

# An in Situ Radiolysis Time-Resolved Electron Spin Resonance Study of 2-Methyl-2-nitrosopropane Spin Trapping Kinetics<sup>1</sup>

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**Abstract:** Results are presented for an in situ radiolysis ESR study of simple  $\pi$  and  $\sigma$  radical spin trapping by 2-methyl-2-nitrosopropane (MNP) in dilute aqueous solution. The parent radicals investigated include alkyl radicals (methyl, ethyl, 1-propyl, and 2-propyl), hydroxyalkyl radicals (hydroxymethyl, 1-hydroxyethyl, 1-hydroxypropyl, 2-hydroxy-2-propyl, and 1,2-dihydroxyethyl), nonreducing substituted alkyl radicals (carboxymethyl, 2-hydroxy-2-methyl-1-propyl, and 2-oxo-1-propyl),  $\sigma$  radicals (sulfite, carboxyl, and *p*-carboxyphenyl), and the radicals produced by radiolysis of water (hydroxyl radical, hydrated electron, and hydrogen atom). The *g* factors and hyperfine coupling constants from steady-state ESR experiments, measured under nearly identical solvent conditions, reveal substituent effects in the spin adducts that have been masked by differential solvent effects in previous studies. The aminoxyl nitrogen couplings and *g* factors of the hydroxyalkyl-MNP spin adducts are sensitive to changes in parent radical structure at the  $\beta$  carbon site. The rate constants for MNP spin trapping were measured by time-resolved ESR using pulse radiolysis for parent radical production. The trapping kinetics of the various parent radicals could easily be compared, as a common solvent was used for all experiments in this study. The rate constants varied from less than  $1 \times 10^6$  to  $6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Steric effects are important in controlling trapping rates, but the greatest differences are observed between reducing and nonreducing radicals. This behavior is attributed to the electrophilic nature of the MNP trap.

## Introduction

Spin trapping<sup>2-5</sup> has proved to be a valuable tool for extending the use of electron spin resonance (ESR) spectroscopy to free radical systems where direct ESR observation of the parent radical is difficult as a result of short radical lifetimes, unfavorable magnetic relaxation rates, or complex hyperfine structure.<sup>6,7</sup> Quantitative use of spin trapping, however, requires detailed knowledge of both parent radical trapping and spin adduct decay rates so that the parent radical concentration can be related to the steady-state concentration of the spin adduct radical. To our knowledge, few direct ESR studies of the kinetics of spin trapping by 2-methyl-2-nitrosopropane (MNP) have been made; most of those have been measurements of trapping in organic solvents.<sup>8-24</sup>

In a previous report,<sup>25</sup> the rate constants for trapping some simple  $\pi$  and  $\sigma$  radicals with nitromethane aci anion (NMA) were measured in aqueous solution by using time-resolved ESR (TRESR) to monitor the decay of the parent radical and the production of the nitro anion radical spin adduct. TRESR offers a high-sensitivity monitor of instantaneous radical concentration, with sufficient selectivity to discriminate between the different radicals produced in a multiradical system. Also, since it is possible to directly observe actual decay and growth of the parent and spin adduct radicals, the correctness of the trapping kinetic model can be easily confirmed. In the previous study, a 30-fold variation in trapping rate was found between similar radicals, due to the nucleophilicity of NMA. Direct reduction of the spin trap was also observed under certain pH conditions, yielding a net hydrogen atom-NMA adduct instead of the expected alcohol radical-NMA adduct. The unexpectedly large variation in trapping rate, and the possibility of multiple adduct formation for the same parent radical, showed that studies of this type might be useful for other more popular spin traps, such as the nitroso and nitron traps, which lead to aminoxyl spin adduct radicals. In this study, we report kinetic studies of spin trapping by MNP using a representative sample of small  $\sigma$  and  $\pi$  radicals.

## Experimental Section

Solutions were prepared in reagent grade water from a Millipore Milli-Q water system, or in a few cases, with triply distilled water in experiments where the parent radical was produced by reaction with the solvated electron. Solutions were 0.25-15 mM in MNP. MNP was obtained as the dimer (Aldrich or Sigma) and was used without further purification. All MNP concentrations are reported on a monomer basis, which assumes complete dissociation of the dimer in solution. The structure of MNP (I) and its dimer (II) are given below:

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document NDRL-3327 from the Notre Dame Radiation Laboratory.

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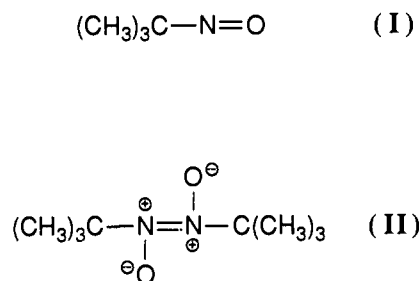
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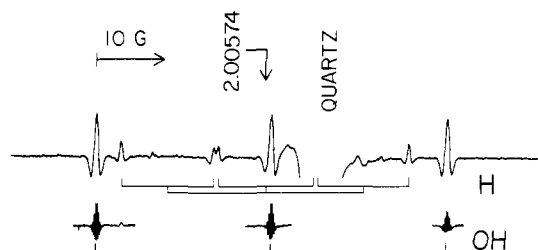


Solutions were prepared by two methods, depending on the solubility of the MNP dimer in the parent material. If the MNP dimer was soluble in the parent material, the parent compound was deoxygenated with nitrogen (Mittler, ultrahigh purity), the MNP dimer dissolved into it, and the mixture added to deoxygenated water. If the MNP dimer was insoluble in the parent material, 0.22 g of MNP dimer was quickly dissolved in 100 mL of nitrogen-purged water at 40 °C, with rapid stirring. A suitable amount of this solution was then added to the deoxygenated parent material/water solution to obtain the desired spin trap concentration. It has been shown that this method of preparation leads to minimal degradation of the spin trap.<sup>26</sup> Experiments using 2-propanol as the parent compound exhibited the same kinetic behavior for either method of preparation. Kinetic measurements were always performed on freshly prepared solutions. Unless otherwise noted, unbuffered solutions near neutral pH were used for kinetic experiments, while solutions buffered with 10 mM sodium borate (pH 9.2) were used for steady-state studies.

