

Substituent Effects on Electron Spin Resonance Spectra and Stability of Free Radicals¹

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The nature of substituent effects in free-radical chemistry has been the subject of considerable work and discussion. Earlier texts on this subject spread the notion that free radicals are stabilized by substituents when and because additional resonance structures can be drawn wherein the unpaired electron is delocalized onto the substituent. More recent work has concentrated on the substituent effect on the rates of free-radical reactions. Some good correlations with the Hammett equation have been found and rationalized in terms of polar transition states.

Electron spin resonance (esr) spectroscopy is ideally suited for a study of the factors influencing the stability of a radical since this technique detects free radicals and at the same time provides information about the delocalization of the unpaired electron. The following introductory material is presented in order to provide a better understanding of how this information is obtainable.

A Brief Introduction to Esr

Esr is a magnetic resonance technique which achieves a response only from those molecules with at least one unpaired electron. The signal obtained from the unpaired electron (say the solvated electron in liquid ammonia solution) is a single line which reflects the net absorption of energy by the electron when the following "resonance" condition is met

$$h\nu = g\beta H$$

where $h\nu$ is the energy of the absorbed photon, β is a constant for the electron, the Bohr magneton, H is the external magnetic field, and g is a constant characteristic of the spin system (approximately 2.0 for organic free radicals). The absorption of energy by the electron corresponds to a change in sign of the electron spin or change in direction of the electron magnetic moment. The external field value for the signal is thus $H = h\nu/g\beta$. If the unpaired electron experiences the field of another spin system, say a nucleus with a spin, the magnetic field felt by the unpaired electron is slightly greater than, or smaller than, the field experienced in the absence of the nuclear spin system, depending on the direction of perturbing additional field. Thus for a spin (I) of $\pm 1/2$ resonance now occurs at $H_1 = H - \delta H$ and $H_2 = H + \delta H$, where $\delta H =$ the

perturbing field. Two signals or lines are observed. The coupling constant (a or A) is defined as the spacing between the observed lines, usually in gauss. Since the original line due to the unpaired electron is "split" into two lines, the spacing is also called a splitting constant. For hydrogen atom the spacing is 500 G, a relatively large value compared to those commonly encountered in organic free radicals.

If the unpaired electron experiences the field of more than one nuclear spin two possibilities arise: either the interaction between each nuclear spin and the unpaired electron is equal for all nuclei (equivalent) or not equal for all nuclei (nonequivalent). For equivalent nuclear spins the system is considered to have a total spin of nI where the number of lines are predicted by the expression $(2nI + 1)$. For nonequivalent nuclei the number of lines is predicted by the product of the individual sets of equivalent nuclei: $(2n_1I_1 + 1) \cdot (2n_2I_2 + 1) \dots$, where n_1 is the number of equivalent nuclei with spin I_1 , n_2 is the number of equivalent nuclei with spin I_2 , etc.

The intensities of the lines produced from an interaction with one nucleus are all equal. The intensities of the lines from interaction with n equivalent nuclei are best obtained from Pascal's triangle, *i.e.*, the coefficients in the expansion of $(1 + x)^n$. The spacings between lines are always symmetrically disposed about the center of the spectrum (to first-order approximation).

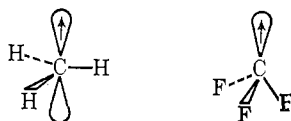
The interaction of two or more unpaired electrons is not handled by this simple picture. However, esr spectra of triplet-state molecules (two unpaired electrons) and transition metal ions with three or any odd number of unpaired electrons have been available for some time and consist of well-understood patterns of lines. Historically the pattern of lines obtained from the interaction of unpaired electrons *with each other* was called fine splitting. The pattern of lines observed from the interaction of the unpaired electron *with nuclear spins* was called hyperfine splitting, and more recently that obtained from the interactions of the unpaired electron with nonbonded nuclei, superhyperfine splitting.

Of interest are the factors which determine the magnitude of the interaction of the unpaired electron with the nuclear spin which is reflected in the magnitude of the hyperfine splitting constant. Three factors are important when the orbital containing the unpaired electron resides on the atom in question: (a) the magnitude of the magnetic moment and spin of the nucleus; (b) (i) the s character of the orbital containing

(1) (a) This paper was prepared for the Second Linear Free Energy Conference, March 27, 1968, at the University of California at Irvine. (b) Since that time a new article on substituent effects has become available: K. W. Bowers in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, p 211.

the unpaired electron (for orbitals with s character) and (ii) the extent of "spin polarization" of the inner shell electrons (for essentially pure p or d orbitals); and (e) the spin density on the nucleus in question. If all other factors remain constant the magnitude of the splitting constant is directly related to the nuclear magnetic moment and inversely related to the spin; for example, for hydrogen atom, $I = 1/2$, $A = 508 \text{ G}$,² and $\mu = 2.793$, and for deuterium atom $I = 1$, $A = 78 \text{ G}$,² and $\mu = 0.857$. Thus $508/78 = (2.793/0.857) \times [1/(1/2)] = 6.51$.

For s orbitals the electron has a finite probability at the nucleus, and thus a direct "contact" between the magnetic moments of the electron and the nucleus is possible. This interaction leads to rather large coupling constants. The electron in a p or d orbital on the other hand has no probability at the nucleus and no hyperfine splitting is expected. Since hyperfine splitting is in fact observed, a polarization mechanism is invoked whereby inner pairs of electrons are made somewhat nonequivalent by the influence of the outer unpaired electron. The extent of this polarization is relatively difficult to calculate. The effect of changing the amount of s character of the orbital containing the unpaired electron is more easily visualized. The methyl radical can be taken as an example.

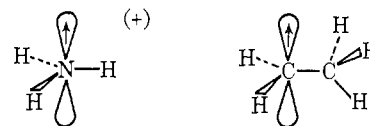


It is generally agreed that the methyl radical is planar with sp^2 hybridization, so that the unpaired electron resides in an essentially pure p orbital. The carbon-13 ($I = 1/2$; $I = 0$ for ^{12}C) hyperfine coupling for methyl radical is 38 G .³ Since it can be calculated that the hyperfine coupling for an electron in a carbon 2s orbital should be 1130 G ,² the value observed reflects either a very small s contribution to the p orbital ($\sim 3\%$) or some spin polarization. The ^{13}C splitting for trifluoromethyl radical, however, is 271 G .³ It can be argued that the orbital containing the unpaired electron has $271/1130 = 24\%$ s character in this radical. This value is close enough to 25% to suggest that the structure of trifluoromethyl radical is tetrahedral.

