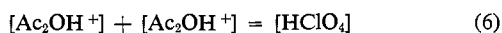


observed exchange rate for low $[\text{Ac}_2\text{O}]$ and high $[\text{AcOH}]$ (Figure 3).

One now has to consider the possibility that the rate constants are such that the exchange is not determined by the most abundant ion. It can be seen from the kinetic equations that reaction IV cannot be important (*i.e.*, rate determining) unless the abundant ion is Ac^+ . This reaction can thus be ruled out. We can then restrict ourselves to the consideration of the two ionic species AcOH_2^+ and Ac_2OH^+ .

Considering the equilibrium between AcOH_2^+ and Ac_2OH^+ due to proton transfer and neglecting the concentration of Ac^+ one finds eq. 6 and 7, where K is an equilibrium constant.



and

$$K = \frac{[\text{Ac}_2\text{OH}^+][\text{AcOH}]}{[\text{AcOH}_2^+][\text{Ac}_2\text{O}]} \quad (7)$$

If we assume that K does not change with composition, the rate of exchange for mechanisms I-III is then given by eq. 8-10.

$$\frac{1}{[\text{HClO}_4]} \frac{d[\text{AcOH}]}{dt} = k_{\text{I}} \frac{[\text{Ac}_2\text{O}][\text{AcOH}]}{[\text{AcOH}] + K[\text{Ac}_2\text{O}]} \quad (8)$$

$$\frac{1}{[\text{HClO}_4]} \frac{d[\text{AcOH}]}{dt} = k_{\text{II}} \frac{K[\text{Ac}_2\text{O}][\text{AcOH}]}{[\text{AcOH}] + K[\text{Ac}_2\text{O}]} \quad (9)$$

$$\frac{1}{[\text{HClO}_4]} \frac{d[\text{AcOH}]}{dt} = k_{\text{III}} \frac{K[\text{Ac}_2\text{O}]}{[\text{AcOH}] + K[\text{Ac}_2\text{O}]} \quad (10)$$

Equations 8 and 9 show that reactions I and II differ only by a constant K and are therefore kinetically indistinguishable.

As discussed earlier, the observed exchange rate is linear in $[\text{Ac}_2\text{O}]$ and independent of $[\text{AcOH}]$ for relatively high $[\text{AcOH}]$ and low $[\text{Ac}_2\text{O}]$. This can be fitted both by eq. 8 (mechanism I) and 9 (mechanism II) if $K \ll 1$, so that $[\text{AcOH}] \gg K[\text{Ac}_2\text{O}]$.

If mechanism II is important we require $Kk_{\text{II}} \approx 560 \text{ sec.}^{-1} M^{-1}$, as is immediately obvious from our previously quoted value of k_{I} and a comparison of eq. 8 and 9. Since $K \ll 1$ this requires a very large rate constant k_{II} which does not seem reasonable for a reaction of this type.

According to mechanism III the rate of exchange should be proportional to acetic anhydride concentration and to the reciprocal of acetic acid concentration. This seems to agree qualitatively with the results at low acetic acid and high acetic anhydride concentration. However, attempts to fit numerically the rates calculated according to mechanism III with the experimental results failed.

Acknowledgment. This work was started in collaboration with Professor S. Meiboom. We would like to express our gratitude for his large contribution to this work and for important comments on the manuscript. We also wish to thank Dr. D. Gill and M. Sasson who designed and built the bridge for measuring dielectric constants and to Professor E. Grünwald for helpful discussion.

Electron Paramagnetic Resonance Spectra of Semiquinones. II. Coupling Constants of β -Nuclei¹

Leon M. Stock and Joseph Suzuki

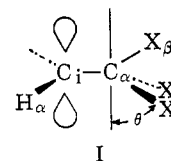
Contribution from the George Herbert Jones Laboratory, University of Chicago, Chicago, Illinois 60637. Received March 15, 1965

The electron paramagnetic resonance spectra of 2-*t*-butyl-, 2-*t*-butyl- C^{13} -, and 2-trifluoromethylsemiquinone and the semiquinones prepared from 1-methyl-2,5-dihydroxy- and 2,5-dihydroxytritycene were obtained. Coupling constants for $\beta\text{-C}^{13}$ and $\beta\text{-F}$ are 0.74 and 2.66 gauss, respectively. The bridgehead hydrogen atoms of the triptycene derivatives are not coupled. The results are discussed with reference to the conclusions of reaction chemistry concerning the relative importance of C-H, C-C, and C-F hyperconjugation.