Most parent radicals were made by reaction of the parent compound with radiolytically produced hydroxyl radicals in N<sub>2</sub>O-purged solutions. Hydroxyl radicals were made by hydrogen abstraction from the following substrates: methanol (0.25 M, Aldrich or Fisher spectroanalyzed), ethanol (0.25 M, Midwest Grain Co. of Illinois), *n*-propanol (0.25 M, Fisher), 2-propanol (0.25 M, Fisher), and ethylene glycol (0.25 M, Fisher). Substituted alkyl radicals were produced from *tert*-butyl alcohol (0.25 M, Fisher), sodium acetate (0.1 M, Baker), and acetone (2 M, Fisher). Sodium formate (0.1 M, Fisher) and sodium sulfite (20 mM, Fisher) were oxidized by hydroxyl radical to give the carboxyl and sulfite radical anions. *p*-Carboxyphenyl radicals were prepared by reaction of hydrated electrons with *p*-bromobenzoic acid (8 mM, Aldrich) in nitrogen-purged solution. Nitrogen-purged solutions of 250 mM potassium phosphate (Aldrich) equimolar in monobasic and dibasic forms reacted with hydrated electrons to give hydrogen atoms in high yield.<sup>27</sup>

Unsubstituted alkyl radicals were derived from reaction of radiolytically produced hydroxyl radical with the appropriate dialkyl sulfoxide.<sup>28–31</sup> Dimethyl sulfoxide was obtained from Burdick and James. Diethyl sulfoxide, di-*n*-propyl sulfoxide, and diisopropyl sulfoxide were prepared from the corresponding dialkyl sulfides (Aldrich) by hydrogen peroxide (Fisher, 30%) oxidation at ice-bath temperatures.<sup>32</sup> Following removal of water at reduced pressure, and drying with magnesium sulfate (Fisher), the resulting sulfoxides were purified by vacuum distillation. Solutions were 1.0, 0.5, 0.25, and 0.1 M in the sulfoxide for dimethyl, diethyl, di-*n*-propyl, and diisopropyl sulfoxide, respectively.

In situ radiolysis ESR spectra were recorded by irradiating flowing cooled aqueous solutions of the parent compound with a 2.8-MeV electron beam from a Van de Graaff accelerator.<sup>33,34</sup> A 2.5- $\mu$ A dc beam was used to produce a steady-state concentration of radicals for field modulation ESR spectra. A pulsed 40-mA beam of 0.5- $\mu$ s duration and 90-Hz repetition rate was used for kinetic measurements. The initial radical concentration for kinetic experiments is approximately 40  $\mu$ M as determined from the period of the bimolecular self-reaction of sulfite radical anion. In the experiments involving unsubstituted alkyl radical trapping, the initial radical concentration was set 10-fold lower, to allow spin trapping to be competitive with radical-radical termination. The solution flow rate was sufficiently fast to ensure the volume of the ESR



**Figure 1.** Second-derivative X-band steady-state ESR spectra of the MNP spin adducts formed by trapping hydroxyl radicals, hydrogen atoms, and hydrated electrons in electron-irradiated nitrogen-saturated 10 mM borate buffer (pH 9.2). The magnetic field increases from left to right. The solution temperature was  $\sim 19$  °C. Stick spectra below the experimental spectra show the lines of each main radical species. At the top are shown the lines of the hydrogen atom-MNP adduct (a triplet of doublets) and the hydroxyl radical-MNP adduct (a triplet) recorded under modulation conditions optimizing the presentation of the former adduct. Below, the lines of the hydroxyl radical adduct are presented under low modulation amplitude conditions, revealing the decet line structure due to *tert*-butyl proton hyperfine coupling.

flat cell was replenished completely between electron beam pulses. Previous kinetic studies had shown that a standard configuration ESR flat cell could not be flushed completely in the period between electron pulses, even at extremely high flow rates, as a result of flow stagnation near the edges of the flat cell. To assure complete flushing, a Suprasil flat cell was constructed with a plate width of 8 mm, matching the 8-mm diameter of the quartz inlet and outlet tubing through a tapered transition region. The interplate spacing was 0.4 mm, with the inner surface of the plates sandblasted to assure efficient washing of the flat cell interior as new solution flowed into the cell. This cell was used for most studies. A rapid mix flat cell of similar configuration was used for sulfite radical trapping studies to combine solutions of sodium sulfite and MNP several milliseconds before irradiation, since MNP and sodium sulfite can undergo thermal reactions leading to decomposition of MNP monomer. The solution temperature was within the range 15–19 °C.

X-band (9.2 GHz) ESR spectra of steady-state radical populations were recorded in second-derivative presentation by using magnetic field modulation at 100 kHz and 200 Hz to determine the line positions for the parent and spin adduct radicals. Magnetic field measurements were made by using NMR method,<sup>33,35</sup> with *g* factors measured with respect to that of the sulfite radical anion, recently redetermined as  $g = 2.00316$ .<sup>36</sup> The line positions were analyzed to derive *g* factors and hyperfine couplings for parent and spin adduct radicals. Literature values for ESR parameters of previously studied MNP spin adducts are summarized in ref 37 and 38 and generally agreed well with our measurements.

Time-resolved ESR kinetic traces were recorded at line positions that did not overlap ESR absorptions from other species. The concentrations of the spin trap and parent radical substrate were adjusted to yield pseudo-first-order trapping kinetics. The line width of the aminoxyl adduct radical lines in this study represented submicrosecond magnetic relaxation times, so the growth and decay of the ESR kinetic traces accurately reflect the chemical kinetics of the radical.<sup>25</sup> These traces were fitted to exponential growths and decays by using the Levenberg-Marquardt nonlinear least-squares fitting procedure of Bevington.<sup>39</sup> Second-order trapping rate constants were derived by a least-squares linear fit of the observed pseudo-first-order rate constants as a function of MNP monomer concentration. In most cases, the ESR kinetic traces for both parent radical decay and spin adduct growth could be observed and were found to exhibit the same kinetic behavior. The complete kinetic analysis was performed upon the ESR traces from spin adduct growth; where this could not be accomplished due to weak adduct ESR absorptions (in the case of the ethyl and propyl radicals), the kinetic

