Structure and Reactivity of Peroxyl and Sulphoxyl Radicals from Measurement of Oxygen-17 Hyperfine Couplings: Relationship with Taft Substituent Parameters

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A series of peroxyl radicals (ROO') with substituent groups of varying electron withdrawing power have been investigated using electron paramagnetic resonance spectroscopy. Sixteen carbon-based radicals have been produced, identified and reacted with ¹⁷O-labelled molecular oxygen to produce the corresponding peroxyl radical. Carbon-centred radical precursors include alkyl, aromatic, halocarbon, lipid and alcohol radicals. The oxygen-17 hyperfine couplings are shown to monitor closely the spin density distribution on the oxygen atoms in the peroxyl radicals. The experimental ¹⁷O couplings suggest a value of -5.7 mT for the anisotropic coupling parameter, *B*, in good agreement with the theoretical value calculated from improved wavefunctions. An increase in the magnitude of the terminal oxygen coupling is shown to correlate with an increase in the reactivity of peroxyl radicals. In addition, the Taft substituent parameter (σ^*) is also correlated with the oxygen-17 couplings. The results allow estimation of peroxyl radical reactivity from oxygen-17 couplings and suggest that complexed superoxide ion may be more reactive than free O_2^{--} . The cysteine sulphonyl peroxyl and thiol peroxyl radicals are discussed in light of the results for carbon-based peroxyl radicals. The sulphonyl peroxyl radical is suggested to be highly reactive and the thiyl peroxyl radical has unique properties which suggest it is of a different nature.

Owing to their biological impact, the reactions of oxygen radicals have become an increasingly important area of research.1ª Carbon-centred free radicals commonly react with molecular oxygen to form peroxyl radicals (ROO') which can sometimes decompose to form the less reactive superoxide ion (O_2^{-}) ^{2,3} Peroxyl radicals typically lie between aliphatic carbon-centred radicals and superoxide ion in their tendency toward hydrogen abstraction, but until recently, little was known about the relative reactivity of different peroxyl radicals. Several investigators have recently shown that the nature of the R group has a considerable effect on the reactivity of the peroxyl group.⁴⁻⁷ For example, the rate of electron transfer from ascorbate ion to substituted methyl peroxyl radicals has been reported to increase as the Taft substituent parameter (σ^*) of the substituted group increases.6

In previous work we have investigated the reactions of both carbon-based and sulphur-based peroxyl radicals.⁸⁻¹¹ In the latter case we have shown via EPR that cysteine or glutathione thiyl radicals react directly with oxygen to form the thiyl peroxyl radical, RSOO[.] ⁹⁻¹³ This species was found to rearrange under visible light to RSO² which, subsequently, reacted with a second oxygen to form RSO₂OO[.] Oxygen-17 hyperfine couplings for RSOO[.] and RSO₂OO[.] suggest that RSO₂OO[.] has a far greater terminal spin density than RSOO[.] ¹²

In this work we have produced a series of carbon-based peroxyl radicals (ROO') with substituent groups of varying electron-withdrawing power. Through oxygen-17 isotopic substitution the spin density distribution on the oxygen atoms in the peroxyl radicals is monitored and correlated to the reactivity of the peroxyl radicals. In addition, the Taft substituent parameter is correlated with the oxygen-17 couplings. The results allow estimation of peroxyl radical reactivity from the oxygen-17 couplings and suggests RSO_2OO° is similar in reactivity to Cl_3COO° .

Experimental

Oxygen-17 (37 mol % ¹⁷O) was obtained from Icon. Other compounds were obtained from Sigma and Aldrich and were

sed without further purification. Solutes were dissolved $(0.01-0.10 \text{ mol } dm^{-3})$ in 12 mol dm^{-3} LiCl (D_2O) and/or 8 mol dm⁻³ NaClO₄ (D₂O) and the solutions equilibrated with O₂ at *ca.* 0.7 atm.¹²† Peroxyl radicals were produced by γ irradiation at 77 K followed by annealing of the sample in situ. Irradiation of 12 mol dm⁻³ LiCl at 77 K results in trapped electrons (e⁻) and Cl₂⁻. The electron is a good reductant and Cl_2^{-} is usually considered a good one-electron oxidant.^{1b} However, none of the compounds studied in LiCl solutions (except for thiols) were oxidized by Cl_2^{-} . Thus, only the electrons are effective in radical production. Photobleaching irradiated LiCl solutions with visible light mobilizes trapped electrons which then react with dissolved solutes. Electron attachment to organic chlorides (RCl) results in dehalogenation to form R⁻ and Cl⁻.^{14,15} Annealing these solutions mobilizes oxygen and results in the formation of the corresponding peroxyl radical ROO^{*}. ¹⁶ Irradiation of 8 mol dm⁻³ NaClO₄ results principally in O^{•-}.¹² This species is both a good oxidant and hydrogen abstracting agent and oxidizes sulphur-containing compounds with results similar to Cl₂⁻. Several neat solvents (methanol, ethanol, 2-methyl-2propanol, toluene and cumene) were also employed. For the alcohols scavengers were used (table 1) to suppress the formation of $O_2^{\star-}$. Irradiation of neat solvents with dissolved isotopically labelled O₂ resulted initially in solvent carbon radicals and subsequent formation of their corresponding peroxyl radicals on annealing.

