An in Situ Radiolysis Time-Resolved ESR Study of the Kinetics of Spin Trapping by 5,5-Dimethyl-1-pyrroline-*N*-oxide

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Abstract: We have measured the reaction rate constants of the nitrone spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) with a number of small alkyl and σ parent radicals in dilute aqueous solution using in situ radiolysis time-resolved electron spin resonance spectroscopy. Unsubstituted alkyl parent radicals (methyl, ethyl, propyl, and 1-methylethyl (2-propyl)) had rate constants ranging from 5.6×10^6 to 1.6×10^7 M^{-1} s^{-1}. Electron-releasing α-hydroxyalkyl radicals (hydroxymethyl, 1-hydroxyethyl, 1-hydroxypropyl, and 1-hydroxy-1-methylethyl (2-hydroxy-2-propyl)) reacted more rapidly than the unsubstituted radicals with rate constants of $(2.2-6.8) \times 10^7$ M^{-1} s^{-1}, while the electron-withdrawing carboxymethyl radical was slower (4.4×10^6 M^{-1} s^{-1}). The bulky 2-hydroxy-2-methylpropyl radical reacted with DMPO, but with a rate constant smaller than 10^6 M^{-1} s^{-1}. σ radicals such as sulfite anion and carboxyl anion were trapped quickly, with rate constants of 1.2×10^7 and 6.6×10^7 M^{-1} s^{-1}, respectively. These results show that the zwitterionic structure of DMPO results in sensitivity to polar effects in the parent radical-spin trap encounter complex, while steric effects are also influential in the reaction of DMPO with bulky alkyl radicals. The rate constants for the reaction of DMPO with the radicals studied herein are, in general, an order of magnitude slower than the same radicals reacting with the nitroso spin trap 2-methyl-2-nitrosopropane.

Introduction

Spin trapping allows the visualization of transient free radical populations by reacting short-lived radicals with a spin trap to produce persistent spin adduct radicals. It has been widely used in the fields of chemical, biological, and medical sciences.[1−6] Kinetic information, including the rate constants of spin adduct formation and decay, is useful for proper design of qualitative spin trapping studies, but essential for quantitative studies, where the final concentration of the spin adduct depends on the competition between spin adduct formation and second-order parent radical decay, for example, by dimerization and disproportionation. The rate of the spin trapping reactions is expected to be dependent upon steric and electronic (polar) interactions in the parent radical-spin trap encounter complex. Such effects have been demonstrated in spin trapping by a nitroso compound.[7,8]

We have studied spin trapping kinetics using in situ radiolysis time-resolved electron spin resonance spectroscopy (TRESR; also known as time-resolved electron paramagnetic resonance, TREPR). This allows us either to follow the spin adduct radical formation and decay processes or to monitor the decay of the short-lived parent radicals directly from their ESR spectra. The unique advantage of TRESR was described in our previous papers.[7,9]

In previous studies, we have examined the adduct formation kinetics of the spin traps (spin trapping reagents) nitromethane *aci*-anion (NMA) and 2-methyl-2-nitrosopropane (MNP).[7,9] In this paper, we examine the kinetics of spin trapping using the nitrone spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) using in situ radiolysis TRESR spectroscopy.

To the best of our knowledge, there are very few reports concerning the kinetics of DMPO spin trapping in dilute aqueous solution, except for those detailing the trapping of hydroxyl or superoxide radicals.[10,11] Using pulse radiolysis and kinetic spectrophotometry, Davies, Forni, and Shuter[12] studied the kinetics of thiyl radical trapping by DMPO in aqueous acetone and 2-propanol solution. Using a similar approach based on competition kinetics, Farragi, Carmichael, and Riesz[13] studied the reaction of the carboxyl anion radical and 1-hydroxy-1-methylethyl radical with DMPO at pH 11. A flash photolysis-ESR study of the reaction of the 1-hydroxy-1-methylethyl radical with DMPO in acidified acetone/2-propanol/water (1:1:2) solution was performed by Chiu, Siemiarczuk, Wong, and Bolton.[14] The conditions for each of these studies differ substantially from those presented here.

