

After thawing, the reaction solutions were mixed and gas samples were withdrawn at various intervals for the mass spectrographic determination of the HD-D₂ ratios. The results of these and other experiments are summarized in Table X.

Synthesis of Ferredoxin Model Compounds.^{12,13} Following the initial report on complexes containing the anions [Fe₄S₄(SR)₄]²⁻, a number of representatives of this class of compounds were synthesized. Initially, the complexes were prepared with R = ethyl, but these were found to undergo slow decomposition under reducing conditions, giving rise to ethylene and ethane derived from the ethylmercaptide residues. In the presence of complex I and reducible substrate, this decomposition is inhibited, but the independent formation of ethylene and ethane from the electron-transfer catalyst was sufficiently disturbing for us not to use this complex anion for our experiments. Instead, we prepared the corresponding anion with R = *n*-propyl, which is more stable under reducing conditions. Although traces of propylene and propane are still formed, these hydrocarbons do not interfere with the gas chromatographic assay for C₂ hydrocarbons in acetylene reduction experiments. The ferredoxin model compounds were either employed in the form of the bis(tetra-*n*-butylammonium) salts or as the dilithium derivatives. The former are less soluble and readily obtained in crystalline form; the latter are more difficult to obtain in substance and were generated *in situ*.

(a) **Synthesis of** [N(*n*-C₃H₇)₄]⁺₂[Fe₄S₄(S-*n*-C₃H₇)₄]²⁻. Anhydrous ferric chloride, 5.2 g (32 mmol), was dissolved in 20 ml of anhydrous methanol. To this solution a methanolic solution of lithium *n*-propylmercaptide was added. The latter was prepared by adding 3.65 g of LiOCH₃ to 40 ml of a solution of 8.6 ml of freshly distilled *n*-propylmercaptan in 40 ml of anhydrous CH₃OH. The reaction of ferric chloride with the lithium mercaptide causes the precipitation of dark green iron *n*-propylmercaptides. These were not isolated but instead reacted further with 1.46 g of solid, anhydrous Li₂S (available from Alfa Inorganics). This produces a dark, bronze-colored homogeneous solution. The complex ion was precipitated by the addition of 9.2 g of N(*n*-C₃H₇)₄Br, dissolved in 40 ml of anhydrous methanol. The black crystalline salt was filtered off, washed with methanol, and dried at room temperature under reduced pressure.

Anal. Calcd for N(*n*-C₃H₇)₄⁺₂[Fe₄S₄(S-*n*-C₃H₇)₄]²⁻: C, 45.37; H, 8.65; S, 22.00 Fe, 19.18. Found: C, 45.22; H, 8.45; S, 23.0; Fe, 19.9.

For the experiments with the lithium salt of the cluster anion, the solution resulting from the addition of Li₂S to the suspension of iron propylmercaptide was employed without further purification. The Fe(II) form of the cluster complex was generated by direct synthesis as described above but with methanolic solutions of FeCl₂ instead of FeCl₃. The FeCl₂ solution was prepared by dissolving 4.06 g of

anhydrous ferric chloride in 20 ml of anhydrous methanol. The resulting solution was converted to the ferrous salt by the addition of iron dust and was used as described above, after removal of excess elemental iron.

(b) **Acetylene Reduction Experiments.** Acetylene-filled (1 atm) reaction vials of 25-ml volume were filled with 1.5 ml of an aqueous solution of 0.106 M complex I in pH 9.6 borate buffer (0.2 M). This was followed by 1.4 ml of the methanolic solution of Li₂Fe₄S₄(S-*n*-C₃H₇)₄ as obtained by the above procedure or by adding the corresponding amount of the tetrabutylammonium salt in methanol. Finally, 0.5 ml of freshly prepared, 1.2 M pH 9.6 buffered solutions of the reducing agents were added (either Na₂S₂O₄ or NaBH₄), followed by 0.5 ml of a freshly prepared 1.2 M solution of ATP, where indicated (see Table IX). Gas samples of 0.1 ml were periodically withdrawn for product analysis by glpc, using a Hewlett-Packard Series 700 laboratory instrument equipped with a phenyl isocyanate-Porasil 80-100 mesh column.