Introduction

Electron paramagnetic resonance spectra offer a method for the determination of spin density at the nuclei of complex free radicals.^{2,3} In brief, radicals

of structure I ($X = \text{H}$) have large spin density at the nonbonded atom. Early theoretical treatments stressed



the significance of C-H hyperconjugation.^{4,5} McLachlan suggested spin polarization as an alternative.⁶ Strauss and Fraenkel subsequently found that the spin-polarization model overestimated the spin density at the α -carbon atom.⁷ Other work revealed that the spin density at nonbonded hydrogen atoms is greater for positive-ion radicals than for negative-ion radi-

(1) This research was supported in part by the National Science Foundation and in part by the Petroleum Research Fund of the American Chemical Society.

(2) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 183 (1963).

(3) A. Carrington, *Quart. Rev. (London)*, **17**, 67 (1963).

(4) R. Bersohn, *J. Chem. Phys.*, **24**, 1066 (1956).

(5) D. B. Chestnut, *ibid.*, **29**, 43 (1958).

(6) A. D. McLachlan, *Mol. Phys.*, **1**, 234 (1958).

(7) H. L. Strauss and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1768 (1961).

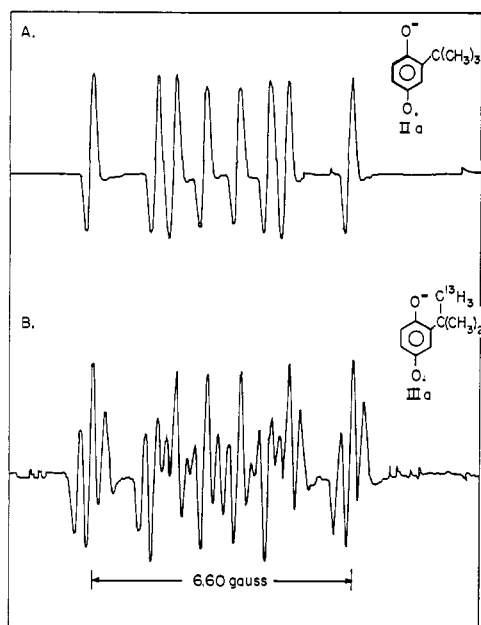


Figure 1. The e.p.r. spectra of 2-*t*-butylsemiquinone (IIa) and its C^{13} derivative (IIIa).

calcs.^{8,9} These investigations have led to the conclusion that the hyperconjugation model offers the most reasonable interpretation.^{2, 3, 8-10}

McLachlan⁶ and Symons¹¹ suggested that the magnitude of the coupling constants for β -hydrogen atoms, $a_{\beta-H}$, depended on $\cos^2 \theta$ (I). Study of the spectra of radiation-damaged, oriented, single crystals of succinic acid confirmed the idea.^{12, 13} Equation 1 accommodates the results with ρ , the spin density at C_i , θ , the dihedral angle, B_0 taken as zero,¹⁴ and B about 45

$$a_{\beta-H} = (B_0 + B \cos^2 \theta)\rho \quad (1)$$

gauss,¹⁴ variable in certain bonding situations¹⁵ and positive.¹⁴⁻¹⁶

Whether e.p.r. observations should be used as a model for the interpretation of chemical reactivity is questionable. Streitwieser points out that spin density at the β -atom is not necessarily indicative of a stabilization influence.¹⁷ Lucken and Dewar comment that the conclusions reached by the study of one-electron properties are not readily transferable to the area of chemical reaction phenomena because the extension of the localized bond model to ion radicals may be unreliable.^{18, 19} Thus, while there is quite

(8) J. A. Brivati, R. Hulme, and M. C. R. Symons, *Proc. Chem. Soc.*, 384 (1961).

(9) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, 5, 31 (1962).

(10) J. P. Colpa and E. de Boer, *ibid.*, 7, 333 (1964).

(11) M. C. R. Symons, *J. Chem. Soc.*, 277 (1959).

(12) C. Heller and H. M. McConnell, *J. Chem. Phys.*, 32, 1535 (1960).

(13) D. Pooley and D. H. Whiffen, *Mol. Phys.*, 4, 81 (1961).