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**Table I.** ESR Parameters of MNP Spin Adducts:<sup>a</sup> Water Radicals, Alkyl Radicals, and Substituted Alkyl Radicals

parent radical	<i>g</i> factor	<i>a</i> (N,NO), <sup>b</sup> G	<i>a</i> (H,R), <sup>c</sup> G	group
H, (e <sub>aq</sub> <sup>-</sup> + H <sup>+</sup> )	2.005 74	14.66	13.94	H
OH	2.005 14	26.43 <sup>d</sup>	0.23	<i>t</i> -Bu
CH <sub>3</sub>	2.005 56	17.40	14.34	CH <sub>3</sub>
CH <sub>2</sub> CH <sub>3</sub>	2.005 54	17.04	11.25	CH <sub>2</sub>
			0.42	CH <sub>3</sub>
CH(CH <sub>3</sub> ) <sub>2</sub>	2.005 64	16.90	1.73	CH
			0.31	CH <sub>3</sub>
CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	2.005 56	16.94	11.14	CH <sub>2</sub>
			0.68	CH <sub>2</sub>
			u.r. <sup>e</sup>	CH <sub>3</sub>
CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	2.005 63	16.15	8.41	CH <sub>2</sub>
CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OH	2.005 72	16.53	11.07	CH <sub>2</sub>
			u.r.	OH
			u.r.	CH <sub>3</sub>
CH <sub>2</sub> C(O)CH <sub>3</sub>	2.005 66	15.72	8.60	CH <sub>2</sub>
			u.r.	CH <sub>3</sub>

<sup>a</sup>All parameters are measured from steady-state ESR spectra. *g* factors are  $\pm 0.000 02$ , hyperfine couplings are  $\pm 0.01$  G. <sup>b</sup>Coupling to nitrogen of aminoxyl function. <sup>c</sup>Coupling to protons of R group. <sup>d</sup>Coupling to nitrogen of nitro group. Parameters for this spin adduct corrected for second-order shifts. <sup>e</sup>Unresolved.

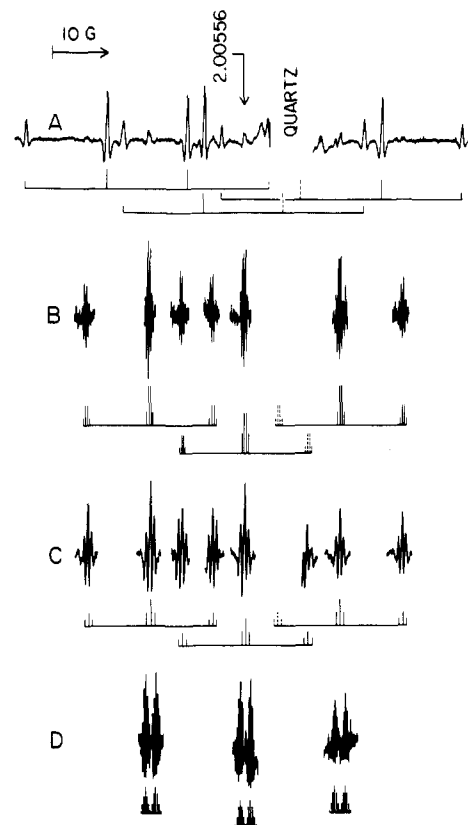
analysis was performed on the decay of the parent radical.

The ESR spectrometer and associated data acquisition system used in both steady-state and time-resolved experiments were as previously described.<sup>25,35</sup> Spectrophotometric pulse radiolysis studies were carried out at the Notre Dame Radiation Laboratory ARCO LP-7 linear accelerator by using 10-ns pulses of 8-MeV electrons to produce initial hydrated electron concentrations of  $\sim 2 \mu\text{M}$ . Transient absorption spectra and kinetic curves were recorded by the computer-controlled pulse radiolysis apparatus described previously.<sup>40,41</sup>

## Results and Discussion

**1. Steady-State ESR Studies. 1.1. Steady-State ESR of Water Transient Spin Adducts.** To develop appropriate experimental conditions for subsequent experiments, the MNP spin adducts from water transients in a borate-buffered (pH 9.2), nitrogen-saturated, aqueous MNP solution (Figure 1) were studied. Water radiolysis produces hydroxyl radicals, hydrated electrons, and hydrogen atoms.<sup>42</sup> Two major spin adducts are present in the experimental spectrum. Their ESR parameters are listed in Table I. The first adduct shows only a nitrogen triplet at low resolution,  $a(\text{N}) = 26.93$  G, with a *g* factor of 2.005 14. Under high-resolution conditions, each line of the nitrogen triplet resolves into a dectet due to nine equivalent protons, with  $a(\text{H}) = 0.23$  G. The low *g* factor and large nitrogen hyperfine coupling of this spin adduct identify it as a nitro radical anion, formed by MNP trapping of the hydroxyl radical at the nitrogen of the nitroso group and subsequent deprotonation of the added hydroxyl moiety. The spectral parameters observed are consistent with those of other aliphatic nitro anions observed in aqueous alcoholic solution<sup>43</sup> and aqueous solution.<sup>44</sup> The low intensity of this adduct radical is due to the second-order termination reaction of nitro anion radicals, which have half-lives of approximately 30 ms.<sup>44</sup> Previous reports of the MNP-hydroxyl radical adduct are unconvincing, since the spectra contained either an extra proton coupling<sup>45,46</sup> or a small nitrogen hyperfine coupling.<sup>46</sup> We therefore propose this species as the authentic hydroxyl radical-MNP spin adduct.

The second radical exhibits hyperfine couplings to nitrogen with  $a(\text{N}) = 14.67$  G and a single proton with  $a(\text{H}) = 13.94$  G. The *g* factor of 2.005 74 is characteristic of an aminoxyl radical. These



**Figure 2.** Second-derivative X-band steady-state ESR spectra of the MNP spin adducts formed by the reaction of hydroxyl radicals with symmetric dialkyl sulfoxides in electron-irradiated nitrous oxide saturated aqueous solution. The sulfoxides used in spectra A–D were dimethyl sulfoxide, diethyl sulfoxide, di-*n*-propyl sulfoxide, and diisopropyl sulfoxide, respectively. The magnetic field increases from left to right. The solution temperature was  $\sim 19^\circ\text{C}$ . Stick spectra below the experimental spectra show the lines of each main radical species. The spectra are assigned as (a) methyl radical-MNP adduct, (b) ethyl radical-MNP adduct, (c) 1-propyl radical-MNP adduct, and (d) 2-propyl radical-MNP adduct.

