ESR Spectra of Some Fluorinated Semiquinones

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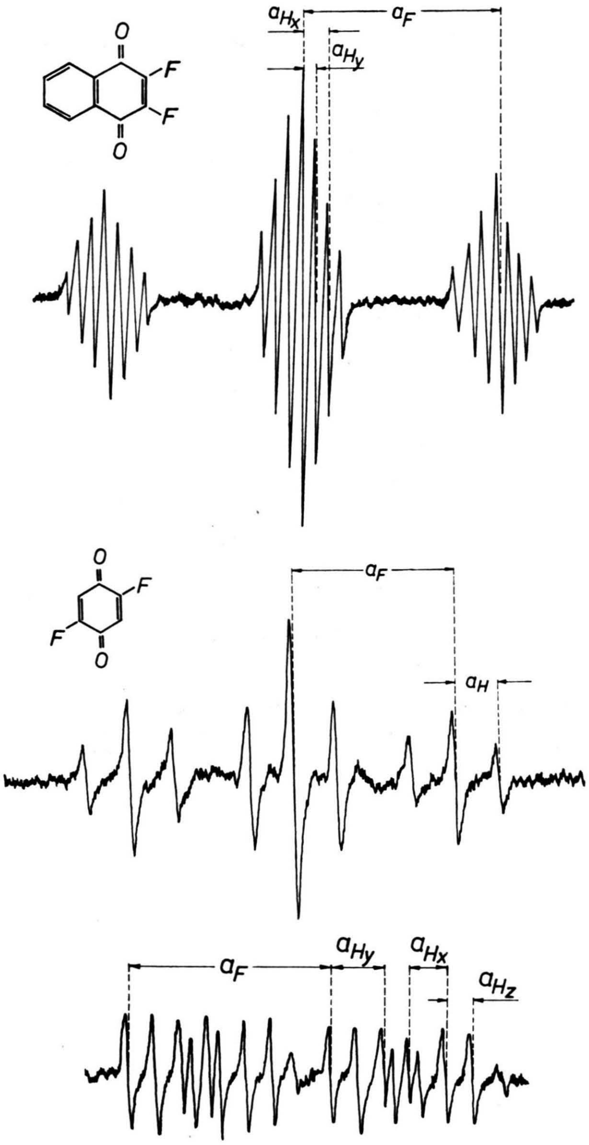
During the course of our investigations of hyperfine interaction in fluorine-containing anion radicals, we have observed the ESR spectra of the anions of 2,3-difluoro-1,4-naphthoquinone (I)[1], 2,5-difluoro-1,4-benzoquinone (II)[2] and of a decomposition product of the latter which may be the anion of 2-fluoro-1,4-benzoquinone (III). The radicals were generated by polarographically reducing a 10^{-3} M solution of I and II in a mixture of 85% dimethoxyethane and 15% acetonitrile, using tetra-n-propylammonium-perchlorate (10^{-1} M) as supporting electrolyte. Reduction at the first half-wave potential of I and II, −0.40 V and −0.32 V vs. SCE, gave the spectra in Fig. 1 a and 1 b, respectively, while at higher potentials the spectrum of Fig. 1 c appeared from a solution of II. ESR spectra were recorded with a Varian V-4500 spectrometer using 100 kHz field modulation.

The spectra consist of 21, 9, and 16 lines, respectively, and are unambiguously interpretable in terms of the following coupling constants:

I: $a_F = 5.31$, $a_{H_x} = 0.74$, and $a_{H_y} = 0.37$ gauss
II: $a_F = 5.24$ and $a_H = 1.42$ gauss
III: $a_F = 5.09$, $a_{H_x} = 1.60$, $a_{H_y} = 1.35$,
and $a_{H_z} = 0.66$ gauss.

The spectrum of the non-fluorinated parent compound of I can be interpreted with three coupling constants $a_{H_x} = 3.31$, $a_{H_y} = 0.30$, and $a_{H_z} = 0.63$ gauss. The latter two are very similar to a_{H_x} and a_{H_y} of I, so that the 3.31 gauss coupling is assigned to the position 2 and 3 protons, and results in a somewhat low, but still reasonable value of $a_F/a_H = 1.61$. On the basis of experimental data, a_{H_x} and a_{H_y} in I remain unassigned. For compound II the assignments are unambiguous if the reasonable supposition that $a_F/a_H > 1$ is made. Under identical conditions the proton splitting in 1,4-benzoquinone is 2.37 gauss, yielding $a_F/a_H = 2.21$.

