Oxygen-17 Semiquinones. The Effect of Fluorine Substitution[1]

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Abstract: A series of fluorinated semiquinone radicals has been studied by electron spin resonance spectroscopy. The isotropic fluorine hyperfine coupling constants, a_F, for 2-fluoro-, 2,5-difluoro-, 2,3,5,6-tetrafluoro-, and 3,6-difluoro-2,5-dioxysemiquinone were found to be 3.50, 5.35, 3.95, and −3.85 G, respectively. Oxygen-17 enrichment of several radicals allowed observation of the values of a_O, and these were found to differ very slightly from the values found in unfluorinated semiquinones. In addition, interactions with naturally abundant carbon-13 were examined and also found similar in magnitude to those reported for unsubstituted semiquinones. The proton coupling constants observed in the partially fluorinated radicals, however, indicated that within the ring, changes of up to 40% in spin density occur upon fluorine substitution. This is the first instance in which fluorination has been found to produce such large redistributions of unpaired electron density.

Fluorine hyperfine coupling constants in free radicals have been the object of considerable investigation by electron spin resonance (esr) spectroscopy. Numerous investigators have attempted to discover a consistent functional relationship between the isotropic fluorine hyperfine splitting, a_F, and the unpaired spin density, ρ_C^π, on the carbon atom to which the fluorine is bonded.[3-10] Such a relationship might be of the form[3,11]

$$a_F = Q^F \rho_C^\pi \qquad (1)$$

where Q^F is an empirical constant or, if spin on fluorine contributes significantly to a_F, analogy to the Karplus–Fraenkel[12] treatment of ^{13}C splittings might be invoked.

$$a_F = Q_{CF}^F \rho_C^\pi + Q_{FC}^F \rho_F^\pi \qquad (2)$$

A number of fluorine couplings are accommodated[7,9,13] by eq 1 using ρ_C^π determined from the analogous hydrogen-containing (hereafter "protonated") radicals and $Q^F = 50 \pm 10$ G; however, largely because of the difficulty in accurately determining the small values of ρ_F^π, no moderately consistent set of parameters has been found for eq 2. The attempts to find such parameters have been reviewed thoroughly by Kaplan, Bolton, and Fraenkel[8] and, more recently but in less detail, by Sinclair and Kivelson.[9]

Previous experimental results[4,8,9] indicated that substitution of fluorine for hydrogen does not noticeably change the spin density distribution, thus allowing these data to be inferred from data for the unsubstituted radical. This approach appears to have been used first by Anderson, *et al.*,[3] in the original work on tetrafluorosemiquinone. The apparent success of this approach stands in contrast to the body of physicochemical data which suggests that the electronic properties of organofluorine compounds are rather different from those of their protonated counterparts.[14] In fact, significant participation by fluorine in π-system conjugation has been postulated by several authors.[15]

The study described here tests the generality of the result that fluorine has little effect on spin densities in aromatic radicals. In order that spin density changes at the positions normally "blind" to esr examination not go undetected, we compare ^{13}C and ^{17}O coupling constants of several fluorosemiquinones with those of the unsubstituted semiquinones in addition to measuring a_F and a_H. Semiquinones were chosen for ease of ^{17}O enrichment and for the extensive data available on the unfluorinated species. Specifically, we compare 2-fluoro- (MFSQ), 2,5-difluoro- (DFSQ), and 2,3,5,6-tetrafluoro-1,4-benzosemiquinone (TFSQ) with 1,4-benzosemiquinone (PBSQ), and compare the trianion of 3,6-difluoro-2,5-dihydroxy-1,4-benzoquinone (fluoranilic acid trianion, FTA) with that of 2,5-dihydroxyquinone (dioxysemiquinone, DOSQ).

The expected small magnitude of the fluorine spin density made an independent estimate of its value desirable, for in a calculation based on conservation of spin density alone small errors in the calculation of the major spin densities could lead to large percentage errors in the estimate of ρ_F^π. Therefore, estimates of ρ_F^π in TFSQ and FTA were made *via* analysis of the variation of the esr line widths of ^{17}O-labeled samples of these radicals, following the method of Kaplan, *et al.*[8]

Experimental Section

Solvents and supporting electrolytes were commercially available and were purified according to established literature procedures.

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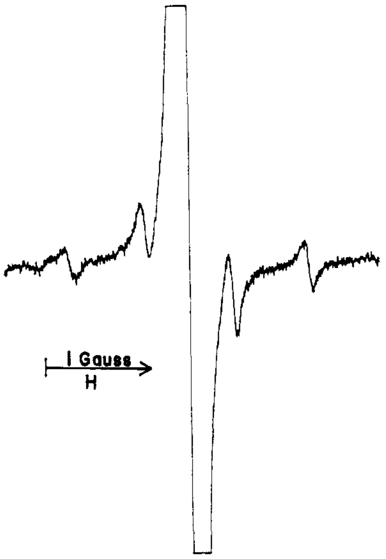

Figure 1. Center line of the first-derivative esr spectrum of tetrafluorosemiquinone showing satellite lines due to two kinds of ^{13}C in natural abundance. The radical was prepared by electrolysis of a dimethoxyethane solution initially 0.3 m*M* in tetrafluoroquinone. The spectrum was recorded at −22°.