Finally the splitting constant is obviously related to the spin density on the nucleus in question since in delocalized systems the interaction between the electron and the nucleus must necessarily reflect the "time" spent in the vicinity of the nucleus. Thus the spin density on each carbon atom in cyclopropenyl radical must be one-third of unity.



Hyperfine splitting is also observed from nuclei which are bonded through one or more bonds to atoms bearing the unpaired electron; e.g., the hydrogen hyperfine coupling is 23 G for the methyl radical, 25 G for the ammonium² radical, and 26 G for the methyl group in the ethyl radical. A spin polarization mechanism is again invoked which argues that the unpaired elec-

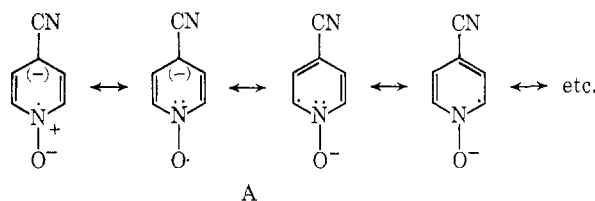


tron in the p orbital "correlates" (Hund's rule) with the electron of the same spin in the σ bond to hydrogen, creating some unpaired electron character in the carbon-hydrogen or nitrogen-hydrogen bond. The methyl splitting in ethyl radical can also be rationalized by a hyperconjugation mechanism.

Although the correct explanation for coupling may be debated it is customary and useful to obtain an empirically derived proportionality constant between the observed hyperfine coupling constant and the spin density on the atom in question. A relationship between the hydrogen hyperfine splitting and the spin density on a sp^2 -hybridized carbon atom was first obtained from the esr spectra of aromatic radical ions of known structure.⁴ A plot of the observed hyperfine splitting vs. the calculated spin density on the carbon atom to which it is attached was found to give a reasonably good straight line fit for a large number of aromatic ionic and neutral radicals. Thus the relationship of eq 1 was predicted, where $A_{\text{C}^{\text{H}}}$ is the coupling

$$A_{\text{C}^{\text{H}}} = Q_{\text{C}^{\text{H}}} \rho_{\text{C}} \quad (1)$$

constant of hydrogen attached to carbon, ρ_{C} is the spin density on carbon, and $Q_{\text{C}^{\text{H}}}$ is the proportionality constant relating the magnitude of the hydrogen coupling constant to the spin density on carbon. Various values of Q have been obtained depending on the system studied: 23 or 24 for hydrocarbon systems, and 27 or 28 for systems containing heteroatoms. In the case of coupling from atoms which are part of a π system contributions from all sources must be taken into account; for example, in the aromatic nitroxide⁵ A, the nitrogen coupling should be proportional to the algebraic sum of all contributions from neighboring



(2) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier Publishing Co., New York, N. Y., 1967.

(3) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965), and references therein.

(4) H. M. McConnell, *ibid.*, **24**, 764 (1956); R. Bersohn, *ibid.*, **24**, 1066 (1956); S. I. Weissman, *ibid.*, **25**, 890 (1956).

(5) E. G. Janzen and J. W. Happ, *J. Phys. Chem.*, **73**, 2335 (1969).

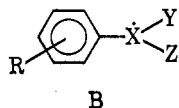
π centers (eq 2). Before an equation of this type can

$$A_N = Q_N^N \rho_N + Q_O^N \rho_O + 2Q_C^N \rho_C \quad (2)$$

be useful for predicting hyperfine splitting parameters, the Q 's need to be evaluated. This is done (or attempted) by varying the conditions which influence the spin distribution in the molecule (*e.g.*, varying the solvent or substituent). The spin densities are calculated from HMO theory and depend on the choice of "heteroatom" coulomb and overlap integral parameters. Finally a search is made for the values of Q which provide the best fit in the above equation. Frequently the values of Q obtained are not precise or unique. However, the availability of even approximate magnitudes of these values can provide much assistance in identifying a radical of unknown structure which might be detected as an intermediate in some reaction of interest.

Substituent Effects on Hyperfine Coupling Constants

The object of this paper is to review and discuss essentially all of the information available in the literature on the substituent effect on the esr hyperfine coupling constant of X in *meta*- and *para*-substituted aryl radicals of type B. The magnitude of the coupling

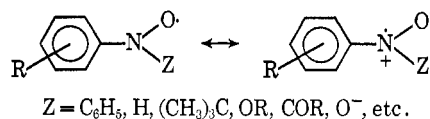


constant of X should reflect the spin density on X primarily, although when Y is also part of the π system, it will be necessary to take the contribution from spin density on Y into account (HMO calculations show spin density on the ring carbon atom adjacent to X is usually small; thus the contribution from this site is ignored).

An associated objective is to evaluate the suitability of Hammett σ constants for correlating esr hyperfine coupling constants and to establish a set of "valid" substituents for the free-radical system under study. It is our contention that the validity of a substituent depends very much on whether the radical is negatively or positively charged or neutral. Thus the following discussion is organized in three parts depending on the nature of the charge on the radical.

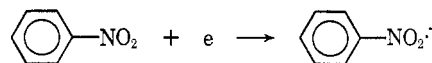
Radical Anions. Although quite a number of stable neutral and charged radicals have been known for some time (*e.g.*, triphenylmethyl, *p*-benzosemiquinone), none was well suited for studies concerning the substituent effect on relevant hyperfine coupling constant because in all cases the atom (or atoms) bearing the major portion of the spin had no nuclear spin ($I = 0$ for ^{12}C and ^{16}O). The synthetic problems of ^{13}C ($I = 1/2$) and ^{17}O ($I = 1/2$) enrichment of suitable sites has retarded growth in this area. In addition the spectra are sometimes difficult to solve (*e.g.*, substituted triphenylmethyl) due to the large number of overlapping lines obtained. Arylnitroxides on the other hand are a

group of radicals which are reasonably stable, easy to



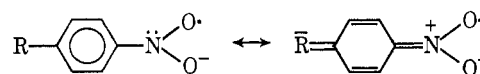
prepare, and give readily understandable esr spectra. Thus quite a few systems of this type have been studied. A special case within the family of nitroxides is nitrobenzene radical anion, where $Z = \text{O}^-$. Enough data are available in the literature at this time to look for some generality in the effect of substituents on a given hyperfine coupling constant in these systems.

