Radical Species Produced from the Photolytic and Pulse-radiolytic Degradation of *tert*-Butyl Hydroperoxide. An EPR Spin Trapping Investigation

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The radicals generated during the photolysis of *tert*-butyl hydroperoxide have been identified by comparison with those generated by reductive pulse radiolysis of the same compound, by photolysis of di-*tert*-butyl peroxide, and by oxidative degradation of dimethyl sulfoxide. While Bu^{t}O$^\bullet$ can definitely be identified as the primary alkoxyl radical intermediate, the identity of the predominantly-formed peroxyl radical is dependent on the generation system.

The univalent reduction of *tert*-butyl hydroperoxide (Bu^{t}OOH) *via* radical species in aqueous solution has been thoroughly studied using EPR spectroscopy and spin trapping. Bu^{t}OOH is catalytically degraded with ferrous iron chelates,[1,2] heme complexes[3,4] or heme proteins.[1,4–7] The most comprehensive spin trapping studies to date are those of Davies[4] and Chamulitrat *et al.*,[7] while Bruice and coworkers[8] and Bennett[9] were mainly concerned with mechanistic and kinetic studies. Davies and Slater[10] have furthermore shown the ease of trapping and identifying these radicals in organic solvents.

We used the photolytic degradation of Bu^{t}OOH [eqn. (1)] in combination with the bleaching of the water-soluble carotenoid crocin to assay the radical-scavenging capabilities of potential antioxidants.[11]

$$(CH_3)_3COOH \xrightarrow{h\nu} (CH_3)_3CO^\bullet + {}^\bullet OH \quad (1)$$

In these studies we assumed that the primary radical species is the alkoxyl radical derived from Bu^{t}OOH, *i.e.* Bu^{t}O$^\bullet$, and knowing its absolute rate constant with crocin,[12] we could convert all relative rate constants from the competition plot of the 'crocin assay' into absolute rate constants of the antioxidants with Bu^{t}O$^\bullet$.[13]

During the metal-catalysed degradation of Bu^{t}OOH, alkoxyl, peroxyl and alkyl radicals have all been observed after spin trapping [eqns. (2)–(6)]:[4,7]

$$(CH_3)_3COOH + Fe^{2+} \longrightarrow (CH_3)_3CO^\bullet + OH^- + Fe^{3+} \quad (2)$$

$$(CH_3)_3CO^\bullet \longrightarrow {}^\bullet CH_3 + (CH_3)_2C{=}O \quad (3)$$

$${}^\bullet CH_3 + O_2 \longrightarrow CH_3OO^\bullet \quad (4)$$

$$(CH_3)_3CO^\bullet + (CH_3)_3COOH \longrightarrow (CH_3)_3COO^\bullet + (CH_3)_3COH \quad (5)$$

$$(CH_3)_3COOH + Fe^{3+} \longrightarrow (CH_3)_3COO^\bullet + H^+ + Fe^{2+} \quad (6)$$

While ${}^\bullet CH_3$ would be the only alkyl radical formed, both Bu^{t}OO$^\bullet$ and $CH_3OO^\bullet$ could represent the trapped peroxyl radical. Of the reactions which have to be primarily considered to take place during the univalent reduction of Bu^{t}OOH, those leading to oxygen-centred alkoxyl and peroxyl radicals are most crucial. We felt it necessary therefore to re-investigate the photolytic degradation of Bu^{t}OOH by EPR spin trapping, using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) and 2-methyl-2-nitrosopropane (MNP) as traps. In parallel experiments we used the method of pulse radiolysis to generate some of the radicals individually.

Experimental

The peroxides used as sources for Bu^{t}O$^\bullet$ were Bu^{t}OOH (80% in Bu^{t}OH) and di-*tert*-butyl peroxide (Bu^{t}O)$_2$ (98%) from Fluka. The spin traps DMPO and MNP and the radical scavengers diphenylamine and mannitol were from Sigma, DMSO from Merck and inositol from Serva. Except for DMPO, which was further purified by charcoal filtration under nitrogen in the dark[14] and kept as frozen stock solution in small vials, all substances were of the highest purity available and used as purchased. All solutions were prepared with 'Milli-Q' water and the pH adjusted by addition of NaOH or $HClO_4$.