After irradiation, spectra were recorded on a Varian E-line Century Series ESR spectrometer with a 9 inch magnet and a variable-temperature Varian E4560 dual cavity. All spectra were calibrated with reference to peroxylamine disulphonate (Fremy's salt, g = 2.0056, $A_N = 1.309$ mT).

Results

In table 1 we report ¹⁷O hyperfine couplings for the peroxyl radicals investigated in this work and a number of others from our previous work on lipids and thiols.^{12,16} For several

^{† 1} atm = 101 325 Pa.

peroxyl radicals more than one matrix was employed but no significant effect of matrix on coupling was found. Fig. 1–3 show the EPR spectra found for several representative carbon-centred radicals and the ¹⁷O labelled peroxyl radicals. They are discussed below. Please note that the sign of the ¹⁷O couplings reported is not measured in this work but is known to be negative from the sign the magnetic moment of the nucleus and the nature of the coupling. For ease of discussion we report magnitudes in the text and tables.

Tetramethylammonium Ion

Irradiation of frozen glassy solutions of tetramethylammonium perchlorate (10 mg cm⁻³) in 8 mol dm⁻³ NaClO₄ at 77 K results chiefly in O⁻⁻ radical. On warming to 175 K for a short period, O⁻⁻ abstracts a hydrogen atom from the tetramethylammonium cation to form the carbon-centred species, $(CH_3)_3N^+CH_2^{-}$ [fig. 1(*a*)]. The spectrum shows a 2.2 mT triplet due to the two protons in the CH₂ group, with anisotropy in the outer lines typical of CH₂^{-.17} A further *ca*. 0.4 mT anisotropic splitting from nitrogen is also present. Further annealing of the sample to 180 K results in the mobilization of labelled oxygen and the formation of the peroxyl radical, $(CH_3)_3N^+CH_2OO^{-}$ [fig. 1(*b*)]. Analysis of this spectrum yields oxygen-17 splittings of 10.28 mT and 5.13 mT from the singly substituted species, $R^{16}O^{17}O^{-}$ and $R^{17}O^{16}O^{-}$, respectively. These splittings are centred near the free-



Fig. 1. First-derivative EPR spectra of a γ -irradiated sample of tetramethylammonium perchlorate and O₂ (37% ¹⁷O) in 8 mol dm⁻³ NaClO₄. (a) The radical (CH₃)₃N⁺CH²₂ is formed by O⁻ attack after annealing (175/150 K). The broad low-field component is due to remaining O⁻. (b) The ¹⁷O-labelled peroxyl radical (CH₃)₃N⁺CH₂OO' forms on further annealing (180/90 K). (c) A firstorder computer simulation which sums the contributions of R¹⁶O¹⁷O' (27%), R¹⁷O¹⁶O' (27%) and R¹⁶O¹⁶O' (47%) using couplings in table 1. The double-substituted species (R¹⁷O¹⁷O) is not included in the simulation, but its (weak) components are found in (b) and are marked. The first temperature is the highest annealing temperature and the second the temperature at which the spectrum was recorded.

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electron g value at 2.003. A simulation based on these parallel couplings (A_{\parallel}) and g values of 2.035, 2.008 and 2.003 is shown in fig. 1(c). The simulation sums the contributions of the species $\tilde{R}^{16}O^{17}O$, $R^{17}O^{16}O$ and $R^{16}O^{16}O$ with A_{\perp} equal to zero; this value of A_{\perp} is used because we do not observe lines from the A_x or A_y principal values in our experimental spectra. However, we believe that A_x (g = 2.008) is near zero and A_y (g = 2.035) may be as large as 1.5 mT (see Discussion); the A_y components are obscured by the spectrum from R¹⁶O¹⁶O. A number of smaller components due to the double-substituted species, R¹⁷O¹⁷O', marked in the figure, are also observed and follow intensity patterns predicted from first-order simulations for two A_{\parallel} couplings whose hyperfine tensors are coaxial. These components are not as readily observed in most other peroxyl radicals. In this radical the 2:1 ratio (10.28/5.13) of hyperfine couplings creates a superposition of A_{\parallel} components of the doublesubstituted species which increases their intensity.