The first study of substituent effects on the esr spectra of radicals was reported in 1961 by Maki and Geske.^{6a} Fifteen *para*-substituted nitrobenzene radical anions were obtained in acetonitrile at room temperature. The nitrogen hyperfine splitting constant (N_{hfsc}) decreases with electron-withdrawing groups and in-



creases with electron-donating groups. However Maki and Geske did not attempt to correlate N_{hfsc} 's with Hammett's σ constant. Kolker and Waters^{6b} obtained a series of substituted nitrobenzene radical anions by alkaline aqueous sodium dithionite reductions of the corresponding nitrobenzenes. These workers plotted some of the N_{hfsc} 's *vs.* σ and σ^+ but were more interested in the correlation with the partial rate factor for *para* nitration of substituted benzenes. The N_{hfsc} 's for *para*-substituted *p*-nitrobiphenyl radical anions were shown to follow Hammett's σ constant reasonably well for seven substituents.^{6a} The nitro group does not fit this correlation, however.

If a plot is made of the nitrobenzene radical anion N_{hfsc} *vs.* σ in a given solvent the correlation is poor for those groups which are strongly electron withdrawing by resonance. This observation suggests the use of σ^- . The choice of this substituent constant is reasonable for nitrobenzene radical anion since this molecule fits the category of compounds σ^- was designed for, because charge can be directly delocalized onto the substituent from the nitro group. A plot of



N_{hfsc} *vs.* σ^- does give a better fit. Figure 1 shows the plot which includes a number of *meta* substituents obtained in our laboratory;⁷ $\rho = -0.31$.^{7b}

(6) (a) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961); see also P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963); (b) P. L. Kolker and W. A. Waters, *ibid.*, 1136 (1964); (c) L. S. Degtyarev, L. V. Ganyuk, A. M. Golubenkova, and A. I. Brodskii, *Dokl. Akad. Nauk SSSR*, **157**, 1406 (1964); *Dokl. Chem., Proc. Acad. Sci. USSR (English Transl.)*, **157**, 808 (1964).

(7) (a) Unpublished work of J. L. Gerlock; (b) $N_{\text{hfsc}}/[(N_{\text{hfsc}}/\sigma)] = \rho$; (c) all σ constants used in this paper were taken from J. E. Lefler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963.

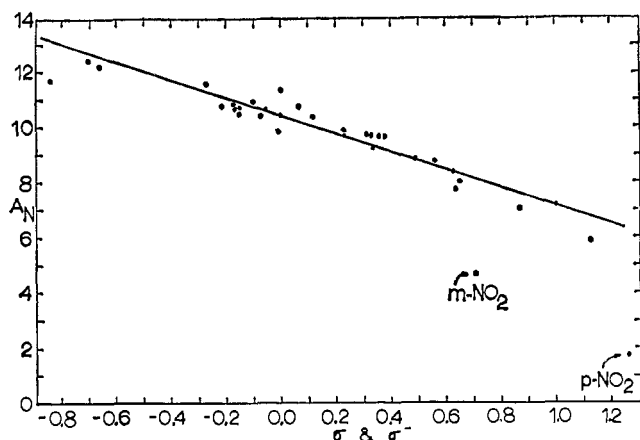


Figure 1. Plot of nitrogen hyperfine coupling constants $\nu\sigma$ and σ^- where applicable for *meta*- and *para*-substituted nitrobenzene radical anions in acetonitrile obtained by electrolytic reduction at room temperature.

It should be noted that the nitro substituent in either the *meta* or the *para* position does not and should not fit this plot. In this case the substituent has gone beyond the bounds of serving as a minor perturbation in the system and in fact *m*- and *p*-dinitrobenzene radical anions should be viewed as unique molecules, not as substituted nitrobenzene radical anions. A logical extension of this interpretation is that when a large fraction of the total spin density is localized on *any* substituent the Hammett relationship will break down. This idea will be formalized in an empirical rule in later discussion.

A discussion of the question of whether the esr hfsc's should be expected to fit the Hammett equation and what the significance of the correlation is, if a fit is obtained, will be reserved until more systems have been described. However at this point it should be clarified that since the hyperfine splitting is directly related to an energy quantity: $h\nu = g\beta(H \pm \delta H)$ where H is the field strength without hyperfine splitting and $2\delta H$ is the hfsc, the Hammett equation can be written in the form

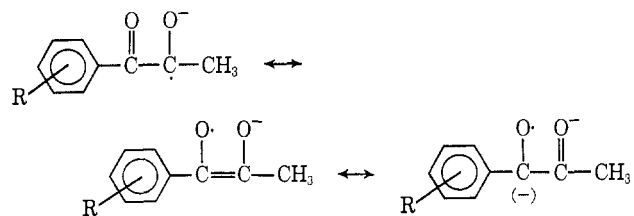
$$N_{\text{hfsc}}/(N_{\text{hfsc}})_0 = \rho\sigma$$

and

$$N_{\text{hfsc}} = \rho'\sigma + \text{constant}$$

The value of ρ is unitless and should reflect the sensitivity of the N_{hfsc} to polar ("substituent") effects in the usual way.

Strom⁸ has discovered another suitable radical-anion system in which substituent effects can be tested. The methyl H_{hfsc} 's for both *meta*- and *para*-substituted phenylpropanesemidiones fit the Hammett equation well when σ^- is used, electron-withdrawing groups decreasing and electron-donating substituents increasing the methyl H_{hfsc} . Since a large N_{hfsc} and no methyl H_{hfsc} could be found in either the *m*- or *p*-



nitro-substituted semidione,^{8b} these radical anions are viewed as substituted nitrobenzene radical anions rather than semidiones.

The Hammett equation asserts that a given substituent exerts the same perturbation on the over-all electron distribution in one system as it does in another. This can be tested for radical anions by plotting the N_{hfsc} in substituted nitrobenzenes $\nu\sigma$ the methyl H_{hfsc} in substituted phenylpropanesemidiones (Figure 2). The good correlation found shows that the substituent effect on the spin distribution in one system parallels that in another system, just as is found in nonradical systems. This observation is a little surprising since the methyl H_{hfsc} is dependent on the spin density of only one atom, the contiguous ketyl carbon, whereas the N_{hfsc} in nitrobenzene radical anion is presumably dependent on both the spin density on the two oxygen atoms and the carbon atom bonded to nitrogen. Rieger and Fraenkel⁹ found $Q_N^N = 99.0 \pm 10.2$ and $Q_O^N = -35.8 \pm 5.9$ (Q_C^N was found to be negligibly small) in

$$A_N = Q_N^N \rho_N + 2Q_O^N \rho_O + Q_C^N \rho_C$$

This means that although the contribution to the nitrogen coupling from spin density on oxygen is sizeable, it apparently does not affect the Hammett correlations. The significance of this observation will be discussed later.