(c) **Nitrogen Reduction Experiments.** The experiments with nitrogen as the substrate were performed under conditions essentially identical with those described in b, except that the vials were initially filled with 99+ % ³⁰N₂ at 1 atm. Product analysis was carried out by the standard hypobromite oxidation method as described above of the degassed and previously acidified reaction solutions or aliquots thereof.

Experiments with Chemically Generated Diimide. Solid dipotassium azodicarboxylate, in portions of 10.0 mg, was added to pH 9.6 borate buffered solutions of the reaction components listed in Table XI. After 15 hr of reaction at 25°, aliquots of 0.4 ml were withdrawn for ammonia and hydrazine analysis by the spectrophotometric methods.

Hydrazine Reduction. The experiments in Table XII were performed in reaction vials containing the amounts of reagents indicated in the footnotes. Ammonia and hydrazine were assayed spectrophotometrically.

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Electron-Carbon Couplings of Aryl Nitronyl Nitroxide Radicals

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Abstract: We have taken ¹³C nmr spectra of a group of aryl nitronyl nitroxide radicals to determine the sign and magnitude of the electron-carbon coupling constants. Lines were observed from the aliphatic carbons on the nitronyl nitroxide ring and from all of the aromatic carbon atoms except the bridgehead carbon. The ¹³C coupling constants of the aromatic carbon atoms are used to estimate spin polarization parameters. The ortho carbon couplings are found to be larger than predicted. The magnitude of these coupling constants can be explained by either an unexpectedly large spin density at the bridgehead carbon or by a long range interaction with spin in the nitronyl nitroxide ring. The coupling constants of the saturated carbons on the nitronyl nitroxide ring are discussed in terms of a mechanism involving polarization of the saturated bonds by spin at the nitroxide group.

The low natural abundance of ¹³C generally makes electron spin resonance measurements of electron-carbon hyperfine coupling constants difficult or im-

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possible. Carbon couplings which have been measured have come from compounds in which the carbon hyperfine lines either lie outside of the main part of the esr spectrum or are spaced between other hyperfine

components. The signs of ^{13}C coupling constants measured by esr are determined through an analysis of line width variations.² The sign and magnitude of carbon splitting constants can be determined from the nmr spectra of organic radicals in some instances.³ In cases in which the electron spin energy levels are rapidly averaged by spin exchange, one may observe a single shifted line from each set of equivalent carbon nuclei. The shift (ΔH) is related to the coupling constant (A) by

$$\Delta H = -A \left[\frac{\gamma_e}{\gamma_N} \right] \left[\frac{g\beta H}{4kT} \right] \quad (1)$$

This type of experiment is difficult because of the low natural sensitivity of ^{13}C nmr along with the large shifts and broad lines which are found in the ^{13}C nmr spectra of organic radicals. These problems can be overcome in some cases by using a high powered pulsed nmr spectrometer which is interfaced to a computer for signal averaging.

We have used a pulsed nmr spectrometer to obtain the ^{13}C nmr spectra of the nitronyl nitroxide radicals shown in Figure 1. Lines were observed from all of the aromatic carbons except the bridgehead carbon. The line from this carbon should have a large shift and the signal is probably overlapped with the line from the β -methyl carbons. Lines were detected from the α and β carbons of the nitronyl nitroxide ring, but the signal from the bridgehead carbon of this ring was not observed. The splitting from this carbon (12 G) has been determined by esr.⁴ Proton coupling constants for these radicals have previously been reported along with a theoretical treatment of the spin distribution.⁵