Alcohol Peroxyl Radicals

A series of alcohol peroxyl radicals were produced by irradiation of neat alcohols with electron scavengers (table 1) or of alcohols in LiCl matrices. No solvent effect was found on the ¹⁷O hyperfine couplings (table 1). The alcohol radicals produced from methanol (HOCH₂), ethanol [HO(CH₃)CH] and 2-propanol [(CH₃)₂CH] were identified in irradiated samples without oxygen. The spectra show the anisotropic lineshapes and hyperfine couplings characteristic of each of these species. For alcohol samples without an electron scavenger considerable amounts of labelled superoxide ion are found immediately after radiation. This is due to electron attachment to molecular oxygen, rather than the result of the well-known decomposition of alcohol peroxyl radicals to $O_2^$ and aldehyde, since in the presence of CCl₃Br or CFCl₃, O₂ is not found.^{1a} All of the alcohol peroxyl radicals investigated have similar oxygen-17 couplings, near 9.5 mT and 5.8 mT (table 1).

Halocarbon Peroxyl Radicals

A series of halocarbon peroxyl radicals were also investigated (table 1). Fig. 2(a) shows the spectrum of CCl₃ produced by the y-irradiation of CCl₃Br dissolved in methanol. Electron attachment to CCl₃Br produces CCl₃ whereas the positive hole results in the methanol species, 'CH₂OH. Annealing to 93 K results in the formation of both CCl₃OO' and HOCH₂OO'; however, the lines from CCl₃OO' are narrower and stand out clearly in the spectrum [fig. 2(b)]. The simulation shown in fig 2(c) is based on couplings of 10.26 mT and 4.92 mT with a 0.4 mT linewidth. Upon annealing to 98 K the CCl₃OO' radical disappears and only the methanol peroxyl species is found. This is indicative of the high reactivity of the trichloromethyl peroxyl radical, which is likely to attack the methanol solvent through hydrogen abstraction [reaction (I)]

$$CCl_3OO' + CH_3OH \rightarrow CCl_3OOH + CH_2OH.$$
 (I)

The mono-, di- and tri-chloromethyl peroxyl radicals show couplings in which $|A_{\parallel}(1)|$ increases with additional chlorine substitution and $|A_{\parallel}(2)|$ decreases concomitantly. Even larger values of $|A_{\parallel}(1)|$ are found for fluorinated species (table 1). The largest value of $|A_{\parallel}(1)|$ and smallest value of $|A_{\parallel}(2)|$ we observed were for the peroxyl radical(s) formed from CClF₂CCl₂F (CClF₂CClFOO[•] and CCl₂FCF₂OO[•]), which gave $|A_{\parallel}(1)| = 10.50$ mT and $|A_{\parallel}(2)| = 4.52$ mT. The largest value of $|A_{\parallel}(1)|$ reported is for the terminal peroxyl radical

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Table 1. Oxygen-17 hyperfine couplings of peroxyl radicals