(14) There is some uncertainty about the value of B_0 . The problem is discussed by E. Stone and A. H. Maki, *J. Chem. Phys.*, 37, 1326 (1963).

(15) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, 84, 4100 (1962).

(16) (a) J. R. Morton and A. Horsfield, *J. Chem. Phys.*, 35, 1142 (1961); (b) C. Heller, *ibid.*, 36, 175 (1962).

(17) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 158, 159.

(18) (a) M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962, pp. 86-101; (b) M. J. S. Dewar, *Tetrahedron*, 19, 89 (1963).

uniform agreement concerning the interpretation of magnetic resonance data in terms of hyperconjugation, the extension of the idea to reaction chemistry remains a matter of concern.

As an empirical approach to this problem, it appeared desirable to search for a relationship, if any, between the findings of reaction chemistry and e.p.r. spectroscopy for three nuclei—hydrogen,^{20a} carbon,²⁰ and fluorine²¹—for which hyperconjugative interactions have been proposed. The existence of spin density at β -F²² and β -C²³ is established and the relevance of the results to the concept of hyperconjugation has been discussed.²⁴ However, data for a closely related series of compounds which would permit a comparison of the relative importance of the transfer of spin density to β -nuclei are not available. Accordingly, we have examined the e.p.r. spectra of 2-substituted semiquinones.²⁵ It was apparent that the e.p.r. hyperfine spectrum of a radical akin to 2-chloro-2-methyldibenzobicyclo[2.2.2]octadiene would be valuable to contrast the stereochemical dependence of kinetic isotope effects in solvolysis²⁶ with the results for magnetic resonance. The semiquinones of 1-methyl-2,5-dihydroxy- and 2,5-dihydroxytryptcene were selected for study of this question.

Results

Preparation of Hydroquinones. Unlabeled 2-*t*-butylhydroquinone (II) was available. 2-*t*-Butyl- β -C¹⁸-hydroquinone (III) was prepared by the alkylation of hydroquinone with *t*-butyl alcohol- β -C¹⁸ obtained from the Grignard reaction of methyl iodide- C^{13} (48.1% C^{13}) with acetone. Trifluoromethylhydroquinone (IV), 2,5-dihydroxytryptcene (V), 1-methyl-2,5-dihydroxytryptcene (VI), and the Diels-Alder adduct of benzoquinone with anthracene (VII) were prepared by conventional methods. The compounds were purified by chromatography on silicic acid or by recrystallization.

Spectra. The semiquinones were formed by air oxidation of the hydroquinones in acetonitrile in the presence of added base. Sodium hydroxide, tetramethylammonium hydroxide, and sodium hydride provided identical spectra within an uncertainty of ± 0.03 gauss.

(19) (a) A. Fairbourn and E. A. C. Lucken, *J. Chem. Soc.*, 258 (1963); (b) E. A. C. Lucken, *Tetrahedron*, 19, 93 (1963).

(20) (a) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, 63, 41 (1941); (b) E. Berliner and F. J. Bondhus, *ibid.*, 70, 854 (1948); (c) P. D. Bartlett, *J. Chem. Educ.*, 30, 22 (1953); (d) C. A. Vernon, *J. Chem. Soc.*, 423 (1954); (e) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, 79, 1897 (1957); (f) R. W. Taft and I. C. Lewis, *Tetrahedron*, 5, 210 (1959).

(21) (a) W. F. Hammer and F. A. Matsen, *J. Am. Chem. Soc.*, 70, 2482 (1948); (b) J. D. Roberts, R. L. Webb, and E. A. McElhill, *ibid.*, 72, 408 (1950); (c) J. Hine, *ibid.*, 85, 3239 (1963).

(22) (a) H. N. Rexrod and W. Gordy, *J. Chem. Phys.*, 30, 599 (1959); (b) D. R. Eaton, A. D. Josey, and W. A. Sheppard, *J. Am. Chem. Soc.*, 85, 2689 (1963); (c) M. T. Rogers and D. H. Whiffen, *J. Chem. Phys.*, 40, 2662 (1964).

(23) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, 82, 4424 (1960).

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(25) Preliminary reports: L. M. Stock and J. Suzuki, *Proc. Chem. Soc.*, 212 (1962); L. M. Stock and J. Suzuki, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963, p. 81Q.