For the UV photolysis of the peroxides, the 254 nm emission of a low-pressure Hg lamp with a flux of 1 mW cm^{-2} at the sample location was employed, using various illumination times. The pulse radiolysis experiments were performed using the Febetron set-up described earlier,[15] the transfer of irradiated samples to the EPR cavity taking about 35–45 s. The EPR spectra were recorded on a Bruker ESP 300 spectrometer, the experimental parameters were: modulation amplitude 0.1 G, sweep rate 2.8 s G^{-1} at a frequency of 9.75 GHz and a gain of 1×10^6.

Results

Photolysis of Bu^{t}OOH.—*Spin trapping by DMPO.* As shown in Fig. 1, at 3 mmol dm^{-3} DMPO (less than 10% of the amount usually employed) only trapped peroxyl radicals are detectable, whereas at 25 mmol dm^{-3} DMPO alkyl, alkoxyl, peroxyl, and hydroxyl radicals are trapped, the latter radical being generated simultaneously during the photolytic homolysis of Bu^{t}OOH. Fig. 2 depicts the simulation of Fig. 1(*b*) as a composite of the four radicals listed above. As the DMPO–OH signal is strongly superimposed over the RO$^\bullet$ adduct signal, these two radicals cannot be easily distinguished. In order to improve the interpretation of the EPR signals, we selectively scavenged the ${}^\bullet OH$ radicals by adding the scavengers mannitol or inositol, which react only poorly with alkoxyl radicals.[10] The radicals of these carbohydrates did not produce observable spin adducts with DMPO, yet only at the lower concentrations of the spin trap can we be sure that the ${}^\bullet OH$ radicals are scavenged sufficiently by mannitol or inositol.

The UV photolysis of (Bu^{t}O)$_2$ is an alternative source of Bu^{t}O$^\bullet$ without the complementary formation of ${}^\bullet OH$ radicals [eqn. (7)].

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO^\bullet \quad (7)$$

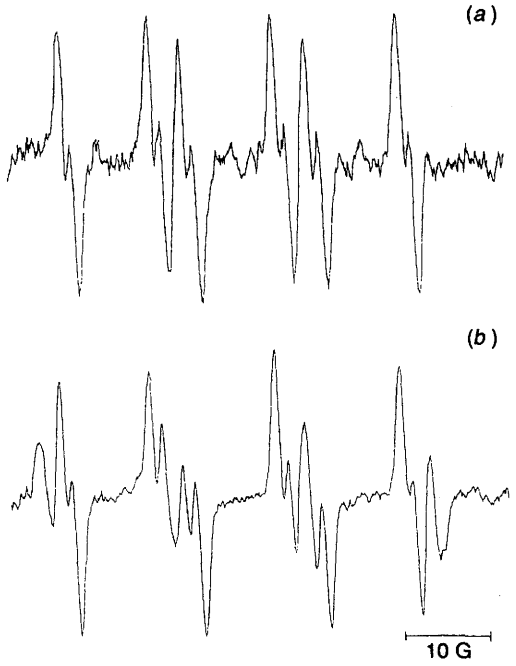

Fig. 1 EPR spectra of DMPO spin adducts after photolysis of Bu^{t}OOH: (*a*) [DMPO] = 3 mmol dm^{-3}, only ROO$^\bullet$ species are trapped; (*b*) [DMPO] = 25 mmol dm^{-3}, composite spectrum containing hydroxyl, alkyl, alkoxyl and peroxyl radicals