In this study we will concentrate on the kinetics of spin

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trapping reaction by 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) using in situ radiolysis TRESR spectroscopy. Among popular water-soluble spin traps, DMPO is one of the most frequently used traps, making this kinetic information timely. In this paper we report a TRESR study of DMPO spin trapping kinetics for some representative parent π and σ radicals in dilute aqueous solution; the use of a common solvent for all parent and spin adduct radicals facilitates the comparison of the trapping kinetics. The ESR spectral parameters of the parent radicals and DMPO adduct radicals were described in the preceding papers.[6,15]

Experimental Section

The experimental procedures and techniques were generally the same as in our previous studies.[7,10] Flowing, cooled (10−15 °C) aqueous solutions were irradiated within the microwave cavity of the ESR spectrometer with a 100 mA, 0.5 μs pulsed beam of 2.8 MeV electrons from a Van de Graaff accelerator. TRESR experiments were performed at a 25 or 100 Hz repetition rate. The instantaneous electron beam intensity was monitored continuously using the collected beam current from the ESR cell. Since DMPO spin adducts of carbon-centered radicals have appreciably longer lifetimes than those from MNP and nitromethane *aci*-anion, and nitroxide radicals are known to react very rapidly with radicals formed by water radiolysis (hydroxyl radicals, hydrated electrons, and hydrogen atoms),[16,17] special effort was expended to ensure that a fresh volume of solution was irradiated with every electron pulse. A special Suprasil aqueous flat cell, with four parallel channels delineated by internal Suprasil fibers, having an internal cross-section of 0.4 mm × 7.5 mm, tubulated with 8 mm o.d. tubing, was constructed to eliminate the flow stagnation characteristic of standard aqueous flat cell designs.[18] A low pulsation continuous-flow syringe pump system was employed to reliably sustain the high flow rates (∼32 mL/min) needed in these studies.

X-band (9.2 GHz) ESR experiments were performed using the apparatus described previously.[19] All ESR experiments were performed at microwave powers well below saturation. Magnetic field measurements were by NMR methods and were measured as offsets from the central feature of the irradiated quartz flat cell, $g = 2.00043$. This field position was verified daily by calibration against the sulfite radical anion, $g = 2.00316$.[20] Time-resolved kinetic curves were recorded at line positions corresponding to the parent radical and spin adduct measured in steady-state ESR spectra.[6,15] Lower field lines not overlapping those of other radical species were usually selected for the kinetic recording to avoid ambiguity. Quantitative determinations of trapping kinetics were performed using the decay kinetics of the parent radicals, except in the studies of the carboxyl anion radical, where growth kinetics of the spin adduct were used. The growth kinetics of the corresponding spin adduct radicals essentially mirrored the decay of the parent radicals for all systems reported here. Since the steady-state in situ radiolysis ESR studies suggested second-order parent radical termination processes could compete with radical addition at reasonable concentrations of DMPO, a mixed first- and second-order kinetic model was used in fitting the data.[21] Wherever possible, the pure second-order parent radical decay kinetics in the absence of DMPO were recorded and analyzed, with the resulting second-order rate constant used as a fixed parameter in the mixed-order fitting process. The experimental kinetic curves were analyzed using the Levenberg−Marquardt curve fitting subroutines of the computer program Origin 4.1 (MicroCal Software, Northampton, MA). Plotting the measured pseudo-first-order rate constants as a function of DMPO concentration yielded a straight line through the origin. The slope of this line gives the bimolecular trapping rate constant of the parent radicals by DMPO.

Sample solutions were freshly prepared using reagent grade water from a Millipore Milli-Q water system. Aqueous solutions contained 0.1−1 M parent compound and 1−15 mM DMPO. Unbuffered solutions near neutral pH were used for kinetic experiments, except for the sulfite anion radical measured at pH 9.1. In studies using carboxylic acids to produce parent radicals, equimolar sodium hydroxide (Fisher) was added to neutralize the sample solution. DMPO was obtained from OMRF Spin Trap Source and used without further purification. No aminoxyl radicals were visible in the DMPO-containing solutions prior to irradiation. All solutions were prepared in water deoxygenated by sparging nitrous oxide or nitrogen, as described below. This anoxic environment was maintained through all phases of the experiments.