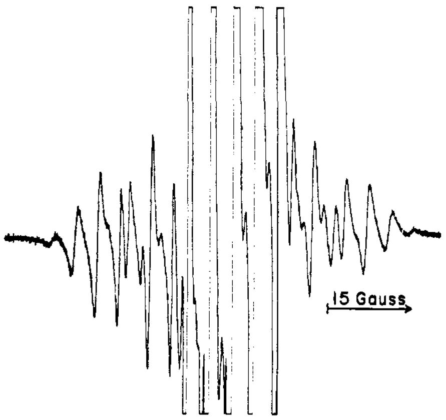

Figure 2. First-derivative esr spectrum of ^{17}O-enriched tetrafluorosemiquinone anion. Radicals were produced by electroreduction of a dimethoxyethane solution initially 1.2 m*M* in tetrafluoroquinone-^{17}O. Lines due to unlabeled radicals are off scale.

Tetrafluoroquinone (Aldrich), tetrachloroquinone (Baker), and 2,5-dichloroquinone (Distillation Products Industries) were purified by sublimation *in vacuo*. 2,5-Difluoroquinone was the gift of the Illinois State Geological Survey and was used as received, mp 173–174°, sealed tube (lit.[16] 171.5–172°). Monofluoroquinone was synthesized by oxidation of 3-fluoro-4-aminophenol following the method of Hodgson and Nicholson.[17] It was purified by vacuum sublimation, mp 80–82°, sealed tube (lit.[17] 80°). This compound appeared to be quite unstable when not rigorously protected from moisture and had to be resublimed before each use. The phenol precursor was synthesized by the method of Hammond.[18] Fluoranilic acid, prepared by basic hydrolysis of tetrafluoroquinone,[19] was also purified by reduced pressure sublimation.

^{17}O enrichment of tetrafluoro- and difluoroquinone was accomplished by mixing 0.1 g of each compound in benzene solution with 0.5 g of water enriched to 15.56% in ^{17}O (Miles Laboratories, Inc.) according to the method previously described.[20] Product recovery was 74% for tetrafluoroquinone and 45% for difluoroquinone; mass spectral analysis of the products showed in each case that about 27% of the molecules contained a single ^{17}O, in agreement with the value anticipated for total random exchange. Tetrachloroquinone-^{17}O was prepared by the same method using water recovered from the difluoroquinone exchange. The ^{17}O enrichment of FTA was conveniently effected by rapid isotope exchange through the radical as suggested previously:[20] natural fluoranilic acid was reduced with sodium dithionite in 0.5 *M* aqueous base using ^{17}O-enriched water. The other radicals studies were generated electrochemically, either by the *intra muros* technique[21] or externally in cells of the type previously described.[22,23] MFSQ and DFSQ-^{17}O were obtained at useful concentrations and free of secondary radicals only by the flow electrolysis method of McKinney and Geske.[24]

The dependence of the ^{13}C coupling constants in TFSQ upon the composition of a dimethoxyethane (DME)—ethanol mixture was determined in the following manner. A DME solution of TFQ was electrolyzed externally to the microwave cavity. A small portion of this solution was withdrawn into an evacuated tube which contained a measured amount of ethanol. The volume of DME was then estimated by pouring the mixture into a calibrated side arm and assuming additivity of volumes. It was found that under these conditions stable TFSQ samples could not be obtained above N_{EtOH} (mole fraction of ethanol) $\cong 0.25$. The solvent dependence of the oxygen coupling constant was measured by making successive additions of ethanol to a DME solution about 0.8 m*M* in TFQ-^{17}O and then generating the radical *intra muros*. Radical decay was sufficiently rapid above $N_{\mathrm{EtOH}} \cong 0.35$ that reproducible data could not be obtained.

Instrumentation for esr, including magnetic field calibration, and for electrochemical measurements is described elsewhere.[20,25]

Results

Tetrafluorosemiquinone. Total electrolytic reduction of a DME solution *ca.* 0.3 m*M* in TFQ at 0° yielded a yellow solution which exhibited an esr spectrum similar to that reported by Anderson, *et al.*,[3] reflecting interaction of the odd electron with four equivalent fluorine nuclei. At higher gain, two sets of satellite lines were revealed which we attributed to hyperfine coupling with two sets of ^{13}C nuclei present in natural abundance (1.1%).[26] Assignments of these splittings to molecular positions were made on the basis of intensities. The satellites with the larger coupling constant were *ca.* 1.2% of the parent line intensity (theoretical 1.12% for two equivalent ^{13}C's). The second two satellites were incompletely resolved from the parent line and thus appear of lower intensity, *ca.* 1.7% of the parent line, than that predicted (2.24%) for four equivalent ^{13}C's.

