Electron Paramagnetic Resonance, ENDOR and TRIPLE Resonance of some 9,10-Anthraquinol Radicals in Solution

Part 4. —Anthraquinolsulphonates†

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EPR, ENDOR and TRIPLE resonance spectra are recorded for 9,10-anthraquinol-1-sodium sulphonate, 9,10-anthraquinol-2-sodium sulphonate, 9,10-anthraquinol-1,5-disodium sulphonate and 9,10-anthraquinol-2,6-disodium sulphonate cation radicals. The splittings of the 9,10-anthraquinol cation radical have been assigned by deuteration. The spectra of the deuterated anthraquinol cation radicals and the assignment of hyperfine coupling constants are discussed.

Quinones are considered to be electron acceptors; the quinone cation, however, is formed by removing an electron from quinone.[1] It has been shown that semiquinones are stable in strongly acidic media, where, as revealed by deuteration, they exist as double protonated cations.[2]

We have found an improved method of producing free radicals in solution, especially cation radicals.[3] Cation radicals are normally produced by chemical or electrochemical oxidation. Usually the oxidation potential needed to generate the cation radical is higher than the reduction potential needed to generate the corresponding anion radical, and more specific procedures are needed.

Aromatic hydrocarbons have electron affinities of 0.1–1.0 eV and ionization potentials varying between 7 and 10 eV.[4] The oxidizing agent is chosen so that the oxidation potential approximately corresponds to the first vertical ionization potential of the substrate.[5] A good solvent for the cation radicals has low melting point, low viscosity and an appropriate relative permittivity. At room temperature and in trifluoroacetic acid, the benzoquinone cation radical is persistent up to an hour after irradiation and can be used as a charge-transfer agent to form another cation radical in trifluoroacetic acid.[6]

The sulphonated compounds are more soluble in water than the anthraquinones but under anhydrous conditions are only sparingly soluble in the present solvent systems. There are few reports in the literature concerning the EPR spectroscopy of anthraquinolsulphonate cations.

Experimental

Materials

9,10-Anthraquinone (purum) from Fluka, 9,10-anthraquinone-1-sodium sulphonate (practical grade, m.p. > 280 °C) from K&K Labs, 9,10-anthraquinone-(quinalizarin, p.a.) 1,5-disodium sulphonate (m.p. > 300 °C, techn.) from EGA-CHEMIE, 9,10-anthraquinone-2-sodium sulphonate (puriss p.a. 99%) from Fluka, 9,10-anthraquinone-2,6-disodium sulphonate (m.p. > 325 °C) and 2-chloro-9,10-anthraquinone (97%) from Aldrich were used without further purification. Other chemicals were D_2SO_4 (Merck, 96–98%, deuteration degree not less than 99%), CF_2SO_3H (Fluka, purum), FSO_3H (Fluka, techn.), SO_2ClF (Cationics Inc.), CF_3COOD (Merck, Uvasol) and CCl_3D (Merck, Uvasol).

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Equipment

EPR spectra were measured on Bruker ESP-300 and Varian E-9 spectrometers, and ENDOR and TRIPLE spectra were measured on a Bruker ER 200D-SRC spectrometer, as described earlier.[3] UV illumination was provided by an Airam HGU 300 W mercury lamp and a Philips HP 3133 460 W lamp.

Sample Preparation

Samples were prepared by a high-vacuum technique as described elsewhere.[3] A closed-loop flow system driven by argon gas or a special cuvette system equipped with vacuum stopcocks was used to detect the optimum conditions. The 2-(^{2}H)-9,10-anthraquinol cation radical was prepared by pumping the solvent mixture away from the anion sample cuvette (part 3). The residue was extracted with CCl_3D and the solution was transported into the cuvette. After evaporating CCl_3D in vacuum, CF_3CO_2D and D_2SO_4 were added.

Results

9,10-Anthraquinone

Fig. 1 shows the EPR spectrum of the deuterated cation radical generated in a mixture of CF_3CO_2D and D_2SO_4. The hyperfine coupling constants are shown in table 1. Bolton *et al.*[2] have published the EPR spectrum of the 9,10-anthraquinol cation radical with both OH protons deuterated. Comparison of the coupling constants of the 9,10-anthraquinol cation radical generated in D_2SO_4 with the coupling constants of the deuterated cation radical indicates that the coupling constant 0.159 mT belongs to the proton at position 1, and on this basis all protons can be assigned. Two splittings, 0.159 and 0.105 mT, were detected from the ENDOR

Table 1. Hyperfine coupling constants (/mT) of undeuterated and deuterated 9,10-anthraquinol cation radicals obtained in various solvents at 293 K