Most parent radicals were produced by the reaction of radiolytically produced hydroxyl radicals with the starting substrate. In these cases, to maximize ESR signal intensity, and to minimize cross-reactions, sample solutions were deoxygenated with nitrous oxide (U.S.P. grade, Mittler) to convert radiolytically produced hydrated electrons into hydroxyl radicals via the following processes:[22]

$$H_2O \rightsquigarrow {}^{\bullet}OH\ (\sim 45\%) + e^{-}_{aq}\ (\sim 45\%) + {}^{\bullet}H\ (\sim 10\%) \quad (1)$$

$$e^{-}_{aq} + N_2O + H_2O \rightarrow {}^{\bullet}OH + OH^{-} + N_2 \quad (2)$$

Alkyl radicals were derived from reaction of the hydroxyl radicals with the appropriate dialkyl sulfoxides via reaction 3:[23,24]

$$R_2SO + {}^{\bullet}OH \rightarrow R_2S(OH)O^{\bullet} \rightarrow R^{\bullet} + RS(O)OH \quad (3)$$

Dimethyl sulfoxide (DMSO) was used as obtained from Fisher. Diethyl sulfoxide (DESO), dipropyl sulfoxide, and diisopropyl sulfoxide were prepared from the corresponding dialkyl sulfide (Aldrich) by hydrogen peroxide (Fisher, 30%) oxidation at ice-bath temperatures, and purified by multiple distillations under reduced pressure.[7,25] Concentrations of DMSO, DESO, dipropyl sulfoxide, and diisopropyl sulfoxide employed were 0.25, 0.2, 0.2, and 0.025 M, respectively.

Hydroxyalkyl radicals were made by hydroxyl radical-induced hydrogen abstraction from the following alcohols: methanol (0.25 M, Fisher), ethanol (0.25 M, Midwest Distilling), 1-propanol (0.1 M, Fisher), 2-propanol (0.1 M, Fisher), and 2-methyl-2-propanol (*tert*-butyl alcohol, 0.1 M, Fisher). σ radicals were generated by the reaction of hydroxyl radical with sodium formate (0.2 M, Aldrich) and sodium sulfite (0.2 M, Mallinckrodt).

We also tried to measure the DMPO trapping rate constants of malonic acid (0.1 M, Aldrich) radical ${}^{\bullet}CH(CO_2^{-})_2$ and tartronic acid (hydroxymalonic acid, 0.1 M, Aldrich) radical ${}^{\bullet}C(OH)(CO_2^{-})_2$ from the decay time profile of these radicals. However, they are apparently too slow to be measured via TRESR.

Carboxymethyl radical was produced by the reaction of the hydrated electron with bromoacetic acid (0.4 M, Aldrich); in this case, 0.4 M NaOH (Fisher) was added to the nitrogen-deoxygenated (ultrahigh purity nitrogen, Mittler) solution to observe the kinetics in the region near neutral pH. In one experiment, sodium formate was added to scavenge radiolytically produced hydroxyl radicals, hoping to increase the yield of carboxymethyl radical by electron transfer from ${}^{\bullet}CO_2^{-}$ radical to bromoacetic acid. However, this reaction proved too slow to be useful for these studies. We therefore added no additional hydroxyl radical scavenger, allowing ${}^{\bullet}OH$ to react directly with DMPO.

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Table 1. Spin Trapping Rate Constants with DMPO and MNP as Spin Traps in M^{-1} s^{-1}

parent radical		DMPO[a]	MNP[b]
methyl	$^{\bullet}CH_3$	1.4×10^7	1.7×10^7
ethyl	$^{\bullet}CH_2CH_3$	1.6×10^7	5.3×10^7
propyl	$^{\bullet}CH_2CH_2CH_3$	5.6×10^6	6.9×10^7
1-methylethyl	$^{\bullet}CH(CH_3)_2$	5.8×10^6	4.6×10^7
hydroxymethyl	$^{\bullet}CH_2OH$	2.2×10^7	1.4×10^8
1-hydroxyethyl	$^{\bullet}CH(OH)CH_3$	4.1×10^7	3.2×10^8
1-hydroxypropyl	$^{\bullet}CH(OH)CH_2CH_3$	3.0×10^7	1.3×10^8
1-hydroxy-1-methylethyl	$^{\bullet}C(OH)(CH_3)_2$	6.8×10^7	6.9×10^8
2-hydroxy-2-methylpropyl	$^{\bullet}CH_2C(CH_3)_2OH$	*c*	$<1 \times 10^6$
carboxymethyl	$^{\bullet}CH_2CO_2^-$	4.4×10^6	7.0×10^6
carboxyl anion	$^{\bullet}CO_2^-$	6.6×10^7	1.7×10^9
sulfite anion	$^{\bullet}SO_3^-$	1.2×10^7	4.3×10^7
hydrated electron	e^-_{aq}	3.2×10^9 [d]	6.2×10^9
hydroxyl radical	$^{\bullet}OH$	2.8×10^9 [d]	2.5×10^9

[a] This work, except two data at the bottom. Errors in the range of 10%. [b] Reference 7. Trapping rates ±20%. [c] Only the gradual growth of the spin adduct radical was observed. [d] Reference 10.

