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AN ENDOR AND ESR STUDY OF THE RADICAL CATION OF N,N'-BIS-(4-FLUOROPHENYL)-4,4'-BIPYRIDYLIUM DICHLORIDE

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Abstract—The ESR and ENDOR spectra of the radical cation of N,N'-bis-(4-fluoro-phenyl)-4,4'-bipyridylium dichloride (fluorophenylquat FPQ) in methanol was studied over a temperature range from +40° to −90°. The ENDOR technique was used to obtain accurately the splitting constants for a highly complicated ESR spectrum and computer simulation showed excellent agreement. Fluorine ENDOR resonance was clearly observed with a line width similar to that of the protons. On decreasing the temperature the concentration of the radical cation decreases until at −90° the ESR intensity was very small. This process is reversible and concentration studies indicate that the radical cation is in equilibrium with a diamagnetic dimer species. The thermodynamic parameters ΔH°, ΔG° and ΔS° for the process are reported.

Bipyridylium salts which are used as herbicides[1] as well as redox indicators[2] have received a great deal of attention over the past few years. They are easily reduced and form highly coloured radical cations by a one electron reduction which is completely reversible.

We have recently carried out an ESR and ENDOR study on methanol solutions of various alkyl N,N'-substituted bipyridylium radical cations[3,4] showing that on decreasing the temperature the radical cations dimerised to form a plane to plane configuration diamagnetic dimer; the two monomer molecules being linked together by a π-π' bond. The ESR spectra show that the electron is delocalised over the entire molecule.

In this paper we report both the ESR and the ENDOR spectra for the radical cation of N,N'-bis-(4-fluorophenyl)-4,4'-bipyridylium-dichloride (FPQ) in methanol. The ESR spectrum was too difficult for reliable analysis hence the use of ENDOR to obtain the correct splitting constants. The ENDOR clearly shows absorptions due to the fluorine nucleus, amongst absorptions arising from the protons. This is the first time the fluorine ENDOR enhancement have been detected in this type of system.

The concentration of the radical cation was found to decrease with decrease of temperature and the process was found to be reversible. An equilibrium between the radical cation and a diamagnetic dimer was observed and the thermodynamic constants obtained are compared with those of a similar equilibrium for the radical cation of the unsubstituted N,N'-diphenyl-bipyridylium system (Phenylquat DPQ).

EXPERIMENTAL

Materials. N,N'-Bis-(4-fluorophenyl)-4,4'-bipyridylium dichloride (FPQ) was prepared by a similar method to that of Allen[5], m.p. >350° dec. The structure was confirmed by proton and fluorine NMR.

MeOH was dried by standing over anhyd $CaSO_4$ distilled under dinitrogen and outgassed before use.

Procedure. The radical cation was prepared by passing MeOH soln over a freshly prepared Zn film. Samples were sealed under vacuum in quartz tubes for ESR and ENDOR analysis. A Varian E109 ESR spectrometer fitted with a variable temp control unit was used for the measurement of ESR spectra. ENDOR measurements were made using a digital Bruker ENDOR unit interfaced with the Varian E109. Radical concentrations were measured by comparison with freshly prepared MeOH solns of diphenyl picryl hydrazyl (dpph). Integration of the ESR spectra was carried out using a micro processor.

RESULTS AND DISCUSSION

ESR and ENDOR spectra

The development of the ENDOR technique has proved to be invaluable for the accurate determination of hyperfine splitting constants especially when ESR spectra are complicated. Up to now most of the reported ENDOR absorptions are for protons, however, since F nuclei (^{19}F) have a gyromagnetic ratio similar to that of protons both F and proton ENDOR enhancements should be observed in the same frequency range if both have splitting constants of comparable size. Hence the unravelling of complex hyperfine patterns of F substituted aromatic radicals should be more easily and accurately achieved. Allendoerfer and Maki[6] have investigated a series of F substituted triphenylmethyl radicals in toluene at −70°. In all cases they were able to observe proton ENDOR but unable to detect ENDOR signals from the ^{19}F nucleus although, the ^{19}F hyperfine splitting constant could be determined from the ESR spectra, and therefore, the frequency of the ENDOR resonances could be calculated. Their reason for the non-detection of ^{19}F ENDOR was due to the broadening of the signal at low temperature; the broadening being due to the contribution of the unaveraged dipole–dipole part of the coupling. The F nucleus has a 4 times larger anisotropy than a proton referring to equal isotropic coupling and therefore the saturation of the ENDOR transitions can be difficult to achieve.

