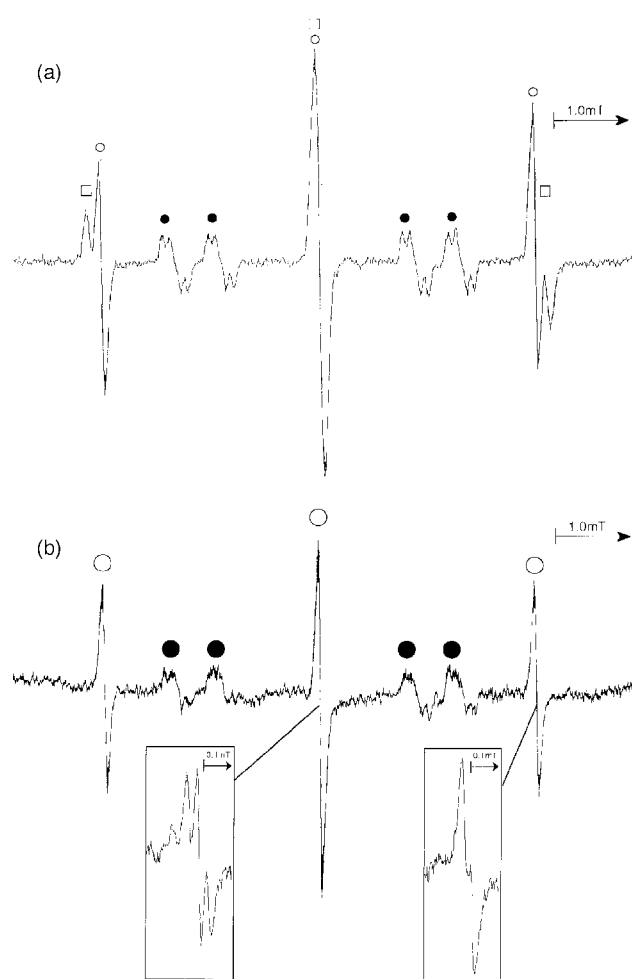

Fig. 4 EPR spectrum observed for the reaction of *myo*-inositol (0.033 mol dm^{-3}) at pH *ca.* 2.5 with: (a) HO$^\bullet$, $\bigcirc$ (**26**) and (**31**), $\bullet$ (**27**) and (**28**), $\square$ (**29**) and (**30**); (b) SO$_4^{-\bullet}$, $\bigcirc$ (**26**), $\bullet$ (**27**) and (**28**), with inset, signals obtained under photolytic conditions (see text).

gave a spectrum which indicates similar reactivity to that observed for its reaction with α-D-glucose; the broad nature of the spectrum (Fig. 3b) makes a precise assignment difficult but it is clear that the dominant radicals formed are C^2- and C^6-derived.

c) *myo*-Inositol

A study of compound **25** allows us in principle to investigate the intrinsic difference in reactivity of axial and equatorial C–H bonds, although stereoelectronic effects (*e.g.* reflecting the geometry of the β-OH) and steric effects may also be important. The spectrum obtained with HO$^\bullet$ (Fig. 4a) has been described previously: it is analysed in terms of one signal (assigned to **27** and **28**) with one axial and one equatorial β-hydrogen atom and three signals due to radicals with two axial β-hydrogens (assigned to **26**, **29** and **30**, and **31**).[27]

The spectrum from the reaction of SO$_4^{-\bullet}$ with *myo*-inositol (Fig. 4b), clearly shows some differences, most notably the loss of the outside lines. Still present are signals from **27** and **28**, which have one axial β-C–H bond and one equatorial β-C–H bond. There is also a sharp and dominant triplet signal: we believe this to be due to a single species with two equivalent β hydrogens. At high resolution (best obtained using photolytic initiation) the outer lines are observed as very small doublets (0.03 mT) and the central line appears as a triplet, as expected for a symmetrical radical exhibiting a second-order effect (see Fig. 4b inset). Given the symmetric nature thereby implied for the radical (*i.e.* either **26** or **31**), the long-range doublet splitting must be from a δ-proton.