compound	radical	matrix	$ A_{ }(1) /\mathrm{mT}^{a}$	<i>A</i> (2) /mT ^a	T/K	ref.
carbon-based peroxyl radicals ^b nrimarv						
tetramethylammonium perchlorate	$(CH_3)_3N^+CH_2OO^-$	8 mol dm ⁻³ NaClO ₄ /D ₂ O	10.28	5.13	60	this work
chloroacetic acid	$(CO_{1}H)CH_{2}OO$	12 mol dm ^{-3} LiCl/D ₂ O	9.8	5.84	77	this work
glycine	$(CO_2^-)CH_2OO^-$	12 mol dm ^{-3} LiCl/D ₂ O	9.6	5.76	<i>LL</i>	this work
$\hat{\beta}$ -chloroalanine	$NH_3^+CH(CO_2^-)CH_2OO$	12 mol dm ⁻³ LiCl/ D_2O	9.81	5.89	<i>LL</i>	12
cyanomethane	NCCH,00	8 mol dm ⁻³ NaClO ₄	9.84	5.72	94	this work
3-chloro-1,2-propanediol	HOCH, CH(OH)CH, OO'	12 mol dm $^{-3}$ LiCl/D,O	9.80	5.80	107	this work
3-chloropropanol	HOCH, CH, CH, OO	12 mol dm ⁻³ LiCl/D,O	9.75	5.80	100	this work
benzyl alcohol	фСН ₂ 00'/фСН(0Н)00'	neat	9.56	5.7	<i>LT</i>	this work
benzyl bromide	¢CH ₂ 00'/HOCH ₂ 00'	methanol	9.54	5.66	LL	this work
utcorot methanol	HOCH-DO	CH,OH/CCL,Br	9.48	5.68	06	this work
ethanol	HOCHICH, JOO.	C,H,OH/CCI,Br	9.48	5.82	11	this work
isopropyl alcohol (IPA)	HOC(CH ₃),00	1:112 mol dm ⁻³ LiCl: IPA	9.59	5.75	66	this work
secondary	8					
DL-alanine	(CO ²)CH(CH ³)OO	12 mol dm ^{-3} LiCl/D ₂ O	9.44	5.93	100	12
methyl oleate	RCH-CHCH(OO')R'	urea clathrate	9.48	5.87	108	16
methyl stearate	RCH ₂ CH(00')CO ₂ CH ₃	urea clathrate	9.46	5.97	108	16
tertiary						
tert-butyl bromide	(CH ₃) ₃ COO	methanol	9.40	5.90	77	this work
cumene	$\phi C(CH_3)_2 OO$	neat	9.50	6.03	77	this work
halocarbon						
bromochloromethane	CCIH ² 00.	12 mol dm ^{-3} LiCl/D ₂ O	9.75	5.55	100	this work
bromodichloromethane	CCI ₂ HOO	12 mol dm ⁻³ LiCl/D ₂ O	10.08	5.13	105	this work
bromotrichloromethane	CCI300.	methanol	10.26	4.92	93	this work
1,1,2-trichloro-1,2,2-trifluoroethane	CCIF ₂ CFCIOO	neat	10.50	4.52	<i>LL</i>	19
polytetrafluoroethane	$R - (CF_2)_{n} - CF_2 00$	polymer	10.7	4.6	77	19
sulphur-based peroxyl radicals						
cysteine	NH ⁺ ₃ CH(CO ⁻ ₂)CH ₂ SOO	8 mol dm ⁻³ NaClO ₄ /D ₂ O	8.10	6.40	77	12
cysteine	$NH_{1}^{+}CH(CO_{2}^{-})CH_{2}SO_{2}OO$	8 mol dm ^{-3} NaClO ₄ /D ₂ O	10.60	4.46	77	12
cysteine sulfinic acid	$NH_3^+CH(CO_2^-)CH_2SO_2OO^-$	12 mol dm ^{-3} LiCl/D ₂ O	10.50	4.48	100	12
superoxide ion	0:-	12 mol dm ^{-3} LiCl/D ₂ O	7.73	7.73	<i>TT</i>	this work
⁴ Theoretical calculations suggest that all coup	olings are negative. Most splittings are	accurate to ± 0.1 mT. However, those ir	n the range 5.6-6.0 mT	have line components	that overlap w	th other lines in

the spectrum and are accurate only to ± 0.2 mT.^b g values for carbon-based peroxyl radicals are 2.035, 2.008 and 2.003 and vary only slightly for different radicals.^c Two radicals are likely to be present. The two sets of couplings were not resolved.

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Fig. 2. EPR spectra found after γ -irradiation of a sample of CCl₃Br/O₂(¹⁷O) in methanol; (*a*) immediately after radiation at 77 K ('CCl₃); (*b*) after annealing to allow for oxygen to become mobile and for the formation of CCl₃OO' (93 K). (*c*) Simulation as in fig. 1(*c*), which sums the contributions of the expected species, based on the parameters in table 1 and a 0.4 mT linewidth.

formed in Teflon, R-(CF₂)_nCF₂OO', with $|A_{\parallel}(2)| = 4.6 \text{ mT}$ and $|A_{\parallel}(1)| = 10.7 \text{ mT}^{18,19}$ (table 1).

Secondary Peroxyl Radicals

Three substituted secondary hydrocarbon peroxyl radicals of the type RR'CHOO' show couplings near 9.5 mT and 5.9 mT (table 1). This is in spite of the fact that they have different structures and are produced in very different matrices. For example, the alanine peroxyl radical,¹² CH₃CH(OO)CO₂, is produced in 12 mol dm⁻³ LiCl whereas, the methyl stearate radical,¹⁶ RCH₂CH(OO)CO₂CH₃ and the methyl oleate radical,¹⁶ RCH=CH-CH(OO)R', were investigated in urea clathrates, yet all have nearly identical couplings.

Primary Peroxyl Radicals

Peroxyl radicals from primary hydrocarbon sites, *i.e.* RCH₂OO', generally also show couplings for $|A_{\parallel}(1)|$ near 9.8 mT. For example, NH₃⁺CH(CO₂⁻)CH₂OO', 9.81 mT; HOCH₂CH₂CH₂OO', 9.75 mT; CNCH₂OO', 9.84 mT and HOCH₂CH(OH)CH₂OO', 9.80 mT. Exceptions are found for HOCH₂OO', 9.48 mT; (CO₂⁻)CH₂OO', 9.6 mT and (CH₃)₃N⁺CH₂OO', 10.28 mT. These deviations are discussed below in terms of the electron-withdrawing power of the substituent group.