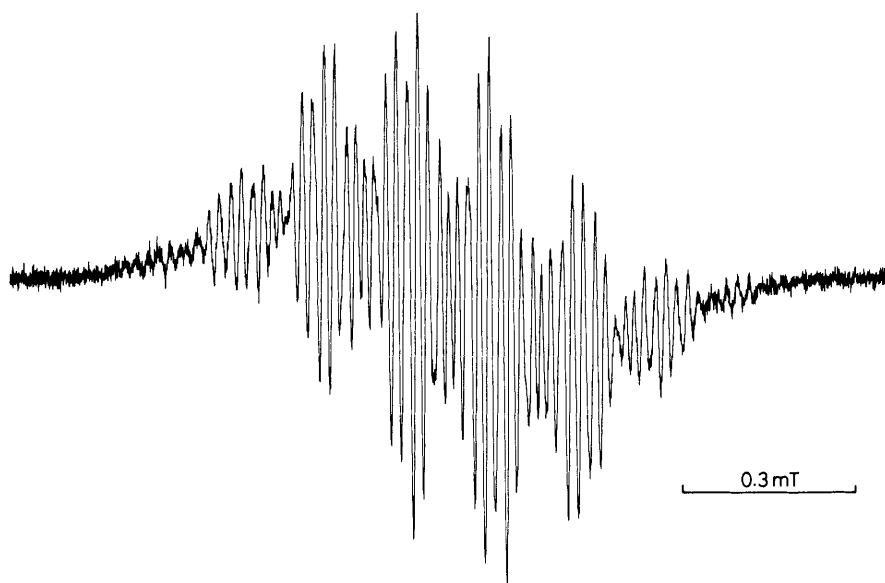| position | hyperfine coupling constants | |
	9,10-anthraquinol in CF_3SO_3H	2-(^{2}H)-9,10-anthraquinol in CF_3CO_2D–D_2SO_4
1	0.162	0.159
2	0.105	0.018 = D
3	0.105	0.105
	0.119 = OH	0.018 = OD
g	2.00308	

Fig. 1. The EPR spectrum of deuterated 2-(^{2}H)-9,10-anthraquinol cation radical generated with UV light in a mixture of CF_3CO_2D and D_2SO_4 at 288 K.

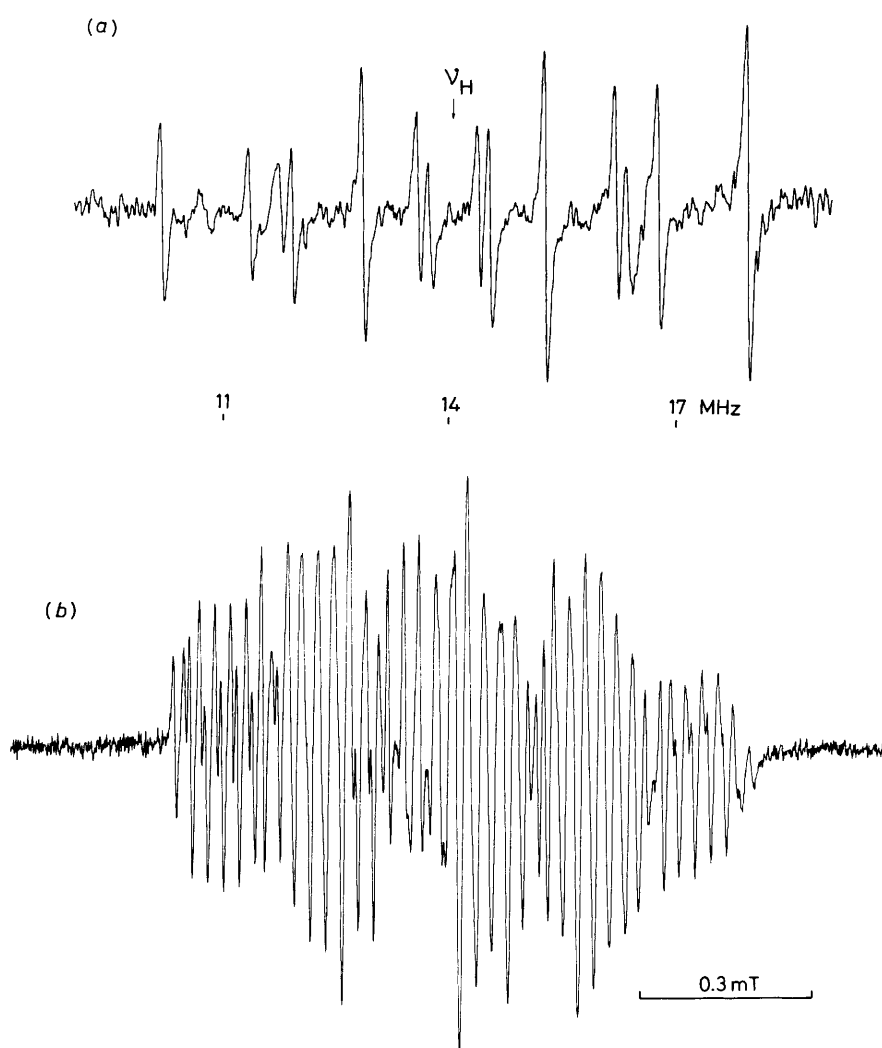**Fig. 2.** (a) The ENDOR spectrum of the cation radical derived from 9,10-anthraquinone-1-sodium sulphonate with UV light in CF_3SO_2H at 253 K. (b) The EPR spectrum of the deuterated cation radical generated from 9,10-anthraquinone-1-sodium sulphonate with UV light in a mixture of SO_2ClF and D_2SO_4 at 285 K.

