An *in-situ* Radiolysis EPR Study of Spin Trapping by 2-Methyl-2-nitrosopropane: Steric and Electronic Effects Influencing the Trapping of Hydroxyalkyl Radicals Derived from Pentanols and Substituted Pentanols

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The spin adducts formed by reaction of bulky hydroxyalkyl radicals with the nitroso spin trap 2-methyl-2-nitrosopropane (MNP) were studied using *in-situ* radiolysis EPR. Parent hydroxyalkyl radicals were produced in aqueous solution either by hydroxyl-radical reaction with unsubstituted and methyl-substituted alcohols (propanols, pentanols and cyclohexanols) or by reaction of the corresponding ketone with the hydrated electron. The parent radicals included 1-hydroxypentyl, 1-hydroxy-1-methylbutyl, 1-ethyl-1-hydroxypropyl, 1-hydroxy-1-isopropyl-2-methylpropyl, 1-hydroxy-2,2-dimethylpropyl, 1,3-dihydroxy-2,2-dimethylpropyl, 1-hydroxycyclohexyl, 1-hydroxy-2-methylcyclohexyl, and 1-*tert*-butyl-1-hydroxy-2,2-dimethylpropyl radicals. All but the bulkiest radicals reacted with MNP by addition at the nitroso nitrogen site to form the MNP–C(OH)RR' spin adduct. In contrast with previous MNP spin-trapping studies using hydroxymethyl, hydroxyethyl, and 1-hydroxy-1-methylethyl parent radicals, steric interactions strongly modulated the yields of the spin adducts produced. Strongly reducing hydroxyalkyl radicals also reacted with MNP to produce the MNP–H adduct by direct reduction of MNP. Steric hindrance between the parent radical and MNP was sufficient in the most extreme case to shut off MNP–R production with concomitant production of MNP–H. Spin-adduct persistence was measured for the MNP–hydroxyalkyl and MNP–alkyl spin adducts. Hydroxyalkyl spin adduct lifetimes varied from seconds (MNP–1-hydroxy-1-methylbutyl) to one year (MNP-1-hydroxycyclohexyl), correlating with the level of aminoxyl function shielding afforded by its substituent groups. MNP spin adducts formed from other non-hydroxyalkyl alcohol radicals had short lifetimes of less than 18 hours.

Spin trapping[1-4] facilitates the study of free radicals by converting transient species into persistent radicals. A spin trap, typically a nitrone or nitroso compound, is added to the system where the free radicals are formed. The transient parent radical reacts by addition to the unsaturated portion of the spin trap, resulting in the formation of a longer-lived aminoxyl (nitroxide) radical, the spin adduct. The increased persistence of the spin adduct allows its examination by conventional spectroscopic techniques, the most commonly employed being electron paramagnetic resonance (EPR).[5] The *g* factors and hyperfine couplings of the spin adduct radical contain contributions from the interaction of the parent radical nuclei and electronic system with the unpaired electron that is mainly localized on the aminoxyl nitrogen and oxygen. Thus, the structure of the parent radical can be deduced from the EPR spectrum to provide qualitative information on the free radicals present in the system.

Quantitative use of spin trapping ('spin counting')[6] to determine transient radical concentrations requires knowledge of the rate constants for parent radical termination, spin-adduct formation, and spin-adduct termination. Only in the case where both parent-radical and spin-adduct termination are slow, with rapid spin-adduct formation, will spin-adduct EPR line intensities give direct measurement of transient radical concentration. Our previous studies of free-radical spin trapping using MNP[7] showed that trapping rate constants for small carbon-centred radicals varied from $< 1.0 \times 10^6$ to 1.7×10^9 dm^3 mol^{-1} s^{-1}. The variation in these rate constants was correlated with electronic and steric effects when the parent radicals were alkyl radicals, but the hydroxyalkyl radicals studied were little influenced by the steric factors involved in the radical-trap encounter complex. We have extended the earlier studies to examine electronic and steric effects upon the spin trapping of bulky primary and secondary hydroxyalkyl radicals by MNP.

Previous studies of MNP-hydroxyalkyl radical trapping with hydroxymethyl, hydroxyethyl and 1-hydroxy-1-methylethyl radicals[7,8] showed that trapping rates were directly correlated with the reducing power of the parent hydroxyalkyl radical. Schwarz and Dodson[9] determined the redox potentials of these radicals in aqueous solution, finding values of −1.18, −1.25 and −1.39 V, respectively, for protonated radicals, and −1.81, −1.93 and −2.10 V for the dissociated radicals. Additionally, the MNP–H spin adduct became a major product as the reduction potential of the parent radical increased in this series,[8] indicating that direct trap reduction[10] was contributing to the production of aminoxyl radicals. Steric hindrance did not seem a factor impeding hydroxyalkyl radical trapping in this selection of parent radicals.

Still, one would expect that steric effects would be important given a radical of sufficient bulk, since the MNP monomer active site itself is well shielded by the tertiary butyl group adjacent to the nitroso function. One needs to establish the point at which the facilitation of hydroxyalkyl radical trapping by parent radical reducing capacity is balanced by retardation of trapping by steric hindrance between the parent radical and the spin trap. To probe this balance, we have studied the spin trapping of hydroxyalkyl radicals formed from substituted and unsubstituted pentanols, propanols and cyclohexanols.

The 1-ethyl-1-hydroxypropyl radical from pentan-3-ol serves as a prototype system for these studies, as it is a strongly reducing secondary hydroxyalkyl radical, like 1-hydroxy-1-methylethyl, but with longer side chains attached to the radical centre. The degree of steric hindrance during trapping can be increased by the addition of methyl groups at the carbons adjacent to the radical centre. Since symmetric parent radicals will produce MNP spin adducts with the simplest spectral characteristics, we will also examine the trapping of the 1-hydroxycyclohexyl, 1-hydroxy-1-isopropyl-2-methylpropyl and 1-*tert*-butyl-1-hydroxy-2,2-dimethylpropyl radicals. Since these

secondary hydroxyalkyl radicals are strong reductants, these studies should also reveal the competition between trap reduction and adduct formation as a function of trap–radical approach distances.

Expansion of these studies to include asymmetrical hydroxyalkyl radical trapping will use radicals from the propanol and cyclohexanol homologous series. We wish to examine primary and secondary hydroxyalkyl species to examine the effect of reducing power *vs.* steric effects in less reducing parent radicals. It will be useful in these cases to use spectral information from symmetrical radicals for assignments of asymmetric spin adducts.

Since these complex hydroxyalkyl radicals studied bear significant resemblance to the structure of carbohydrate free radicals in size and complexity, we feel that such studies will be useful as a model system for sugar radical spin-trapping kinetics to test the applicability of analytical methods recently developed.[11] Finally, these steady-state EPR experiments are a prelude to time-resolved EPR (TREPR) studies. They will determine appropriate line positions for kinetic studies of spin adduct formation, and provide qualitative information on spin adduct stability.