Figure 1 shows the two sets of satellites symmetrically flanking the center hyperfine line of the spectrum. The high-field line of each satellite pair is of larger derivative amplitude, and hence narrower, than the corresponding low-field line. Since the carbon spin densities are positive (*vide infra*), this asymmetry indicates negative coupling constants for both types of carbons in the radical.[27]

Electroreduction of a DME solution 1.2 m*M* in TFQ-^{17}O gave the esr spectrum displayed in Figure 2. Lines indicating the presence of radicals containing a single ^{17}O ($I = {}^5/_2$) are clearly distinguished. The high-field oxygen lines have a smaller derivative ampli-

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(26) At temperatures above *ca.* 0°, low-intensity lines due to a secondary radical appeared; in time, these obscured the ^{13}C satellites. At lower temperatures no spurious lines were observed.

(27) E. deBoer and E. L. Mackor, *J. Chem. Phys.*, **38**, 1450 (1963).

Table I. Coupling Constants (Gauss) of Simple Semiquinones in Aprotic Solvents (A) and Dioxysemiquinones in Alkaline Water (B)

A

Radical	Solvent	$-a_O$	$-a_{C_1}$	$-a_{C_2}$	$-a_H$	a_F
p-Benzosemiquinone	DME	9.54 ± 0.05[a]	2.21 ± 0.02[b]	0.12[b,c]	2.40 ± 0.002[b]	
Tetrafluorosemiquinone	DME	9.46 ± 0.05[d,e]	2.19 ± 0.02[d,e]	0.80 ± 0.01[d,e]		3.95 ± 0.02[d]
2,5-Difluorosemiquinone	MeCN	9.41 ± 0.08[d]			1.41 ± 0.01[d]	5.35 ± 0.02[d]
2,5-Dichlorosemiquinone	MeCN	9.28 ± 0.02[f,g]			2.16 ± 0.02[d]	
Tetrachlorosemiquinone	DME	8.80 ± 0.05[d]	2.57 ± 0.04[d]			
Monofluorosemiquinone	MeCN				(1.85)[d,i]	
					(1.95)	3.50[d]
					(3.15)	

B

Radical	$-a_O$	a_{C_1}	$-a_{C_3}$	a_X
Dioxysemiquinone	4.57 ± 0.02[f]	2.63 ± 0.007[b]	6.60 ± 0.005[b]	+0.79 ± 0.001 (X = H)[b]
Fluoranilic acid trianion	4.78 ± 0.03[d]	2.55 ± 0.01[d]	8.02 ± 0.04[d]	−3.85 ± 0.01 (X = F)[d]
Chloranilic acid trianion	4.79 ± 0.02[h]	2.71[h]	8.17[h]	|0.18| ± 0.01 (X = Cl)[h]

[a] From ref 20. [b] From ref 29. [c] This value calculated in ref 29 for dimethyl sulfoxide solution from data obtained in other media. [d] Value determined in this work. Uncertainties are given at the 95% confidence level. [e] Values obtained at −22°. Slight temperature variations were observed for a_{C_1} and a_F. These coupling constants had increased *ca.* 1.5 and 1.0%, respectively, when the temperature reached 16°. [f] From ref 33. [g] Value given for dimethylformamide solution. [h] M. Broze and Z. Luz, *J. Phys. Chem.*, **71**, 3690 (1967). [i] Values which produced the best fit of a computed spectrum. These were assigned, respectively, to proton splittings at the 3, 5, and 6 positions by comparison with calculated spin densities (see text).

Table II. Tetrafluorosemiquinone Coupling Constants in a Dimethoxyethane–Ethanol Mixture[a]

N_{EtOH}[b]	$-a_{C_1}$	$-a_{C_2}$	$-a_O$	a_F
0.000	2.19 ± 0.02	0.80 ± 0.01	9.46 ± 0.05	3.95 ± 0.02
0.021			9.45 ± 0.03	
0.048			9.37 ± 0.03	
0.079			9.34 ± 0.03	
0.085	1.90 ± 0.02	0.91 ± 0.01		3.91 ± 0.02
0.116	1.80 ± 0.02	0.92 ± 0.01		
0.120			9.33 ± 0.02	
0.162			9.33 ± 0.02	
0.210	1.74 ± 0.02	0.96 ± 0.02		3.90 ± 0.01
0.227	1.56 ± 0.01	0.97 ± 0.01		
0.231			9.33 ± 0.02	
0.290			9.33 ± 0.03	
0.355			9.31 ± 0.06	

[a] Coupling constants in gauss with uncertainties at the 95% confidence level. [b] Mole fraction of ethanol.

tude than the corresponding lines at low field. Since this observation was reproducible over a period of several hours, the difference in amplitudes is ascribed to the greater breadth of the high-field components. Thus, a negative sign for the oxygen coupling constant is required (*vide infra*). Coupling constants for all the radicals studied are collected in Table I.