(26) (a) A. Streitwieser, R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, 80, 2326 (1958); (b) V. J. Shiner, *ibid.*, 82, 2655 (1960); (c) V. J. Shiner, B. L. Murr, and G. Heinemann, *ibid.*, 85, 2413 (1963); (d) V. J. Shiner and J. S. Humphrey, *ibid.*, 85, 2416 (1963).

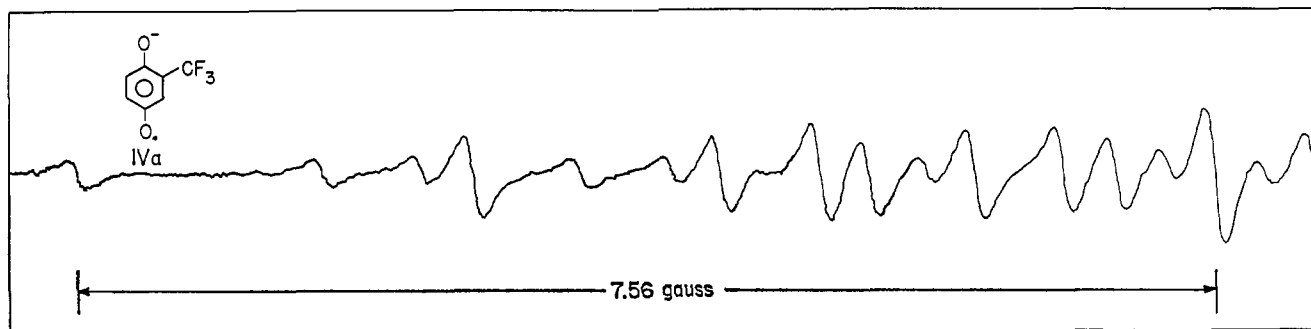


Figure 2. The e.p.r. spectrum of 2-trifluoromethylsemiquinone (IVa). Only one-half of the spectrum is shown.

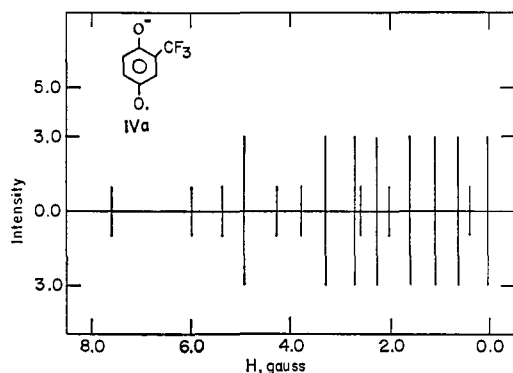


Figure 3. A synthetic e.p.r. spectrum of 2-trifluoromethylsemiquinone (IVa) based on the experimental coupling constants. Only one-half of the spectrum is shown.

The spectra of 2-*t*-butylsemiquinone (IIa) and 2-*t*-butyl- β -C¹³-semiquinone (IIIa) are shown in Figure 1.

A fully resolved eight-line spectrum (Figure 1A) was obtained with the unlabeled material. The coupling constants for the three nonequivalent ring hydrogen atoms are 2.85, 2.10, and 1.65 gauss. The isotopically enriched sample containing 52% IIa and 48% IIIa is more complex (Figure 1B). Each line of IIa is flanked by two lines of approximately one-half intensity. The satellite lines are particularly evident in the fully resolved wings and indicate $a_{\beta\text{-C}^{13}}$ is 0.74 gauss.

An incompletely resolved spectrum of 29 (32 possible) lines was observed for 2-trifluoromethylsemiquinone (IVa), Figure 2.

The coupling constants are $a_{\beta\text{-F}} = 2.66$ and 3.37, 2.19, and 1.62 gauss for the three aryl hydrogens. A synthetic spectrum based on these values is shown in Figure 3. Good agreement (± 0.02 gauss) is found. However, the intense center line (Figure 2) is anomalous. This line apparently results from the overlap of the two lines displaced by only ± 0.07 gauss from the center of the synthetic spectrum (Figure 3).