Experimental

Solutions were prepared in reagent-grade water from a Millipore Milli-Q water system. MNP was obtained as the dimer (Aldrich), and was used without further purification. All MNP concentrations are reported on a monomer basis, which assumes complete dissociation of the dimer in solution. Because of the incompatibility of the MNP monomer with certain of the alcohols used in these studies, two solutions, one containing alcohol and another containing the spin trap were prepared for each study. A stock solution containing MNP was prepared by deoxygenating 100 cm^3 of water by purging with ultra-high purity nitrogen (Mittler), heating the water to 40 °C, then quickly dissolving 0.22 g of MNP dimer in the water with gentle stirring. A suitable amount of this solution was then added to additional deoxygenated water to obtain the desired spin-trap concentration. It has been shown that this method of preparation leads to minimal degradation of the spin trap.[12] A second solution containing alcohol was prepared by dissolving the parent alcohol in water deoxygenated with nitrous oxide (Mittler, USP grade). The two solutions were connected to a dual syringe pump, through a set of check values, and then to a small mixing tee attached to the bottom of a conventional EPR aqueous cell. The parent alcohol and the spin trap were mixed roughly 4 s prior to entry into the flat region of the aqueous cell holder. EPR measurements were always performed on freshly prepared solutions. The solutions were unbuffered for these steady-state studies.

Most parent radicals were made by reaction of the parent compound with radiolytically produced hydroxyl radical. Hydroxyalkyl radicals for spin trapping experiments were made by hydrogen abstraction from the following alcohols: pentan-1-ol (100 mmol dm^{-3}, Aldrich), pentan-2-ol (100 mmol dm^{-3}, Aldrich), pentan-3-ol (200 mmol dm^{-3}, Aldrich), 2,4-dimethylpentan-3-ol (75 mmol dm^{-3}, Aldrich), 2,2-dimethylpropan-1-ol (100 mmol dm^{-3}, Aldrich), 2,2-dimethylpropane-1,3-diol (100 mmol dm^{-3}, Aldrich), cyclohexanol (100 mmol dm^{-3}, Aldrich) and 2-methylcyclohexanol (100 mmol dm^{-3}, Aldrich). The concentration of MNP was chosen to be a factor of 0.01 to 0.015 of that of the parent alcohol so that greater than 99% of the hydroxyl radicals would react with the parent alcohol. 1-*tert*-Butyl-1-hydroxy-2,2-dimethylpropyl radicals were prepared by reaction of the hydrated electron with 2,2,4,4-tetramethylpentan-3-one (5–10 mmol dm^{-3}, Aldrich). In this case 0.1 mol dm^{-3} 2-methylpropan-2-ol (*tert*-butyl alcohol, Fisher) was usually added to the deoxygenated solution to scavenge radiolytically produced hydroxyl radicals.

The solutions containing alcohol were saturated with nitrous oxide to convert radiolytically produced hydrated electrons into hydroxyl radicals. The reactions leading from water radiolysis to MNP-hydroxyalkyl spin adduct formation are given in eqns. (1)–(5).

$$H_2O \rightsquigarrow e_{(hyd)}^- (45\%) + {}^{\bullet}OH (45\%) + H^{\bullet} (10\%) \quad (1)$$

$$e_{(hyd)}^- + N_2O + H_2O \rightarrow N_2 + {}^{\bullet}OH + OH^- \quad (2)$$

$$R^1CH(OH)R^2 + {}^{\bullet}OH \rightarrow {}^{\bullet}C(OH)(R^1)R^2 + H_2O \quad (3)$$

$$R^1CH(OH)R^2 + H^{\bullet} \rightarrow {}^{\bullet}C(OH)(R^1)R^2 + H_2 \quad (4)$$

$$MNP + {}^{\bullet}C(OH)(R^1)R^2 \rightarrow [MNP\text{–}C(OH)(R^1)R^2]^{\bullet} \quad (5)$$

Eqns. (6)–(9) are reactions competing with eqns. (2)–(5).

$$MNP + {}^{\bullet}OH \rightarrow (MNP\text{–}OH)^{\bullet} \quad (6)$$

$$MNP + H^{\bullet} \rightarrow (MNP\text{–}H)^{\bullet} \quad (7)$$

$$MNP + e_{(hyd)}^- \rightarrow (MNP^-)^{\bullet} \quad (8)$$

$$(MNP^-)^{\bullet} + H^+ \rightarrow (MNP\text{–}H)^{\bullet} \quad (9)$$

We have attempted to minimise the effects of reactions (6)–(9) by a suitable choice of reactant concentrations in our solutions.

In an N_2O-saturated aqueous solution at a pressure of one atmosphere, the nitrous oxide concentration is approximately 27 mmol dm^{-3}; the rate constant for reaction (2) is 9.1×10^9 dm^3 mol^{-1} s^{-1}.[13] MNP and the hydrated electron react somewhat more slowly, with a rate constant of 6.2×10^9 dm^3 mol^{-1} s^{-1}.[7] However, since the concentration of MNP is low (*ca.* 1 mmol dm^{-3}), MNP does not compete with nitrous oxide in scavenging the hydrated electron.

The high alcohol concentration used in these studies also guarantees that MNP does not react appreciably with the hydroxyl radical or hydrogen atom water transients. The rate constants for reactions (6) and (7) are 2.5×10^9 and 9.1×10^8 dm^3 mol^{-1} s^{-1}, respectively.[7] The rate constants for the reaction of hydroxyl radical with alcohols is roughly the same order of magnitude as that for MNP; the reaction of hydrogen atom with secondary alcohols is roughly an order of magnitude slower.[14] Under our conditions, reaction (6) does not proceed to any appreciable extent. The competition between reactions (4) and (7) is shown by the small amount of MNP–H seen in the top spectrum of Fig. 1.

Since the hydroxyl radical is a strongly oxidizing species, there might be concern over the production of alkoxyl radical from the parent alcohol. Asmus, Möckel and Henglein[15] show that reaction of hydroxyl radical in neutral aqueous solutions of propan-2-ol results in greater than 98% hydrogen abstraction at C–H sites; alkoxyl radicals formed by hydrogen abstraction at C–OH represent merely a trace (1.2%) of the total radical yield. In the case of propan-1-ol and butan-1-ol, the alkoxyl radical yield was even lower, less than 0.5% of the total radical yield. For the bulky primary and secondary alcohols studied here, we would expect similar chemistry; essentially all alcohol radicals are formed by hydroxyl-radical abstraction of methylenic protons.