The variations of ^{13}C, ^{17}O, and ^{19}F coupling constants in TFSQ produced by increases in the ethanol content of a DME–ethanol mixture are summarized in Table II. The solvent effect upon the carbon and oxygen coupling constants closely parallels that reported for PBSQ[20,28,29] in the range of ethanol contents we were able to study. Radical instability precluded study of the effect of added water.

2,5-Difluorosemiquinone. *Intra muros* electrolysis of a 1 m*M* solution of DFQ in acetonitrile (MeCN) gave a spectrum composed of three sets of triplets as expected for hyperfine interaction with two groups of two equivalent spins of one-half. This spectrum was essentially identical with that reported for DFSQ by Fischer and Zimmerman.[30] Assignment of the coupling constants (Table I) to interacting nuclei was made on the basis that the fluorine splitting was expected to be the larger and was confirmed by line-width variations, which were more pronounced among the triplets with the larger coupling constant.[31]

Flow electrolysis of a 1.2 m*M* solution of DFQ-^{17}O in MeCN gave a spectrum in which additional interaction with a single ^{17}O nucleus was evident. The signs of the coupling constants (Table I) were again determined from the line-width variations.

Monofluorosemiquinone. Flow electrolysis of a 1 m*M* solution of MFQ in MeCN gave the spectrum displayed in Figure 3a. The spectrum shown in Figure 3b was computed[32] on the basis of hyperfine interaction with four inequivalent spins of one-half using the coupling constants designated in Table I. Line-width analysis could not provide the basis of a choice between the two largest coupling constants in assigning the fluorine splitting because of insufficient resolution of the spectrum. Therefore, assignments to molecular positions were made *via* comparison of the experimental

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(28) E. W. Stone and A. H. Maki, *J. Am. Chem. Soc.*, **87**, 454 (1965).

(29) M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).

(30) P. H. H. Fischer and H. Zimmerman, *Z. Naturforsch.*, **23a**, 1399 (1968). These workers report that a new radical is obtained when DFQ is reduced at potentials more cathodic than $E_{1/2}$ and suggest that it could be MFSQ. We found no new species produced at potentials as negative as −1 V *vs.* sce. Our esr results show clearly that the secondary radical observed by these workers is *not* MFSQ.

(31) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 944 (1964).

(32) E. W. Stone and A. H. Maki, *ibid.*, **38**, 1999 (1963). This program was executed on an IBM 360·65 computer.

Table III. Polarographic Results

Compound	Dimethylformamide $-E_{1/2}$[a]	Dimethylformamide $-(E_{3/4} - E_{1/4})$[b]	Dimethylformamide i_d/C[c]	Acetonitrile $-E_{1/2}$[a]	Acetonitrile $-(E_{3/4} - E_{1/4})$[b]	Acetonitrile i_d/C[c]
Monofluoroquinone	0.30	67	3.90	0.38	69	6.55
	1.14	93	6.43	1.06	..	13.4
Difluoroquinone	0.21	65	3.96	0.26	67	8.08
	1.12	64	6.56	1.04	60	14.1
Tetrafluoroquinone	−0.04	50	5.54	0.02	64	8.04
	0.85	64	10.75	0.79	..	13.7
p-Benzoquinone	0.54[d]	..	4.31	0.51[d]	..	8.05
	1.23[d]	..	7.63	1.14[d]	..	15.5

[a] Volts *vs.* aqueous saturated calomel electrode. [b] Millivolts. [c] μA/m*M*; maximum, not average, polarographic currents. [d] Data from M. E. Peover, *J. Chem. Soc.*, 4540 (1962).

splittings with the results of molecular orbital calculations. Choosing $Q_{CH}^{H} = -27$ G, the calculated spin densities yielded −1.78, −2.03, and −3.11 G for the expected proton splittings at the 3, 5, and 6 positions, respectively.

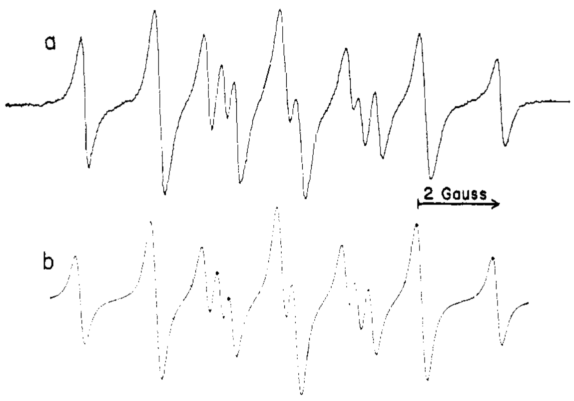

Figure 3. (a) The first-derivative esr spectrum of monofluorosemiquinone. Radicals were generated by electrolysis of a 1 m*M* solution of the parent quinone in acetonitrile at a platinum gauze cathode in a flow system. (b) Spectrum computed with four spins of one-half with coupling constants of 1.85, 1.95, 3.15, and 3.50 *g*. A Lorentzian line shape was employed and a line width of 0.260 G.