ESR parameters match those of the MNP-hydrogen atom adduct reported previously.<sup>47</sup> Upon addition of the electron scavenger nitrous oxide to the solution, the intensity of this ESR signal decreases appreciably. This shows that a net MNP-hydrogen atom adduct results from reduction of MNP by hydrated electrons, followed by protonation. The remaining portion of the MNP-hydrogen atom adduct arises from the intrinsic hydrogen atom yield in water radiolysis, roughly 10% of the total radical yield.<sup>42</sup>

**1.2. Steady-State ESR of Alkyl and Substituted Primary Alkyl Radicals.** Radiolytically produced hydroxyl radicals react with the symmetric dialkyl sulfoxides at near-diffusion-controlled rates, producing sulfenic acid radicals that quickly dissociate to produce alkyl radicals.<sup>28–30</sup> Lagercrantz and Forshult used this chemistry to produce the alkyl radical adducts to the related spin trap 2-methyl-2-nitrosopropan-1-one.<sup>31</sup> We have used this chemistry to generate the MNP spin adducts from the methyl, ethyl, 1-propyl, and 2-propyl radicals. Our ESR spectra are shown in Figure 2, and the ESR parameters are in Table I. The methyl-MNP spin adduct ESR parameters are in good agreement with earlier studies of Chamulitrat et al.<sup>48</sup> and Rustgi et al.<sup>49</sup> These studies found  $a(\text{N,NO}) = 17.30\text{--}17.35$  G and  $a(\text{H,CH}_3) = 14.20\text{--}14.40$  G. Chamulitrat et al.<sup>48</sup> reported the ethyl-MNP spin adduct parameters as  $a(\text{N,NO}) = 17.05$  G,  $a(\text{H,CH}_2) = 11.25$  G, and  $a(\text{H,CH}_3) = 0.45$  G, which agree well with our work. The

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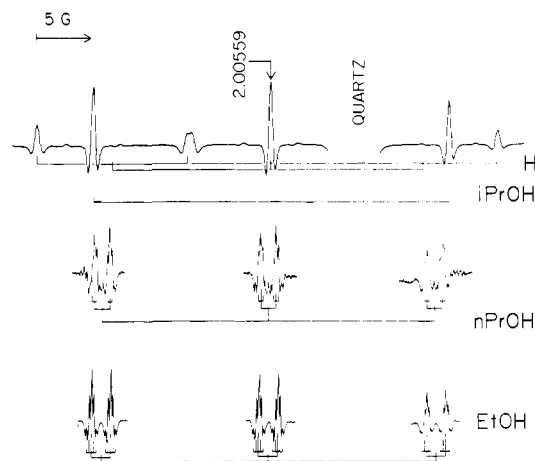
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**Figure 3.** Second-derivative X-band steady-state ESR spectra of the MNP spin adducts formed by the reaction of radiolytically produced hydroxyl radicals with 2-propanol, *n*-propanol, and ethanol, respectively, in electron-irradiated 10 mM borate buffer (pH 9.2). The spectra are assigned (from top to bottom): 2-hydroxy-2-propyl-MNP adduct, 1-hydroxypropyl-MNP adduct, and 1-hydroxyethyl-MNP adduct.

2-propyl spin adduct parameters of Perkins,<sup>50</sup>  $a(\text{N,NO}) = 16.80$  G and  $a(\text{H,CH}) = 1.80$  G, are in accord with ours, although the small methyl proton coupling,  $a(\text{H,CH}_3) = 0.31$  G, was not observed in the early study. The observed 1-propyl adduct parameters are similar in magnitude to those reported by Rosenthal et al.,<sup>51</sup> who found  $a(\text{N,NO}) = 15.78$  G,  $a(\text{H,CH}_2 \alpha) = 10.39$  G, and  $a(\text{H,CH}_2 \beta) = 0.53$  G. The lack of precise agreement is probably due to the mixed solvent (water/DMSO, 2:3) used in their work. Couplings to the protons of the terminal methyl group were unresolved in both studies.

Substituted alkyl radicals were produced by hydroxyl radical attack on sodium acetate, *tert*-butyl alcohol, and acetone. Hydrogen abstraction results in a substituted primary alkyl radical in all cases. The carboxymethyl radical,  $\text{CH}_2\text{CO}_2^-$ , gives an MNP adduct with ESR parameters essentially as those previously reported<sup>52</sup> by Lagercrantz and Forshult,  $a(\text{N,NO}) = 16.10$  G and  $a(\text{H,CH}_2) = 8.42$  G. Minegishi et al.<sup>53</sup> studied the radical adduct from perdeuterated 2-hydroxy-2-methyl-1-propyl radical,  $\text{CD}_2\text{C}(\text{CD}_3)_2\text{OD}$ , finding ESR parameters of  $a(\text{N,NO}) = 16.30$  G and  $a(\text{D,CD}_2) = 1.66$  G at 25 °C. We found very similar couplings, taking into account the difference in gyromagnetic ratio between the deuteron and proton. Proton couplings to the distant methyl groups were unresolved. Our coupling constants from the 2-oxo-1-propyl adduct radical agree with those measured by Leastic and co-workers,<sup>54</sup> who found a spin adduct with  $a(\text{N,NO}) = 15.40$  G and  $a(\text{H,CH}_2) = 8.50$  G, with couplings to the terminal methyl group unresolved.

**1.3. Steady-State ESR Studies of Hydroxyalkyl Radicals.** The abstraction of a methylenic proton at an alcohol  $\alpha$  carbon atom by radiolytically produced hydroxyl radicals efficiently produces hydroxyalkyl radicals. We list the ESR parameters for the MNP spin adducts of these radicals in Table II. The ESR spectra are presented in Figure 3. The major hyperfine couplings for the hydroxymethyl adduct agree well with the values  $a(\text{N,NO}) = 15.50$  G and  $a(\text{H,CH}_2) = 6.10$  G, as previously reported.<sup>55</sup> In this study, we also observed the hydroxyl coupling,  $a(\text{H,OH}) = 0.27$  G, and determined the  $g$  factor as 2.00574. Previous reports