In situ radiolysis EPR spectra were recorded by irradiating flowing cooled aqueous solutions of the parent compound and MNP with a 2.8 MeV electron beam from a Van de Graaff accelerator.[16,17] A 2.5 μA DC beam was used to produce a steady-state concentration of radicals for field-modulation EPR

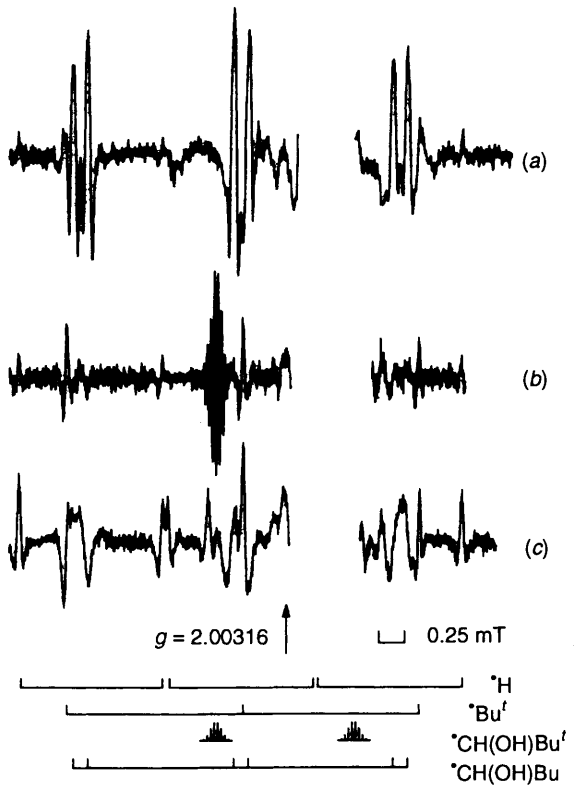

Fig. 1 Second-derivative X-band *in-situ* radiolysis EPR spectra of radicals formed during continuous electron irradiation of aqueous solutions containing 0.1 mol dm^{-3} primary alcohols and 1 mmol dm^{-3} MNP; (*a*) pentan-1-ol, (*b*) 2,2-dimethylpropan-1-ol, and (*c*) 2,2-dimethylpropane-1,3-diol. The stick figures below show the EPR line positions for the MNP–hydrogen atom spin adduct, MNP–tertiary butyl radical adduct (di-*tert*-butylaminoxyl), 1-hydroxy-2,2-dimethylpropyl radical, and MNP–CH(OH)Bu spin adduct radical.

spectra. The solution temperature was within the range 15–19 °C. The solution flow rate varied between 20 and 32 cm^3 min^{-1}. The use of such a fast flow minimises the intensity of spurious long-lived secondary radical products relative to the spin-adduct radicals.

X-Band (9.2 GHz) *in situ* radiolysis EPR spectra of steady-state radical populations were recorded in second-derivative presentation using magnetic field modulation at 100 kHz and 200 Hz to determine the line positions for the parent and spin adduct radicals. The EPR spectrometer and associated data acquisition system are described elsewhere.[18] The magnetic field was measured by NMR methods,[16,18] with *g* factors measured with respect to that of the sulfite radical anion, recently redetermined as $g = 2.003\,16$.[19] EPR line positions were measured using the Lorentzian/Gaussian fitting functions included in the IBM PC-based data analysis program ORIGIN.[20] The line positions were analysed to derive *g* factors and proton hyperfine couplings for parent and spin adduct radicals. The spin adduct parameters are presented in Table 1. Spectral simulation of the MNP–1-hydroxycyclohexyl and MNP–1-hydroxy-2-methylcyclohexyl spin adducts was performed using the SIMEPR program,[21] kindly provided by Dr. David Duling of the Laboratory of Molecular Biophysics, NIEHS, NIH.

Persistent radicals from spin trapping reactions were produced by 1–2 min γ-irradiation of alcohol (ketone)–MNP solutions within a Sheppard model 109 ^{60}Co irradiator, having a dose rate of 1.17×10^4 rad min^{-1}. Total radical concentrations were 73–146 μmol dm^{-3}. Initial spectra were usually acquired a minimum of 2 min following sample irradiation. An IBM/Bruker ER100 spectrometer was used to acquire X-band (9.8 GHz) EPR spectra of persistent radicals in second-derivative presentation by detecting the second harmonic of the 50 kHz modulation frequency. An alkaline aqueous solution of Fremy's salt (peroxylamine disulfonate dianion radical) with a *g* factor of 2.005 54[22] was used for the calibration of line positions measured using this instrument.

Results and Discussion

An unexpected result obtained at the start of these experiments was observation of the chemical incompatibility of pentan-3-ol and the MNP monomer. The first preparation of the solution was made as a single solution, with the MNP dimer quickly dissolved in deoxygenated pentan-3-ol, and that solution added to the nitrous oxide purged water, as was done in the studies of ref. 7. The characteristic blue colour of the MNP monomer faded in a matter of minutes, simultaneously with the disappearance of the spin adduct signals from the *in situ* radiolysis EPR spectrum. This prompted the use of the mixing system to prevent depletion of MNP monomer during the course of the experiments.

After adoption of the mixing system, the expected radicals could be observed during the irradiation of aqueous alcohol–MNP solutions. Given the parent radical •C(OH)RR′, we would have expected MNP–C(OH)RR′ spin adduct from direct hydroxyalkyl radical addition, MNP–H from trap reduction followed by protonation (if the hydroxyalkyl radical is strong enough a reductant), and MNP–R–CH(OH)R′ from alkyl radicals formed by alcohol hydrogen abstraction at sites other than hydroxyalkyl carbon. A number of spin adducts observed are, to the best of our knowledge, reported for the first time in this work. The spin Hamiltonian parameters for the spin-adduct radicals observed in this study are listed in Table 1. The spin Hamiltonian parameters for selected parent radicals are listed in Table 2.

(*a*) *Primary Alcohols and Steric Hindrance.*—The EPR spectrum observed during electron irradiation of aqueous 0.1 mol dm^{-3} pentan-1-ol containing 1.3 mmol dm^{-3} MNP is shown in the upper trace of Fig. 1. This is a clean MNP–CH(OH)Bu spectrum, with little MNP–H [$g = 2.005\,74$, a(N, NO) = 1.466 mT, and a(H, NH) = 1.394 mT][7] absorption seen; the small MNP–H signal represents the competition between pentan-1-ol and MNP for the 10% yield of hydrogen atoms produced in the radiolysis of water.[14] The spin Hamiltonian parameters for the MNP–CH(OH)Bu compare favourably with those observed previously[7] for MNP spin adducts of hydroxymethyl, hydroxyethyl and hydroxypropyl radicals. However, since the linewidth is greater for this spin adduct owing to unresolved proton couplings from distant protons, the hydroxyl coupling was not observed in this adduct. Although the spectrum is dominated by the MNP–CH(OH)Bu adduct, there are some low-intensity EPR lines which might originate from MNP–alkyl absorptions; these represent little of the spectral intensity. Clearly, although the 1-hydroxypentyl radical is not a strongly reducing radical, the low steric hindrance experienced between this radical and MNP during trapping allows facile production of the primary hydroxyalkyl spin adduct.