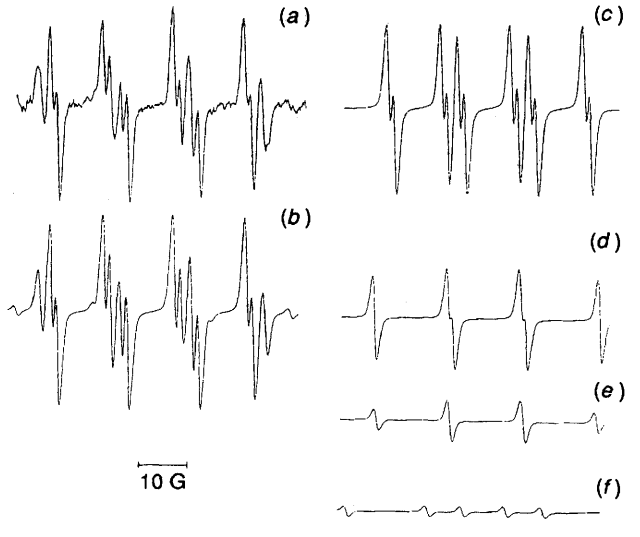

Fig. 2 Simulation of composite spectrum in Fig. 1(*b*): (*a*) experimental results [for details see Fig. 1(*b*)]; (*b*) simulation of Fig. 1(*b*), composite spectrum; (*c*) DMPO–OOR adduct signal; (*d*) DMPO–OR adduct signal; (*e*) DMPO–OH adduct signal; (*f*) DMPO–R(CH_3) adduct signal

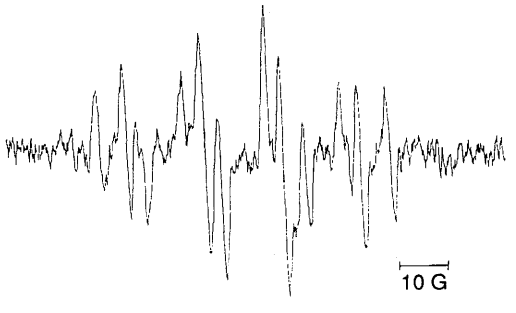

Fig. 3 EPR spectrum of DMPO spin adducts after photolysis of (Bu^{t}O)$_2$ [DMPO] = 18 mmol dm^{-3}, composite spectrum containing the same species as in Fig. 1(*b*)

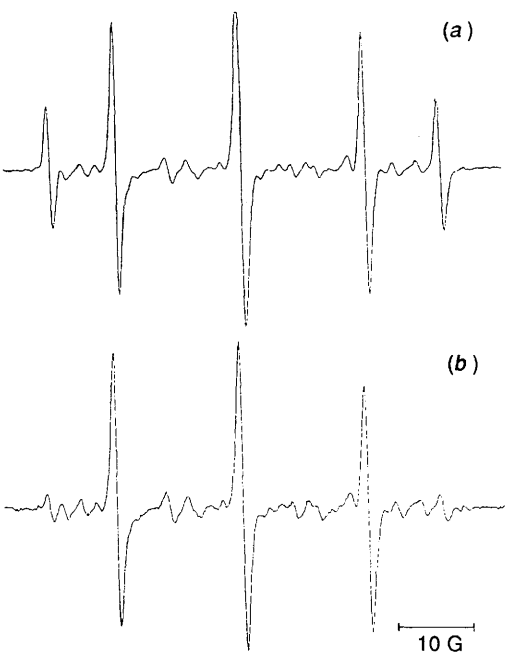

Fig. 4 EPR spectra of MNP spin adducts after photolysis of Bu^{t}OOH: (*a*) [MNP] = 15 mmol dm^{-3}, spectrum contains unspecific three-line signal and 26.6 G signal of Bu^{t}O$^\bullet$; (*b*) [MNP] = 15 mmol dm^{-3}, [DPA] = 0.4 mmol dm^{-3}, Bu^{t}O$^\bullet$ signal is absent

Nevertheless, even under these conditions we obtained EPR signals representing $^\bullet CH_3$, $(CH_3)_3CO^\bullet$, $CH_3OO^\bullet$ and $^\bullet OH$ (Fig. 3). Since this "$^\bullet OH$' signal was not inhibited by mannitol, it is most likely derived from photolysis of DMPO itself,[16] which we confirmed independently by photolysis of DMPO alone.