Substituent data on a number of other radical-anion systems are also available in the literature. Seven substituted acetophenone radical anions have been obtained,^{7,10} although only three substituents are valid. Both the *m*- and *p*-nitro derivatives are in fact substituted nitrobenzene radical anions since large N_{hfsc} 's are obtained and the methyl H_{hfsc} is vanishingly small. At least ten substituted benzonitrile radical anions have also been made;¹¹ however no correlation exists between N_{hfsc} and σ . This can be readily rationalized by considering that *m*- and *p*-nitrobenzonitrile radical anions are really *m*- and *p*-cyanonitrobenzene radical anions and *p*-formyl- and *m*- and *p*-acetylbenzonitrile radical anions are really ketyl radicals. The *m*- and

(9) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963); see however W. M. Fox, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc.*, **A**, 448 (1966); J. M. Gross and M. C. R. Symons, *ibid.*, **A**, 451 (1966); W. M. Gulick, Jr., W. E. Geiger, Jr., and D. H. Geske, *J. Am. Chem. Soc.*, **90**, 4218 (1968).

(10) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962); N. Steinberger and G. K. Fraenkel, *ibid.*, **40**, 723 (1964).

(11) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963); P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

(8) (a) E. T. Strom, *J. Am. Chem. Soc.*, **88**, 2065 (1966); (b) private communication.

Table I
Difference in Half-Wave Reduction Potentials^a

R	$\text{C}_6\text{H}_5\text{NO}_2^-$	$\text{C}_6\text{H}_5\text{C}(\text{O}^-)=\text{C}(\text{O}^-)\text{Me}$	$\text{C}_6\text{H}_5\text{C}(\text{O}^-)\text{Me}$	$\text{C}_6\text{H}_5\text{-CN}^-$	$\text{C}_6\text{H}_5\text{CO-C}_6\text{H}_5^-$	$\text{C}_6\text{H}_5\text{-NO}^-$	$\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5^-$	$\text{C}_6\text{H}_5\text{-COCF}_3^-$	$\text{C}_6\text{H}_5\text{-SOMe}^d$	$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}^e$
	-1.15	$\sim -0.7^b$	-1.99	-2.34	-1.72	0.1	-0.72	-1.4 ^c	-2.15	-2.37
	$E_{1/2}$ of System									
	$E_{1/2}$ of System - $E_{1/2}$ of $\text{C}_6\text{H}_5\text{R}$									
NO_2	0.00	0.4	-0.84	-1.19	-0.57	1.0	0.4	-0.25	-1.0	-1.25
CHO^f	0.65	1.1	-0.19	-0.54	0.08	1.7	1.1	0.4	-0.35	-0.60
CH_3CO	0.84	1.3	0.00	-0.35	0.27	1.9	1.3	0.6	-0.15	-0.40
CN	1.19	1.6	0.35	0.00	0.62	2.2	1.6	0.9	0.19	0.0

^a $E_{1/2}$ of system - $E_{1/2}$ of $\text{C}_6\text{H}_5\text{R}$; $E_{1/2}$ measured *vs.* see mainly in aqueous ethanol or dimethylformamide; taken from L. Meites, "Polarographic Techniques," Interscience Publishers, New York, N. Y. 1964, pp 674-711. ^b Estimated from benzil (-0.75 V) and biacetyl (-0.72 V). ^c Value obtained by J. L. Gerlock. ^d Or $\text{C}_6\text{H}_5\text{SO}_3\text{CH}_3$. ^e Or $\text{C}_6\text{H}_5\text{CHCH}_2$. ^f $E_{1/2}$ for benzaldehyde is -1.80 V.

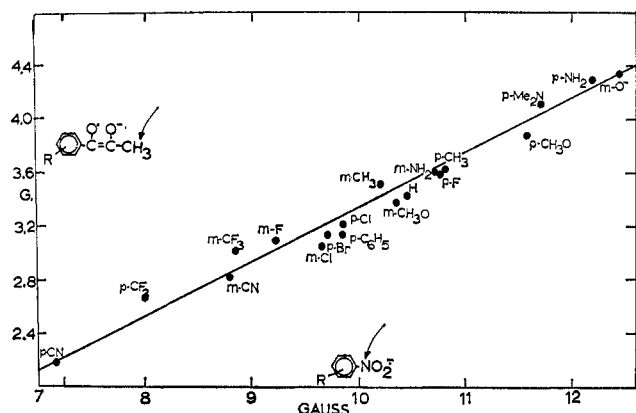


Figure 2. Plot of methyl hydrogen hyperfine coupling constant in substituted phenylpropanesemidiones *vs.* nitrogen hyperfine coupling constant in substituted nitrobenzene radical anions.

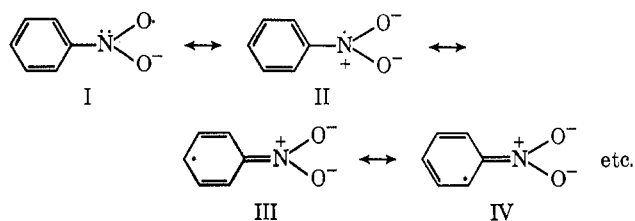
p-cyano groups are also not valid substituents since by symmetry the same spin density must reside on the substituent as on the system site.

A good method whereby the validity of a group as a *bona fide* substituent could be predicted in advance would be useful. A rule of thumb that appears to satisfy this need is that the more easily a group is reduced, the more likely it is to become the system. The difference in reduction potential between the system under consideration and the group when attached to benzene appears to be a measure of the validity of the substituent; thus if $E_{1/2}$ of system - $E_{1/2}$ of $\text{C}_6\text{H}_5\text{R}$ is positive, R will probably be a (Hammett) well-behaved substituent in the given system. Table I illustrates this approach for common electron-withdrawing groups. If the value of the difference is fairly large and positive (greater than 0.5) the group should fit a Hammett plot. If the difference value is small (0.4 or less) or negative the "substituent" will actually be the radical-anion system and Hammett behavior is not expected. In spite of the fact that the reduction potentials are only approximately comparable since the data were not all obtained in the same solvent, it is clear that the procedure correctly predicts the validity of groups as substituents: the nitro group in the phenylpropanesemidiones and acetophenones and

the nitro, acetyl, and formyl groups in the benzonitriles are predicted not to fit the Hammett plot of the system. This method could be made more accurate by obtaining reduction potentials in the same solvent and by taking *meta* or *para* orientation into account.

