Electron Spin Resonance of the Acenaphthylene Anion Radical

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The electron spin resonance spectra of the anion radicals of an aromatic system provide much interesting information about these molecules. In particular, the approximate proportionality between the proton hyperfine constant and the π-electron spin density has yielded valuable information about the distribution of the unpaired electron, enabling one to test theoretical predictions.[1-11] However, some radicals produced by alkali metal reduction have been shown to exhibit some anomalous hyperfine structures, which can be attributed to the interaction of the radicals with the metal ions.[12-14]

The present investigation was undertaken to obtain more refined hyperfine coupling constants of the acenaphthylene anion radical than those previously reported and to examine the effects of the presence of metal ions on the hyperfine structure of this radical.

Experimental

To prepare the anion radical, both alkali metal reduction and electrolytic reduction methods were applied. In the former, the entire series of alkali metals, i. e., lithium, sodium, potassium, rubidium and cesium were used as reducing agents, with dioxane, tetrahydrofuran (THF), dimethoxyethane (DME), and dimethylformamide (DMF) as the respective solvents. In the latter, DMF, acetonitrile and a mixture of DMF and dioxane were used as solvents, tetra-*n*-propylammonium perchlorate as the supporting electrolyte, and the reduction was carried out in the electrolysis cell with a platinum anode and a mercury pool cathode, which was so designed that the electrolysis was possible within the microwave cavity. The ESR spectra were measured with a Hitachi X-band ESR spectrometer, model MPU-3B, employing field modulation at 100 kc./s. The preparation of the radicals and the measurement of the ESR spectra were carried out at room temperature (22.0$\sim$24.0°C).

Results and Discussion

The ESR Spectra and the Effect of Metal Ion Association on the Hyperfine Structures.— Figure 1 shows the ESR spectrum of the radical prepared with sodium in THF, together with the reconstruction based on the hyperfine coupling constants listed in Table I. As may be seen from this figure, the spectrum may be completely interpreted as arising from the coupling with four sets of two equivalent protons of the acenaphthylene anion radical. In the cases of the radicals other than those derived from the reduction with rubidium or cesium in DME, THF or dioxane, with lithium sodium or potassium in dioxane, and with potassium in THF respectively, the spectra show hyperfine splittings, similar to, though not strictly identical with, that given in Fig. 1. Figure 2, for example, shows the spectrum obtained from the radical prepared with sodium in DME: it should be compared with the spectrum given in Fig. 1.

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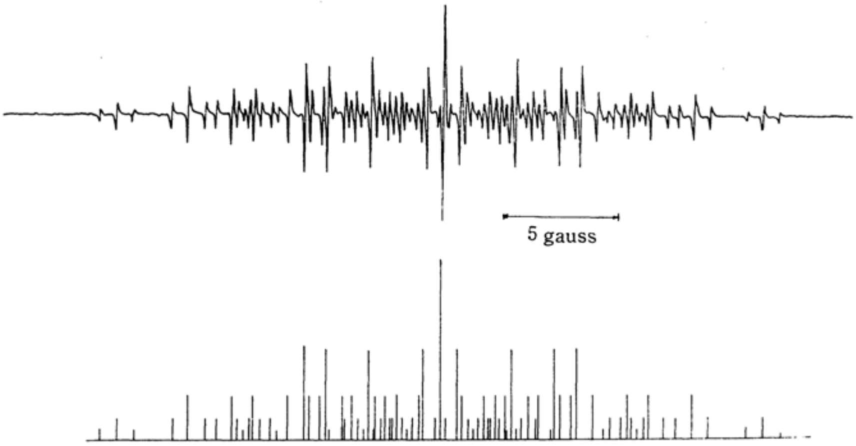


Fig. 1. The ESR spectrum of acenaphthylene anion radical prepared by the reduction with sodium in THF and the reconstruction based on the assumed coupling constants.

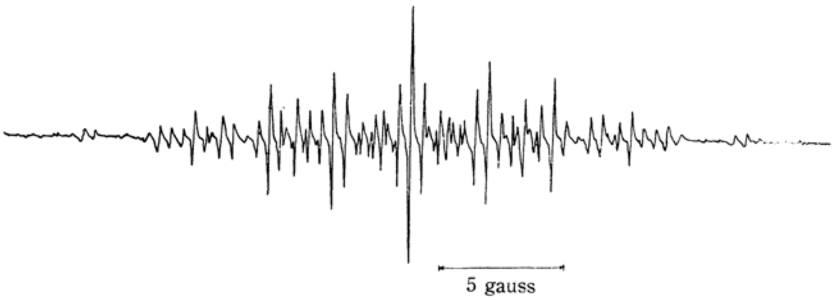


Fig. 2. The ESR spectrum of acenaphthylene anion radical prepared by the reduction with sodium in DME.