Table 2. Hyperfine coupling constants (/mT) of cation radicals generated from 9,10-anthraquinone-1-sodium sulphonate and 9,10-anthraquinone-2-sodium sulphonate with UV light in various solvents and at various temperatures

hyperfine coupling constants					
9,10-anthraquinol-1-sodium sulphonate			9,10-anthraquinol-2-sodium sulphonate		
pos.	CF_3SO_3H at 298 K	$SO_2ClF–D_2SO_4$ at 298 K	pos.	$SO_2ClF–FSO_3H$ at 278 K	$SO_2ClF–D_2SO_4$ at 278 K
5	0.163	0.171	6	0.089	0.092
4 or 8	$\begin{cases}0.190\\0.087\end{cases}$	$\begin{cases}0.197\\0.080\end{cases}$	3 or 7	$\begin{cases}0.155\\0.112\end{cases}$	$\begin{cases}0.162\\0.113\end{cases}$
not assigned	$\begin{cases}0.275\\0.153\\0.037\\0.025\end{cases}$ 0.159 = OH	$\begin{cases}0.282\\0.150\\0.029\\0.017\end{cases}$ 0.027 = OD	not assigned	$\begin{cases}0.182\\0.162\\0.112\\0.089\end{cases}$ 0.142 = OH 0.134 = OH	$\begin{cases}0.179\\0.162\\0.113\\0.092\end{cases}$ 0.024 = OD 0.024 = OD
g	2.00280			2.00314	

spectrum of the deuterated cation radical. Sullivan has investigated the temperature dependence of the hydroxyl proton splitting constant of the 9,10-anthraquinol cation radical by EPR and has assigned the coupling constants correctly by theoretical calculations.[7]

9,10-Anthraquinone-1-sodium Sulphonate

The ENDOR spectrum of the cation was observed after UV irradiation of 9,10-anthraquinone-1-sodium sulphonate in a mixture of CF_3SO_3H (triflic acid) and D_2SO_4, using a high-vacuum technique. A similar spectrum was observed using only trifluoromethanesulphonic acid, a high-vacuum technique and UV light [(fig. 2(a)]. Analysis of the EPR and ENDOR spectra gives the hyperfine coupling constants shown in table 2. The EPR spectrum of the cation radical produced in a mixture of D_2SO_4 and SO_2ClF is shown in fig. 2(b) and the coupling constants in table 2. According to molecular symmetry, the 9,10-anthraquinol-1-sulphonate cation contains nine chemically non-equivalent protons, two OH protons and seven aromatic protons. The ENDOR spectrum shows seven coupling constants and the EPR spectrum eight, confirmed by simulation. Temperature (253–298 K) had only a slight effect on coupling constants. Deuteration allowed detection of one hydroxyl proton coupling constant.

9,10-Anthraquinone-2-sodium Sulphonate

The cation radical was generated in four different solvent systems: trifluoromethane sulphonic acid and mixtures of FSO_3H and SO_2ClF, D_2SO_4 and SO_2ClF or FSO_3H and D_2SO_4. Samples were sealed under high vacuum and irradi-

ated with UV light. The radical concentration was strong and sometimes side reactions took place and a fluorine splitting was detected by ENDOR; EPR spectra showed strong temperature dependence. The hyperfine splitting constants are shown in table 2. Only six coupling constants were detected by ENDOR (fig. 3). The coupling constants of the OH protons were identified on the basis of the EPR spectrum of the deuterated system. According to the general TRIPLE spectrum the coupling constants of the very unstable cation radical have the same relative sign.

9,10-Anthraquinone-1,5-disodium Sulphonate

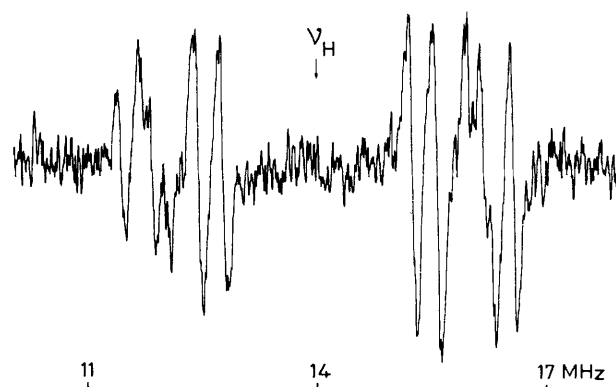This cation radical is very hard to generate, probably because of poor solubility in the solvent used: CF_3SO_3H,

Fig. 3. The ENDOR spectrum of the 9,10-anthraquinol-2-sodium sulphonate cation radical measured under UV illumination in a mixture of SO_2ClF and FSO_3H at 253 K.