Spin trapping by MNP. Fig. 4 shows the adduct signals of at least two radical species, one of which decays with a half-life of about 90 s. The yield of the same radical adduct is diminished in a concentration-dependent manner after addition of diphenylamine, a scavenger of alkoxyl radicals.[17] We therefore consider this signal to represent the Bu^{t}O$^\bullet$ radical adduct, in agreement with Chamulitrat *et al.*,[7] and were able to confirm this assignment by again using (Bu^{t}O)$_2$ as a source of Bu^{t}O$^\bullet$. The remainder were the strong three-line signal attributed to di-*tert*-butylnitroxide[18] and the adduct of the acetonitrile alkyl radical, which was used at 6.3 mol dm^{-3} to enhance the solubility of MNP (which we confirmed by independent generation and trapping, data not shown).

Determination of rate constants of DMPO and MNP with Bu^{t}O$^\bullet$ *by competition with crocin.* This regularly employed test for the reactivity of Bu^{t}O$^\bullet$ with various substances[11] in aqueous solution gave absolute rate constants (dimension: dm^3 mol^{-1} s^{-1}) with DMPO of 9×10^6 and MNP of 1.3×10^8. These values and the inverse order stand in contrast to 5×10^8 and 1.5×10^6 for the reaction of Bu^{t}O$^\bullet$ with DMPO and MNP determined in benzene solution.[19]

Pulse Radiolysis of Bu^{t}OOH.—*Spin trapping by DMPO.* Using mannitol or inositol (0.1 mol dm^{-3}) to scavenge $^\bullet OH$ radicals in analogy to the photolytic experiments (see Fig. 1), we found only alkyl and hydrogen atom spin adducts of DMPO (3 mmol dm^{-3}) after pulse radiolysis of N_2-saturated solutions of Bu^{t}OOH (5 mmol dm^{-3}) (Fig. 5). The same results were obtained using cumene hydroperoxide (CuOOH) as the radical source (spectra not shown). Table 1 gives a compilation of the hyperfine splitting constants of all radical species trapped by DMPO in the previously described experiments.

Spin trapping by MNP. After irradiation of Bu^{t}OOH (1 mmol dm^{-3}) in N_2-saturated aqueous solutions, *i.e.* reducing it with

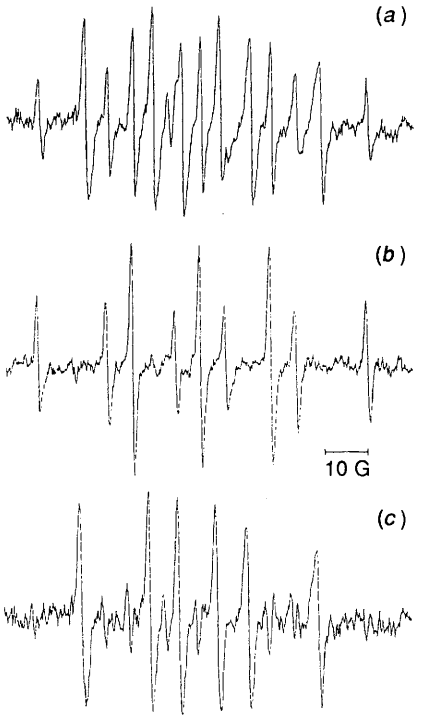

Fig. 5 EPR spectra of DMPO spin adducts after pulse radiolysis of Bu^{t}OOH (N_2-saturated solutions, phosphate-buffered at pH 7.5): (*a*) [DMPO] = 3 mmol dm^{-3}, [mannitol] = 100 mmol dm^{-3}, [Bu^{t}OOH] = 5 mmol dm^{-3}, spectrum contains $^{\bullet}H/e^-_{aq}$ and alkyl ($^{\bullet}CH_3$) adduct; (*b*) [DMPO] = 3 mmol dm^{-3}, [mannitol] = 100 mmol dm^{-3}, no Bu^{t}OOH present, spectrum contains only $^{\bullet}H/e^-_{aq}$ adduct; (*c*) difference spectrum (*a*) − (*b*), reflects only $^{\bullet}CH_3$ adduct

Table 1 Hyperfine splitting constants of DMPO radical adducts observed after photolytic and radiolytic degradation of organic (hydro)peroxides and dimethyl sulfoxide