The spectra (Figure 4) of semiquinones prepared from 2,5-dihydroxytryptene (V) and 1-methyl-2,5-dihydroxytryptene (VI) indicate the coupling constants

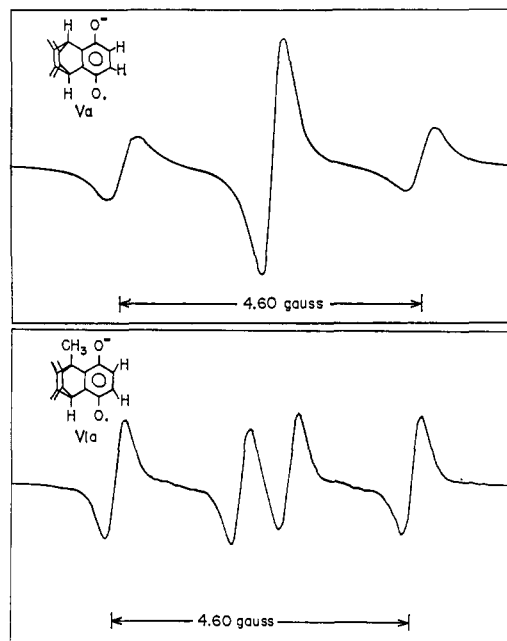
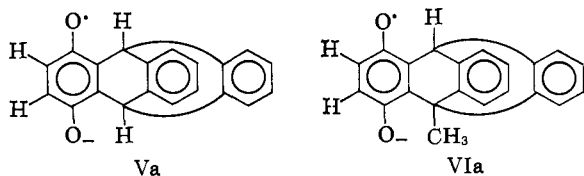


Figure 4. The e.p.r. spectra of triptycene semiquinones Va and VIa.

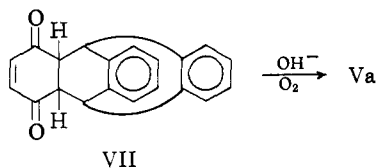
are 2.31 (Va) and 2.62 and 1.98 gauss (VIa), respectively, indicative of coupling with only the aryl hydrogen atoms. Second derivative spectra also failed to reveal further hyperfine splitting by the bridgehead hydrogen atoms. The line widths and the knowledge that signals separated by 0.25 gauss are resolved by our equipment indicate the coupling constants for the bridgehead hydrogen atoms are certainly < 0.3 and probably < 0.2 gauss.

These results are somewhat at variance with another report of the spectrum of Va.²⁷ Chiu found that the treatment of V with excess base yielded Va, as evident by the triplet spectrum. However, a more complex spectrum was observed with small quantities of base. Chiu interpreted his observation to mean that the bridgehead hydrogen atoms were coupled. This analysis of the complex spectrum is not satisfactory because the line positions and intensities are incompatible with a further hyperfine splitting by the bridgehead nuclei.

In view of these conflicting results, it was desirable to verify the assignment of the simple triplet spectrum to Va. Spectra of solutions of V with variable amounts

(27) T. Chiu, *K'o Hsueh T'ung Pao*, 574 (1960).

of base were recorded. The triplet resonance was observed in each sample. These results suggested an impurity in Chiu's sample was responsible for the complex spectrum. This notion was confirmed by study of the spectra of the products of the reaction of VII with base. In principle VII may be converted to Va. In fact, the complete conversion is accomplished only when the base/VII mole ratio is greater than 6.



Complex spectra as reported by Chiu²⁷ were recorded for lower base/VII ratios. Variation of the base/VII ratio did not change the line positions, but the relative intensities varied appreciably, permitting the identification of the triplet resonance of Va and the doublet resonance (± 1.10 gauss) of a second radical.²⁸ The doublet resonance is compatible with the presence of a 3-substituted 2,5-dihydroxytritycene semiquinone in solution. Nucleophilic (or free radical) substitution of VII and oxidation to a semiquinone is not unlikely under the conditions of these experiments. That VII was the precursor of the new radical was confirmed by the addition of VII to a solution of V and base (each 0.01 M). The original triplet resonance of Va was replaced by a composite spectrum of Va and the ± 1.10 gauss doublet. These experiments secure the assignment of the triplet resonance to Va.

Discussion

The isotropic spectra of Va and VIa reveal the bridgehead hydrogen atoms are not coupled. The hydrogen atoms of the methyl group in 2-methylsemiquinone exhibit $a_{\beta-H} = 1.8$ gauss.²⁹ The large decrease in $a_{\beta-H}$ for the triptycene derivatives may be confidently ascribed to the fact that the hydrogen atoms are constrained to the nodal plane of the orbital containing the unpaired spin.