Tertiary Peroxyl Radicals: Cumene Peroxyl Radical and the t-Butyl Peroxyl Radicals

Irradiation of t-butyl bromide (10% in methanol) results predominantly in the signal of the t-butyl radical at 77 K



Fig. 3. EPR spectra found after γ -irradiation of a sample of t-butylbromide/O₂(¹⁷O) in methanol. (a) The t-butyl radical at 77 K. Some methanol radical (°CH₂OH) is expected and is likely to contribute to the underlying broad spectrum. (b) Spectrum of the ¹⁷O-labelled t-butyl peroxyl radical found at 89 K after annealing to 97 K.

showing the expected 10-line pattern separated by 2.3 mT, fig. 3(a). Annealing to 89 K results in the formation of the t-butyl peroxyl radical [fig. 3(b)]. The methanol peroxyl radical, HOCH₂OO⁺, is also expected but not found. The measured oxygen-17 couplings for (CH₃)₃COO⁺ of 9.40 mT are the smallest found for a carbon-based species. Irradiation of neat cumene in the absence of oxygen results in the quite stable cumyl radical, ϕ C(CH₃)₂. Irradiation in the presence of ¹⁷O-labelled oxygen results in the cumyl peroxyl radical which shows oxygen couplings of 9.50 and 6.03 mT.

Sulphur Peroxyl Radicals

In previous work we have investigated two sulphur peroxyl species from cysteine, CysSOO' and CysSO₂OO', where CysSH is cysteine, $NH_3^+CH(CO_2^-)(CH_2SH)$.¹² The pattern of couplings are very different for the two radicals (table 1). CysSO₂OO' shows couplings (10.60 mT, 4.47 mT) comparable to those of fluorinated hydrocarbon peroxyl radicals while CysSOO' shows couplings (8.10 mT, 6.40 mT) which are unlike those displayed by any other peroxyl species measured to date.

Superoxide Anion Radical

Oxygen-17 labelled superoxide anion radical, O_2^{-} , was produced in two matrices (methanol, 12 mol dm⁻³ LiCl) with identical results for the $|A_{\parallel}|$ ¹⁷O hyperfine coupling, 7.73 mT. As for the peroxyl radicals investigated, the perpendicular couplings (A_{\perp}) were not observed. Since the oxygen couplings are identical, the double-substituted components are easily observed in the ESR spectra. The spectra of the double-substituted species have twice the extent of the signal of substituted species showing strong alignment of the p orbitals. The values found here are in good agreement for labelled uncomplexed O_2^{-} found in other systems.^{20,21}

Discussion

Nature of the Hyperfine Coupling

In fig. 4 (top) we show a diagram depicting the spin-density distribution in a typical peroxyl radical. The spin density is localized primarily in the p_z orbitals of the two oxygens as shown. Anisotropic hyperfine couplings from spin density in such p_z orbitals should follow approximate axial symmetry with

$$A_{\parallel} = (a+2B)\rho^{\pi} \tag{1a}$$

$$A_{\perp} = (a - B)\rho^{\pi} \tag{1b}$$

where ρ is the spin density in the p_z orbital.²² Our experimental hyperfine couplings are in accord with this model. We observe one large hyperfine coupling (denoted by A_{\parallel}); the two remaining couplings (A_{\perp}) are both much smaller in magnitude than A_{\parallel} and are in regions of the spectra where overlapping line components prevent their observation. From the previously measured isotropic oxygen-17 couplings for $(CH_3)_3OO$ (table 2),²³ our values of the anisotropic couplings and the assumption that $\rho^{\pi}(1) + \rho^{\pi}(2) = 1$, we calculate B = -5.7 mT and a = -3.8 mT. (Note that $a\rho^{\pi} = a_{iso}$.) This value of B is in excellent agreement with the value of -6.01mT calculated by Morton and Preston with improved p-orbital functions.²⁴ From eqn (1b) the values $A_{\perp}(1) = 1.1$ mT and $A_{\perp}(2) = 0.76$ mT are obtained; the average, 0.9 mT, is close to the analogous off-parallel average of 0.8 ± 0.3 mT found for $O_2^{-2.25}$ Note that since the p orbitals are not actually in a strict axial environment, the two components (A_x, A_y) that make up A_1 should differ, e.g. see values for O_2^{*-1} in table 2, footnote b.

For O_2^- , each orbital has $\frac{1}{2}$ unit spin and $A_{\parallel} = -7.73$ mT; a_{iso} can be estimated as -2.1 mT from the measured magnitude and assumed signs of the principle values for O_2^- on MgO (table 2).^{25,26} With this data, we obtain B = -5.6 mT, which is excellent agreement with the value from (CH₃)₃OO.