Radical adduct	Solute[a]	System[b]	Hyperfine splitting constants a_N	$a_{H\beta}$	a_H	Comment
$H^{\bullet}/e^-_{aq}$	Bu^{t}OOH	PR	16.6	22.4/2	—	*c*
	CuOOH	PR	16.6	22.4/2	—	*c*
$^{\bullet}OH$	N_2O	PR	14.9	14.9	—	*c*
	Bu^{t}OOH	*hv*	14.9	14.9	—	*d*
"$^{\bullet}OH$"	$(Bu^tO)_2$	*hv*	14.9	14.9	—	*d*
	—	—	14.95	14.95	—	*e*
$^{\bullet}CH_3$	Bu^{t}OOH	PR	16.3	23.5	—	*d*
	DMSO	PR	16.3	23.5	—	*c*
	—	—	16.43	23.46		*e*
Bu^{t}O$^{\bullet}$	Bu^{t}OOH	*hv*	14.9	16.0	—	*d*
	$(Bu^tO)_2$	*hv*	14.9	16.0	—	*d*
	—	—	14.7	16.2	—	*e*
$CH_3OO^{\bullet}$	Bu^{t}OOH	*hv*	14.5	10.6	1.4	*c*
	$(Bu^tO)_2$	*hv*	14.5	10.6	1.4	*d*
	DMSO	*hv*	14.5	10.6	1.3	*c*
	DMSO	PR	14.5	10.6	1.4	*d*

[a] Bu^{t}OOH: *tert*-butyl hydroperoxide; $(Bu^tO)_2$: di-*tert*-butyl peroxide; CuOOH: cumene hydroperoxide; DMSO: dimethyl sulfoxide. [b] PR: pulse radiolysis; *hv*: photolysis. [c] Experiment used to determine hfsc. [d] Experiment where spin adduct was observed as component. [e] Average literature value (ref. 7).

Table 2 Hyperfine splitting constants of MNP radical adducts observed after photolytic and radiolytic degradation of organic (hydro)peroxides and dimethyl sulfoxide

Radical adduct	Solute	System	Hyperfine splitting constants a_N	$a_{H\beta}$	Comment
$^{\bullet}CH_3$	Bu^{t}OOH	PR	17.1	14.1/3	*a*
	DMSO	PR	17.2	14.4/3	*b*
	Bu^{t}OOH	—	17.33	14.34/3	*c*
Bu^{t}O$^{\bullet}$	Bu^{t}OOH	*hv*	26.6	—	*b*
	$(Bu^tO)_2$	*hv*	26.6	—	*b*
	Bu^{t}OOH	—	26.7	—	*c*

[a] Experiment where spin adduct was observed as component. [b] Experiment used to determine hfsc. [c] Average literature value (ref. 7).

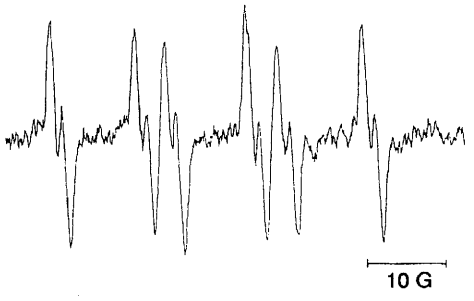

Fig. 6 EPR spectrum of the DMPO spin adduct of $CH_3OO^{\bullet}$ after photolysis of DMSO in oxygenated solutions containing H_2O_2: [DMSO] = 100 mmol dm^{-3}, [DMPO] = 15 mmol dm^{-3}, [H_2O_2] = 5 mmol dm^{-3}, pH = 7.5

e^-_{aq} to Bu^{t}O$^{\bullet}$, we observe only $^{\bullet}CH_3$ radicals and the three-line signal of di-*tert*-butylnitroxide,[18] after trapping with 10 mmol dm^{-3} MNP. In control experiments the methyl radical was generated much more efficiently and specifically from DMSO + $^{\bullet}OH$ in N_2O-saturated solutions and corroborated the identification in the Bu^{t}OOH system (spectra not shown). The fact that Table 2 lists only the hfsc values of the two radicals $^{\bullet}CH_3$ and Bu^{t}O$^{\bullet}$ clearly shows the limitations of this spin trap as compared to DMPO (*cf.* Table 1).