Tetrachlorosemiquinone and 2,5-Dichlorosemiquinone. Both of these radicals have been studied previously. ^{17}O coupling constants for both were measured in dimethylformamide (DMF) by Broze, *et al.*,[33] and a_H for DCSQ was reported from experiments in ethanol–water.[34] For the sake of accurate comparison, we measured a_H for DCSQ in MeCN and a_O for TCSQ in DME (Table I). In addition, at high gain the spectrum of natural TCSQ revealed satellite lines (*ca.* 1% of the major line's intensity) which we assigned to hyperfine splitting by ^{13}C at position 1.

Fluoranilic Acid Trianion. The spectrum of FTA consists of a triplet due to hyperfine interaction with two equivalent fluorine nuclei. At high gain the presence of 11 of the 12 expected ^{13}C satellites was readily detected (Figure 4). Since the larger carbon coupling constant is only slightly more than twice the fluorine coupling constant, overlap with the central line obscured the 12th satellite except in one experiment when particularly narrow lines were obtained. The satellites associated with the larger coupling constant each had an intensity of 1.20 ± 0.40% relative to their parent line and those associated with the smaller coupling were 2.18 ± 0.21% of the parent intensity. On this basis the former were assigned to the C_3 (fluorine-carrying) carbon and the latter to the C_1 carbon. Signs of the coupling constants (Table I) were obtained following the arguments of Das and Fraenkel.[29]

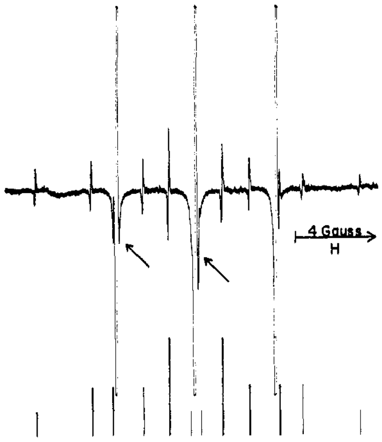

Figure 4. First-derivative esr spectrum of fluoranilic acid trianion in alkaline water. Splittings from two different kinds of ^{13}C in natural abundance are shown. Eleven of the 12 expected satellite lines are detected in this spectrum. Lines indicated with arrows are due to impurities. The stick diagram represents a theoretical reconstruction of the ^{13}C structure.

Six equally intense triplets from the singly enriched FTA-^{17}O were observed as anticipated. Components of a high-field triplet were broader than those of a corresponding low-field triplet, thus allowing determination of the sign of a_O.

Voltammetry. The polarographic behavior of the simple fluoroquinones in DMF and MeCN was determined in the course of this investigation. These data are presented in Table III, where data for PBQ are also given for comparison. $E_{3/4} - E_{1/4}$ for the first reduction is in each case fairly close to the value of −56 mV expected for a reversible, one-electron reduction.[35] Cyclic voltammetry, however, provided more information regarding the stability of these radicals. In DMF

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(33) M. Broze, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, 46, 4891 (1967).

(34) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *ibid.*, 30, 1006 (1959).

(35) J. Tomes, *Collection Czech. Chem. Commun.*, 9, 12, 81, 150 (1937).

at a sweep rate of 0.17 V/sec, the ratio of anodic to cathodic peak currents was 0.99 for TFQ, 0.65 for DFQ, and 0.31 for MFQ. These data are consistent with the relative radical stabilities we observed qualitatively by esr.

Line-Width Studies. The techniques involved in precise measurement of line-width variations in esr spectra have been discussed in several publications by Fraenkel, *et al.*[8,31,36] In the study of TFSQ and FTA, low-field modulation and power amplitudes were employed to prevent distortion of the line shape. Data from about ten scans, sweeping the magnetic field in both directions, were averaged and the widths thus obtained were fitted to the equation[8]

$$\Delta_k = A + \sum_i B_i\tilde{M}_i + \sum_i C_i\tilde{M}_i^2 + \sum_{i \neq j} E_{ij}\tilde{M}_i\tilde{M}_j \qquad (3)$$

where Δ_k is the peak-to-peak derivative width of the kth line, $\tilde{M}_i$ and $\tilde{M}_j$ are the spectral index numbers,[36] and the coefficients are constants characteristic of the radical. The values of the coefficients obtained for TFSQ are $A = 669$, $B_F = 25.6$, $C_F = 26.3$, $B_O = 66.7$, $C_O = 58.3$, $E_{OF} = 82.4$; and those for FTA are $A = 332$, $B_F = 6.4$, $C_F = 6.2$, $B_O = 16.0$, $C_O = 11.6$, $E_{OF} = 17.0$, $B_{C_1} = 14.6$, and $E_{C_1F} = 10.2$ (all values in milligauss).