Fig. 4. The p-orbital system of a typical peroxyl radical (top) and the major contributing resonance structures (I and II). The depicted spin densities which result are calculated as the ratio: (measured hyperfine)/15.4 mT, 15.4 mT = |a + 2B|.

For O_2^{-} in aqueous solution, hydrogen bonding results in a non-axial environment which lifts the degeneracy in the π -orbital system and confines the spin to a pair of p orbitals.²⁷⁻²⁹

Using previous results for the polytetrafluoroethylene (PTFE) peroxyl radical (table 2),^{18,19} the value of *B* calculated is -5.7 mT, again in excellent agreement with the values from $(CH_3)_3COO^{\circ}$ and O_2^{--} . This commonality in values of *B* for such disparate species is in keeping with a model which places unpaired spin density in near pure p orbitals for all peroxyl-type radicals. The average value of the isotropic coupling, *a*, for unit spin density is -4.0 ± 0.2 mT for O_2^{--} , PTFE peroxyl radical and $(CH_3)_3COO^{\circ}$. This value is a measure of the s-orbital spin density, *i.e.* division of 4.0 mT by the calculated isotropic coupling for unit spin in a 2s orbital on oxygen (165 mT)³⁰ yields 2.4% s-orbital character for the unpaired electron MO; this result is in keeping with a model which places the spin density in pure p orbitals, especially after consideration of the spin polarization mechanism.

A good estimate of the spin-density distribution in the p_z orbitals of peroxyl radicals can be obtained from the relation, $\rho^{\pi}(i) = |A_{\parallel}(i)|/15.4 \text{ mT}$, 15.4 mT = |a + 2B|. From this relation we estimate that the terminal oxygen spin-density values vary from 0.61 to 0.70 for carbon-based peroxyl radicals. The sum of the two A_{\parallel} couplings for carbon-based peroxyl radicals is nearly constant (-15.0 to -15.5 mT) which suggests little spin-density delocalization into the R group of ROO'. Finally, the fact that in the double-substituted species (R¹⁷O¹⁷O), the $A_{\parallel}(1)$ principal axis is aligned with that of $A_{\parallel}(2)$ shows that the principal axes of two oxygen p_z orbitals are parallel, as pictured in fig. 4.

The use of the parallel coupling to determine spin density depends on the absence of significant dipolar cross interactions in the parallel orientation. The hydrogen dipolar coupling tensor is ca. 1.0, -1.0, 0 mT for the >C-H fragment with unit spin density on carbon.³⁰ The minimum value (0 mT) is directed in the 'parallel' orientation. For the -O-O fragment, a much smaller tensor for cross-coupling is expected, owing to the small value of the ¹⁷O gyromagnetic ratio $(1/7.4 \text{ of that of } ^1\text{H})$ and owing to the increased bond distance (again with the near-zero value along the parallel orientation). More sizeable isotropic cross interactions may be expected. However, since the isotropic coupling makes up only ca. $\frac{1}{4}$ of the parallel coupling and since the isotropic couplings correlate in near-linear fashion with the overall A_{\parallel} couplings, cross interactions have only a small effect on the estimated spin density.

Hyperfine Coupling and Radical Structure

The variation in the hyperfine couplings reported in table 1 indicates that the electron-withdrawing ability of the X group(s) in $X_nCH_{3-n}OO$ affects these couplings and, consequently, the spin-density distribution in the OO group. (As X becomes more electron withdrawing, the hyperfine coupling

Table 2. Values of ¹⁷O anisotropic (B) and isotropic (a) coupling for O_2^{-} and $RO_{(2)}O_{(1)}^{+}$ radicals^a

radical	A ₁ (1)	A (2)	$a_{iso}(1)$	$a_{iso}(2)$	$B(\rho^{\pi}=1)$	$a(\rho^{\pi}=1)$
O_2^{-} (CH ₃) ₃ COO' -(CF ₂) _n CF ₂ OO'	-7.73 -9.4 -10.7 ^d	-7.73 -5.9 -4.6 ^d	-2.1^{b} -2.18 ^c -2.65 ^d	-2.1^{b} -1.64 ^c -1.3 ^d	5.6 5.7 5.7	-4.2 -3.8 -3.95
				average theoretical value ^e	- 5.7 - 6.01	-4.0

^a All values in mT. ^b From A tensor (7.7, 1.5, 0 mT) reported by A. J. Tench and P. J. Holroyd [ref. (26)]. Signs of tensor elements assumed in this work (-7.7, 1.5, 0). ^c Ref. (23). ^d Ref. (19). ^e Ref. (24).