Since the rate constants of parent compounds with hydroxyl radicals range from 5.2×10^8 (for 2-methyl-2-propanol) to 5.8×10^9 M^{-1} s^{-1} (for DMSO)[26] and that of DMPO is 2.8×10^9 M^{-1} s^{-1},[10] greater than 79% of the hydroxyl radicals react with the parent compounds at 5 mM DMPO. About 98% of the hydrated electron reacts with bromoacetic acid at 13 mM DMPO, since the rate constant of bromoacetic acid anion with hydrated electron is 6.2×10^9 M^{-1} s^{-1} [26] and that of DMPO is 3.2×10^9 M^{-1} s^{-1}.[10]

Results and Discussion

The DMPO trapping rate constants for all radicals studied here are summarized in Table 1. The MNP trapping rate constants for the same parent radicals are listed for comparison. Rate constants for the reaction of both spin traps with radiolytically produced hydrated electron and hydroxyl radical are included for reference.

Figures 1 and 2 show typical TRESR curves for methyl and 1-hydroxyethyl radical trapping by DMPO. Figure 1 shows the time profile of the decay of methyl radical, with pseudo-first-order rate constants of 3.0×10^4, 6.4×10^4, and 1.2×10^5 s^{-1} for 2.1, 4.5, and 8.6 mM DMPO, respectively. Plotting these pseudo-first-order rate constants against the concentration of DMPO, as shown in the inset of Figure 1, followed by linear least-squares fitting, resulted in a calculated second-order rate constant of $(1.4 \pm 0.2) \times 10^7$ M^{-1} s^{-1} for the trapping reaction of DMPO and methyl radical.

Figure 2 shows TRESR traces for the decay of 1-hydroxyethyl radical, and the complementary growth of its spin adduct in the presence of 7.5 mM DMPO. Pseudo-first-order rate constants are 3.0×10^5 and 2.3×10^5 s^{-1}, respectively. The difference between these two rate constants is attributable to the second-order termination process of the parent radical; this population of radicals is not trapped by DMPO. Plotting the pseudo-first-order decay rate constant of 1-hydroxyethyl radical as a function of DMPO concentrations leads to a second-order rate constant of $(4.1 \pm 0.5) \times 10^7$ M^{-1} s^{-1}. The range of errors is about 10%.

(1) Alkyl Radical Trapping. The unsubstituted alkyl radicals form a homologous series of simple carbon-centered π radicals in which steric interactions and electron-releasing tendencies are expected to increase with radical size. As the size of unsubstituted straight chain radicals increases in the order of methyl, ethyl, and propyl, the trapping rate shows little variation (1.4×10^7, 1.6×10^7, and 5.6×10^6 M^{-1} s^{-1}, respectively). The similarity of the reaction rate constants for methyl and ethyl radicals shows that the increased electron-releasing capability of the ethyl radical has canceled the increase in steric hindrance between the parent radical and DMPO spin trap near the parent radical's singly occupied molecular orbital (SOMO) in the encounter complex. Further extension of the alkyl chain in the 1-propyl radical provides only a modest increase in electron-releasing power compared to ethyl radical, as both are primary alkyl radicals, but with a significant increase in steric hindrance at the radical center, since only the straight-chain conformer will mimic the low steric constraints of the ethyl radical. The result is a DMPO trapping rate constant one-third of that of the