The middle trace of Fig. 1 shows the EPR spectrum recorded during electron irradiation of an aqueous solution of 0.1 mol dm^{-3} 2,2-dimethylpropan-1-ol (*neo*-pentyl alcohol) in the presence of 1 mmol dm^{-3} MNP. This trace was recorded under the same conditions as in the top trace, but with the signal channel gain decreased by a factor of 0.82. The most obvious change is that there is no visible contribution from the MNP–CH(OH)R radical, as well as no substantial MNP–alkyl adduct. Notably, the greatest spectral intensity resides in a multiplet ascribed to the parent radical. This species is identified from the

Table 1 Spin Hamiltonian parameters for MNP spin adducts

Parent radical (Parent substrate)	*g* Factor	*a*(N,NO)/ mT	*a*(H,R)/ mT[a]	R
$CH(OH)Bu$ (pentan-1-ol)	2.005 79	1.559	0.142 ur	CH C(OH)
$C(OH)MePr$ (pentan-2-ol)	2.005 60	1.662	ur ur ur	CH_3 CH_2 C(OH)
$C(OH)Et_2$ (pentan-3-ol)	2.005 67	1.655	0.166	C(OH)
$CH_2CH_2CH(OH)Et$ (pentan-3-ol)	2.005 64	1.692	1.335 0.972 0.071	CH_2(H1) CH_2(H2) CH_2
$CH_2CH(Me)CH(OH)Pr^i$ (2,4-dimethylpentan-3-ol)	2.005 66	1.693	2.439 0.071	ΣCH_2(H1,H2)[b] CH
$CH(OH)C(Me)_2CH_2OH$ (2,2-dimethylpropane-1,3-diol).	2.005 9[c]	1.592[c]	ur ur	CH COH
c-$C(OH)(CH_2)_5$ (cyclohexanol)	2.005 61	1.665	0.150 0.108 0.075	CH_2 C(OH) CH_2
c-$C(OH)CH(CH_3)(CH_2)_4$ (2-methylcyclohexanol)	2.005 6	1.665	0.165 0.165 0.085 0.025 0.020	CH C(OH) CH_3 CH CH

[a] ur = Hyperfine splitting is unresolved. [b] Since the central line of a triplet due to CH_2 protons is too broad to be observed, the overall coupling constant is given. See the text. [c] These are estimates, due to spectral overlap and unresolved hyperfine interactions. Line positions were estimated by a parabolic fit to the experimental absorption.

Table 2 Spin Hamiltonian parameters for selected parent radicals

Parent radical (Parent substrate)	*g* Factor	*a*(H,R)/mT[a]	R
$C(OH)Pr^i_2$ (2,4-dimethylpentan-3-ol)	2.003 02	1.072 0.180	CH (×2) C(OH)
$CH(OH)Bu^t$ (2,2-dimethylpropan-1-ol)	(2.003 16)[b]	(1.353)[c] 0.035 ur	CH Bu^t C(OH)
$C(O^-)Bu^t_2$ (pH 14) (2,2,4,4-tetramethylpentan-3-one)	2.003 22	0.019	Bu^t (×2)
$C(OH)Bu^t_2$ (neutral pH) (2,2,4,4-tetramethylpentan-3-one)	(2.003 22)[b]	0.023 (0.36)[c]	Bu^t (×2) C(OH)

[a] ur = Hyperfine splitting is unresolved. [b] Assumed *g* factor; see the text. [c] Calculated using assumed *g* factor; see the text.

low-field line group of the 1-hydroxy-2,2-dimethylpropyl radical. The central six lines of the 0.035 mT 1:9:36:84:126:126:84:36:9:1 dectet are visible above the noise level in this spectrum. Assuming a typical hydroxyalkyl radical *g* factor of 2.003 16,[23] the alpha-proton splitting is estimated as 1.353 mT, near the 1.27 mT value reported by Dixon and Norman for the similar 1-hydroxy-3-methylbutyl radical observed during oxidation of 3-methylbutan-1-ol by the titanous ion–hydrogen peroxide couple.[24] The high-field line group is obscured by the intense EPR signal from the colour centres in the irradiated quartz flat cell. The intensity of this parent radical EPR spectrum, and the lack of any obvious concentration of MNP–primary hydroxyalkyl spin adduct show that steric hindrance has completely overcome the ability of this ketyl radical to add to MNP. This establishes the limiting level of steric interaction necessary to shut down adduct formation for primary hydroxyalkyl radicals. This primary hydroxyalkyl radical is not expected to reduce MNP to the MNP anion radical. Experimentally, no increase in MNP–H signal intensity is seen over that observed in the pentan-1-ol–MNP system. EPR lines of MNP–*tert*-butyl [di-*tert*-butylaminoxyl g = 2.005 59 and a(N,NO) = 1.722 mT][22] were also observed as a minor spectral component.

The lower trace of Fig. 1 shows the EPR spectrum obtained when an aqueous solution of 0.075 mol dm^{-3} 2,2-dimethylpropane-1,3-diol is irradiated in the presence of 1 mmol dm^{-3} MNP. This EPR spectrum shows three aminoxyl species: MNP–H, MNP–*tert*-butyl, and MNP–$CH(OH)CMe_2CH_2OH$.

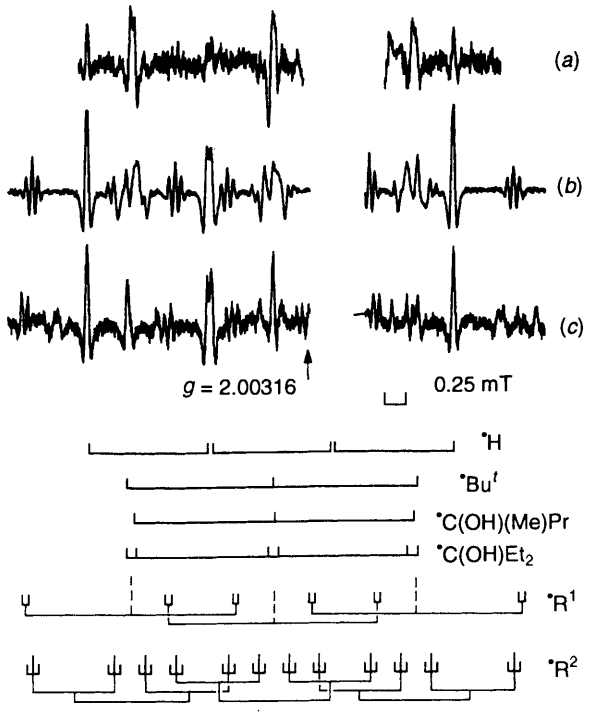

Fig. 2 Second-derivative X-band *in-situ* radiolysis EPR spectra of radicals formed during continuous electron irradiation of aqueous solutions containing secondary alcohols and 1 mmol dm^{-3} MNP; (*a*) 0.1 mol dm^{-3} pentan-2-ol, (*b*) 0.1 mol dm^{-3} pentan-3-ol, and (*c*) 75 mmol dm^{-3} 2,4-dimethylpentan-3-ol. The stick figures below show the EPR line positions for the MNP spin adducts of the indicated radicals (top to bottom): hydrogen atom, *tert*-butyl radical, 1-hydroxy-1-methylbutyl (hydroxyalkyl radical from pentan-2-ol), 1-ethyl-1-hydroxypropyl (hydroxyalkyl radical from pentan-3-ol), R^1 (3-hydroxy-2,4-dimethylpentyl radical from 2,4-dimethylpentan-3-ol; dashed lines show position of central line for motionally narrowed CH_2 hyperfine triplet), and R^2 (3-hydroxypentyl radical from pentan-3-ol).