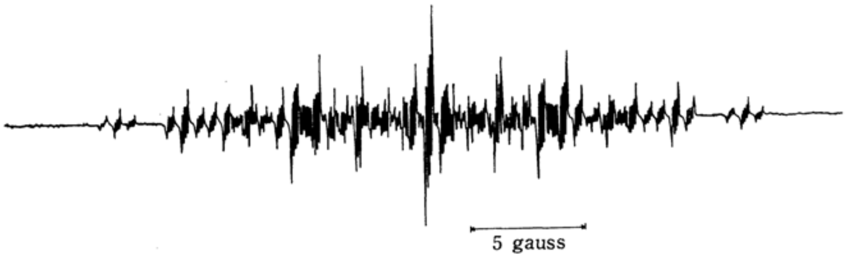


Fig. 3. The ESR spectrum of acenaphthylene anion radical prepared by the reduction with potassium in dioxane.

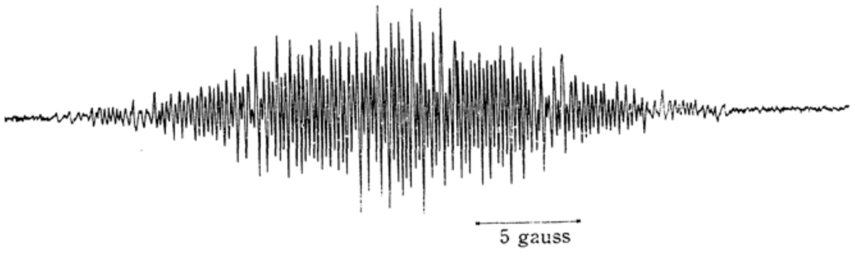


Fig. 4. The ESR spectrum of acenaphthylene anion radical prepared by the reduction with rubidium in dioxane.

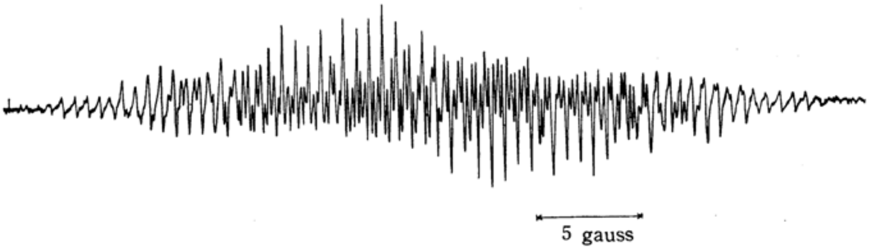


Fig. 5. The ESR spectrum of acenaphthylene anion radical prepared by the reduction with cesium in dioxane.

TABLE I. EXPERIMENTAL HYPERFINE COUPLING CONSTANTS (in gauss)

a) Li-acenaphthylene anion radical

Position	DMF	DME	THF	Dioxane
1, 2	3.06	3.10	3.20	3.19
3, 8	4.51	4.58	4.75	5.23
4, 7	0.46	0.48	0.62	0.94
5, 6	5.60	5.72	5.80	6.01
Metal	—	—	—	0.14

b) Na-acenaphthylene anion radical

Position	DMF	DME	THF	Dioxane
1, 2	3.06	3.09	3.09	3.10
3, 8	4.51	4.63	4.95	5.17
4, 7	0.46	0.55	0.71	0.79
5, 6	5.60	5.71	5.87	6.03
Metal	—	—	—	0.06

c) K-acenaphthylene anion radical

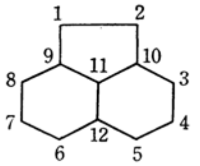
Position	DMF	DME	THF	Dioxane
1, 2	3.06	3.06	3.08	3.03
3, 8	4.51	4.75	4.87	4.94
4, 7	0.46	0.59	0·62	0.65
5, 6	5.60	5.78	5.89	5.90
Metal	—	—	0.07	0.09

d) Cs-acenaphthylene anion radical

Position	DMF	DME	THF	Dioxane
1, 2	3.06	2.99	2.93	2.93
3, 8	4.51	4.73	4.69	4.77
4, 7	0.46	0.58	0.59	0.61
5, 6	5.60	5.79	5.87	5.76
Metal	—	1.07	1.17	1.22

e) Electrolytic reduction

Position	In DMF, acetonitrile and a 1 : 1 mixture of DMF and dioxane
1, 2	3.06
3, 8	4.51
4, 7	0.46
5, 6	5.60



In contrast, the spectra from the radicals prepared with rubidium or cesium in DME, THF or dioxane, with lithium, sodium or potassium in dioxane and with potassium in THF show more complicated hyperfine structures than those expected from the couplings with only the protons of the acenaphthylene anion radical. For examples, Figs. 3—5 show the spectra from the radicals prepared in dioxane with potassium, rubidium and cesium respectively. In the cases of the reduction with lithium, sodium or potassium in dioxane, and with potassium in THF, each line of the normal hyperfine pattern of the acenaphthylene radical is further split into four lines with equal intensities, while in the cases with cesium in DME, THF or dioxane, each line is further split into eight lines with equal intensities. These additional splittings can be explained by the interaction of the odd electron with each metal nucleus, viz., lithium, sodium or potassium of spin 3/2, and cesium of spin 7/2 respectively. In the cases of reduction with rubidium, too, we believe that the anomalous feature in the hyperfine structures is due to the interaction of the odd electron with two kinds of rubidium nuclei of spin 5/2 and 3/2, although the analysis of the spectra has not yet been completed.