The large influence of the bridgehead methyl substituent on the coupling constants ($a_{\alpha-H} = 2.62$ and $a_{\alpha-H} = 1.98$ gauss) of the aryl hydrogen atoms of VIa is unexpected. The acidity of 4-methylbicyclo[2.2.2]octane-1-carboxylic acid indicates the polar effect of the methyl group bonded to sp^3 carbon to be negligibly different from that of hydrogen.³⁰ The significant change in $a_{\alpha-H}$ resulting from the methyl substituent is reasonably ascribed to a steric interaction of the methyl group with the nearby oxygen. Both steric desolvation and steric compression interactions would decrease the negative charge density on oxygen and alter the distribution of spin density. The latter idea has been advanced to account for the failure of theory to account for the coupling constant of *t*-butylsemiquinones.^{19a} In view of the importance of solvent effects on the spectra of semiquinones,^{29,31} the steric desolvation viewpoint is somewhat more attractive.

(28) Two other lines were also detected. These signals were always weak relative to the triplet and doublet resonance and were not observed in most experiments.

(29) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

(30) H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5188 (1964).

(31) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

Delocalization of the spin density to neighboring phenyl nuclei is not detected in these semiquinones. Triptycene negative ion would offer a far better test of the significance of this interaction, but the analysis of the ultraviolet spectrum suggests the delocalization would be quite small.³²

The finding that $a_{\beta-H}$ for the bridgehead hydrogen atom is undetectably small parallels the results of Shiner and his students concerning the influence of stereochemistry on the secondary isotope effects in the solvolysis of 2-chloro-2-methylbicyclo[2.2.2]octadienes.^{26,33} Thus, the results for the e.p.r. model and reaction chemistry are parallel.

Coupling Constants for $\beta-X$. The isotropic coupling constants $a_{\beta-H} = 1.8$, $a_{\beta-C} = 0.74$, and $a_{\beta-F} = 2.7$ gauss reflect only the Fermi contact term of the spin Hamiltonian and are proportional to the spin population in the *s*-orbitals of the β -nuclei. The spin population might be estimated from the ratio, $a_{\beta-X}/G_X$, where G_X is the hyperfine splitting constant for an *s*-orbital of the X atom.³⁴ Thus, the coupling constants correspond to spin populations of 0.0035 in H (1s), 0.00067 in C^{13} (2s), and 0.00015 in F^{19} (2s). The spin populations at the β -nuclei also depend on the spin density at the adjacent aryl carbon atom, $\rho(C_i)$. The application of eq. 1 with $a_{\beta-H} = 1.8$ gauss, $B = 45$ gauss, and $\cos^2 \theta = 0.5$ suggests $\rho(C_i)$ is about 0.08 for 2-methylsemiquinone. Theory yields an equivalent result.³⁵ Since the polar properties of the alkyl groups differ only slightly, $\rho(C_i)$ for 2-*t*-butylsemiquinone should be negligibly different from 0.08.³⁶ Presumably, $\rho(C_i)$ is somewhat smaller for 2-trifluoromethylsemiquinone because of the polar effect of the substituent. The use of eq. 1 with $a_{\beta-F} = 2.7$ gauss, $B^F = 77$ gauss,^{22b} $\cos^2 \theta = 0.5$ indicates $\rho(C_i)$ is 0.07. The coupling constants for the aryl hydrogen atoms of this semiquinone differ only modestly from those of the alkylsemiquinones. The assignments are in doubt but it is evident that no major change in $\rho(C_i)$ occurs. The spin populations for unit spin density at C_i are then 0.044 for H (1s), 0.0084 for C^{13} (2s), and 0.0022 for F^{19} (2s).

The viewpoint that spin density is transferred to $\beta-H$ by hyperconjugation prompted our study of 2-*t*-butyl- $\beta-C^{13}$ -semiquinone as a model for C-C hyperconjugation.²⁵ The detection of spin density at $\beta-C$ suggests the effect is significant.^{24,25} One inference of the hyperconjugative mechanism is that the spin at the β -nuclei reflects the spin density in the C-X bond. Thus, the spin populations at $\beta-X$ also depend on the character of the C-X bonding orbital. As a first approximation, we assume that the spin populations at

(32) C. F. Wilcox, *ibid.*, **33**, 1874 (1960); A. C. Craig and C. F. Wilcox, *J. Org. Chem.*, **26**, 2491 (1961).