The formation of this hydroxyalkyl radical adduct is enhanced by the presence of an internal hydrogen bond in the parent radical between the hydroxy groups at the C-1 and C-3 positions, an interaction not present in the 1-hydroxy-2,2-dimethylpropyl radical. This interaction tends to open up the space near the unpaired electron orbital centred on C-1, relieves the steric hindrance in the trap–parent radical encounter complex, and allows the spin adduct to be formed. This hydrogen bonding interaction also appears to have an electronic effect, that of making the parent hydroxyalkyl radical somewhat more reducing, as the yield of MNP–H is distinctly greater than in the two previous examples.

(*b*) *Secondary Alcohols, Reducing Power and Steric Hindrance.*—The EPR spectrum of the aminoxyl radicals formed when aqueous 0.1 mol dm^{-3} pentan-2-ol is electron-irradiated with 1 mol dm^{-3} MNP is shown at the top in Fig. 2. Compared to the 1-pentanol/MNP system, there is a greater concentration of MNP–H adduct, indicating this secondary hydroxyalkyl radical has greater reducing power than the primary species described in the preceding section. This is consistent with the results for spin trapping less sterically hindered primary and secondary hydroxyalkyl radicals.[7] Also, there is a lower steady-state concentration of MNP–C(OH)MePr adduct than is observed under similar experimental conditions with the primary hydroxyalkyl radicals mentioned above, an indication that steric hindrance at the ketyl radical centre has become sufficient to retard parent radical trapping.

The central EPR spectrum in Fig. 2 shows an analogous experiment using 0.1 mmol dm^{-3} pentan-3-ol as the parent substrate in the presence of 1 mmol dm^{-3} MNP. Compared with the pentan-2-ol system there is a greater concentration of MNP–H adduct, showing that this secondary hydroxyalkyl radical can function as a strong reductant for the MNP spin trap. Also, there is a rather small steady-state concentration of MNP–$C(OH)Et_2$. Here the location of the hydroxyalkyl radical centre between two bulky, electron-releasing alkyl functions has had a dual effect; the increased steric hindrance has retarded adduct formation, while the increased reducing power of this radical increases the formation of MNP–H. Thus trap reduction is promoted at the expense of adduct formation.

The central spectrum of Fig. 2 also shows that the MNP–$CH_2CH_2CH(OH)Et$ spin adduct is formed in good yield. The stick diagram at the bottom of the figure labelled $•R^2$ shows the splitting of this spin adduct. In this parent radical–trap system, a chiral centre is generated in the spin adduct at the C-3 position of the parent radical. This has the effect of rendering the two methylenic protons adjacent to the aminoxyl nitrogen magnetically inequivalent, as observed previously by Gilbert and Trenwith[25] and Janzen and Lopp.[26] The spin Hamiltonian parameters are given in Table 1. The effect of the chiral atom observed here is a weaker effect than observed previously in MNP spin trapping, since previous observations were of spin adducts with the chiral centre two atoms from the nitrogen atom of the aminoxyl group. In this case, the chiral carbon is three atoms away. The only precedent we know for this behaviour is the observation of such a chiral effect in the trapping of sulfur-centred radicals using nitromethane *aci*-anion; the couplings of the alpha-methylenic protons in CXYZ–S–$CH_2NO_2^{•-}$ show inequivalent hyperfine couplings.[27]

The rate constants for reaction of the hydroxyl radical with pentan-3-ol and pentan-3-one have been measured. For the ketone, the rate is 1.4×10^9 dm^3 mol^{-1} s^{-1};[28] for the alcohol, the rate is 2.1×10^9 dm^3 mol^{-1} s^{-1}.[29] These rate constants show that during the radiolysis of aqueous pentan-3-ol solutions the terminal methyl groups are the sites for a significant fraction of hydrogen abstraction events. The high intensity observed for this spin adduct in the *in situ* radiolysis EPR spectrum is consistent with these rate constants. The intensity of this spin adduct is deceptive, however; previous kinetic studies from these laboratories show that MNP–alkyl radical trapping is slow, with the rate constant of MNP–methyl radical trapping being approximately one-tenth the rate constant of MNP–hydroxymethyl trapping.[7] Thus the *in-situ* radiolysis experiment shows the presence of the MNP–alkyl spin adduct, but understates its yield. The time scale of spin adduct radical decay is also important in determining the intensity of the observed spectrum; this particular spin adduct has a moderately fast termination rate, since the MNP–$CH_2CH_2CH(OH)Et$ radical is not observed 18 h after ^{60}Co-γ irradiation, as shown in Fig. 4(*b*). The MNP–$C(OH)Et_2$ spin adduct has a slower termination rate, and therefore has an intense long-term EPR spectrum even twenty days after γ-irradiation.

The EPR spectrum produced during electron irradiation of 0.1 mol dm^{-3} cyclohexanol solution containing 1 mmol dm^{-3} MNP is shown in Fig. 3(*a*). Direct comparison with the pentan-3-ol–MNP system reveals the influence of steric effects in trapping of secondary hydroxyalkyl radicals with similar reducing capabilities, since both have secondary hydroxyalkyl centres with ethyl or 'ethyl-like' substituents. However, the 1-hydroxycyclohexyl radical has a semi-occupied molecular orbital (SOMO) that is less shielded than the 1-ethyl-1-hydroxypropyl radical SOMO, since the ring conformation locks the side chains in place, away from the semi-occupied π-orbital. The cyclohexanol–MNP trapping system, compared with pentan-3-ol trapping, produces the MNP–C(OH)RR′ species in good yield, along with the reduction product, MNP–H.