**Table II.** ESR Parameters of MNP Spin Adducts:<sup>a</sup> Hydroxyalkyl Radicals and  $\sigma$  Radicals

parent radical	$g$ factor	$a(\text{N,NO})$ , <sup>b</sup> G	$a(\text{H,R})$ , <sup>c</sup> G	group
$\text{CH}_2\text{OH}$	2.005 74	15.51	6.20 0.27	$\text{CH}_2$ OH
$\text{CH}(\text{OH})\text{CH}_3$	2.005 75	15.74	1.79 0.23 0.23	CH OH $\text{CH}_3$
$\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$	2.005 79	15.60	1.43 u.r. <sup>d</sup> 0.21	CH OH $\text{CH}_2$
$\text{C}(\text{OH})(\text{CH}_3)_2$	2.005 59	16.70	u.r. u.r.	OH OH
$\text{CH}(\text{OH})\text{CH}_2\text{OH}$	2.005 89	15.17	1.49 0.22 0.27	CH OH $\alpha$ $\text{CH}_2$
$\text{CO}_2^-$	2.005 97	12.08	0.14	<i>t</i> -Bu
$\text{SO}_3^-$	2.005 59	14.68		
$\text{C}_6\text{H}_4\text{CO}_2^-$ (para)	2.005 59	14.29	1.93 0.99	H ortho H meta

<sup>a</sup> All parameters are measured from steady-state ESR spectra.  $g$  factors are  $\pm 0.00002$ , hyperfine couplings are  $\pm 0.01$  G. Solutions contained 10 mM borate (pH 9.2). <sup>b</sup> Coupling to nitrogen of aminoxyl function. <sup>c</sup> Coupling to protons of R group. <sup>d</sup> Unresolved.

of hydroxyethyl spin adduct radicals give couplings  $a(\text{N,NO}) = 15.60$ – $15.75$  G and  $a(\text{H,CH}) = 1.80$ – $1.85$  G<sup>48,56</sup> and are essentially in agreement with our findings. We also measured the hydroxyl and methyl proton couplings in this adduct,  $a(\text{H,OH}) = a(\text{H,CH}_3) = 0.23$  G with a  $g$  factor of 2.005 75. To our knowledge, the MNP spin adducts from the 1,2-dihydroxyethyl, 1-hydroxypropyl, and 2-hydroxy-2-propyl radicals have not been reported in aqueous solution. The 1,2-dihydroxyethyl radical-MNP adduct has a  $g$  factor of 2.005 89 and resolved hyperfine couplings of  $a(\text{N,NO}) = 15.17$  G,  $a(\text{H,CH}) = 1.49$  G,  $a(\text{H,OH } \alpha) = 0.22$  G, and  $a(\text{H,CH}_2) = 0.27$  G. We found the 1-hydroxypropyl-MNP spin adduct to have resolved hyperfine couplings to the  $\alpha$  and  $\beta$  methylene protons of the parent radical,  $a(\text{H,CH}) = 1.43$  G and  $a(\text{H,CH}_2) = 0.21$  G, with  $a(\text{N,NO}) = 15.60$  G and  $g = 2.005 79$ . The 2-hydroxy-2-propyl-MNP adduct has  $a(\text{N,NO}) = 16.70$  G and  $g = 2.005 59$ , with all other proton hyperfine couplings unresolved.

The top spectrum of Figure 3 shows the ESR spectrum of the 2-hydroxy-2-propyl-MNP adduct, recorded in 10 mM borate buffer (pH 9.2). Noteworthy in this spectrum is an intense hydrogen atom-MNP spin adduct. The intensity of the hydrogen atom adduct is roughly equal to that of the 2-hydroxy-2-propyl radical adduct. However, the reaction half-life of radiolytically produced hydrogen atoms in 0.25 M 2-propanol is  $\sim 10$  ns, so that the intense hydrogen atom adduct signal cannot be due to direct hydrogen atom addition to MNP. We propose that, in basic solution, 2-hydroxy-2-propyl radical first reduces MNP by electron transfer and then reacts to give either the hydrogen atom adduct or alcohol radical adduct. At neutral pH, however, no H atom adduct is seen; the 2-hydroxy-2-propyl-MNP adduct is the sole product in the ESR spectrum. The kinetic studies of hydroxyalkyl radical trapping by MNP in this report were all conducted at near neutral pH; trapping studies in basic and acidic media will be considered in a subsequent report.

**1.4. Comparison of Alkyl and Hydroxyalkyl Spin Adduct ESR Parameters.** 1-Hydroxyalkyl radical-MNP spin adducts have smaller nitrogen splittings and larger  $g$  factors than the analogous alkyl radical spin adducts due to the electron-withdrawing hydroxyalkyl moiety attached to the aminoxyl nitrogen. This effect can be explained by considering the relative contributions of the two canonical forms of the aminoxyl radical:

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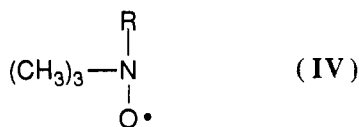
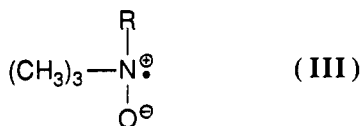
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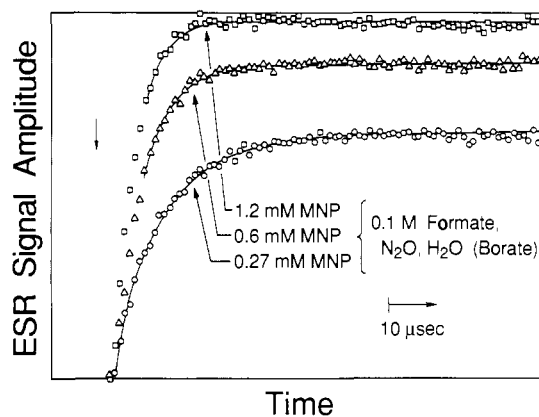
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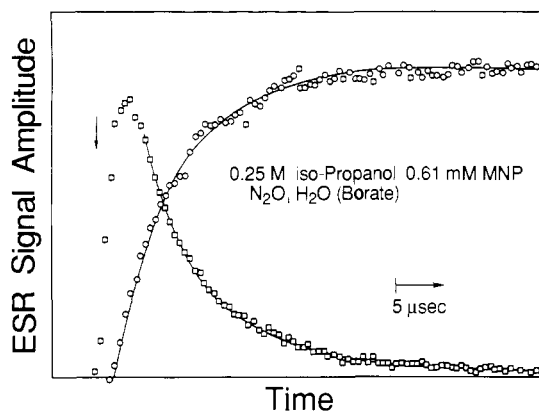