The sign of the product $a_i\rho_i$ for nucleus i can be determined from the sign of B_i.[8,37] Our results show that $a_F\rho_F$ is positive in both TFSQ and FTA, consistent with the conclusions of investigators who have determined the sign of this quantity for other fluorinated radicals.[8,38] The positive value of B_O implies a negative sign for $a_O\rho_O$ in each radical,[20] and the positive sign of B_{C_1} in FTA implies that $a_{C_1}\rho_{C_1}$ is positive in this radical.[27,37] These implications are corroborated by the values found for the coefficient of the cross term, E_{ij}, from which the relative signs of *pairs* of products are established. When coupled with the spin densities calculated for these radicals, the signs of these coefficients form the basis upon which the signs of the coupling constants in Table I have been affixed. While the reliability of molecular orbital calculations is open to question, all of the spin densities predicted, except those for fluorine, are large enough that we feel confident of their *signs*.

A further utilization of the coefficients of eq 3 is the approximate evaluation of *ratios* of spin densities in these radicals. Thus, if we accept the ability of molecular orbital calculations to give reasonable values of ρ_O, it is possible to estimate ρ_F in a way which does not rely on direct MO calculation of this small quantity. The evaluation of the spin density ratios depends upon the relation of the measured line-width coefficients to the dipolar coefficients, $D_i^{(m)}$, which are functions of the spin density distribution and geometry of the radical. These are described in detail elsewhere.[37] The theoretical basis of the relations between the coefficients of eq 3 and the $D_i^{(m)}$ has been given by Freed and Fraenkel,[39] reviewed recently by Fraenkel,[37] and used previously by several authors.[8,31,36] Neglecting contributions from $D_i^{(\pm2)}$ which are small in TFSQ,[40] we state the results of the theoretical development as eq 4–7.

$$B_O/B_F = \epsilon_O\epsilon_F \cdot \xi_O/\xi_F \cdot D_O^{(0)}/D_F^{(0)} \qquad (4)$$

$$C_O/E_{OF} = 5\epsilon_O\epsilon_F/16 \cdot \xi_O/\xi_F \cdot D_O^{(0)}/D_F^{(0)} \qquad (5)$$

$$E_{OF}/C_F = 2\epsilon_O\epsilon_F \cdot \xi_O/\xi_F \cdot D_O^{(0)}/D_F^{(0)} \qquad (6)$$

$$C_O/C_F = 5\xi_O^2/8\xi_F^2 \cdot [D_O^{(0)}]^2/[D_F^{(0)}]^2 \qquad (7)$$

Here, following previous usage,[37,39] $\xi_i = (1/2\pi)|\gamma_e\gamma_i\hbar$ and $\epsilon_i = -a_i/|a_i|$. In the case in which nonlocal contributions to the $D_i^{(0)}$ may also be neglected[8]

$$D_i^{(0)}(\text{local}) = (6/25)^{1/2}\langle r^{-3}\rangle\rho_i \qquad (8)$$

The nonlocal contributions, in addition to being small with respect to the local contributions,[40] require knowledge of the spin density distribution for the radical if a highly accurate evaluation is to be made. Equations 4–8, however, provide an estimate of spin density ratios, albeit approximate, independent of molecular orbital calculations.

The line-width coefficients and eq 4–7 provide four sources of estimation of $D_O^{(0)}/D_F^{(0)}$ which for TFSQ yield, respectively, 18.09, 15.35, 10.88, and 13.12. The average value is 14.36. We calculate[40] $D_O^{(0)} = (16.45\rho_O - 0.0206) \times 10^{-24}$ cm^{-3} and $D_F^{(0)} = (24.95\rho_F - 0.023) \times 10^{-24}$ cm^{-3}. In these expressions the first term refers to the local contribution and the second is due to the nonlocal effects. The purely local terms, combined with the average value of $D_O^{(0)}/D_F^{(0)}$ in TFSQ, yield

$$|\rho_F^\pi| = 0.046\rho_O^\pi \qquad (9)$$

and if $\rho_O^\pi = 0.173$ (see following discussion), then $\rho_F^\pi = 0.0079$. Inclusion of nonlocal effects, evaluated approximately, would raise this estimate about 10%.

A similar treatment of FTA yields values of 17.36, 15.16, 9.51, and 12.01 from eq 4–7 and an average of 13.51. This in turn leads to the result that for FTA

$$|\rho_F^\pi| = 0.049\rho_O^\pi \qquad (10)$$

and if $\rho_O^\pi = 0.0896$, then $\rho_F^\pi = -0.0044$. The negative sign is introduced on the assumption that the sign of a_F will be the same as that of ρ_C^π of the contiguous carbon[5a,6] ($a_F\rho_F > 0$).

Molecular Orbital Calculations. Spin densities in several radicals were evaluated from molecular orbital calculations using Hückel theory and the approximate configuration interaction method suggested by McLachlan.[41] The value of k_{CO}[42] used throughout was 1.20; h_O was taken as 1.40 in DME solution and 1.60 in water, the values recommended by Das and Fraenkel[29] for PBSQ in these solvents. In order to establish suitable values for h_F and k_{CF}, these quantities were

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(36) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 1815 (1964).

(37) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967).