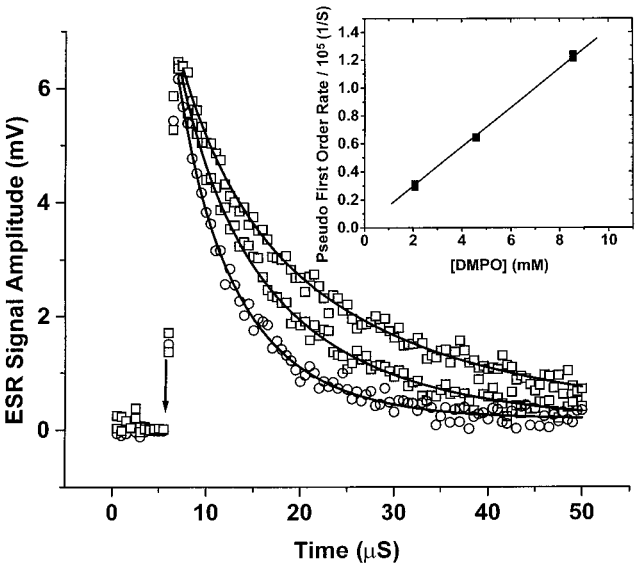

Figure 1. Three TRESR kinetic profiles of methyl radical decay in nitrous oxide saturated aqueous solutions of 0.25 M DMSO and 2.1 (upper curve), 4.5 (middle curve), and 8.6 (lower curve) mM DMPO at neutral pH. The 0.5 μs electron beam pulse occurs at the time indicated by the vertical arrow. The pseudo-first-order rate constants for methyl radical decay are 3.0×10^4, 6.4×10^4, and 1.2×10^5 s^{-1}, respectively. The inset drawing shows the linear least-squares fitting regression for the trapping pseudo-first-order rate constants as a function of DMPO concentration, yielding a bimolecular trapping rate constant of 1.4×10^7 M^{-1} s^{-1}.

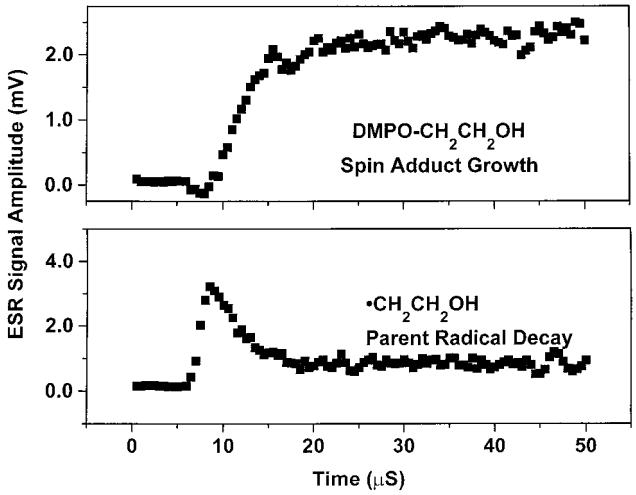

Figure 2. TRESR kinetic profiles of 1-hydroxyethyl radical decay (lower curve) and concomitant growth of its spin adduct (upper curve) for 0.25 M ethanol and 7.5 mM DMPO at neutral pH. Pseudo-first-order rate constants are 3.0×10^5 and 2.3×10^5 s^{-1}, respectively. The difference between these two rate constants is ascribed to the parent radical decay in competition with DMPO spin trapping.

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methyl radical. Thus, DMPO does not exhibit the strong electrophilic character seen with MNP.

Spin trapping of 1-methylethyl (2-propyl) radical by DMPO is influenced by opposing electronic and steric factors. The electron-releasing abilities of this secondary radical are appreciably greater than those of the primary alkyl radicals described above and will tend to increase the trapping rate with an electrophilic spin trap. However, the steric environment around the SOMO of this secondary radical is appreciably more crowded than the primary alkyl radicals. The trapping rate constant of 5.8×10^6 M^{-1} s^{-1} is lower than that of the ethyl radical, indicating that steric effects dominate electronic effects in this case.

There is indirect evidence from in situ radiolysis steady-state ESR spectra that larger alkyl radicals are trapped more slowly with DMPO than methyl radical.[6] In the steady-state radiolysis studies DMPO−H, produced via eq 1 above, serves as a low-yield intensity standard representing ∼10% of the radiolytic free radical yield. The low intensity of DMPO−propyl or DMPO−1-methylethyl spin adducts relative to DMPO−H adducts suggests that larger parent alkyl radicals are lost via recombination or disproportionation processes competing with spin trapping by DMPO. Since second-order termination rate constants are similar for methyl, ethyl, and propyl radicals,[27−29] the steady-state result confirms the direct observation that higher members of the alkyl radical homologous series are trapped slowly by DMPO in aqueous solution.