Carbon couplings in aromatic rings can be accounted for by interactions between the unpaired spin in the $2p\pi$ system and the $1s$ and $2s$ electrons of a given carbon atom. The equation which has been used to account for aromatic carbon coupling constants was first proposed by Tuttle⁶ and later formalized by Karplus and Fraenkel.⁷ The Karplus and Fraenkel equation is given by

$$A_C = [S^C + \sum_i Q_{C\text{X}_i}^C] \rho^\pi + \sum_i Q_{\text{X}_i\text{C}}^C \rho_i^\pi \quad (2)$$

The first terms in this expression account for polarization of the $1s$ electrons and the electrons in the sp^2 hybrid orbits by spin in the $2p$ orbit of the atom in question. S^C is the spin polarization parameter for the $1s$ electrons and the $Q_{C\text{X}_i}^C$'s are the spin polarization parameters for the sp^2 electrons. The second term accounts for polarization of the electrons in the sp^2 hybrid orbitals by unpaired spin density in the p orbitals of adjacent carbon atoms. The spin polarization parameters for this type of interaction are denoted as $Q_{\text{X}_i\text{C}}^C$. The spin density at the atom in question is given by ρ^π while the ρ_i^π 's are the spin densities at adjacent carbon atoms.

The spin polarization parameters calculated by Karplus and Fraenkel are $S^C = -12.7$ G, $Q_{\text{CH}}^C = 19.5$, $Q_{\text{C-C}'}^C = 14.4$ G, and $Q_{\text{C-C}''}^C = -13.9$ G. A

(2) E. de Boer and E. L. Mackor, *J. Chem. Phys.*, **38**, 1450 (1963).

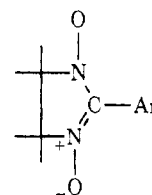
(3) G. F. Hatch and R. W. Krellick, *J. Chem. Phys.*, **57**, 3696 (1972); G. F. Hatch and R. W. Krellick, *Chem. Phys. Lett.*, **10**, 490 (1971).

(4) J. A. D'Anna and J. H. Wharton, *J. Chem. Phys.*, **53**, 4047 (1970).

(5) M. S. Davis, K. Morokuma, and R. W. Krellick, *J. Amer. Chem. Soc.*, **94**, 5588 (1972).

(6) T. R. Tuttle, *J. Chem. Phys.*, **32**, 1579 (1960).

(7) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).



I, Ar = phenyl III, Ar = 4-pyridyl
II, Ar = 2-pyridyl IV, Ar = 3-pyridyl

Figure 1. Compounds investigated.

second set of theoretical parameters has been suggested by Yonezawa in a more recent calculation.⁸

The various spin polarizations in the Karplus and Fraenkel equation can be combined to yield two effective terms for an aromatic carbon atom and the equation may be rewritten as

$$A_C = Q^C \rho^\pi + \sum_i Q_{\text{C}'-C}^C \rho_i^\pi \quad (3)$$

For an unsubstituted aromatic carbon atom, Karplus and Fraenkel's value of $Q_{\text{C}'-C}^C$ is 35.6 G while $Q_{\text{C}'-C}^C$ is -13.9 G. When a nitrogen atom is bonded to the carbon atom in an aromatic ring, eq 3 must be modified to account for the carbon-nitrogen and nitrogen-carbon spin polarization parameters. Values suggested for these spin polarization parameters are $Q_{\text{C-N}}^C = 4 \pm 4$ G and $Q_{\text{N-C}}^C = -20.5 \pm 4$ G.⁹

In order to determine the spin polarization parameters in eq 3 experimentally, it is necessary to measure the sign and magnitude of a series of carbon coupling constants and to have an independent evaluation of the spin distribution in the aromatic ring. With this experimental information a plot of A_C/ρ^π vs. $\sum_i \rho_i^\pi/\rho^\pi$ should yield a straight line with a slope equal to $Q_{\text{C}'-C}^C$ and an intercept of Q_{C}^C .