(38) A. L. Buchachenko and A. M. Vasserman, *Zh. Strukt. Khim.*, **8**, 27 (1967); *J. Struct. Chem. USSR*, **8**, 21 (1967).

(39) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

(40) A detailed consideration of the dipolar coefficients for TFSQ may be found in the Ph.D. thesis of W. E. G. The local contributions to $D_i^{(0)}$ were calculated from $\langle r^{-3}\rangle$ values tabulated by J. R. Morton, *Chem. Rev.*, **64**, 453 (1964), or by C. M. Hurd and P. Coodin, *J. Phys. Chem. Solids*, **28**, 523 (1967). The ratios of $D_O^{(0)}/D_F^{(0)}$ were independent of the source of $\langle r^{-3}\rangle$ values to ~1%. Nonlocal contributions to $D_i^{(0)}$ and $D_i^{(\pm2)}$ were calculated using a computer program kindly made available by Mr. D. S. Leniart. However, in order to include the $D_i^{(\pm2)}$, knowledge of the complete g tensor, information not currently available, is required. Since the nonlocal contributions to $D_i^{(0)}$ were of the same order of magnitude as $D_i^{(\pm2)}$, both were neglected. Calculations of this type were not carried out for FTA since the requisite structural data are not available for that radical.

(41) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(42) These parameters are defined in the usual way: $h_X = (\alpha_X - \alpha_C)/\beta_{CC}$ and $k_{CX} = \beta_{CX}/\beta_{CC}$.

Table IV. Calculated Spin Densities

Radical	Position	Spin density	Radical	Position	Spin density
p-Benzosemiquinone	1	0.148	Dioxysemiquinone	1	0.190
	2	0.084		3	−0.0568
	7	0.184		7	0.0895
2,5-Difluorosemiquinone	1	0.152	Fluoranilic acid trianion	1	0.190
	2	0.108		3	−0.0548
	3	0.052		7	0.0896
	7	0.176		F	−0.0038
	F	0.0104			
Tetrafluorosemiquinone	1	0.156			
	2	0.078			
	7	0.173			
	F	0.0076			
2-Fluorosemiquinone	1	0.155			
	2	0.081			
	3	0.066			
	4	0.135			
	5	0.075			
	6	0.115			
	7[a]	0.201			
	8	0.164			
	F	0.0082			

[a] Position 7 is the oxygen closer to fluorine.

varied over the ranges 1.80–3.00 and 0.60–0.74, respectively, until the calculated C_3 spin density in DFSQ agreed with the value obtained from the experimental proton coupling constant using $Q_{CH}^{H} = -27$ G.[29] It was necessary, in addition, to employ the "auxiliary inductive parameter"[43] (AIP) for the fluorine-carrying carbons to approximate the effect of fluorine on the Coulomb integral of these atoms. This parameter was varied over the range 0.10–1.05. The best fit was achieved using AIP = 0.15, h_F = 2.00, and k_{CF} = 0.70, all values within the ranges recommended by Streitwieser.[43] Application of these parameters to the fluorinated radicals gave the results in Table IV.

Discussion

Data presented here show that fluorine substitution makes essentially no changes in the oxygen coupling constants of the radicals investigated. The values of a_O found for TFSQ and DFSQ are both equivalent to that in PBSQ within the precision of the measurements. The carbonyl carbon coupling constant in TFSQ is also unchanged from PBSQ. These facts strongly suggest that the spin densities in the carbonyl fragment of the two radicals are very similar. This conclusion is supported by the near identity of the solvent effects observed for these radicals. The large percentage difference between a_{C_2} in TFSQ and that in PBSQ may not be particularly significant. Since $\rho_{C_2}^{\pi}$ is small, undetectably small changes in the other spin densities might accumulate to cause a large *relative* change at this position. In the equation describing a_{C_2} for TFSQ, Q_{CH}^{C} must be replaced by Q_{CF}^{C} and an additional term, $Q_{FC}^{C}\rho_F^{\pi}$, should be included. Also, the remaining σ–π parameters for this atom are likely to be sensitive to fluorine substitution.[12,44]

The proton coupling constants of DFSQ and MFSQ are the first experimental demonstration of a subtantial redistribution of spin density caused by fluorine substitution. A decrease of nearly 40% in the spin density at the C_3 position in DFSQ is evidenced by comparison of the proton coupling constant with that in PBSQ, while the increase in the value of a_F over that in TFSQ indicates a significant increase in spin density at the C–F fragment. The oxygen coupling constant suggests that the carbonyl group is again unaffected, although the lack of ^{13}C data prevents proof of this point.

On the basis of data presented here, it seems general that *partial* fluorination causes spin redistribution within the ring, but does not affect the carbonyl group. By regarding fluorine as insufficiently potent to redistribute spin from a carbonyl group, it is possible to understand the near identity of spin distributions in PBSQ and TFSQ, and in DOSQ and FTA: there is no source of easily polarized spin density.