(2) Hydroxyalkyl and Carboxyalkyl Radical Trapping. The hydroxyalkyl radicals form a series of strongly reducing carbon-centered π radicals. The tendency of the hydroxyalkyl radicals to undergo electron transfer increases in the following order; hydroxymethyl < 1-hydroxyethyl ≅ 1-hydroxypropyl < 1-hydroxy-1-methylethyl (2-hydroxy-2-propyl). The corresponding trapping rate constants with DMPO are 2.2×10^7, 4.1×10^7, 3.0×10^7, and 6.8×10^7 M^{-1} s^{-1}, respectively. It is noteworthy that the rate constants for hydroxymethyl and hydroxyethyl radicals are not significantly larger than those for the unsubstituted methyl and ethyl radicals. Even the strongly reducing 1-hydroxy-1-methylethyl radical reacts with DMPO only three times faster than the hydroxymethyl radical, whereas with MNP the increase is nearly a factor of 50, again showing that DMPO, unlike MNP, does not have a strongly electrophilic nature to induce electron transfer from hydroxyalkyl radicals.

Steric effects on primary hydroxyalkyl radical trapping are revealed by 1-hydroxyethyl and 1-hydroxypropyl, with corresponding trapping rates of 4.1×10^7 and 3.0×10^7 M^{-1} s^{-1}. Using molecular models to compare steric factors in the DMPO−1-hydroxyethyl and DMPO−1-hydroxypropyl radical encounter complex, one finds that the steric constraints of the 1-hydroxyethyl radical should be similar to those of the 1-methylethyl radical, while the additional methylene function in 1-hydroxypropyl imparts sufficient side chain flexibility to permit configurations with greater steric strain than in the 1-hydroxyethyl case. The decrease in the trapping rate in these two radicals possessing similar reducing power shows that steric interactions can modulate the trapping rate of even strongly reducing radicals. Still, sufficient reducing power can overcome unfavorable steric factors in DMPO hydroxyalkyl radical trapping, as demonstrated by the strongly reducing 1-hydroxy-1-methylethyl radical. Figure 3 shows the mixed order decay of the radical as a function of DMPO concentration. In the inset

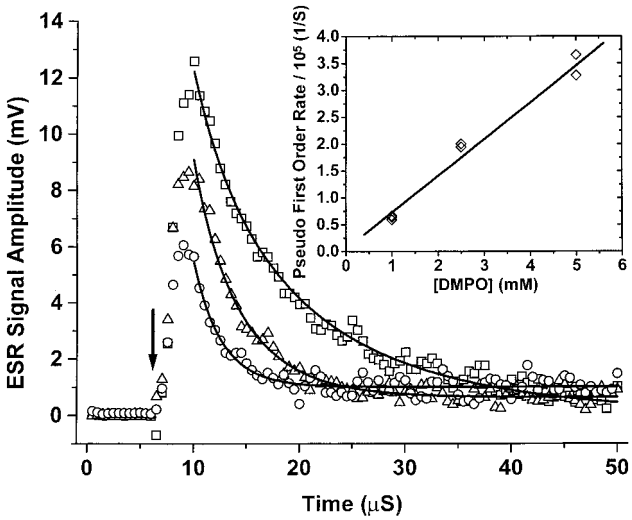

Figure 3. Three TRESR kinetic profiles of 1-hydroxy-l-methylethyl radical decay in nitrous oxide saturated aqueous solutions of 0.1 M 2-propanol and 1 (upper curve), 2.5 (middle curve), and 5 (lower curve) mM DMPO at neutral pH. The 0.5 μs electron beam pulse occurs at the time indicated by the vertical arrow. The pseudo-first-order rate constants for 1-hydroxy-1-methylethyl radical decay are 7.2×10^4, 1.8×10^5, and 3.5×10^5 s^{-1}, respectively. The inset drawing shows the linear least-squares fitting regression for the pseudo-first-order rate constants as a function of DMPO concentration, yielding a bimolecular trapping rate constant of 6.8×10^7 M^{-1} s^{-1}.

of Figure 3, the first-order component is plotted against DMPO concentration; linear least-squares fitting gives a second-order trapping rate constant of 6.8×10^7 M^{-1} s^{-1}, the fastest π radical reaction rate measured in the present study.

The severity of steric interference for the radicals studied here reaches maximum in the trapping of the 2-hydroxy-2-methylpropyl radical that reacts slowly with DMPO. The SOMO of this β-hydroxyalkyl radical is surrounded by the methyl and hydroxyl groups of the radical, encasing the radical's π orbital in a pocket that prevents good overlap between the radical SOMO and the nitrogen−carbon π orbital of the trap. Although the 2-hydroxy-2-methylpropyl radical spin adduct can be observed with additional proton coupling due to the hydroxyl proton hydrogen bonded to the aminoxyl oxygen in the steady-state ESR experiments,[6] only gradual growth of spin adduct was observed by TRESR.