The presence of a strongly electron withdrawing group such as a hydroxyalkyl function strengthens the partial positive charge on the aminoxyl nitrogen, destabilizing the ionic canonical form (III) relative to the neutral form (IV). This produces a net shift in spin population from the aminoxyl nitrogen atom to the aminoxyl oxygen, yielding an increase in  $g$  factor and a decrease in the nitrogen hyperfine coupling. The effects of electron withdrawal are essentially the same for all primary hydroxyalkyl radicals studied, as the  $g$  factor and nitrogen hyperfine values vary little in the series hydroxymethyl, hydroxyethyl, and 1-hydroxypropyl. Electron-releasing alkyl functions, which as a class stabilize the ionic canonical structure, show opposite behavior, resulting in an increased aminoxyl nitrogen hyperfine interaction and diminished  $g$  factor. Further substitution at the radical center can enhance or diminish this effect. The 2-hydroxypropyl-MNP adduct has ESR parameters more similar to the alkyl adducts than the hydroxyalkyl adducts. Here the electron-releasing abilities of the two methyl groups must dominate the electron-withdrawing power of the hydroxyl function at the  $\alpha$  carbon of the spin adduct (which was the radical center in the parent radical). The opposite effect is manifest in the ethylene glycol-MNP adduct, where a second hydroxyalkyl group adjoins the parent radical center. The electron withdrawal by the hydroxyalkyl substituent intensifies the positive charge at the  $\alpha$  carbon of the spin adduct, destabilizing the ionic aminoxyl form. This raises the  $g$  factor and lowers the aminoxyl nitrogen coupling to a greater extent than in the unsubstituted hydroxyalkyl spin adducts.

**1.5. Steady-State ESR Studies of  $\sigma$  Radicals.** The spin trapping of  $\sigma$  radicals should be facile, due to their high reactivity. In this study, we have examined the MNP spin adducts of the sulfite radical, the  $p$ -carboxyphenyl radical, and the carboxyl radical. The ESR parameters are listed in Table II. The nitrogen hyperfine coupling of the sulfite radical-MNP adduct,  $a(\text{N},\text{NO}) = 14.68$  G, is in excellent agreement with those of Stolze et al.,<sup>56</sup> the  $g$  factor we report in this study is 2.00559. Rustgi and Riesz<sup>57</sup> characterized the carboxyl radical-MNP adduct by using specific carbon-13 labeling as proof of their assignment; our observed nitrogen hyperfine coupling of 12.08 G agrees closely with their value of 12.0 G. In addition, it was possible to resolve proton hyperfine couplings to the *tert*-butyl group of the MNP, with a magnitude of 0.14 G. We report the  $g$  factor of this species as 2.00597; this high value serves as a further signature of this radical adduct. Chignell et al.<sup>58</sup> studied the  $p$ -carboxyphenyl radical adduct to MNP, finding a nitrogen coupling of 13.65 G, with phenyl ring proton couplings of 1.95 and 0.97 G to the ortho and meta protons, respectively. Our measurement yields  $a(\text{N},\text{NO}) = 14.29$  G, with the proton couplings in agreement to within 0.02 G. The observed  $g$  factor was normal at 2.00559. The deviation in nitrogen coupling magnitude is likely due to differential media effects in the two solutions. Although we could produce this adduct in the steady-state experiment, the  $p$ -carboxyphenyl radical proved impossible to study in kinetic experiments due to the strong tendency of the parent molecule to trap phenyl radicals. The rate for self-trapping is  $7.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>59</sup>



**Figure 4.** TRESR kinetic profile of carboxyl radical-MNP spin adduct growth in a nitrous oxide saturated aqueous solution of 0.1 M sodium formate and 10 mM sodium borate (pH 9.2), containing 0.27 (○), 0.6 (△), and 1.2 (□) mM MNP. The 0.5- $\mu\text{s}$  electron pulse occurs at the time indicated by the vertical arrow.



**Figure 5.** TRESR kinetic profile of 2-hydroxy-2-propyl radical decay and concomitant MNP spin adduct growth in a nitrous oxide saturated aqueous solution of 0.25 M  $\alpha$ -propanol, 0.61 mM MNP, and 10 mM sodium borate (pH 9.2). The 0.5- $\mu\text{s}$  electron beam pulse occurs at the time indicated by the vertical arrow. The pseudo-first-order rate constant for spin adduct growth is  $1.6 \times 10^5 \text{ s}^{-1}$ ; that for 2-hydroxy-2-propyl radical decay is  $1.4 \times 10^5 \text{ s}^{-1}$ .

**Table III.** Trapping Rate Constants of Alkyl, Hydroxyalkyl,  $\sigma$ , and Water Radiolysis Radicals with MNP<sup>a</sup>

parent radical	radical structure	trapping rate constants, $\text{M}^{-1} \text{ s}^{-1}$
methyl	$\text{CH}_3$	$1.7 \times 10^7$
ethyl	$\text{CH}_2\text{CH}_3$	$5.3 \times 10^7$
carboxymethyl <sup>b</sup>	$\text{CH}_2\text{CO}_2^-$	$7.0 \times 10^6$
1-propyl	$\text{CH}_2\text{CH}_2\text{CH}_3$	$6.9 \times 10^7$
2-propyl	$\text{CH}(\text{CH}_3)_2$	$4.6 \times 10^7$
2-methyl-2-hydroxy-1-propyl	$\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$	$<1 \times 10^6$
2-oxo-1-propyl	$\text{CH}_2\text{C}(\text{O})\text{CH}_3$	$3.7 \times 10^7$
hydroxymethyl	$\text{CH}_2\text{OH}$	$1.4 \times 10^8$
hydroxyethyl	$\text{CH}(\text{OH})\text{CH}_3$	$3.2 \times 10^8$
hydroxypropyl	$\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$	$1.3 \times 10^8$
2-hydroxy-2-propyl	$\text{C}(\text{OH})(\text{CH}_3)_2$	$6.9 \times 10^8$
1,2-dihydroxyethyl	$\text{CH}(\text{OH})\text{CH}_2\text{OH}$	$3.4 \times 10^7$
sulfite anion	$\text{SO}_3^-$	$4.3 \times 10^7$
carboxyl anion <sup>b</sup>	$\text{CO}_2^-$	$1.7 \times 10^9$
hydrated electron <sup>b</sup>	$e_{\text{aq}}^-$	$6.2 \times 10^9$
hydrogen atom <sup>c</sup>	$\text{H}$	$9.1 \times 10^8$
hydroxyl radical <sup>b</sup>	$\text{OH}$	$2.5 \times 10^9$

<sup>a</sup> In neutral aqueous solution at  $\sim 18^\circ\text{C}$ . Trapping rates  $\pm 20\%$ . <sup>b</sup> In 10 mM borate buffer (pH 9.2). <sup>c</sup> In 250 mM phosphate buffer (pH 7).