Identity of Peroxyl Adduct.—In contrast to the metal- or enzyme-catalysed degradation of Bu^{t}OOH,[4,7] during photolysis or pulse radiolysis peroxyl radicals are only formed as secondary species. To determine whether these radical adducts are either those of $(CH_3)_3COO^{\bullet}$ (=Bu^{t}OO$^{\bullet}$) or $CH_3OO^{\bullet}$, we generated the latter radical specifically from DMSO + $^{\bullet}OH$ + O_2 either photolytically or by pulse radiolysis and trapped it with DMPO. Fig. 6 shows exclusively the $CH_3OO^{\bullet}$ adduct after DMSO oxidation during UV photolysis of H_2O_2 with very similar results for the pulse radiolysis experiments (not shown).

Discussion

The main problem, when using the photolytic generation of Bu^{t}O$^{\bullet}$ in conjunction with the bleaching of the carotenoid crocin, concerns the identity of the respective radicals. Pulse radiolysis studies showed that while crocin is effectively bleached by a number of radicals,[20] no reaction was observed with $O_2^{\bullet-}$ or $^{\bullet}CH_3$.[21] Furthermore, while a kinetic difference between RO$^{\bullet}$ and ROO$^{\bullet}$ was observed,[22] no absolute rate constants with peroxyl radicals are known.

During the photolysis of Bu^{t}OOH in aqueous solution, Bu^{t}O$^{\bullet}$ radicals were trapped unequivocally by DMPO [Figs. 1(*b*), 2] and by MNP (Fig. 4), in agreement with Chamulitrat *et al.*[7] We consider the good correlation of the simulated spectra as suffi-

Table 3 Comparison of hyperfine splitting constants of various alkylperoxyl radicals

Radical adduct	Solute	System	Hyperfine splitting constants a_N	$a_{H\beta}$	a_H	Comment
$CH_3OO^\bullet$	Bu^tOOH	*hv*	14.5	10.6	1.4	*a*
	$(Bu^tO)_2$	*hv*	14.5	10.6	1.4	*b*
	DMSO	*hv*	14.5	10.6	1.3	*a*
	DMSO	PR	14.5	10.6	1.4	*b*
$Bu^tOO^\bullet$	Bu^tOOH	—	14.4	10.53	1.48	*c*
$EtOO^\bullet$	EtOOH	—	14.65	11.05	1.25	*c*
$CuOO^\bullet$	CuOOH	—	14.56	10.64	1.28	*c*

[a] Experiment used to determine hfsc. [b] Experiment where spin adduct was observed as component. [c] Average literature value (ref. 7).

cient proof that $Bu^tO^\bullet$ radicals are clearly the primary photolysis products reacting with either crocin or the prospective antioxidant.[11] Since crocin is such an efficient scavenger of $Bu^tO^\bullet$ radicals (3×10^9 dm^3 mol^{-1} s^{-1}, ref. 12), it is unlikely that under the conditions of the 'crocin assay' peroxyl radicals are involved.

In contrast, we consistently find signals for peroxyl adducts with DMPO after photolysis of Bu^tOOH. We consider this to be due to the fact that DMPO is a far less efficient trap for $Bu^tO^\bullet$ than crocin (9×10^6 dm^3 mol^{-1} s^{-1}, see above) and that $Bu^tO^\bullet$, in aqueous solution, fragments very rapidly in a first-order reaction into $^\bullet CH_3$ and acetone, eqn. (3). With $^\bullet CH_3$ adding O_2 in a diffusion-controlled reaction, eqn. (4), and the potential contribution of eqn. (5), both $(CH_3)_3COO^\bullet$ and $CH_3OO^\bullet$ could occur. Yet from the quite similar hfsc values in Table 3, it is unlikely to resolve this question merely by spin trapping experiments. Therefore, we have used a kinetic approach to determine the probabilities of the different radicals being trapped under photolytic or radiolytic conditions. This requires the knowledge of the concentrations of the participating substrates and the respective rate constants, which are either known or are assumed to be similar to those of comparable radicals. Under photolytic conditions we took into consideration the reactions listed below [dimension: dm^3 mol^{-1} s^{-1}, except for eqn. (3), s^{-1}; * denotes those reactions for which no literature values are known or which have yet to be determined]. These reactions are fewer than those considered in a recent kinetic EPR study,[9] but the latter only concern radical–radical recombinations which can be neglected under steady-state conditions.