The above results indicate that an electron-withdrawing radical, such as the carboxymethyl radical, would be expected to react more slowly with DMPO than unsubstituted alkyl radicals. This is indeed the case; the DMPO−carboxymethyl reaction proceeds with a rate constant of 4.4×10^6 M^{-1} s^{-1}, 31% of the methyl radical trapping rate, and the slowest rate constant measured in this study. For carboxyalkyl radical trapping, steric interactions also play an important role, since the π system of the carboxyl function is of sufficient size that the approach to the nitrogen−carbon π system of the trap is impeded in any trajectory of radical approach. In the steady-state ESR spectrum of this spin adduct, a small, exchangeable coupling was observed, a common characteristic of DMPO spin adducts with a β-hydroxyl group on the parent radical, indicating a hydrogen bond between the β-hydroxyl group and the aminoxyl oxygen. This interaction profoundly affects the stability of the spin adduct radical,[15] and also the formation kinetics (vide infra).

(3) σ Radical Trapping. Two σ radicals, the sulfite anion radical and the carboxyl anion radical, were studied. Figure 4 shows TRESR traces for the spin adduct growth of carboxyl

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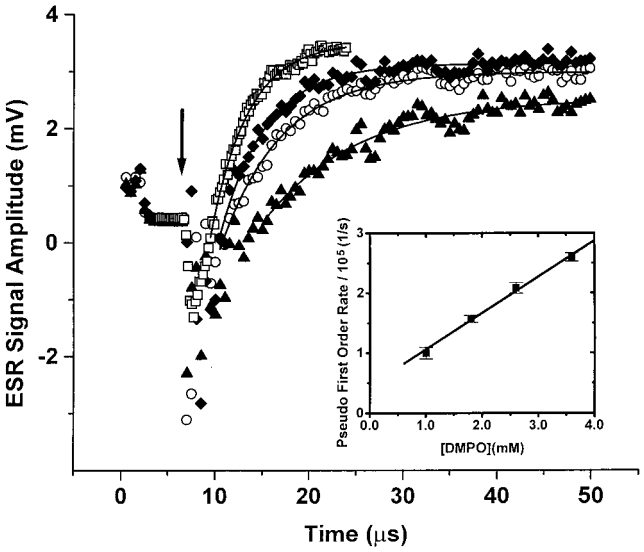


Figure 4. Four TRESR kinetic profiles of spin adduct growth of carboxyl anion radical in nitrous oxide saturated aqueous solutions of 0.2 M sodium formate and 1.0 (▲), 1.8 (○), 2.6 (◆), and 3.6 (□) mM DMPO at pH ~6.4. The pseudo-first-order rate constants for spin adduct radical growth are 1.0×10^5, 1.6×10^5, 2.1×10^5, and 2.6×10^5 s^{-1}, respectively. The inset drawing shows the linear least-squares fitting regression for the trapping pseudo-first-order rate constants as a function of DMPO concentration, yielding a bimolecular trapping rate constant of 6.6×10^7 M^{-1} s^{-1}.

anion radical, with pseudo-first-order rate constants of 1.0×10^5, 1.6×10^5, 2.1×10^5, and 2.6×10^5 s^{-1} for 1.0, 1.8, 2.6, and 3.6 mM DMPO, respectively. The second-order trapping rate constant was obtained by plotting these pseudo-first-order rate constants against the concentration of DMPO as shown in the inset of Figure 4. The strongly reducing carboxyl anion radical is trapped rapidly with a calculated rate constant of 6.6×10^7 M^{-1} s^{-1}, while the oxidizing sulfite anion radical has a lower trapping rate constant of 1.2×10^7 M^{-1} s^{-1}. Here, electronic effects dominate the trapping reaction since steric effects are not significantly different in these two σ radicals.