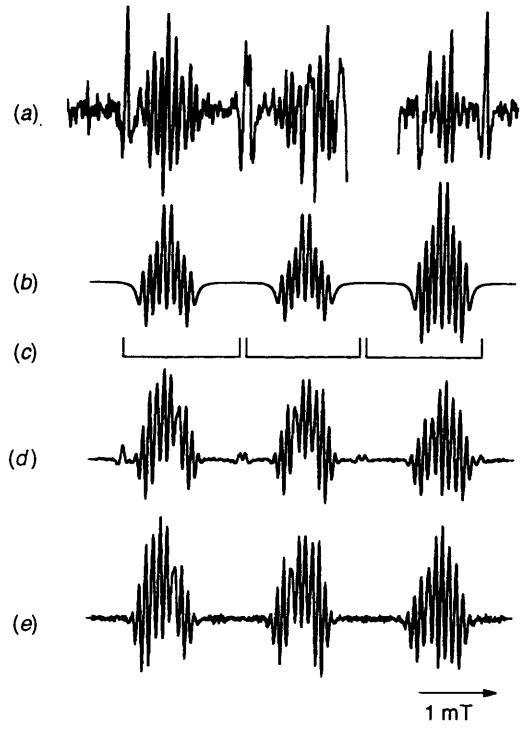

Fig. 3 Experimental and simulated second-derivative X-band EPR spectra of radicals formed by irradiation of aqueous solutions containing 0.1 mol dm^{-3} cyclohexanol and 1 mol dm^{-3} MNP; (*a*) *in situ* radiolysis EPR spectrum, containing MNP–H and MNP–1-hydroxycyclohexyl spin adduct, (*b*) spectral simulation of MNP–1-hydroxycyclohexyl radical spin adduct, (*c*) stick diagram of MNP–H spin adduct, (*d*) EPR spectrum of a ^{60}Co-γ irradiated solution several minutes after irradiation, (*e*) as in (*d*), but 18 h later.

The eight-peak multiplet assignment for this hydroxyalkyl radical adduct is not straightforward; assuming a Lorentzian line shape, and nitrogen quantum-number-dependent linewidths of 0.050, 0.053 and 0.045 mT, from lowest to the highest field line group, respectively, and using the spin Hamiltonian parameters a(N, NO) = 1.665 mT, a(H, CH_2) = 0.075 mT, a(H,CH_2) = 0.150 mT, and a(H, OH) = 0.108 mT (also listed in Table 1), we obtain the spectral simulation presented in Fig. 3(*b*). Although the observed spectral asymmetry shows that multiple minor adducts are present in the EPR spectrum, there are no EPR lines obviously associated with the alkyl radical adduct MNP–C(H)R, where R is the cyclohexanol ring. This implies that in the cyclohexanol system, the concentration of hydroxycycloalkyl spin adduct is greater than that of the various MNP–cycloalkyl species.

Similar results were obtained from electron- or γ-irradiated 0.1 mol dm^{-3} 2-methylcyclohexanol solution containing 1 mmol dm^{-3} MNP. Major EPR spectral components are three sets of eight peaks with intense MNP–H lines as in the case of the cyclohexanol–MNP spin trapping system. The former aminoxyl radical can be ascribed to 1-hydroxy-2-methylcyclohexyl radical adduct to MNP; its spin Hamiltonian parameters are listed in Table 1. These parameters are determined by the same procedure mentioned above and they are consistent with those of MNP–1-hydroxycyclohexyl adduct radical.

The EPR spectrum observed during electron irradiation of aqueous solutions containing 40 mmol dm^{-3} 2,4-dimethylpentan-3-ol and 1 mmol dm^{-3} MNP is shown in Fig. 2(*c*). Compared with the spectrum observed in MNP–pentan-3-ol spin trapping, we note that there is a sizable concentration of MNP–H seen in this spectrum, but that no visible trace of MNP–C(OH)RR′ is found. The interpretation we propose is that steric hindrance at C-3 has become so great in the radical–trap encounter complex as to 'suppress' hydroxyalkyl spin trapping completely, while the trap reduction reaction involving electron transfer still occurs, producing MNP–H. The implication is that with a strongly reducing radical, trap reduction can occur at a greater trap–parent radical distance than spin trapping.

In the spectrum there are also EPR absorptions due to the reaction of the minor end-chain hydrogen abstraction product with MNP, yielding MNP–CH_2CH(Me)CH(OH)CH$(Me)_2$. The stick diagram for this species is labelled as $^{\bullet}R^1$ in Fig. 2. In this spectrum we observe some selective line-broadening due to hindered internal rotation and/or the presence of a chiral carbon adjacent to the terminal CH_2 group of the parent radical. The broadened lines represent the inner line of a 1:2:1 triplet produced by two equivalent protons in a motionally narrowed CH_2 group; these are indicated by dashed lines in the stick diagram. The same argument advanced concerning the deceptive nature of the alkyl spin adduct intensity in the pentan-3-ol system is valid here. However, the effect is further exaggerated here as the steric hindrance of the 3-hydroxy-2,4-dimethylpentyl radical approaches that of the 2-hydroxy-2-methylpropyl radical from 2-methylpropan-2-ol, whose MNP spin trapping has been studied previously.[7] Kinetic measurements showed that direct trapping was essentially shut down, with the observed steady-state concentration of MNP–2-hydroxy-2-methylpropyl adduct representing merely a fraction of the total production of the parent radical. The small steady-state concentration of spin adduct which this EPR signal represents shows that steric interactions between this alkyl radical and MNP are more favourable than in the case of the MNP–2-hydroxy-2-methylpropyl encounter complex.

The ultimate test of the effects of steric hindrance in the homologous series of methyl-substituted pentanols occurs in the trap–radical encounter complex of MNP–1-*tert*-butyl-1-hydroxy-2,2-dimethylpropyl radical. This radical is formed by addition of the hydrated electron to 2,2,4,4-tetramethylpentan-3-one; to our knowledge, this is the first report of this radical in aqueous solution. In nitrogen-purged 5 mmol dm^{-3} alkaline aqueous 2,2,4,4-tetramethylpentan-3-one solution (1 mol dm^{-3} KOH), the deprotonated ketyl radical shows an 11-line multiplet, the central features of the 19-line multiplet from 18 equivalent protons. The proton hyperfine coupling is 0.019 mT, with a g factor of 2.003 22. Upon reduction of the ketone in neutral aqueous solution, a nine-line multiplet with the proper intensity ratios as the inner features of the preceding species, was found centred at a magnetic field corresponding to a g factor of 2.004 32, with a proton coupling to 18 equivalent protons of 0.023 mT. We believe this is the low-field line group of the protonated form of the ketyl radical, with the high-field line group obscured by the EPR signal from the silica flat cell. If we assume that the g factor of this radical is the same as the deprotonated form, the hydroxy proton hyperfine coupling would be 0.36 mT. A tertiary-butyl proton hyperfine coupling of 0.012 mT (g = 2.003) was measured for the potassium ion-paired ketyl radical in tetrahydrofuran by Hirota and Weissman.[30]