$$(CH_3)_3CO^\bullet \xrightarrow{1.5 \times 10^6} {}^\bullet CH_3 + (CH_3)_2C{=}O \quad (3)^{12}$$

$$^\bullet CH_3 + O_2 \xrightarrow{4.7 \times 10^9} CH_3OO^\bullet \quad (4)^{23}$$

$$(CH_3)_3CO^\bullet + (CH_3)_3COOH \xrightarrow{1.2 \times 10^6} (CH_3)_3COO^\bullet + (CH_3)_3COH \quad (5)^9$$

$$^\bullet CH_3 + {}^\bullet CH_3 \xrightarrow{1.4 \times 10^9} CH_3 - CH_3 \quad (8)^{24}$$

$$CH_3OO^\bullet + (CH_3)_3COOH \xrightarrow{<10^2} (CH_3)_3COO^\bullet + CH_3OOH \quad (9)^*$$

$$CH_3OO^\bullet + CH_3OO^\bullet \xrightarrow{3.5 \times 10^8} \text{termination products} \quad (10)^{25}$$

Added to these are the following individual trapping reactions:

$$(CH_3)_3CO^\bullet + DMPO \xrightarrow{9 \times 10^6} DMPO - OR \quad (11a) \text{ (this work)}$$

$$(CH_3)_3CO^\bullet + MNP \xrightarrow{1.3 \times 10^8} MNP - OR \quad (11b) \text{ (this work)}$$

$$(CH_3)_3COO^\bullet + DMPO \xrightarrow{<10^6} DMPO - OOR \quad (12)^*$$

$$CH_3OO^\bullet + DMPO \xrightarrow{5 \times 10^5} DMPO - OOR \quad (13)^*$$

$$^\bullet CH_3 + DMPO \xrightarrow{<10^7} DMPO - CH_3 \quad (14a)^*$$

$$^\bullet CH_3 + MNP \xrightarrow{1.7 \times 10^7} MNP - CH_3 \quad (14b)^{26}$$

The reaction probabilities for the most likely reactions are defined as follows:

$$r_p(Bu^tO^\bullet) = k_3 + k_5[Bu^tOOH] + k_{11a}[DMPO] \quad (15)$$

$$r_p(^\bullet CH_3) = k_4[O_2] + k_8[^\bullet CH_3] + k_{14a}[DMPO] \quad (16)$$

$$r_p(CH_3OO^\bullet) = k_9[Bu^tOOH] + k_{10}[CH_3OO^\bullet] + k_{13}[DMPO] \quad (17)$$

According to eqn. (15), with [Bu^tOOH] at 1 mmol dm^{-3} and [DMPO] at 25 mmol dm^{-3}, k_5 would have to be $> 1.5 \times 10^9$ dm^3 mol^{-1} s^{-1} to account for $(CH_3)_3COO^\bullet$—the recently determined value of 1.2×10^6 dm^3 mol^{-1} s^{-1} [9] for this reaction is far too low. Furthermore, with a value for k_3 of 1.5×10^6 s^{-1} [12] and k_{11a} of 9×10^6 dm^3 mol^{-1} s^{-1} ($k_{11b} = 1.3 \times 10^8$ dm^3 mol^{-1} s^{-1}) from the competition experiments with crocin, most $Bu^tO^\bullet$ would decay *via* reaction (3), rather than being trapped by MNP or DMPO. We thus have mainly $^\bullet CH_3$ radicals, for which eqn. (16) gives a considerable preference to form $CH_3OO^\bullet$ [eqn. (4)] even in air-saturated aqueous solutions ([O_2] = 0.3 mmol dm^{-3}), assuming that k_{14a} of 10^7 dm^3 mol^{-1} s^{-1} is a reasonable estimate. Again the radical–radical recombination of reaction (8) has no impact whatsoever. Eqn. (17) shows the clear preference of $CH_3OO^\bullet$ to be trapped by DMPO *via* reaction (13) as opposed to reaction with Bu^tOOH [reaction (9)] or second-order self decay reaction (10). Reaction (9) is merely a chain-propagating change from one peroxyl radical to another with the value given as an upper limit, whereas the rate constant for eqn. (10) is the sum of three possible decay reactions measured in the gas phase.[25] Aside from reaction (9), $Bu^tOO^\bullet$ could also be regenerated in reaction (5)—both reactions, however, are negligible as are all the proposed termination reactions of $Bu^tOO^\bullet$.[9] Altogether, at lower DMPO concentrations (3 mmol dm^{-3} *vs.* 25 mmol dm^{-3}) we may assume an almost quantitative conversion of $Bu^tO^\bullet$ *via* reactions (3) and (4) into $CH_3OO^\bullet$, which is the only species trapped, as indeed has been found [Fig. 1(*a*)].