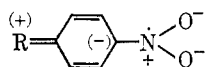
The necessity of considering the validity of a group as a substituent in a given system cannot be over-emphasized. In a recent publication^{1b} a new set of σ values was calculated based on the N_{hfsc} 's obtained for substituted nitrobenzene radical anions in dimethyl sulfoxide, dimethylformamide, and acetonitrile. The values were essentially those which provided the best fit for all substituents including the nitro group. However we have shown that if σ^- is used and the nitro groups ignored (justifiably we think), an adequate fit is obtained (Figure 1). There seems to be no need to develop new σ constants for radical anions if σ^- is used and care is taken to consider the validity of the group as a substituent.

It is noteworthy that in the systems described valid substituents have very little effect on the total delocalization of the unpaired electron into the phenyl ring. While the N_{hfsc} goes from 12 to 7 G in *p*-amino- to *p*-cyanonitrobenzene radical anion, the change in the *ortho* H_{hfsc} is small (~ 0.1 G). The main effect of the substituent is not to delocalize the electron but to exert a polar effect on the spin distribution in the function. Thus a certain contribution from each of the resonance structures, I, II, III, etc., to the nitrobenzene radical anion is expected. Electron-withdrawing substituents



would favor resonance structure I, and thus the N_{hfsc} is smaller in these derivatives than in nitrobenzene radical anion itself since more spin will be located on the oxygen atoms (recall $A_{\text{N}} = 99.0\rho_{\text{N}} - 71.6\rho_{\text{O}}$ for nitro-

benzene radical anions⁹) in the substituted nitrobenzene radicals than in the unsubstituted molecule. The *extra* decreasing effect on the N_{hfsc} by groups which are strongly electron withdrawing by resonance is consistent with this explanation since such groups would favor additional resonance structures where charge is directly delocalized onto the substituent. These structures place more spin on oxygen and lead to smaller N_{hfsc} 's. Similarly it is expected that electron-donating groups should favor resonance structure II since the nitrogen atom is electron deficient in this structure. In this structure more spin resides on the nitrogen atom and thus the N_{hfsc} is expected to be



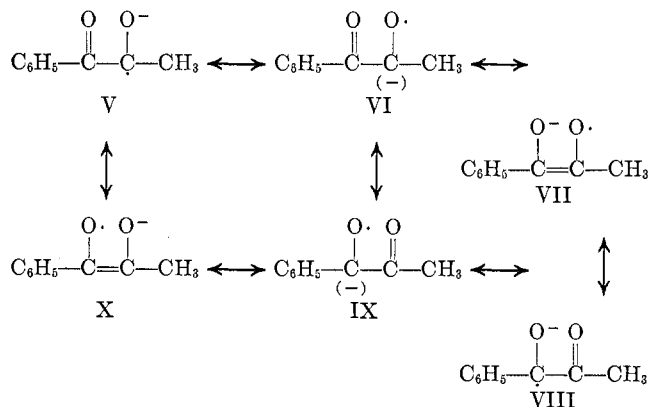
greater in the substituted than in the unsubstituted nitrobenzene radical anion. The substituent effect on the N_{hfsc} can thus be completely rationalized in terms of a polar effect on the electron distribution *on the function* with very little effect on the distribution of the unpaired electron in the aromatic ring. From the latter observation it can be shown that the *spin density on nitrogen* also obeys the Hammett equation. Thus from an application of the McConnell equation⁴ to the observed ring proton hyperfine coupling constants it can be estimated that the total spin density in the ring is approximately 0.4. The spin density on the nitro function is thus $0.6 = \rho_N + 2\rho_O$ where ρ_N and $\rho_O =$ the spin densities on nitrogen and oxygen, respectively. Combining eq 2 and the Hammett equation

$$Q_N^N \rho_N + 2Q_O^N \rho_O = \rho' \sigma$$

(unfortunately ρ is used both for the slope in the Hammett equation and for spin density). After substituting

$$\begin{aligned} \rho_O &= (0.6 - \rho_N)/2 \\ \rho_N(Q_N^N - Q_O^N) + 0.6Q_O^N &= \rho' \sigma \\ \rho_N &= 1/(Q_N^N - Q_O^N)[\rho' \sigma - 0.6Q_O^N] \\ \rho_N &= \rho'' \sigma + \text{constant} \end{aligned}$$

In the phenylpropanesemidiones, electron-withdrawing substituents would favor structures IX and X.

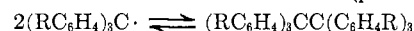


Since σ^- gives a better fit for the data it is clear that IX and X make important contributions to the over-all spin distribution in the radical. The substituent effect

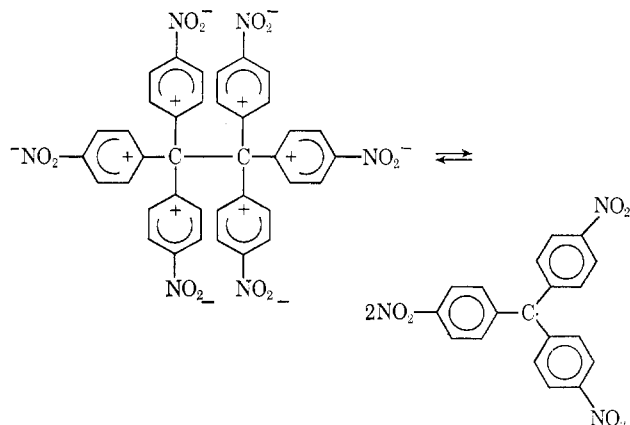
on the contributions from the other resonance structures is not particularly clear, but since the slope of the Hammett plot of methyl H_{hfsc} vs. σ is negative, apparently V is favored by electron-donating groups.

The factors influencing the *stability* of radical anions as a function of substituent have not been studied systematically. From general observations it is clear that electron-withdrawing substituents usually increase the stability of radical anions inasmuch as the rates of formation of the radical anions are increased and rates of decay are decreased. Even the modes of decay have not been studied. Presumably these include disproportionation, protonation, and dimerization. The stabilizing effect of the electron-withdrawing group on radical anions is probably a polar effect and may have little to do with the extent of delocalization of the unpaired electron as such. More attention to this area is clearly needed.