Table 3. Hyperfine coupling constants (/mT) of cation radicals produced from 9,10-anthraquinone-1,5-disodium sulphonate and 9,10-anthraquinone-2,6-disodium sulphonate with UV light in protonated and in deuterated solvents at various temperatures

hyperfine coupling constants				
9,10-anthraquinol-1,5-disodium sulphonate		9,10-anthraquinol-2,6-disodium sulphonate		
pos.	CF_3SO_3H at 298 K	pos.	CF_3SO_3H at 314 K	$CF_3CO_2D–D_2SO_4$ at 325 K
4	0.107	3	0.157	0.157
2 or 3	$\begin{cases}0.173\\0.079\end{cases}$	1 or 4	$\begin{cases}0.115\\0.111\end{cases}$ 0.145 = OH	$\begin{cases}0.115\\0.111\end{cases}$ 0.020 = OD
g	2.00251		2.00316	

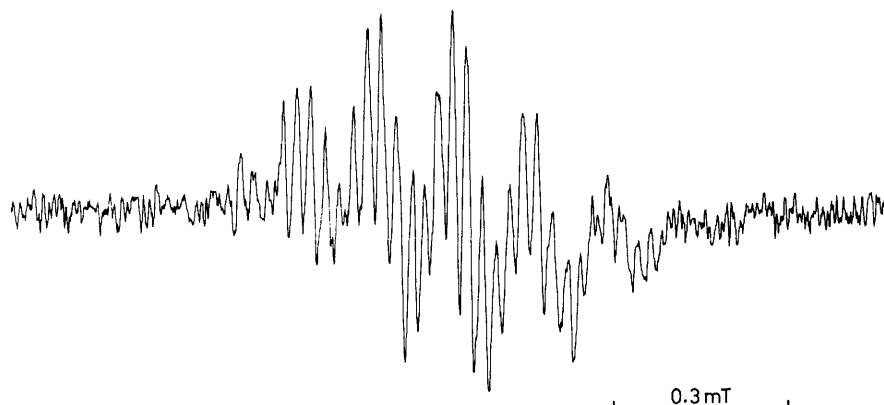**Fig. 4.** The EPR spectrum of 9,10-anthraquinol-2,6-disodium sulphonate cation radicals generated with UV light in a mixture of CF_3CO_2D and D_2SO_4 at 303 K.

D_2SO_4–FSO_3H or CF_3SO_3H–D_2SO_4. We have not yet been able to scan an ENDOR spectrum of the normal or deuterated cation. The hyperfine coupling constants are listed in table 3 and a high temperature was required to scan the EPR spectrum.

9,10-Anthraquinone-2,6-disodium Sulphonate

The cation radical was generated by UV irradiation in a high-vacuum cuvette using CF_3SO_3H, CF_3SO_3H–D_2SO_4, FSO_3H–D_2SO_4 or CF_3CO_2D–D_2SO_4 as solvent. Where deuterated and undeuterated acids were used together, a mixture of deuterated and undeuterated cation radicals was produced.

Fig. 4 shows the EPR spectrum of the deuterated cation radical. The splitting constants are shown in table 3. The analysis of the best ENDOR spectrum gives three coupling constants; the largest coupling constant is highly temperature dependent and a high temperature is necessary to obtain a good signal-to-noise ratio.

Discussion

Generation of the cation radicals required use of UV irradiation and a strong acidic medium. Trifluoroacetic acid was used because of its acidity and low nucleophilicity, which contribute to the stabilization of the cation radicals. Anthraquinonesulphonates are photosensitisers: 2- and 2,6-sulphonates are strong sensitisers and 1- and 1,5-sulphonates are weak sensitisers. Therefore, the cation radicals of 2- and 2,6-sulphonates are more easily generated than those of 1- and 1,5-sulphonates, and side reactions also take place more often.

The assignment of the 9,10-anthraquinol cation radical is clear but the assignments of the other compounds are tentative owing to symmetry, which makes it impossible to assign all the coupling constants. More substituted compounds will need to be investigated. INDO calculations could also be performed but a modified program is needed rather than the standard.[8] Deuteration is a technique that always gives the correct assignment, but this procedure is tedious. However, the halogen-substituted quinones are easily deuterated by generating an anion radical in a deuterated solvent system.

References

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