The coupling constants of the aliphatic carbons in the nitronyl nitroxide ring should be mainly due to polarization of the electrons in the sp^3 hybrid orbitals by spin in the nitrogen's $2p$ orbital. The carbon atom in the ring is α to one of the nitrogens and β to the other nitrogen. The methyl carbons are β to one nitrogen and γ to the other. The coupling constants of the ring carbon atoms are probably dominated by a direct polarization of the nitrogen-carbon bond by unpaired spin at the nitrogen. Beta couplings in nitroxide radicals have been found to depend on the angle (θ) between the nitrogen's $2p$ orbital and the α - β carbon-carbon bond.³ The relation between the β coupling constant, θ , and the nitrogen spin density (ρ_N) is given by¹⁰

$$A = [B_0 + B_1 \cos^2 \theta] \rho_N \quad (4)$$

Smaller interactions with spin at the oxygen atoms may also contribute to the coupling constants of the aliphatic carbon atoms.

Experimental Section

(A) **Samples.** The preparation of the nitronyl nitroxide radicals has previously been described.⁵ Saturated solutions of the radicals

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(10) G. R. Underwood and V. Vogel, *J. Amer. Chem. Soc.*, **93**, 1058 (1971); C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

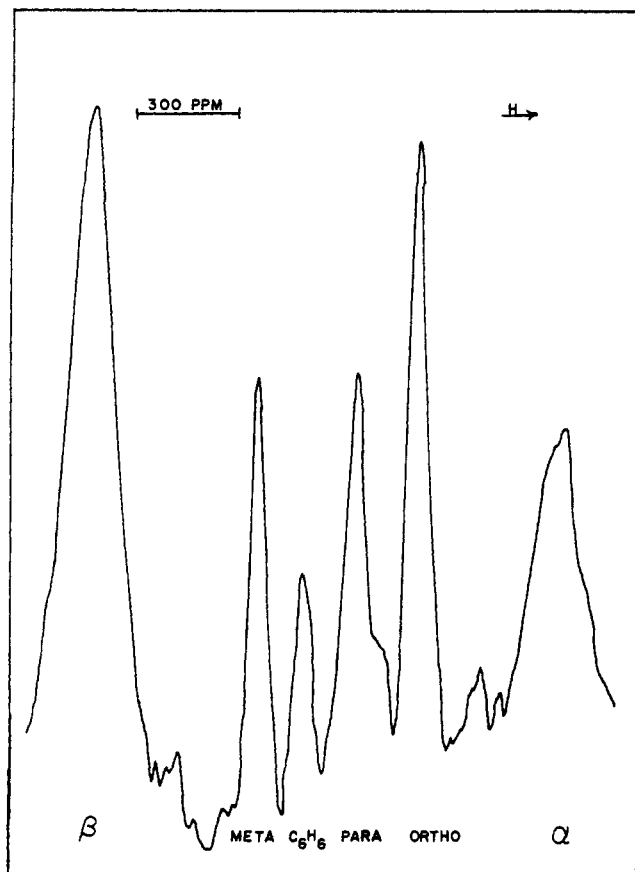


Figure 2. ^{13}C nmr spectrum of radical I. The lines in the center of this spectrum are partially saturated.

in methylene chloride were made for the nmr measurements. The radicals interact strongly with the solvent's carbon atoms and the solvent line is shifted and broadened. Benzene was used as an internal reference for the aromatic carbon atoms. The shifts of the aliphatic carbons were measured with respect to the methyl carbons of 2,2,6,6-tetramethylpiperidine.

(B) **Instrumental.** The spectra were taken with a high powered pulsed nmr spectrometer operating at 25.1 MHz. The radio-frequency pulse was directed to a magic tee which divided the signal between a $50\text{-}\Omega$ termination and the probe. A single coil probe capable of accepting 10-mm sample tubes was used and the bridge was balanced by adjusting a series capacitor and an impedance matching capacitor until the probe had an impedance of $50\ \Omega$.¹¹

Two techniques were used to obtain the spectra. The first technique involved the use of a boxcar integrator to monitor the signal after radiofrequency detection. The gate of the boxcar integrator was triggered with the pulse and left open for a period long compared to the duration of the free induction decay. With this mode of operation the boxcar integrator monitors the dc component of the signal and a normal constant wave spectrum is observed as the field is swept. The signal from the boxcar integrator was averaged with a Digital Equipment Corp. PDP-12 computer to improve the signal to noise. Four to eight hours of averaging was normally necessary to obtain a reasonable signal-to-noise ratio.