(33) The value of $\Delta\Delta F^*$ for hydrogen compared to deuterium in solvolysis reactions is approximately linear in $\cos^2 \theta$. The major uncertainties in the actual dihedral angle in the transition state and the conformational factors discussed by Shiner²⁶ render the relationship inexact. The difficulty is illustrated by the variation in k_H/k_D for *cis*- and *trans*-2-deuteriocyclopentyl tosylate, 1.22 and 1.16, respectively^{28a}; *i.e.*, different isotope effects are found although the incipient carbonium ion is the same.

(34) G_H (1s) is 508 gauss. Theoretical values, $G_{C^{13}}$ (2s) 1110 gauss and $G_{F^{19}}$ (2s) 17,200 gauss, are presented in ref. 2, p. 335.

(35) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).

(36) This notion is supported by the similar coupling constants for the aryl hydrogen atoms in the alkylsemiquinones. For 2-methyl: $a_3 = 1.95$ and $a_6 = 2.44, 2.70^{29}$; and for 2-*t*-butyl: $a_3 = 1.65$ and $a_6 = 2.10, 2.85$ gauss, respectively. The assignments are based on theory.^{19a,36}

β -X vary directly with the per cent s-character of the X bonding orbitals (H, 100%; CH₃, 25%). On this basis, the relative importance of the interaction between the spin density at C₁ with the C-H and C-C bonds is in the ratio 0.044:0.032. This interpretation implies that C-H hyperconjugation is only 1.3-fold more significant than C-C hyperconjugation.

Analyses of the role of alkyl groups in reaction chemistry, particularly for the alkylbenzenes, have led to the conclusion that C-H and C-C hyperconjugation are of similar importance.^{20b-f} Dewar points out that the ratio of the Hammett σ -constants, $\sigma_{p-Y}/\sigma_{m-Y}$, is about 1.2 for all substituents incapable of resonance.³⁷ The σ^+ -constants³⁸ are also in the ratio 1.2 for groups incapable of donor resonance. A substantial increase is observed for the alkyl groups: $\sigma_{p-R}/\sigma_{m-R}$ is 2.4 for Me and 2.0 for *t*-Bu; $\sigma^+_{p-R}/\sigma^+_{m-R}$ is 4.0 for Me and 2.6 for *t*-Bu. It may be inferred from these larger ratios that both *p*-alkyl groups enhance reactivity through hyperconjugation. The additional contribution may be estimated by the difference $\sigma^+_{p-R} - 1.20\sigma^+_{m-R}$: -0.19 for Me, -0.15 for *t*-Bu. Thus, there is only a nominal difference between C-H and C-C hyperconjugation with C-H only 1.3-fold greater. The conclusions reached through the e.p.r. model and reaction chemistry are again compatible.

The spin population at β -F (2s), 0.0022, is much less than at β -H (1s), 0.044. The hyperconjugation model with the s-character of the F-bonding orbital taken as 25%³⁹ implies that C-H hyperconjugation is fivefold more important than C-F hyperconjugation. However, other experimental data suggest C-F hyperconjugation is responsible for only a minor portion of the spin population at β -F. The e.p.r. spectra of perfluorosuccinic acid radical in the solid state reveal the couplings of the β -F atoms are highly anisotropic, indicative of a large spin density in p-orbitals.^{22c} Calculations suggest that 0.13 of the p spin density may contribute to isotropic couplings.^{22c} Thus, the entire spin population at β -F (2s) may arise from spin density in p-orbitals rather than through the C-F bond *via* hyperconjugation. Indeed, it has been proposed that a direct interaction between the p-orbitals of F and the orbital containing the spin density occurs.⁴⁰ Few results are currently available for β -F, but other interactions appear more significant than C-F hyperconjugation.

Chemical evidence relative to the problem is meager. The finding that σ_{p-CF_3} (0.53) was greater than σ_{m-CF_3} (0.42) prompted the proposal that C-F hyperconjugation was significant.^{21b} However, these parameters are in the ratio 1.2, unchanged from the ratio for other substituents without resonance.³⁷ The parameter $\sigma^+_{p-CF_3}$ is appreciably larger, 0.74,^{21b} indicative of an additional contribution of the same magnitude observed for the alkyl groups. Sheppard⁴⁰ has examined the results for several perfluoro substituents and concludes that the overlap of fluorine orbitals with adjacent orbitals has a major influence on the apparent substituent effects. Further study is desirable to confirm this proposal. However, the results for reaction chemistry

(37) Reference 18a, pp. 153-173.