Upon reduction at higher potentials, a solution of compound II exhibited the well resolved 16 line spectrum of Fig. 1 c, all lines being of equal intensity. It is explicable in terms of the four spin $I = 1/2$ couplings already cited. The similarity of the largest splitting to the fluorine splitting of I and II indicate a fluorine splitting in III also. Three further non-equivalent spin $I = 1/2$ nuclei are consistent with the idea that III may be the anion of 2-fluoro-1,4-benzoquinone, formed through loss of one fluorine atom. The loss of fluorine during electro-reduction of highly fluorinated species has been previously observed[3, 4].



Figs. 1 a, b, and c. ESR spectra of anions of 2,3-difluoro-1,4-naphthoquinone, 2,5-difluoro-1,4-benzoquinone, and unknown species.

As an aid in assignment of coupling constants and as part of an extensive program to determine fluorine spin polarisation parameters, we have performed calculations according to Hückel's LCAO method for I, II, and the suspected III. Introduction of an approximation to configuration interaction has been accomplished via McLachlan's method. Table 1 presents the Hückel, McLachlan, and experimental spin densities.

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[1] Gift of Prof. Dr. K. Wallenfels, Freiburg.

[2] Prepared according to G. C. Finger, F. H. Reed, D. M. Burness, D. M. Fort, and R. R. Blough, J. Am. Chem. Soc. **73**, 145 [1951].

[3] P. H. H. Fischer, unpublished results.

[4] J. K. Brown and W. G. Williams, Trans. Faraday Soc. **64**, 298 [1968].

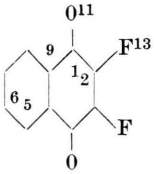
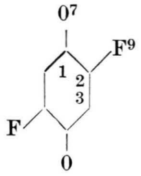
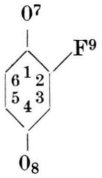
Molecule	Posit.	Hückel [a]	McLachlan [b]	Experimental [c]
	1	0.13127	0.13837	
	2	0.11489	0.11869	
	5	0.02905	0.01527	0.0156
	6	0.03996	0.03688	0.0312
	9	0.05063	0.05463	
	11	0.12383	0.13004	
	13	0.01036	0.00611	
	1	0.12921	0.12849	
	2	0.13387	0.15839	
	3	0.08081	0.05512	0.0599
	7	0.14268	0.14839	
	9	0.01344	0.00960	
	1	0.13370	0.13089	
	2	0.11726	0.13346	
	3	0.08027	0.06059	0.0570 [d]
	4	0.11880	0.11624	
	5	0.13683	0.13809	0.0279 [d]
	6	0.11683	0.10922	0.0675 [d]
	7	0.15336	0.16289	
	8	0.13661	0.14047	
	9	0.01209	0.00823	

Table 1. Calculated and experimental spin densities. [a] The Coulomb and exchange integrals are written as $\alpha_r = \alpha_c + h_r \beta_{cc}$ and $\beta_{rs} = k_{rs} \beta_{cc}$, respectively, and $h_0 = 1.5$, $k_{co} = 1.6$, $h_c(co) = -0.15$, $h_F = 2.25$, and $k_{cF} = 0.72$ were employed. [b] $\lambda = 1.2$. [c] $|Q_{CH}| = 23.7$ gauss is assumed. [d] Assignments uncertain.

On the basis of the MO calculations for I, we assign the 0.74 gauss splitting to the position 6 and 7 protons, the 0.37 gauss coupling to the 5 and 8 protons. Excellent agreement is then found between experimental and calculated spin densities. For II the experimental and calculated spin densities at carbons 3 and 6 are also in excellent agreement.

Although the spectrum in Fig. 1 c is consistent with the idea that it arises from a species containing four non-equivalent spin $I = 1/2$ nuclei, such as 2-fluoro-1,4-benzosemiquinone (III), the LCAO calculation on this (III) system does not support this idea. In fact, a rather poor agreement between experimental and calculated spin densities is found, at least for two spin densities as in Table 1. The identity of III remains unknown.

We thank Prof. Dr. K. Wallenfels for the gift of 2,3-difluoro-1,4-naphthoquinone and Prof. Dr. K. H. Hausser for his continued interest in this work.