The McLachlan[41] calculations which we fitted to DFSQ have given spin density estimates which are at least consistent for this group of radicals. In agreement with experiment, only small differences in spin densities at either the oxygen or carbonyl carbon are predicted among PBSQ, DFSQ, and TFSQ. The excellent agreement between the observed and calculated proton coupling constants in MFSQ supports the feeling that the MO calculations are meaningful for these systems.

The molecular orbital calculations for DOSQ and FTA predict essentially no difference between the two. This is anticipated, for in Hückel theory the molecular orbital occupied by the unpaired electron has a node at the C_3 position, and configuration interaction must be invoked to predict the small negative spin density which is accepted as present at this position.[29] As one might expect, the oxygen splittings and calculated spin densities are approximately half of the simple semiquinone value in the dioxysemiquinones.

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(43) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 5.

(44) H. Fischer, *Z. Naturforsch.*, **20a**, 428 (1965).

The agreement between the spin density ratios, ρ_F^π/ρ_O^π, obtained *via* line-width analyses and those obtained from the McLachlan calculations is rather remarkable and probably fortuitous. Thus, for TFSQ the two methods give $|0.046|$ and 0.044, respectively, while for FTA we compare $|0.049|$ with -0.043. The accuracy of estimating these ratios from the line widths is believed[8] to be only of the order of a factor of 2.

Failure to obtain reasonably constant estimates of Q^F from our data suggests that, as previous authors have also concluded,[5,8,45] eq 1 is an inadequate description of a_F. One might hope to use the calculated spin densities to evaluate the coefficients of eq 2; however, an attempt to do so leads to inconsistencies of both magnitude *and sign*. This is almost certainly a reflection of the fact that the errors in determining the spin densities, particularly ρ_F^π, are appreciable compared with the *differences* in spin densities among these radicals.

One striking aspect of the data in Table I is the small magnitude of a_O for TCSQ. Chlorine substitution, examined *via* proton couplings, is a considerably smaller perturbation than is fluorine substitution. Proton couplings for DFSQ and DCSQ in the table and comparison of the present data for MFSQ with those reported for 2-chlorosemiquinone by Venkataraman, *et al.*,[34] illustrate this point. These observations are in accord with the chemical evidence[46] which suggests that chlorine interacts with a π system less strongly than does fluorine. For these reasons, the ^{17}O coupling constants in the chlorosemiquinones appear anomalous.

Comparing TCSQ with either PBSQ or TFSQ, we find that the magnitude of a_O in the former is smaller by about 8%, while the absolute value of a_{Cl} is larger by more than 15%. These coupling constants depend upon two or three spin densities, respectively. Examination of the relevant equations, however, shows that the observations for TCSQ require a *net loss* of spin from the carbonyl function. This loss of spin density was not predicted by McLachlan calculations of the type we found successful for the fluorinated radicals. Previous workers[33,47] had found that the data for the chlorosemiquinones could be approximated in MO calculations only by treating the C–Cl moiety as a single heteroatom. The physical significance of the success of such a treatment is obscure.

The effect of solvent variation (from aprotic solvent to water) upon the oxygen coupling constant is considerably smaller for TCSQ (+0.64 G) than for PBSQ (+0.98 G).[20,33] We have carried out McLachlan calculations for TCSQ, TFSQ, and PBSQ treating the halogens as individual heteroatoms and employing the usual[20] changes in h_O to simulate the solvent effect. These calculations predict that all three radicals should exhibit identical solvent effects.

An explanation of these anomalous data, as well as the inability to simulate them by ordinary MO methods, might be embodied in the hypothesis that a direct, nonbonding interaction occurs between chlorine and oxygen which stabilizes negative charge on the latter atom. A direct field effect between chlorine and oxygen has recently been proposed by Golden and Stock[48] to account for the anomalous acidity of a chlorinated ethano-bridged anthracenecarboxylic acid. We note that within the framework of the MO method the experimental observations cannot be approximated by a bonding interaction; calculations which include a finite resonance integral between chlorine and oxygen predict spin density shifts opposite to those required by the data.

Conclusions

We have studied the first series of free radicals in which partial fluorination produces relatively large redistributions of spin density. It is worthwhile to note that the majority of previous studies of partially fluorinated aromatic radicals involved molecules which are generally insensitive to substituent effects. Since those radicals[4,7,8,13,49] contained a strongly electron-withdrawing group, the perturbation caused by the addition of a fluorine substituent was minimized.[50]

For three of the radicals studied here, we found $a_F\rho_F$ is positive. In accord with the only experimental determinations of the signs of fluorine coupling constants[5a,6] we have assumed that a_F has the same sign as the spin density on the contiguous carbon atom, an assumption which is corroborated by the signs of the fluorine spin densities obtained from the McLachlan calculations.

Chlorine produces smaller changes in ring spin densities than fluorine does, presumably because of its smaller mesomeric interaction. It appears, however, that chlorine exerts upon the carbonyl group of the semiquinones a specific effect which we hypothesize may be a direct nonbonding interaction between chlorine and oxygen.

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