Fig. 5. The relationship between the Taft substituent parameter (σ^*) and oxygen-17 hyperfine coupling constant on the terminal oxygen of peroxyl radicals. $A_{\parallel}(1) = 9.41 + 0.33\sigma^*$, $r^2 = 0.912$. The regression line was calculated using only those radicals for which reliable Taft parameters could be calculated (\bigcirc). Four radicals for which Taft parameters could only be estimated are shown (\triangle), but not included in the regression fit. See table 3 for data used.

on the terminal oxygen increases and that on the inner oxygen decreases.) Fig. 5 shows the hyperfine coupling on the terminal oxygen $[A_{\parallel}(1)]$ as a function of the Taft parameter, σ^* , ³¹ for those radicals for which Taft parameters are available (table 3). The parameter is a measure of the localized electron-withdrawing (or electron-donating) effect of the substituent and is appropriate for use in non-aromatic compounds. A reasonable fit to a straight line is found $(r^2 = 0.912)$. For Taft values between -0.3 and 1 the correlation is weak and other factors must play a role. For the more highly electron-withdrawing substituents, *i.e.* $\sigma^* > 1$, the variance in the hyperfine coupling correlates well with the Taft parameter.

The electron-withdrawing effect of X on the hyperfine coupling can be explained by considering the two principal valence-bond structures, I and II, that can be envisioned for a peroxyl radical (fig. 4, bottom, with $R = X_n CH_{3-n}$). Bonding to the $X_n CH_{3-n}$ group results in a unit formal charge on both oxygens in II and a correspondingly higher energy for II than

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for I. Thus while for O_2^- both analogous structures I and II contribute equally, in peroxyl radicals structure I is favoured, resulting in greater terminal oxygen spin density and $|A_{\parallel}(1)| > |A_{\parallel}(2)|$. Highly electron-withdrawing groups (X) result in increased positive charge on the already positively charged oxygen, which further lessens the contribution of II to the ground-state wavefunction of the radical. As the importance of II becomes smaller, the spin density on the terminal oxygen increases and that on the internal oxygen decreases, resulting in the experimentally observed trends in hyperfine couplings with substituent.

Hyperfine Coupling and Reactivity of Peroxyl Radicals

The preceding results, coupled with the recent finding by Neta et al.⁶ that the rate constant for electron transfer by peroxyl radicals increases as the Taft, σ^* , substituent parameter increases, suggest that the rate of electron transfer is dependent on the spin density of the terminal oxygen. For reactions with ascorbate, eight rate constants and associated terminal oxygen-17 hyperfine splittings are available and are plotted in fig. 6 (lower curve). This figure shows a clear trend toward higher reactivities for higher couplings. The three chlorocarbon peroxyl radicals have somewhat higher reactivities than found for non-halogenated carbon peroxyl radicals of similar couplings. From their results Neta and coworkers⁶ suggested that the chlorocarbon peroxyl radicals reacted via a different mechanism. The reactions of peroxyl radicals with TMPD, N,N,N',N'-tetramethyl-p-phenylenediamine (upper line in fig. 6), show a definite but somewhat less pronounced trend toward higher reactivity with oxygen-17 coupling. The rate of reaction of t-butyl peroxyl radical with TMPD (darkened circle) is far below that expected from its hyperfine coupling. It is likely that the bulky t-butyl group sterically hinders the electron-transfer process.

Based on its oxygen-17 hyperfine coupling of 7.7 mT, the predicted rate (pk) for O_2^- reaction with ascorbate is quite small, *ca.* 1. This might explain why attempts at measuring electron transfer for ascorbate to O_2^- have been unsuccessful. The rate of addition of O_2^- to ascorbate is faster (pk = 4.5)³² than the predicted electron-transfer rate, hence addition is likely to occur in preference to electron transfer.

Table 3. Taft Parameters and pk (electron transfer) for peroxyl radicals

radical	Taft parameter $(\sigma^*)^a$	pk (ascorbate) ^b	pk (TMPD)⁰	A _∥ (1)/mT
(CH ₃) ₃ COO'	-0.30		6.04	9.40
RCH=CHCH(OO')R'	0.00 ^c			9.48
$\phi C(CH_3)_2OO'$	0.020			9.50
HOCH, CH, CH, OO'	0.030 ^d			9.75
φCH ₂ OO'/φCH(OH)OO'	0.215	6.40		9.56
HOC(CH ₃),OO'	0.35			9.59
HOCH(CH ₃)OO	0.45 ^e			9.48
HOCH ₂ OO [°]	0.555	6.67	7.86	9.48
R'CH ₂ CH(OO')CO ₇ CH ₃	0.92°			9.46
(CO ₅)CH,OO		6.34	7.78	9.6
$(CO_2H)CH_2OO$	1.05			9.8
CCIH ₂ OO'	1.05	8.08	8.62	9.75
NCCH ₂ OO'	1.30	7.30	8.46	9.84
$(CH_3)_3 N^+ CH_2 OO^*$	1.90	8.60		10.28
CCl ₂ HOO'	1.94	8.85	8.87	10.08
$CCl_{3}OO$	2.65	8.95	9.23	10.26
CCIF ₂ CFClOO	3.07°			10.50

^a Ref. (31). All values are as tabulated in reference except as noted. ^b For electron transfer, from ref. (6). ^c Estimated assuming additivity of substituent groups and σ^*s from the following structural approximations: for RCH=CHCH, use 0.13 from CH₃CH=CHCH₂; for R', use -0.13 from n-butyl; for CClF₂CH₂ use 0.92 from CF₃CH₂. ^d Estimated using standard relay factor of 2.8 and value of 0.555 for OH. ^e Calculated assuming additivity of OH and CH₃ substituent groups.