(38) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 89, 130 (1963).

(39) J. H. Goldstein and R. T. Hobgood, *J. Chem. Phys.*, **40**, 3592 (1964).

(40) W. A. Sheppard, *J. Am. Chem. Soc.*, **87**, 2410 (1965).

and e.p.r. spectroscopy do suggest C-F hyperconjugation is less significant than C-H hyperconjugation.

In conclusion, comparison of the data for these several systems reveals that the results for appropriate model compounds in e.p.r. spectroscopy and for reaction chemistry do correspond. Clearly, further study is desirable to establish the applicability of the hyperconjugation model for β -C¹³ with more confidence and to define the interactions responsible for β -F couplings.

Experimental⁴¹

2-t-Butyl- β -C¹³-hydroquinone (III). Compound III was prepared by a two-step synthesis from methyl iodide-C¹³. The Grignard reagent was prepared from methyl iodide (48.1% C¹³, 1.0 g., 7.04 mmoles) in ether (5 ml.) and magnesium (0.34 g., 14.1 mg.-atoms) in a reaction vessel similar to that described by Cheronis.⁴² After 10 min., the mixture was warmed for 2-3 min. to ensure completion of the reaction. The Grignard reagent was then filtered through sintered glass into a flask containing acetone (1.2 ml.) and ether (5 ml.). The reaction mixture was hydrolyzed with aqueous ammonium chloride after 30 min. The pH was adjusted to 7 and the heterogeneous mixture distilled. The fraction, b.p. 65-100°, approximately 1 ml., was collected in a dropping funnel.

The method of Young and Rogers was employed for the reaction of *t*-butyl alcohol- β -C¹³ with hydroquinone.⁴³ A heterogeneous mixture of hydroquinone (1.55 g., 14.1 mmoles), phosphoric acid (85%, 6 ml.), and xylene (6 ml.) was heated to 115°. The distillate containing the labeled alcohol and water was added rapidly while the solution was stirred vigorously. The hot xylene layer was removed after 30 min. and the hot acid phase extracted with more xylene. The xylene was removed *in vacuo* to yield 0.76 g. of crude product. The mixture was chromatographed on silicic acid-Celite (1:1, 35 g.) with chloroform. 2,5-Di-*t*-butylhydroquinone (m.p. 208-210°, 0.14 g., 27%) and 2-*t*-butyl- β -C¹³-hydroquinone (m.p. 125-128°, 0.36 g., 30%) were obtained.

Other Hydroquinones. Trifluoromethylhydroquinone (IV), m.p. 110-111°, lit.⁴⁴ m.p. 109° (di-*p*-nitrobenzoate, m.p. 232-232.5°, lit.⁴⁴ m.p. 230°), was prepared by the method of Whalley⁴⁴ in 10% yield. The known dihydroxytritylenes V and VI were prepared by the conventional method.⁴⁵ These compounds were recrystallized until the carbonyl frequency was not detectable in the infrared spectrum.

E.p.r. Spectra. All spectra were recorded for dilute (10⁻¹-10⁻³ M) solutions of the hydroquinones in acetonitrile. No differences in the spectra were detected with different bases (sodium hydroxide, tetramethylammonium hydroxide, or sodium hydride). A Varian Model V4500 spectrometer was used for all experiments. The coupling constants were determined by field calibration with tolylsemiquinone or 2,5-di-*t*-butylsemiquinone. The *g* value was not assessed with accuracy but was not significantly different among the several radicals.

(41) All melting points are uncorrected.

(42) N. D. Cheronis, "Micro and Semimicro Methods," Vol. VI, "Techniques of Organic Chemistry," A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1954, p. 347.

(43) O. S. Young and G. F. Rogers, U. S. Patent 2,722,556 (1955).

(44) W. B. Whalley, *J. Chem. Soc.*, 3016 (1949).

(45) P. D. Bartlett, *et al.*, *J. Am. Chem. Soc.*, **64**, 2649 (1942).