The addition of 1–2 mmol dm^{-3} MNP to a nitrogen-purged 5 mmol dm^{-3} 2,2,4,4-tetramethylpentan-3-one solution causes the appearance of a strong MNP–H signal; the multiplet from the parent radical is the other major radical species. Minor signals are observed from MNP–OH [g = 2.005 14 and a(N, NO) = 2.643 mT][7] and MNP–Bu^t. No trace of an MNP–C(OH)Bu^t_2 spin adduct is observed. In nitrogen-purged solutions containing 5 mmol dm^{-3} MNP, 5 mmol dm^{-3} tetramethylpentanone, and 1 mol dm^{-3} KOH, the spin adducts seen are MNP–OH, MNP–Bu^t, and a third MNP radical adduct consisting of a 1.69 mT triplet. Makino[31] assigned such a triplet to the MNP hydrogen abstraction product $^{\bullet}CMe_2CH_2NO$, formed after the isomerisation reaction of

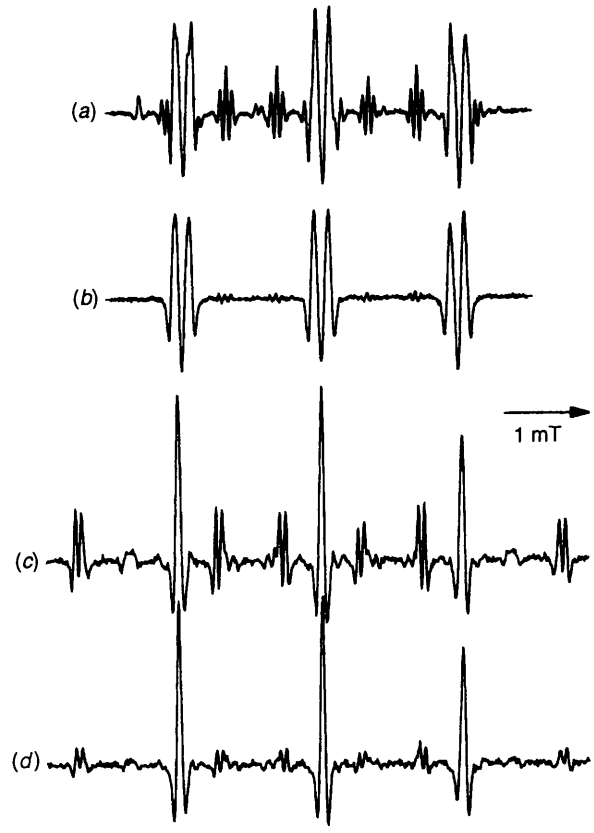

Fig. 4 Second-derivative X-band EPR spectra of radicals formed during ^{60}Co-γ irradiation of aqueous solutions containing secondary alcohols and 1 mmol dm^{-3} MNP; (*a*, *b*) 0.1 mol dm^{-3} pentan-3-ol (central portion of EPR spectrum), and (*c*, *d*) 75 mmol dm^{-3} 2,4-dimethylpentan-3-ol. Spectra (*a*) and (*c*) were recorded several minutes after irradiation; spectra (*b*) and (*d*) were recorded 18 h later.

MNP caused by irradiation. Again, no trace of an MNP–C(OH)Bu$^t_2$ spin adduct is observed. Finally, in the EPR spectrum seen immediately after a 2 min ^{60}Co-γ irradiation of an aqueous solution of 10 mmol dm^{-3} 2,2,4,4-tetramethylpentan-3-one, 1 mmol dm^{-3} MNP, and 100–500 mmol dm^{-3} 2-methylpropan-2-ol, the only major radicals observed are MNP–H and a radical of the form MNP–CH_2R. This radical has the spectral characteristics of MNP–2-hydroxy-2-methylpropyl spin adduct [g = 2.005 72, a(N, NO) = 1.653 mT, and a(H, CH_2) = 1.107 mT],[7,32] but on structural grounds could be the product of the $^{\bullet}CH_2CMe_2C(O)Bu^t$ radical formed by hydrogen abstraction from 2,2,4,4-tetramethylpentan-3-one. However, the preponderance of 2-methylpropan-2-ol in solution as starting material allows unequivocal assignment of this species as the MNP–$CH_2C(Me)_2OH$ spin adduct.

Under all three conditions, we find that as in 2,4-dimethylpentan-3-ol spin trapping, steric hindrance has made MNP–C(OH)Bu$^t_2$ formation impossible; MNP–H formation is the only channel available for the hydroxyalkyl radical reaction, and is produced in sizable yield. However, the increase in parent radical bulk has retarded the trap reduction pathway, since the parent ketyl radical is still observed as a strong signal in neutral solution during the continuous irradiation experiment. The trap–radical encounter distance here must therefore be appreciably greater than in the case of MNP–2,4-dimethylpentan-3-ol system from consideration of the C-3 crowding inherent in the parent ketone molecule. This sets the limiting distance for effective hydroxyalkyl radical–MNP electron transfer.

Konaka and co-workers studied the effect of steric hindrance in the trapping of alkyl and hydroxyalkyl radicals in benzene by 2,4,6-tri-*tert*-butyl(nitroso)benzene.[33] When this extremely sterically hindered trap reacted with reducing hydroxyalkyl radicals, radical addition to the oxygen of the nitroso function was observed, yielding an anilinyl radical as well as the expected aminoxyl spin adduct. A mechanism for the formation of the anilino spin adduct was proposed by Tordo and co-workers.[34] Spin-trap reduction by the hydroxyalkyl radical, yielding the 2,4,6-tri-*tert*-butyl(nitroso)benzene anion radical, was followed by nucleophilic attack on the ketone produced by the electron transfer. This, in turn, yields an aminoxyl if the attacking site were the nitroso nitrogen, or anilinyl radical if the attacking site were the nitroso oxygen. Konaka found the level of steric hindrance in the trap–parent radical encounter controlled the ratio of aminoxyl to anilino radicals as the parent hydroxyalkyl radical changed from hydroxyethyl (1:0), to hydroxypropyl (3:1), to hydroxybutyl (1:2); the relative anilino radical concentration increases at each step in this series. Radical addition to oxygen becomes favoured only when the steric hindrance is so great that the parent species cannot get close to the nitrogen atom of the trap. In the present study, differential trap steric hindrance between the nitrogen and the oxygen is not so great, and the nitrogen atom remains accessible to parent radical approach; therefore no anilino radical is observed in the current work.

(*c*) *Stability of the Spin Adduct Radicals.*—We have followed the evolution of the spin adduct radicals from millisecond to one year post-irradiation times, to observe effects of spin-adduct decay, and possibly post-irradiation spin-adduct growth[35] in hydroxyalkyl radical spin trapping. In these studies, we saw no evidence of post-irradiation growth for these spin adducts, although there is no guarantee that the stability observed for the larger alcohol radical spin adducts is not enhanced by a subtle post-irradiation growth effect. We can say that for any given solution studied, we observed no EPR spectrum that increased in intensity with time; the only temporal behaviour was either steady spectral intensity, or spectral decay.