The second technique which was used involved averaging the free induction decay directly in the computer and carrying out a Fourier transformation to obtain the absorption spectrum. The 90° pulse width for carbon was 2–3 μsec with a resulting bandwidth of about a 100 kHz. The carbon relaxation times in organic radicals are normally very short and a fast analog to digital converter (ADC) must be used. A Hybrid Systems Corp. Model 525-8 ADC capable of carrying out an 8-bit conversion in 2 μsec was used. The signal from the ADC was directed to the direct memory access bus of the computer and added to memory. The cycle time of the computer limited the system to a maximum acquisition rate of 6 $\mu\text{sec}/\text{word}$ and

(11) M. P. Klein and D. E. Phelps, *Rev. Sci. Instrum.*, **38**, 1545 (1967).

Table I. Shifts, Coupling Constants, and Spin Densities

Compd	Position	Shift, ppm	A , G	$P \times 10^{2a}$
I	Ortho	342	-1.17	-1.65
I	Meta	-157	0.54	0.65
I	Para	138	-0.47	-1.41
I	α	630	-2.1	
I	β	-746	2.6	
II	Ortho	283	-0.98	-1.1
II	Meta	-83	0.29	0.5
II	Para	112	-0.38	-1.1
III	Ortho	360	-1.24	-1.8
III	Meta	-149	0.51	0.46
III	α	698	-2.4	
III	β	-750	2.6	
IV	Ortho	348	-1.09	-1.61
IV	Meta	-123	0.42	0.7
IV	Para	159	-0.55	-1.61
IV	α	655	-2.2	
IV	β	-732	2.5	

^a The spin densities are calculated assuming Q_{CH} is -27.

a bandwidth of 83.3 kHz. There were 512 triple precision (36 bit) words taken. About 30 min of averaging was required to obtain a reasonable signal-to-noise ratio.

After carrying out the Fourier transformation the phase of the absorption spectrum was adjusted with separate linear and nonlinear phase corrections. The nonlinear phase adjustment gave a maximum phase correction of 12π radians. Correct phasing of the broad lines observed from the aliphatic carbons was difficult and phase correction errors lead to some error in the values of the shifts for these lines. The broad lines were phased better in the spectra taken with the boxcar integrator.

Results and Discussion

A representative ^{13}C nmr spectrum of radical I is shown in Figure 2. The ^{13}C shifts and coupling constants are listed in Table I along with the spin densities in the aromatic rings. The assignment of lines to the various carbon atoms was made on the basis of areas and changes in the spectra when a nitrogen was substituted for a carbon atom. The lines from the ortho and para carbon atoms are shifted to high field while the line from the meta carbon atom is shifted to low field. The line from the α -nitronyl nitroxide ring carbon is shifted to high field while the line from the β -methyl carbons is shifted to low field.

The lines from the α - and β -aliphatic carbons of the *o*-pyridyl nitronyl nitroxide radical were very broad and we were unable to measure their shifts. The line from the ortho carbon atom in this radical was considerably broader than the corresponding signals in the other compounds, and it was difficult to measure the shift accurately. The spectra of this compound contained a number of diamagnetic impurity lines and the solubility of this compound was less than that of the other radicals.