Neutral Radicals. Many of our ideas concerning substituent effects in free radicals probably come from early studies of the triarylmethyl-hexaarylethane equilibrium. It is well known that tris(*p*-nitrophenyl)-



methyl radical is more stable than trityl radical. However trityl radicals are apparently also stabilized by electron-donating substituents. This work needs re-investigation since recent studies indicate that trityl radical in fact dimerizes to some extent in the *para* position,¹² a route not as readily available to *para*-substituted derivatives. Nonetheless the extent of delocalization of the unpaired electron in trityl radicals as a function of substituent is very small. Thus the *ortho* H_{hfsc} is 2.50, 2.53, and 2.89 G in tris(*p*-nitrophenyl)methyl, triphenylmethyl, and tris(*p*-methoxyphenyl)methyl radical, respectively.¹³ This change in spin density distribution in the phenyl ring would seem to be much too small to account for the large difference in stability of these radicals. An alternate explanation involves an electrostatic repulsive interaction between the rings in the dimer to account for the stability of radicals such as the trisnitro radical^{14a}



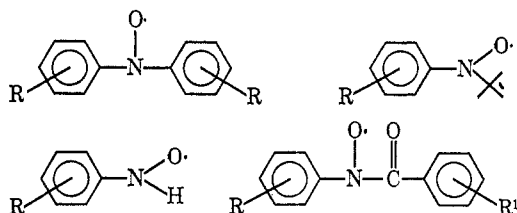
(12) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Letters*, 249 (1968).

(13) J. Sinclair and D. Kivelson, *J. Am. Chem. Soc.*, **90**, 5074 (1968).

(14) (a) See also E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 155; (b) C. M. Himel, private communication.

One would expect that if trityl radicals with different substituents were mixed in the same solution, the radical concentration should diminish or vanish. Such observations have in fact been made.^{14b}

Numerous studies of substituent effects on the esr spectra of nitroxides have been reported. The N_{hfsc} 's in diphenyl-,¹⁵ *t*-butylphenyl-,¹⁶ *t*-alkenylphenyl-,¹⁷ phenylhydro-,¹⁸ and phenylbenzoylnitroxides¹⁹ can all



be correlated by σ in the Hammett equation. Plots are given in the first three references. We find correlations are considerably improved by using σ^- . A plot of the N_{hfsc} and H_{hfsc} in substituted phenylhydro-nitroxides vs. σ and σ^- is shown in Figure 3. The slopes of the two lines are the same. This observation has some very important implications. Since the H_{hfsc} depends *only* on the spin density on nitrogen, the spin density on nitrogen must also follow the Hammett equation. The N_{hfsc} on the other hand is also correlated by the Hammett equation. When the same σ values are used, the same slope, or sensitivity to "polar" substituent effect, is obtained. This means that a correlation between the *nitrogen hfsc* and σ is a correlation between the *spin density on nitrogen* and σ for substituted phenylnitroxides. This constitutes an independent proof of our earlier development of this point using nitrobenzene radical-anion data. We believe this relationship to be general for all nitroxides and nitrobenzene radical anions.²⁰

It is clear that the nitroxide function is sensitive to the polar effect of substituents in much the same way as the nitro anion function is. The nitroxide bond is a three- π -electron two-atom function wherein resonance structure XI is favored when the substituent is electron withdrawing, which causes a decrease in the N_{hfsc} , and XII is favored when the substituent is electron donating, which causes an increase in the N_{hfsc} . The same

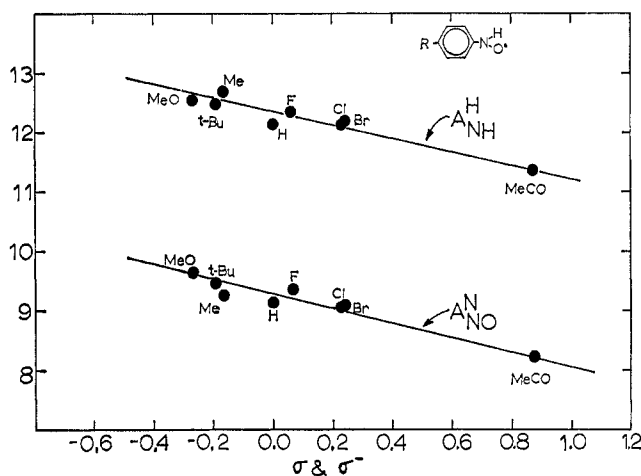


Figure 3. Plots of the nitrogen and hydrogen coupling constants in *para*-substituted phenylhydro-nitroxides vs. σ and σ^- (where applicable).

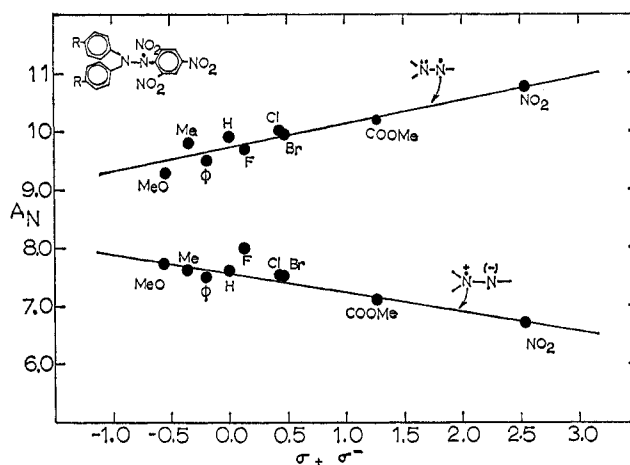
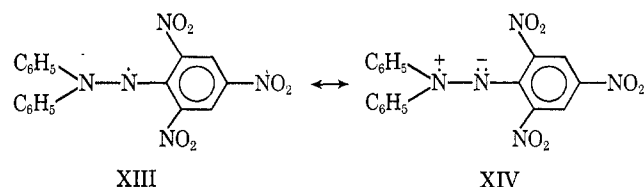


Figure 4. Plots of the nitrogen hyperfine coupling constants in *para*-substituted diphenylpicrylhydrazyls vs. σ and σ^- (where applicable).

interpretation accommodates the substituent effect in substituted diphenylpicrylhydrazyls (XIII and XIV).



A plot of these data²¹ is shown in Figure 4. It should be pointed out that, as in the case of the substituted radical anions, very little change in spin density distribution in the phenyl ring of phenylnitroxides is observed as a function of substituent.

The substituent effect on the N_{hfsc} in nitroxides in general is smaller than in nitrobenzene radical anions. In phenylbenzoylnitroxides the effect is even smaller whether groups are substituted in the A or B ring.¹⁹

(21) M. M. Chen, K. V. Sane, R. I. Walter, and J. A. Weil, *J. Phys. Chem.*, **65**, 713 (1961); R. I. Walter, *J. Am. Chem. Soc.*, **88**, 1923 (1966).

(15) E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, **32**, 3853 (1967).

(16) H. Lemaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. France*, 372 (1965).

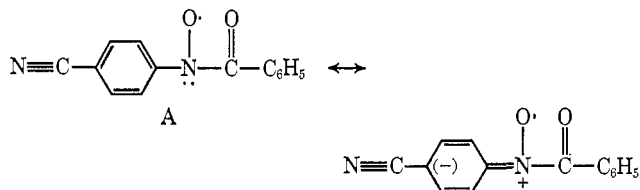
(17) A. B. Sullivan, *J. Org. Chem.*, **31**, 2811 (1966).