Looking at the pulse-radiolytic data and taking into account the above-listed rate constants, it can easily be understood why under these conditions *no* peroxyl radical whatsoever can be

observed. In the anaerobic system of N_2O-saturated solutions, the necessarily low concentrations of DMPO and MNP can only trap $^{\bullet}CH_3$, which is present in micromolar rather than nanomolar concentrations. At higher concentrations of the spin traps $^{\bullet}OH$ or alkyl adducts of the $^{\bullet}OH$ scavengers would obscure the signal–not even MNP, with its higher rate constant as compared to DMPO, traps the $Bu^tO^{\bullet}$ radical under pulse-radiolytic conditions. Only by irradiating DMSO at various O_2 concentrations could we observe $CH_3OO^{\bullet}$ radicals in addition to $e_{aq}^-/H^{\bullet}$ and $^{\bullet}CH_3$ radical adducts.

It is thus obvious that under photolytic conditions the only peroxyl radical trapped is $CH_3OO^{\bullet}$ rather than $(CH_3)_3COO^{\bullet}$, which was corroborated by generating $CH_3OO^{\bullet}$ selectively by pulse radiolysis of DMSO in N_2O/O_2-saturated solutions. From the data in Table 3 and in ref. 7, it is evident that one cannot distinguish between the various peroxyl adducts of DMPO as the hfsc values for $CH_3OO^{\bullet}$, $CH_3CH_2OO^{\bullet}$, $(CH_3)_3COO^{\bullet}$ and $C_6H_5(CH_3)_2COO^{\bullet}$ (cumene peroxyl radical) are too similar.

What, then, about the identity of the peroxyl radicals trapped in metal-catalysed systems? Assuming the same reaction probabilities as given for the photolytic system—*i.e.* eqns. (15)–(17), with reactions (12) + (18) in addition then the reaction prob-

$$2(CH_3)_3COO^{\bullet} \xrightarrow{2.5\times10^4} \text{products} \qquad (18)^{27}$$

ability is given by eqn. (19). Using the rate constant given for

$$r_p(Bu^tOO^{\bullet}) = 2k_{18}[Bu^tOO^{\bullet}] + k_{12}[DMPO] \quad (19)$$

reaction (18) in water of 2.5×10^4 dm^3 mol^{-1} s^{-1} [27] and assuming 10^4 dm^3 mol^{-1} s^{-1} for k_{12} as well as steady-state concentration of the radicals maximally at 10 nmol dm^{-3}, it is thus clear that all of the peroxyl radicals trapped after metal- or enzyme-catalysed degradation of Bu^tOOH are indeed $Bu^tOO^{\bullet}$ rather than $CH_3OO^{\bullet}$ radicals.

In conclusion, we have shown that using known or newly established rate constants of spin trapping reactions and applying these to calculations of reaction probabilities, one can *predict* which radicals are likely to be observed. In line with a similar conclusion on the importance of rate constants for the *interpretation* of spin trapping experiments,[28] we propose to use this approach to optimize the experimental conditions for selective spin trapping of specific radicals.

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