The spin polarization parameters in eq 3 were estimated from a plot of A_C/ρ^π vs. $\sum_i \rho_i^\pi/\rho^\pi$ (Figure 3). The spin density at the bridgehead carbon cannot be experimentally determined and data from the ortho carbons are omitted from this plot. Data from carbon atoms adjacent to nitrogen atoms are also omitted from this plot. The plot includes data for the meta and para carbon atoms of radical I, the meta carbon atom of radical IV, and the meta and para carbon atoms of radical II. Data from benzene,¹² naphthalene,^{6,13} and anthracene¹⁴ nega-

(12) J. R. Bolton, *Mol. Phys.*, **6**, 219 (1963).

(13) T. R. Tuttle and S. I. Weissman, *J. Chem. Phys.*, **25**, 189 (1956).

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tive ion radicals are included. The slope and intercept of this plot depend on the value of Q_{CH} which is used to calculate the spin densities. The plot shown in Figure 3 assumes that Q_{CH} is -27 G for all of the radicals except the benzene negative ion for which Q_{CH} is set equal to -22.5 G. A least-squares fit of these data gives a value of $Q_{C^C} = 29.6$ G and $Q_{C'-C^C} = -9$ G. If Q_{CH} is assumed to be -22.5 for all of the radicals then a least-squares fit gives $Q_{C^C} = 24$ G and $Q_{C'-C^C} = -7.6$ G.

Some of the scatter in data for the meta carbon of the various nitronyl nitroxide radicals comes from inaccurate determinations of the ortho and para proton coupling constants. The nmr lines from these protons are overlapped in all of the radicals except compound I and separate values for the ortho and para coupling constants could not be determined. The carbon atoms at the 2 position of the naphthalene and anthracene negative ion radicals have been assigned negative coupling constants on the basis of esr line-width variations. If the sign determination for these carbons is incorrect, the points for these atoms would lie very close to the least-squares lines.

The coupling constants of the ortho nitronyl nitroxide carbons are about a factor of 2 larger than the coupling constants of the para carbon atoms. The ortho and para spin densities are nearly the same in this group of radicals, and INDO calculations indicate that the bridgehead spin density is almost equal to the spin density of the meta carbon.⁵ In order to account for the large values of the ortho coupling constants, one must assume that either the bridgehead spin densities are much larger than predicted or that a second mechanism contributes to the coupling of the ortho position. The bridgehead spin density must be about a factor of 5 greater than the ortho and para spin densities to account for the magnitude of the ortho coupling constants ($\rho_{BH} = 6.9 \times 10^{-2}$, $\rho_M = 6.5 \times 10^{-3}$, and $\rho_{O,P} = 1.6 \times 10^{-2}$). A second mechanism which might make a contribution to the ortho coupling constants involves a direct polarization of the electrons in the sp^2 hybrid orbit of the bridgehead ortho carbon-carbon bond by spin at the N-O group. The ortho carbon is γ to the nitrogen atom in these radicals. The γ carbon coupling constants in saturated nitroxide radicals have values up to about -0.4 G.³ The ortho carbon atom is β to the bridgehead carbon of the nitronyl nitroxide ring (2 carbon) which is predicted to have a negative spin density ($\rho = -1.27 \times 10^{-1}$).¹⁵ An interaction between spin at the 2 carbon and the bridgehead ortho bond would also yield a negative coupling at the ortho position. If the relative geometry of the nitronyl nitroxide ring and the aromatic ring is correct, polarization of the bridgehead ortho bond could account for the observed increase in the ortho coupling constant.

The shift of the bridgehead aromatic carbon can be estimated from the spin density at the 2 carbon of the nitronyl nitroxide ring and the ortho and bridgehead spin densities of the aromatic ring. If one uses the value of the bridgehead spin density from the INDO calculation, one predicts a bridgehead coupling constant of 1.65 G and a shift of -11.3 G. The nmr

(15) D. G. B. Boocock, R. Darcy, and E. F. Ullman, *J. Amer. Chem. Soc.*, **90**, 5945 (1968).