(18) T. A. J. W. Wajer, A. Mackor, T. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 1941 (1967).

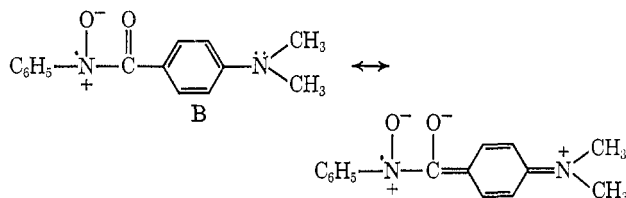
(19) E. G. Janzen, O. W. Maender, and J. L. Gerlock, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. S73; O. W. Maender, "An Electron Spin Resonance Study of Substituted α -Ketonitroxides and Related Systems," Thesis, University of Georgia, Athens, Ga., 1969.

(20) See, however, ref 15.

The slopes for the plot of $N_{\text{hfsc}}/(N_{\text{hfsc}})_0$ vs. σ are 0.0024 and 0.012 for *meta* and *para* substituents in the A and B rings, respectively. The best fit is obtained when σ^- is used in the A ring and σ^+ in the B ring. This indicates that electron-pair delocalization is significant when the substituent in the A ring is strongly electron withdrawing by resonance



or when the substituent in the B ring is strongly electron donating by resonance



If we conclude from the body of data cited that the N_{hfsc} depends on the magnitude of the spin density on nitrogen, the constancy of the N_{hfsc} as a function of substituent in this radical shows that the spin (and charge) density on the nitrogen atom remains constant. Since no changes in the H_{hfsc} 's in the phenyl ring are observed, the spin distribution here also must remain constant as a function of substituent. Although it is not possible to monitor the spin density on the oxygen or carbon atoms it is probably safe to say that the spin density throughout the radical remained essentially constant as a function of *meta* or *para* substituent in the A or B ring. It was interesting to find, however, that the stability of the radical is strongly effected by substituent, electron-withdrawing groups destabilizing the radical. Plots of the N_{hfsc} and rates of decay as a function of σ are shown in Figure 5 for ring A and in Figure 6 for ring B. Clearly the substituent effect on the rate of decay is greater than the substituent effect on the spin density on the nitrogen atom of the radical *in the ground state*. If we permit ourselves to equate the lack of change in spin distribution in the radical as a function of substituent with an essentially fixed energy of the ground state,²² we can conclude that the substituent exerts its effect solely on the transition state of the decay reaction. Since the plot of the rates of decay as a function of substituent fits σ^- better than σ^+ , the nitrogen electron pair probably is not delocalized into the phenyl ring in the transition state. However the nitrogen atom must be more negatively charged

(22) The assertion that the relatively small change in spin density distribution in the radical is an indication of a fixed ground-state energy assumes that the sensitivity of the energy of ground state to changes in spin density distribution is small.

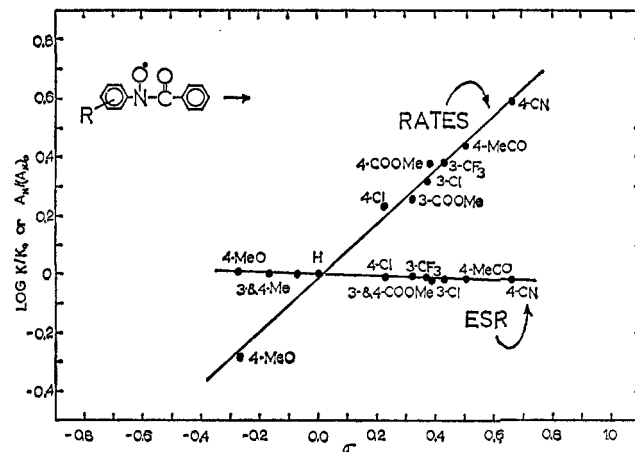


Figure 5. Plots of the nitrogen hyperfine coupling constants and initial rates of decay (log ratio of first-order rate constants) vs. σ and σ^- (where applicable) for *meta*- and *para*-substituted phenylbenzoylnitroxides.

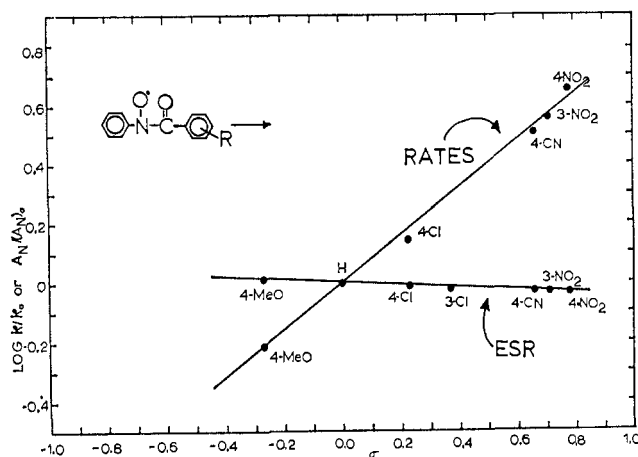
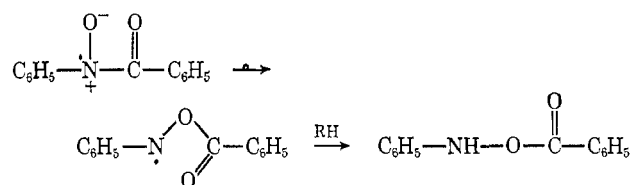


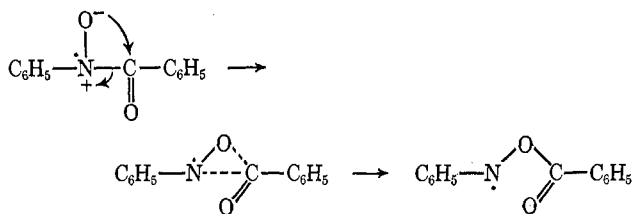
Figure 6. Plots of the nitrogen hyperfine coupling constants and initial rates of decay (log ratio of first-order rate constants) vs. σ and σ^+ (where applicable) for *meta*- and *para*-substituted phenylbenzoylnitroxides.

in the transition state than in the ground state since electron-withdrawing groups facilitate decomposition. The mode of decomposition is thought to be a rearrangement to an unstable nitrogen radical which abstracts hydrogen to give O-benzoylphenylhydroxylamine



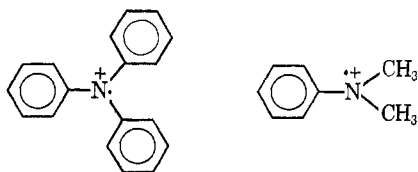
The transition state visualized is one where the nitrogen atom is gaining charge and the oxygen is acting as a nucleophile in bond formation with the benzoyl group.