25

26 27 28

29 30 31
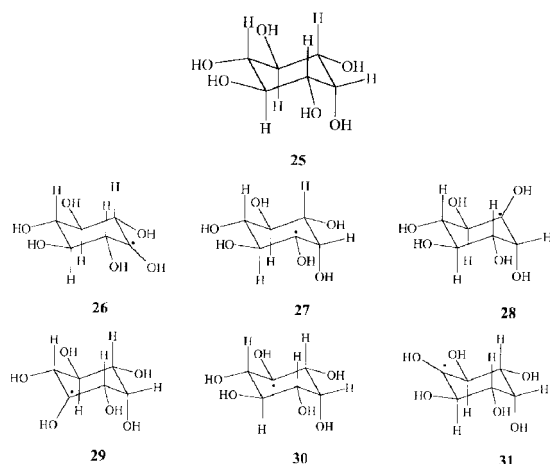
It is clear from the observation of only two signals that attack by $SO_4^{-\bullet}$ is more selective than $HO^\bullet$. The formation of **27** (and of **28**) *via* axial C–H abstraction is notable: this is understandable in terms of the stabilisation of these radicals by the optimum interaction of the unpaired electron at the developing radical centre with the adjacent axial β-OH group (for example, as for the α-D-2-glucosyl radical **7**). Given that axial C–H bond abstraction is not normally encouraged in the absence of other stabilising effects (note, for example, the relative lack of abstraction of the axial hydrogen atoms from the C^3- and C^4-positions of D-glucose and derivatives) we propose that the other radical detected with two axial β-H and a single δ-proton splitting is **26**, formed by abstraction of the single equatorial hydrogen. This evidence is consistent with that presented earlier, (see **3** and **4**, ref. 21) that suggest equatorial hydrogen atom abstraction is preferable in the absence of a ring oxygen. Angular dependent long range γ- and δ-splittings have been resolved for some cyclic aminoxyls with six-membered rings and for some substituted cyclohexyl derivatives:[28,29] for the cyclohexyl radical itself it has been shown that $a_\gamma = -0.106$, 0.095 mT and $a_\delta = 0.038$, 1.02 mT (axial and equatorial respectively), the δ-equatorial proton showing a larger splitting reflecting the effectiveness of spin transmission *via* a W geometry. The magnitude of the doublet splitting detected here and assigned to the axial δ-proton from **26** is entirely consistent with the analysis for cyclohexyl (a larger splitting might have been expected for an equatorial δ-proton). If this assignment is correct the radicals **29** and **30**, generated *via* attack by $HO^\bullet$ on the unactivated axial C–H bonds, have splitting constants reassigned as follows: **31** (a_{2H} 3.005 mT with equatorial δ-H, *ca.* 0.1 mT), and **29** and **30** (a_{1H} 3.213 mT, a_{1H} 3.093 mT; a_{3H} 0.03 mT).

3. Conclusions

Our observations provide evidence for the influence of polar and stereoelectronic effects, especially in the reactions of $SO_4^{-\bullet}$ with alcohols and ethers, including some carbohydrates. The following rationalisation appears to be self-consistent. Equatorial C–H abstraction is preferred for *myo*-inositol, presumably on account of the ease of approach of the $SO_4^{-\bullet}$ and release of the strain between the axial hydroxy substituent and the axial protons. Attack at axial C–H bonds in a variety of sugars can hence be encouraged by a β-OH group, especially when the latter is already held in a pseudo-eclipsing conformation; the effect is less marked when the parent has rotational mobility.

4. Experimental

EPR spectra were recorded on a Bruker ESP 300 spectrometer equipped with an X-band microwave bridge and 100 kHz modulation. Hyperfine splittings and *g* values were determined

directly from the spectrometer's field scan, this having been calibrated with the signal from Fremy's salt ($a_N = 1.3091$ mT,[30] *g* 2.0055[31]): results shown in Tables 1 and 2 were obtained under conditions of high resolution (low modulation amplitude). Radical concentrations were determined, *via* double integration, by comparison with the spectrum obtained from the radical $^\bullet CH_2OH$, formed *via* the reaction of Ti^{III} and H_2O_2 in the presence of methanol. A mixing chamber was employed which allowed simultaneous mixing of three reagent streams *ca.* 30 ms before passage through the cavity of the spectrometer; flow was maintained using a Watson-Marlow 502s peristaltic pump placed on the inlet tubing. pH measurements were made using a Pye-Unicam PW9410 pH meter with the electrode inserted into the effluent stream. The three solutions typically contained (i) titanium(III) sulfate (0.0024 mol dm^{-3}), (ii) sodium peroxydisulfate (0.025 mol dm^{-3}) and (iii) the substrate (0.3 mol dm^{-3}) and $Cu^{II}SO_4\cdot5H_2O$ (1.05×10^{-4} mol dm^{-3}). For photolysis experiments a single stream was flowed through the cavity of the spectrometer, flow was maintained using a Watson-Marlow 101U peristaltic pump. The sample was exposed to UV light ($\lambda > 250$ nm) using a Hanovia 977B-1 1 kW mercury–xenon compact arc light source. The solution typically contained sodium peroxydisulfate (0.1 mol dm^{-3}) and the substrate (0.1 mol dm^{-3}). All solutions were deoxygenated by nitrogen purge both before and during use.

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