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Fig. 6. The relationship between oxygen-17 hyperfine coupling constants (terminal oxygen) for peroxyl radicals and the negative of the log of the rate constant for electron transfer (pk). The regression line for reaction with TMPD (\bigcirc) is pk = $-9.56 + 1.83A_{\parallel}$, $r^2 = 0.897$ and that for ascorbate, (\triangle) is pk = $-24 + 3.2A_{\parallel}$, $r^2 = 0.83$. The point for the reaction of (CH₃)₃OO[•] with TMPD is shown (\bigcirc), but not included in the regression fit since the bulky t-butyl group is likely to slow the reaction considerably relative to the other radicals indicated. See table 3 for data used.

Note that the oxygen-17 hyperfine couplings of superoxide ion complexed to surface transition metal ions show 1.0–1.2 mT difference between $A_{\parallel}(1)$ and $A_{\parallel}(2)$, which was attributed to both the topological features of adsorption³³ and bonding to the surface.³⁴ In aqueous systems, if a similar inequivalence in oxygen-17 hyperfine couplings is induced by complexation of O_2^- to transition metals, our results would predict an increase in the reactivity of the O_2^- relative to the uncomplexed species.

Sulphoxyl Radicals

In previous work^{11,12} we predicted that the hydrogenabstracting ability of a number of oxygen-containing radicals would show a positive correlation with the ¹⁷O hyperfine coupling of the terminal oxygen. We observed that in frozen matrices containing both CysSO₂OO' and CysSOO', CysSO₂OO' $[A_{\parallel}(1) = 10.6 \text{ mT}]$ abstracts hydrogen from parent thiol at temperatures at which CysSOO' $[A_{\parallel}(1) = 8.1 \text{ mT}]$ appears unreactive with parent thiol.

This correlation between reactivity and ¹⁷O hyperfine coupling is in agreement with the pattern observed in this work for electron transfer to carbon-based peroxyl radicals. Thus, the large coupling to the terminal oxygen in CysSO₂OO' suggests that it may be an extremely reactive species (with regard to electron transfer and/or hydrogen abstraction) and that its reactivity should be comparable to that of CCl₃OO'.

The different nature of the RSOO', relative to other peroxyl radicals is of interest. GSOO', in pulse-radiolysis studies, undergoes a relatively fast electron transfer from ascorbate with $k = 1.75 \times 10^8$ dm³ mol⁻¹ s⁻¹ (pk = 8.24),³⁵ while our hyperfine couplings for the same radical¹² would suggest a lower pk (fig. 6). Evidently the correlation between ¹⁷O coupling and rate of electron transfer does not hold for RSOO'. Interestingly, pulse-radiolysis studies also show that GSOO' undergoes a slow reaction with GSH ($k < 10^6$ dm³ mol⁻¹ s⁻¹),³⁵ in agreement with our observation in frozen

samples that GSOO' does not abstract from GSH. In addition, CysSOO' is the only peroxyl radical reported in table 1 in which the magnitude of the sum of the ¹⁷O couplings is less than 15 mT, $|A_{\parallel}(1) + A_{\parallel}(2)| = 14.5$ mT, indicating that ca. 6% of the spin density is located on the sulphur. CysSOO' also has a more equivalent distribution of spin density on the oxygens (0.42, 0.53) than any other peroxyl radical investigated and shows a visible absorption with $\lambda_{max} = 540$ nm ¹⁰ which is unique for peroxyl radicals. We believe that a significant contribution of the charge-transfer state represented by CysS⁺OO^{• -} would explain the near equivalence of hyperfine splittings (identical to those found in for O_2^{*-} in decationated zeolite),²⁵ as well as the absorption in the visible range. While molecular-orbital calculations have given insight into the structure of sulphonyl radicals,^{12,36} ab initio MO calculations of the spin density and hyperfine couplings of the thiol peroxyl radical, CH₃SOO', incorrectly suggest that this species has spin density and couplings identical to those of the alkyl peroxyl radical, CH₃OO^{.11} Clearly, more experimental and theoretical efforts are needed to characterize this interesting species.

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