**2. Kinetic Studies.** TRESR studies were performed on alkyl, substituted alkyl, hydroxyalkyl,  $\sigma$ , and water transient radicals. Figures 4 and 5 show typical TRESR curves for carboxyl and

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2-hydroxy-2-propyl radical trapping by MNP. TRESR traces for the MNP-carboxyl radical adduct are shown in Figure 4 in the presence of 0.27, 0.6, and 1.2 mM MNP at pH 9.2, with the observed rate of reaction increasing with MNP concentration. Figure 5 shows TRESR traces for the decay of 2-hydroxy-2-propyl radical, with concomitant growth of its spin adduct in the presence of 0.61 mM MNP at pH 9.2.

**2.1. Kinetic Studies of Water Transient Trapping.** To assist the design of subsequent kinetic experiments, it was necessary to measure the reaction rate of hydrated electrons, hydroxyl radicals, and hydrogen atoms with MNP. The MNP trapping rate constants for all radicals studied are listed in Table III. To study the reaction of hydrated electrons with MNP, we monitored the disappearance of hydrated electrons by using optical pulse radiolysis. This was preferable to following the growth of the adduct by using TRESR, since hydrogen atoms produce the identical spin adduct. Aminoxyl radicals have very low extinction coefficients in the visible range, so that the absorption of the hydrated electron could be followed at 686 nm without significant interference from the adduct. The rate constant was  $6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

Reactions of hydrogen atoms and hydroxyl radicals with MNP were studied by using TRESR to observe the growth of the spin adduct ESR signal. Hydrogen atoms were produced radiolytically by using the reaction of the hydrated electron with phosphate buffer at pH 7.<sup>27</sup> *tert*-Butyl alcohol (0.95 M) scavenged hydroxyl radicals. Kinetic analysis of MNP-hydrogen adduct growth gave a rate constant of  $9.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

Measurement of hydroxyl radical reaction with MNP proved challenging, as low concentrations of trap were needed to limit the rise time of the MNP-hydroxyl radical adduct ESR traces. To avoid depletion of the spin trap, the use of low-current electron pulses was required, resulting in poor signal-to-noise kinetic traces. The reaction rate obtained from these data was estimated as  $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . After determining the trapping rate constant for the carboxyl radical (*vide infra*), we performed a second experiment using competition between MNP and sodium formate in hydroxyl radical reaction, observing the amplitude of the adduct signals. This competition experiment gave the rate of MNP-hydroxyl radical reaction as  $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , consistent with the estimate from the direct experiment.

**2.2. Kinetic Studies of Alkyl and Substituted Alkyl Radical Spin Trapping.** The unsubstituted alkyl radicals form a homologous series of simple carbon-centered  $\pi$  radicals in which steric interactions and electron-releasing tendencies increase with radical size. As the unsubstituted straight chain radicals increase in size in the series methyl, ethyl, and propyl, the trapping rate increases monotonically ( $1.7 \times 10^7$ ,  $5.3 \times 10^7$ , and  $6.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively). This trend follows the electron-releasing power of the alkyl radicals, while there is little change in steric interactions between the parent radicals and MNP spin trap near the parent radical's singly occupied molecular orbital (SOMO). The 3-fold increase in trapping rate between methyl and ethyl radical is taken to show that the increased electron-releasing capabilities of the ethyl radical have overcome the small increase in steric hindrance. Further extension of the alkyl chain in the 1-propyl radical provides a modest increase in electron-releasing power together with a minimal increase in steric hindrance at the radical center so that the trapping rate constant is 4 times that of the methyl radical. The electron-withdrawing tendency of the carboxylate anion has the opposite effect in carboxymethyl radical spin trapping, where the trapping rate decreases to 41% of the methyl radical rate. In this case, steric interactions also play an important role, since the  $\pi$  system of the carboxyl function is of sufficient size that approach to the nitrogen-oxygen  $\pi$  system of the trap is impeded in any trajectory of radical approach. For the radicals studied here, the severity of steric interference reaches a maximum in the trapping of the 2-methyl-2-hydroxy-1-propyl radical, which is essentially unreactive to MNP and has a trapping rate constant less than  $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . The SOMO of this radical is surrounded by the methyl and hydroxyl groups of the radical, encasing the radical's  $\pi$  orbital in a pocket that prevents good overlap between the radical SOMO and the nitrogen-oxygen  $\pi$  orbital of the trap. Although

a small amount of the 2-methyl-2-hydroxy-1-propyl radical spin adduct can be observed in the steady-state ESR experiments, TRESR parent radical decay traces show almost pure second-order decay behavior, indicating that trapping is not competitive with radical-radical reaction under our conditions.

Comparison of 2-oxo-1-propyl and 1-propyl radical trapping shows the role of electronic effects in spin trapping of primary alkyl radicals. These radicals have approximately the same shape, so that steric factors should be the same for both. The electron-releasing tendencies for the two radicals will be different since there will be substantial electron release in the 1-propyl species due to the ethyl group attached to the radical center, while the 2-oxo-1-propyl radical will achieve little electron release due to the carbonyl function adjacent to the radical center. As a result, the 2-oxo-1-propyl species is trapped half as quickly as its unsubstituted counterpart ( $3.7 \times 10^7$  versus  $6.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for 1-propyl).

MNP spin trapping of 2-propyl radical 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. 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  $4.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  is comparable to that of the ethyl radical, indicating that steric effects dominate electronic effects in this case.