(4) Comparison between DMPO and MNP Trapping Rate Constants. In situ radiolysis time-resolved ESR studies with the nitroso spin trap MNP have shown that carbon-centered radical trapping is considerably influenced by steric and electronic effects in the MNP−radical encounter complex.[7] Rapid MNP spin trapping is observed with sterically unhindered straight chain alkyl radicals, while bulky branched alkyl radicals such as 2-hydroxy-2-methylpropyl are sufficiently crowded about the radical center that second-order parent radical termination occurs in preference to radical trapping. The electron releasing capability parallels the MNP trapping rate in the order of carboxymethyl < methyl < ethyl < propyl. Steric interactions of the parent radical with MNP are also important, since the reaction of the secondary 1-methylethyl radical is slower than that of the primary 1-propyl species. Strongly reducing hydroxyalkyl radicals such as hydroxymethyl, 1-hydroxyethyl, 1-hydroxypropyl, and 1-hydroxy-1-methylethyl quickly react with MNP despite steric constraints, however, due to favorable electronic interactions between the radical and the polar N═O moiety of MNP.[7,8]

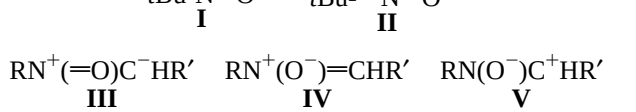
The absolute rate constants for the reaction of DMPO with modest-sized carbon-centered radicals is roughly a factor of 3 smaller that those measured using the MNP spin trap. Consideration of the canonical resonance structures for MNP (structures **I** and **II**) and DMPO (**III**, **IV**, and **V**) shows that the net charge at the site of radical addition to the spin trap is positive for MNP (resonance of structures **I** and **II**, with addend attachment at nitrogen) and weakly negative for DMPO (resonance of structures **III** and **IV**, with addend attachment at C2). Table 2 summarizes the fractional change in spin trapping rate constants for carbon-centered radicals reacting with MNP and DMPO. For MNP, progressing in the sequence methyl, ethyl, and (1-propyl or 2-propyl), the additional electron release provided by the addend radical compensates for the added steric strain in the radical-trap encounter complex; ethyl radical is trapped three times as rapidly as methyl, while 1-propyl and 2-propyl trap as rapidly as ethyl. For DMPO, the electron release is not effective; ethyl is trapped as quickly as methyl, and further substitution impedes spin trapping. These effects are in accord with the differences in trap polarity noted above; MNP is strongly electrophilic, while DMPO is, at most, weakly nucleophilic.

Table 2. Trapping Rate Constant Ratios

trapping rate constant ratio	DMPO[a]	MNP[b]
$k_t(^{\bullet}CH_2CH_3)/k_t(^{\bullet}CH_3)$	1	3
$k_t(^{\bullet}CH_2CH_2CH_3)/k_t(^{\bullet}CH_2CH_3)$	0.4	1
$k_t(^{\bullet}CH(CH_3)_2)/k_t(^{\bullet}CH_2CH_3)$	0.4	1
$k_t(^{\bullet}CH(OH)CH_3)/k_t(^{\bullet}CH_2(OH))$	2	2
$k_t(^{\bullet}CH(OH)CH_2CH_3)/k_t(^{\bullet}CH(OH)CH_3)$	0.8	0.4
$k_t(^{\bullet}C(OH)(CH_3)_2)/k_t(^{\bullet}CH(OH)CH_3)$	2	2

[a] This work. [b] Reference 7.

The spin-addend hydroxyl function of α- and β-hydroxyalkyl spin adduct radicals is known to have a hydrogen-bond interaction with the aminoxyl oxygen of the DMPO spin adduct.[15,30,31] For α-hydroxyalkyl radicals, this interaction is evidenced by a small, exchangeable proton coupling observable in organic solvents; for β-hydroxyalkyl radicals, this coupling is also observed in aqueous solution. In DMPO−hydroxyalkyl spin trapping, this interaction will stabilize structures **IV** and **V**, shifting net positive charge to C2, enhancing the electrophilic character at that site. The kinetic trends for DMPO parallel those of MNP−hydroxyalkyl spin trapping, increasing in the sequence hydroxymethyl < primary hydroxyalkyl < secondary hydroxyalkyl.



Conclusions

The present results show that the rate constants for DMPO spin trapping vary by over an order of magnitude in a series of small carbon-centered radicals. In general, polar effects and steric considerations each only weakly influence spin adduct formation. The reaction rates of alkyl and hydroxyalkyl radicals with DMPO are quite similar whether electron-withdrawing or electron-releasing substituents are present. The measured trapping rate constants with DMPO are, in general, slower than the corresponding rates with a nitroso spin trap, MNP. That is attributed to the weakly nucleophilic character of DMPO, the strongly electrophilic character of MNP, and unfavorable steric factors in the DMPO−radical encounter complex.

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