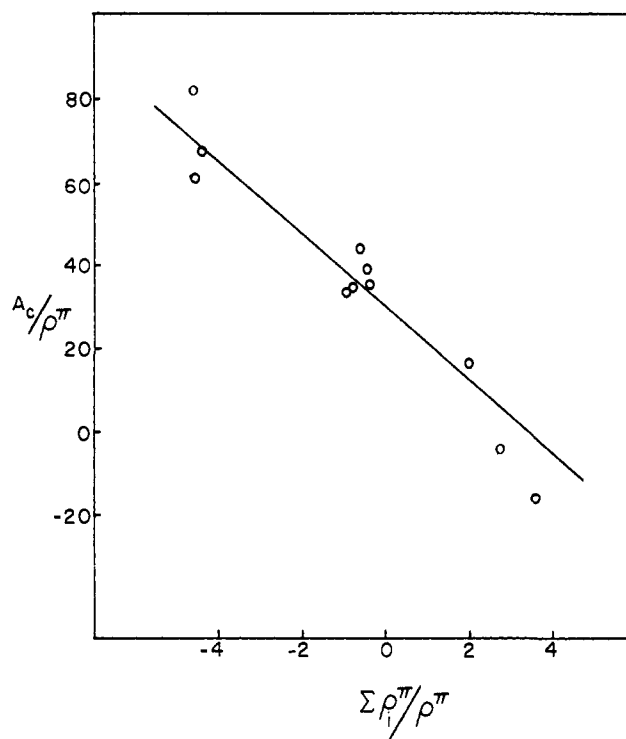


Figure 3. Plot of A_C/ρ^π vs. $\Sigma\rho_i^\pi/\rho^\pi$.

signal from this carbon was not observed and is probably overlapped with the line from the β -methyl carbons.

The coupling constants of carbon atoms adjacent to a nitrogen atom in the pyridyl rings are almost the same as the coupling from a corresponding carbon in the phenyl ring. The spin densities in the aromatic ring do not change very much when a nitrogen atom is substituted for a carbon atom, and the spin density at a pyridyl nitrogen is probably almost the same as that of a corresponding carbon atom. These data indicate that the spin polarization parameters for a carbon-nitrogen bond (Q_{C-N^C} and Q_{N-C^C}) are nearly the same as the carbon-carbon spin polarization parameters.

The coupling constant of the α -carbon atoms in the nitronyl nitroxide ring should be determined by polarization of the electrons in the nitrogen-carbon bond and the α - β carbon-carbon bonds. Both types of polarization should be proportional to the spin density at the nitrogen. One predicts a negative coupling constant from these interactions and this is observed experimentally. Smaller contributions from spin at the oxygen atoms may also occur. These carbon atoms are β to the second nitrogen in the heterocyclic ring, and if the ring is not completely planar, spin at the β -nitrogen atom may contribute to these coupling constants.

If the spin distribution in the N-O group is constant in nitroxide and nitronyl nitroxide radicals, then the ratio of the nitrogen coupling constants should indicate the ratio of the nitrogen spin densities. The ratio of the nitrogen coupling of di-*tert*-butyl nitroxide (DBNO, 16.13 G) to the nitrogen coupling of the nitronyl nitroxides (7.47 G) is 2.16. The ratio of the α -carbon couplings for these radicals is 2.09. These data indicate that the same mechanism makes a dominant contribution to the α -carbon couplings in both types of radicals and that the spin distribution in the N-O group

is nearly the same in nitroxide and nitronyl nitroxide radicals.

The β -carbon atoms coupling constant should depend on the angle (θ) between the α - β carbon-carbon bond and the nitrogen 2p orbit (eq 4). Values for $B_{0\rho_N}$ (0.8 G) and $B_{1\rho_N}$ (6.8 G) have previously been determined from a study of carbon couplings of nitroxide radicals.³ If the heterocyclic ring of the nitronyl nitroxide radicals is flat, one predicts that θ should be 30°. In order to account for differences in spin densities between nitroxide and nitronyl nitroxide radicals, we have divided $B_{0\rho_N}$ and $B_{1\rho_N}$ by the ratio of the respective nitrogen coupling constants. With these constants and the value of the β -carbon coupling constant, one calculates an angle of 33°. This calculation indicates that the values of B_0 and B_1 are consistent for β couplings in nitroxide and nitronyl nitroxide radicals and that the other nitrogen in the nitronyl nitroxide ring makes a negligible contribution to these coupling constants.