**2.3. Kinetic Studies of Hydroxyalkyl Radical Trapping.** The hydroxyalkyl radicals form a series of strongly reducing carbon-centered  $\pi$  radicals. These radicals can directly transfer an electron to suitable electron acceptors and are also facile in donating an electron to MNP to form the C-N bond of the adduct radical. The tendency of the hydroxyalkyl radicals to undergo electron transfer increases in the series hydroxymethyl < 1-hydroxyethyl < 2-hydroxy-2-propyl. The corresponding trapping rate constants are  $1.4 \times 10^8$ ,  $3.2 \times 10^8$ , and  $6.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , significantly larger than for the unsubstituted methyl, ethyl, and 2-propyl radicals. This trend shows the strongly electrophilic nature of MNP. Steric effects on hydroxyalkyl radical trapping are demonstrated in the primary hydroxyalkyl radical series of 1-hydroxyethyl, 1-hydroxypropyl, and 1,2-dihydroxyethyl, with corresponding trapping rates of  $3.2 \times 10^8$ ,  $1.3 \times 10^8$ , and  $3.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . The rapid decrease in the trapping rate in these three radicals possessing similar reducing power shows that steric interactions can modulate the trapping rate of even the most strongly reducing radicals. The magnitude of this effect is surprising, since examination of molecular models reveals little additional crowding in trap-parent radical approach in going from the 1-hydroxyethyl to 1-hydroxypropyl case. Still, reducing power is the dominant factor in hydroxyalkyl radical trapping, as 2-hydroxy-2-propyl radical is the most reactive alcohol radical studied here, in spite of severe steric hindrance during trap-radical encounters.

**2.4. Kinetic Studies of  $\sigma$  Radical Trapping.** Two  $\sigma$  radicals, the sulfite radical and the carboxyl radical anion, were studied.  $\sigma$  radicals have a highly localized SOMO, and in both radicals, this orbital is directed away from the oxygen atoms attached to the central atom of the radical, minimizing steric interference as the parent radical approaches the trap. Therefore, these radicals provide a test of trapping rate variability with steric effects minimized. The strongly reducing carboxyl radical anion is trapped extremely rapidly with a rate constant of  $1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , while the oxidizing sulfite radical anion has a trapping rate constant of  $4.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , among the lowest of the radicals surveyed in this study. Here, electronic effects dominate the trapping reaction since steric effects are not significantly different in these radicals.

## Conclusion

The 2800 spin trapping experiments summarized in the STDBII V4.5 spin trapping database demonstrate the popularity of MNP as a spin trap.<sup>37</sup> Still, to our knowledge, the number of previous studies of MNP spin trapping kinetics is small. Only the work of Maeda, Schmid, Griller, and Ingold<sup>22</sup> is directly comparable

to ours. Their rate constant for 1-hexyl radical trapping by MNP in methanol is  $1.16 \times 10^7$ . This rate constant agrees well with those of the present study, as Maeda et al. showed that spin trapping with nitroso and nitron spin traps becomes faster as solvent polarity increases. Ingold and co-workers<sup>21,23</sup> also measured trapping of 1-hexyl and 2-hexyl radicals by MNP in benzene, finding a rate constant of  $8.8 \times 10^6$  for the primary alkyl radical vs  $6.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for the secondary species. The ratio of these rates, 0.69, closely matches the 0.67 ratio we observed between 1-propyl and 2-propyl radical trapping by MNP in aqueous solution.

The present results show that rate constants for spin trapping can vary by over 2 orders of magnitude in a series of small carbon-centered radicals. Electronic factors primarily control trapping rates, as reducing hydroxyalkyl radicals and substituted alkyl radicals capable of electron release show the fastest rates. Steric effects can greatly retard trapping reactions with parent radicals of marginal electron-releasing capability. Our results show that reaction of hydroxyalkyl radicals with MNP in neutral aqueous media leads only to formation of the hydroxyalkyl-MNP spin adduct. In basic media, however, we have seen formation of net

hydrogen atom-MNP adduct, as well as hydroxyalkyl-MNP spin adduct during reaction of 2-hydroxy-2-propyl radical with MNP; the trapping rate constant of hydroxyalkyl radicals was pH dependent.<sup>60</sup> In biological systems, where spin trapping has found its greatest utility, radicals may be located in regions of greatly varying polarity and effective pH, which potentially could cause site-specific trapping rate variation for a given radical. Experiments in progress are extending trapping rate studies to acidic and basic aqueous solutions to determine the cause of the pH-dependent trapping rate variations. We believe that the time-resolved ESR pulse radiolysis method is uniquely suited to measure the selectivity and efficiency of spin trapping reactions.

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## Magnetic Interaction between the Triplet Centers in Ethynylenebis(phenylnitrenes) and 1,3-Butadiyne-1,4-diylbis(phenylnitrenes)

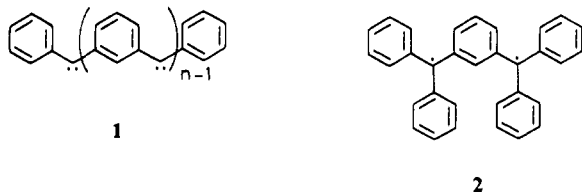
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**Abstract:** The magnetic interaction of the two triplet phenylnitrene units linked together through an acetylene or a diacetylene linkage has been investigated by ESR spectroscopy. Two regioisomeric (meta,para' and meta, meta') diazides of 1,2-diphenylacetylene **12a** and 1,4-diphenyl-1,3-butadiyne **13a** were prepared and photolyzed in a 2-methyltetrahydrofuran glass at 10 K to give the corresponding dinitrenes **12n** and **13n**. The *m,p'*-dinitrenes of **12n** and **13n** showed intense quintet signals which obeyed a Curie law in the temperature range 12-85 K. The *m,m'*-dinitrenes of **12n** and **13n** showed signals due to the thermally populated quintet states, the intensities of which reached a maximum at 50 and 28 K for **12n** and **13n**, respectively. It is concluded that the two remote phenylnitrene units in **12n** and **13n** interact sufficiently strongly through bonds to form quintet states that are concluded to be the ground state in the meta,para' isomers as predicted by theory. In the meta,meta' isomers, the quintet states are thermally populated from ground singlet states, the energy gaps between the two states (ca. 200 and 100 cal/mol for  $-\text{C}\equiv\text{C}-$  and  $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ , respectively) being dependent reasonably upon the distance between the two moieties. The results serve as good guiding principles for designing high-spin conjugated polymers with pendant radical centers.

Since the dicarbene **1** ( $n = 2$ )<sup>1</sup> and the Schlenk hydrocarbon **2**<sup>2</sup> were established to have a quintet and a triplet ground state



in 1967 and 1970, respectively, they have served as the structural basis of further theoretical and experimental studies on organic high-spin molecules.<sup>3</sup> Their structures have in common the  $\pi$ -moiety of 1,3-benzoquinodimethane, for which no stable Kekulé

structure can be drawn. In contrast, the *p*-dicarbene **3**<sup>4</sup> and the Chichibabin and Thiele hydrocarbons (**4** and **5**)<sup>5</sup> are in lower spin

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