Since chemical systems containing multiple radical adducts produce complex overlapping aminoxyl radical spectra, the use of chromatography[11,36] has become widespread in spin trapping studies as a tool for separating the various spin adduct radicals. Since second-order processes are the likely mode of radical termination, concentration of the spin adducts during chromatography can lead to a skewing of the intensity profile derived chromatographically, as radicals form diamagnetic products prior to and during their traverse of the chromatographic medium. At short times after irradiation, in systems producing strongly reducing hydroxyalkyl radicals, significant concentration of the total radical yield will be converted into MNP–H by direct trap reduction.

The MNP–hydroxycyclohexyl radical system serves as an effective illustration of this situation. In Fig. 3(*a*), the EPR spectrum recorded during continuous irradiation shows a strong MNP–H EPR signal, comparable in intensity to the central peak of the MNP–hydroxyalkyl multiplet, indicating high MNP–H yield. Fig. 3(*d*) shows an analogous spectrum acquired several minutes after the conclusion of a 2-min ^{60}Co-γ irradiation. The total duration of the field sweep was 500 s. During the sweep, the EPR lines from the MNP–H spin adduct decay quickly; the high-field line is only one-third the intensity of the low-field line, which was recorded 2 min following irradiation. Fig. 3(*e*) shows that MNP–H decays essentially to zero in the 18 h interval following the irradiation. Thus, any calculation of initial secondary hydroxyalkyl radical concentration based solely on the long-term MNP–hydroxyalkyl spin adduct intensity is likely to lead to an erroneous conclusion. Analogous conclusions can be drawn for the pentan-3-ol [Figs. 2(*b*), 4(*a*) and 4(*b*)] and 2,4-dimethylpentan-3-ol [Figs. 2(*c*), 4(*c*) and 4(*d*)] systems.

As noted above, the spectral intensity of the spin adducts formed by reaction of MNP with substituted alkyl radicals is diminished relative to the hydroxyalkyl spin adducts due to the lower spin trapping rate constants exhibited by alkyl radicals.[7] Another factor involved is the lower persistence of these spin adducts compared with the hydroxyalkyl radical spin adducts. Fig. 4(*a*) shows the central portion of the EPR spectrum of the hydroxylalkyl radical spin adduct obtained from a pentan-3-ol–MNP solution 2 min after ^{60}Co-γ irradiation, with the 1:2:1 triplets from the MNP–$CH_2CH_2CH(OH)Et$ radical. Eighteen hours later, the spectrum of Fig. 4(*b*) is obtained, showing little of the alkyl radical spin adduct remaining. In Figs. 4(*c*) and 4(*d*), analogous spectra are presented for the 2,4-dimethylpentan-3-ol–MNP system. In this case the doublet EPR lines due to MNP–$CH_2CH(Me)CH(OH)Pr^i$ decay to a fraction of the original intensity in 18 h. Of these two systems, only the pentan-3-ol hydroxyalkyl radical adduct shows an EPR spectrum 20 d later. In both studies, the conclusion is that the initial radical concentration of the substituted alkyl radical is severely underestimated owing to the combined effect of slow trapping and poor adduct persistence.

Finally, the persistence of the MNP–hydroxyalkyl radical spin adducts must be considered. The MNP-hydroxyalkyl spin adducts from 1-hydroxymethyl, 1-hydroxyethyl, and 1-hydroxy-1-methylethyl radicals have half-lives of minutes under our irradiation/observation conditions.[3,7] MNP spin adducts from hydroxyalkyl radicals of pentan-1-ol and 2,2-dimethylpropane-1,3-diol are not significantly more stable than the smaller primary hydroxyalkyl spin adducts. Although the MNP-hydroxyalkyl radical from pentan-2-ol was visible only in continuous irradiation experiments, the secondary alcohol radicals from pentan-3-ol and cyclohexanols form MNP–hydroxyalkyl radicals with lifetimes of greater than 20 d [*cf.* Figs. 4(*b*) and 3(*e*)]. Notably, after one year of storage in a refrigerator the MNP spin adduct of the hydroxyalkyl radicals from cyclohexanol and 2-methylcyclohexanol are still intense. The bulk of the substituents surrounding the aminoxyl centre in these adducts apparently shields them against any second-order decay process.

Conclusions

The preceding results show that the effect of steric hindrance can be seen in secondary hydroxyalkyl radicals, although a quite bulky environment is needed to see this effect; the degree of steric hindrance present in the MNP–1-hydroxy-1-methylethyl encounter complex is not sufficient to retard radical trapping. When sufficient hindrance is achieved, however, the effect can be dramatic, as seen from the total suppression of MNP–C(OH)RR′ reaction in the 2,4-dimethylpentan-3-ol and 2,2,4,4-tetramethylpentan-3-one systems.

MNP–H is the alternative product of MNP–hydroxyalkyl radical reaction in a large number of systems involving hydroxyalkyl radicals. Once the reduction potential threshold is reached (roughly the redox potential of the 1-hydroxy-1-methylethyl radical), one can see the proportions of MNP–C(OH)RR′ and MNP–H change as steric hindrance is increased; this implies that MNP reduction by ketyl radicals can occur at greater distances than MNP–ketyl radical trapping. There is a threshold, however, where the trap–radical encounter distance is great enough to interfere with trap reduction; this is attained in the MNP···C(OH)RR′ complex, with R = R′ = *tert*-butyl.

Finally, the intensity ratio of various MNP spin adducts seen in steady-state EPR spectra can be misleading if detailed information concerning trapping rate and adduct radical decay is not known. In the series of MNP–hydroxyalkyl radical spin adducts studied here, only the spin adducts formed from the bulkiest hydroxyalkyl radicals were stable for times greater than hours; the other hydroxyalkyl radical spin adducts investigated here show faster second-order termination processes, decaying to a low level in minutes. Direct reduction of the MNP spin trap converts hydroxyalkyl radicals to the transient MNP–H aminoxyl radical; the rapid decay of MNP–H can leave unaccounted substantial accumulations of parent secondary hydroxyalkyl radicals. Substituted alkyl radicals formed by hydrogen abstraction from C–H groups on paraffinic carbons in the alcohol are underrepresented in spin adduct spectral intensity because of slow trapping and fast termination reactions. Therefore, to gain quantitative knowledge of parent radical yields from spin-trapping experiments, consideration of the rate constants for adduct formation and decay is necessary. Time-resolved EPR kinetic studies are indispensable to quantitative use of spin trapping. The steady-state EPR results presented here can serve as a guide, demonstrating the limiting values of radical reducing power and steric hindrance necessary to influence hydroxyalkyl spin trapping reactions.

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