Conclusion

The ¹³C nmr spectra of a series of nitronyl nitroxide

radicals have been used to determine electron-carbon coupling constants for both aromatic and aliphatic carbon atoms. The data for the aromatic carbon atoms were used along with that from some negative ion radicals to estimate spin polarization parameters. Carbon couplings from atoms adjacent to a nitrogen in an aromatic ring indicated that the spin polarization parameters for a carbon-nitrogen bond are almost identical with those for a carbon-carbon bond. The coupling constants for the ortho carbon atoms were found to be much larger than predicted. The magnitude of these couplings can be explained by either an anomalously high spin density at the aromatic bridgehead carbon or by long range interactions with spin in the nitronyl nitroxide ring. The coupling constants of the aliphatic carbon atoms can be explained in terms of polarization of the electrons in the saturated bonds by spin at the nitrogen atoms. The data obtained for the nitronyl nitroxide radicals are consistent with those from a series of nitroxide radicals which were investigated in an earlier study.

Geometries of the Methoxy Radical (X^2E and A^2A_1 States) and the Methoxide Ion

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Abstract: *Ab initio* self-consistent field electronic structure calculations have been performed on the methoxy radical (CH_3O) in its ground and first excited electronic states and on the methoxide ion (CH_3O^-). The geometries of the three species have been predicted by varying the total energy with respect to the CH and CO bond distances and the OCH bond angle. The three geometries are qualitatively quite different, particularly the CO bond distances. A small Jahn-Teller distortion is predicted for the 2E CH_3O ground state. The excited 2A_1 state of CH_3O is predicted to lie at 3.6 eV.

As the prototype alkoxy radical, CH_3O is one of the simplest fundamentally important organic molecules. This is reflected in its importance in photochemistry² (and photochemical air pollution) and organic radiation chemistry.^{3,4} Although the methoxy radical is inevitably short lived, it may be readily formed by several means, including the photolysis of methyl acetate⁵



and pyrolysis of dimethyl peroxide⁶



(1) (a) University of California; (b) Wilson-Tasheira Fellow; (c) Alfred P. Sloan Fellow; (d) Information Systems Design.

(2) (a) B. A. DeGraff and J. A. Calvert, *J. Amer. Chem. Soc.*, **89**, 2247 (1967); (b) J. Heicklen, *Advan. Chem. Ser.*, No. 76, 23 (1968).

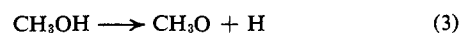
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(4) J. A. Wargon and F. Williams, *J. Amer. Chem. Soc.*, **94**, 7917 (1972).

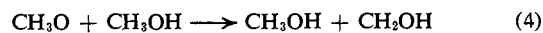
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During the past few years, it has been definitively shown^{3,4} that the methoxy radical is the most abundant radical produced in the radiolysis of liquid methanol



and that the thermodynamically more stable (by 5–10 kcal/mol^{7,8}) hydroxymethyl radical arises primarily from the secondary reaction



The latter hydrogen atom abstraction is typical of the reactions that the methoxy radical undergoes.^{2b} Among the additional thermodynamic data^{2b,7} available for CH_3O are the methanol dissociation energy $D(CH_3O-H) \approx 102$ kcal/mol and the dissociation energy relative to formaldehyde $D(H-CH_2O) \approx 29$ kcal/mol.

In light of the above, it might seem somewhat surprising that the molecular structure of methoxy is unknown. However, in fact, the geometries of only a

(7) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(8) M. A. Haney and J. L. Franklin, *Trans. Faraday Soc.*, **65**, 1794 (1969).