The hyperfine coupling constants of the protons and the metal nuclei obtained from these spectra are listed in Table I. The assignment of the splittings to the respective proton positions was made on the basis of theoretical calculations for the odd-electron distribution. In a previous work,[1)] the lack of resolution made it impossible to obtain a proton coupling at position 4 or to show a difference between positions 3 and 5.

All the spectra observed from the chemically- and electrolytically-produced radicals in the DMF solution agree with each other quite well and yield essentially the same coupling constants. However, in the other solvents, there is some small change in the proton hyperfine splittings as one goes from one metal to another. In the cases of electrolytically-produced radicals, no appreciable variation of hyperfine structures with the solvents was observed. It may be considered, therefore, that the variation of the hyperfine splittings with the solvents or with alkali metals is caused by the association between the anion radical and metal ions.

As may be seen from Table I, the magnitude of the coupling of the cesium nucleus increases in the series of DMF-DME-THF-dioxane. In dioxane, which is nonpolar in nature, the splittings of all the alkali metals were observed. On the contrary, in the DMF solution no splittings due to any metal nuclei were observed. It may be concluded, therefore, that the association between the anion radical and metal ions increases in the series of DMF-DME-THF-dioxane solutions, and that the difference in the proton hyperfine coupling constants from those in the DMF solution is due to metal ion association.

In the dioxane solutions, the difference in proton hyperfine splittings from those in the DMF solutions is largest for the lithium-acenaphthylene anion radical; in going to the cesium-acenaphthylene anion radical it decreases. In view of studies by Mathius and others[15-17] on the optical absorption and reactivities of some radicals, it seems reasonable to consider that the lithium ion affects most strongly the proton hyperfine couplings of the anion radicals and that as the cationic radius increases the effect decreases. However, in the DME solutions, the difference in the proton hyperfine splitting from those in a DMF solutions is largest for the cesium-acenaphthylene radical and smallest for the lithium-acenaphthylene radical. We are not able to offer any explanation of this. However, leaving aside this question, it can be seen from Table I that the hyperfine coupling constants of the protons belonging to the six-membered ring increase by metal ion association, especially at position 3. However, the splitting constant at position 1 is not so affected; rather, it decreases in the case of the cesium-acenaphthylene anion radical.

Since the isotropic proton hyperfine splitting in the π-electron radicals has been shown to be linearly related to the π-lectron spin density,[18] the variation in the proton coupling constants observed here may be attributed to the redistribution of the π-electron spin densities caused by the cationic field of metal ions. According to the spin distribution predicted by McLachlan's method, the increase in the coupling constants at positions 2, 3 and 5 corresponds to the increase in the positive spin densities, and that at position 4, to the increase in the negative spin density.

The change in hyperfine coupling constants caused by metal ion association can be observed in some other aromatic anion radicals, but the magnitudes are not as large as those observed here. Furthermore, it is of interest to note that in the acenaphtylene anion radical the hyperfine coupling of the sodium nucleus is smaller than that of the lithium or potassium nucleus. In many cases reported previously larger couplings have been observed for the sodium nucleus than for the lithium or potassium nuclei.[7,14,19-22] Further work is in progress on the effect of metal ion association on the hyperfine coupling constants of the other aromatic anion radicals; a detailed discussion will be reported at a later date.

Calculated Hyperfine Coupling Constants and Spin Densities.—Table II shows the spin densities and hyperfine coupling constants calculated on the basis of the Hückel and McLachlan[3] methods. When these values are compared with the experimental values obtained in the DMF solution, the agreement seems rather good in spite of the neglect of the variation in the σ-π interaction parameter Q in McConnell's equation with bond angles. However, the total width of the spectrum is much larger than the usual values of 23~27 gauss. It may be considered, therefore, that negative spin densities possibly exist in the acenaphthylene anion radical, as may be expected from the calculations based on the McLachlan method.

TABLE II. CALCULATED HYPERFINE COUPLING CONSTANTS AND SPIN DENSITIES

Position	Hückel method*1		McLachlan method*2	
	Hyperfine constant gauss	Spin density	Hyperfine constant gauss	Spin density
1,2	3.28	0.104	2.90	0.101
2,8	4.76	0.151	4.74	0.196
4,7	0.04	0.014	0.99	−0.041
5,6	5.61	0.178	5.92	0.245
9,10	—	0.053	—	0.027
11	—	0	—	−0.012
12	—	0	—	−0.045

*1 Proportionality constant Q in McConnell's equation is assumed to be -31.5 gauss.

*2 Based on McLachlan's procedure.[3]

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