This picture also accommodates the positive slope for rates of decay as a function of substituent in the B ring.



Further work is necessary to establish the route of the decay reaction. However, regardless of the detailed nature of the decay mechanism, the point of interest here is that the esr spectra give a detailed picture of the substituent effect on the spin distribution in the ground state whereas the rates of decay reflect the substituent effect on the difference between the ground state and transition state. The availability of substituent effect data on both the spin distribution and rate of reaction from electron spin resonance appears to provide a new approach in studying substituent effects on the nature of the ground and transition states in free-radical reactions.

Radical Cations. Substituent effects on two radical-cation systems have been studied: triarylammonium^{21,23} and *N,N*-dimethylanilinium salts.²⁴ The very complex spectra obtained from triarylammonium radical cations precludes ready interpretation of the esr spectra beyond the N_{hfsc} . From analyses of spectra obtained in formic acid^{21,23} Walter concluded that both electron-withdrawing and electron-donating substituents decrease the N_{hfsc} although the scatter in the data does not make such a conclusion obvious. Latta and Taft²⁴ (footnote 27) cite N_{hfsc} 's for five substituted triarylammonium radicals obtained in acetonitrile which show a trend which is consistent with a Hammett relationship, electron-donating groups decreasing the N_{hfsc} and electron-withdrawing groups increasing the N_{hfsc} . A plot of these data also shows serious scatter. Clearly data for more substituents are needed to understand this system.



The study of substituent effects on the esr spectra of *N,N*-dimethylanilinium radical cation ($\text{DMA}\cdot^+$) has provided the first system wherein a significant change in spin distribution in the aromatic portion of the radical as a function of substituent has been observed.²⁴ If the *m*- and *p*-dimethylamino groups are omitted

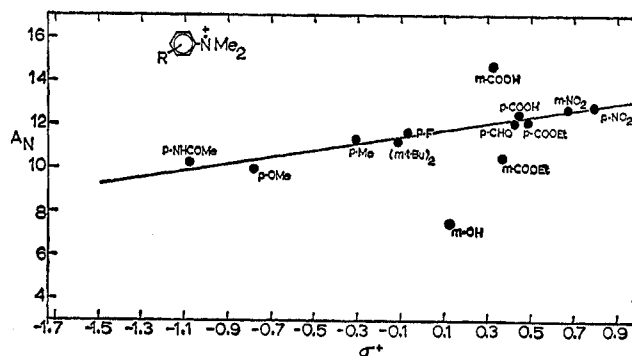
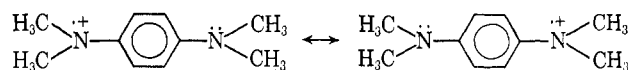


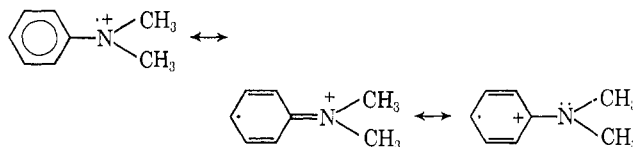
Figure 7. Plot of the nitrogen hyperfine coupling constant in *N,N*-dimethylanilinium radical cation vs. σ and σ^+ (where applicable).

from consideration, because these cannot be valid (Hammett) substituents in the $\text{DMA}\cdot^+$ system (probably the *m*- and *p*-amino groups should also be excluded), the *ortho* H_{hfsc} changes from 4.25 G in *p*-



$\text{CH}_3\text{ODMA}\cdot^+$ to 5.86 G in *p*- $\text{NO}_2\text{DMA}\cdot^+$. A plot of the N_{hfsc} vs. σ and σ^+ gives a reasonable correlation (Figure 7). Note that this interpretation differs substantially from that proposed by Latta and Taft. Based mainly on the unusually large effect of the *m*-amino and *m*-dimethylamino groups on the N_{hfsc} new σ values for *meta* donor substituents were given by these workers for radical-cation systems.

The considerably larger substituent effect on the spin density distribution in the $\text{DMA}\cdot^+$ system than in the previously described two-atom three- π -electron systems appears to be due to the fact that the spin density on nitrogen can only be changed by addition to or removal of spin from the phenyl ring.



In summary, this paper presents evidence for an over-all Hammett behavior of certain hfsc's obtained from the esr spectra of substituted stable free radicals if substituents carrying a large fraction of the spin density are omitted. The use of σ^- and σ^+ is demonstrated. The reasons why small deviations are observed for some valid substituents are not considered in this general treatment. Our main point is that the Hammett substituent constants available today accommodate esr data.

This is not the first consideration of this topic.^{1b,15,21} Walter²¹ has classified a large number of free-radical systems under a Hammett behaving class (class O, for opposite substituent effect) and a Hammett non-

(23) L. Hagopian, G. Köhler, and R. I. Walter, *J. Phys. Chem.*, **71**, 2290 (1967); R. I. Walter, *J. Am. Chem. Soc.*, **77**, 5999 (1955).

(24) B. M. Latta and R. W. Taft, *ibid.*, **89**, 5172 (1967); see also W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 6010 (1964).

behaving class (class S, for same substituent effect). We agree essentially with his treatment of class O. However in our opinion the esr data available at this time (dimerization of triarylmethyl radicals and esr of triarylammonium radicals) are not sufficient to warrant creating a special class of radicals (class S). More recent work shows that the dimerization data of substituted trityl radicals needs reinvestigation.¹² In any event the substituent effect on the spin delocalization into the phenyl rings (as judged by the magnitude of the *ortho* hfsc's) obeys the Hammett equation.¹³ The considerable scatter observed in the plot of the N_{hfsc} 's for the triarylammonium radicals^{21,23,24} does not in our opinion permit this system to be tested. The dimethylanilinium radical-cation system²⁵ is a Hammett-behaving system. Admittedly substituent effects on more radicals are known today. However

it should be pointed out that substituent effects on the hfsc's of a system (*i.e.*, substituent effects on spin distribution) need not parallel the substituent effect on other properties of the radical, *e.g.*, stability, since the substituent effect on the starting state and final state (or transition state) must be taken into account for the latter. Studies attempting to relate the substituent effect on the spin distribution in a radical with the substituent effect on its chemistry will hopefully provide answers to some of these interesting questions.

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