Lubitz *et al.*[7] however have detected F ENDOR in F substituted benzophenone radical anions and they have shown that with an NMR rf field of 4 mT (rotating frame) absorptions can only be expected for couplings no larger than 0.5 mT.

We have also found F absorptions of 0.124 and 0.133 mT in substituted fluorenone radical anions in tetrahydrofuran with sodium as gegen ion.[8]

In this study the ESR spectrum of the green radical cation of FPQ obtained by passing a methanol solution

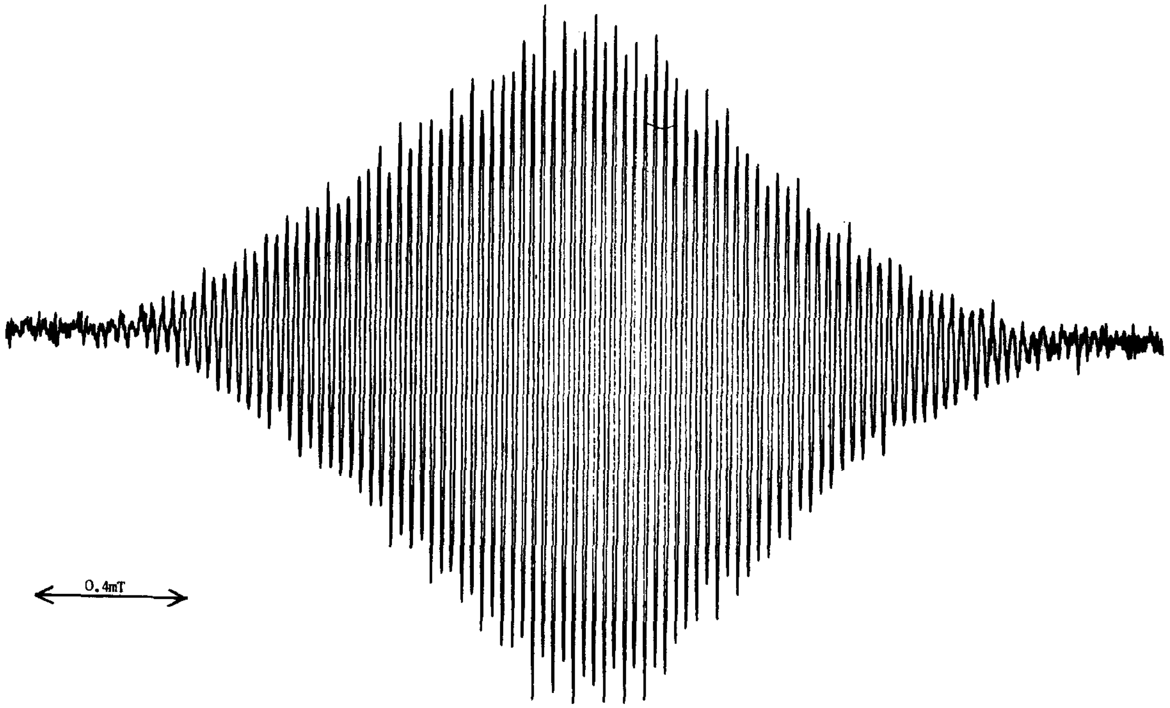


Fig. 1. ESR spectrum of radical cation of FPQ at −40°.

over a zinc film is shown in Fig. 1. The ESR spectrum was too complicated for reliable analysis and could only be interpreted by the use of the ENDOR technique. The ENDOR spectrum is shown in Fig. 2; F enhancement (0.116 mT) with a similar line width to that of the proton ENDOR is clearly observed. This we believe is the first time that F ENDOR has been observed in such radical cation systems. The splitting constants thus obtained are given in Table 1 together with those of Phenylquat DPQ (the unsubstituted N,N′-diphenyl-4,4′-bipyridylium radical cation). It is clearly seen that the unpaired electron is delocalised over the entire molecule and that F substitution does not seriously perturb the unpaired electron density in the molecule as the proton splitting constants are similar. The splitting constant for the F nucleus is approximately twice that of the proton in the similar position in parent hydrocarbon. This is the normally observed ratio for F substituted radical anions.[7] The

$$\frac{|A|_F}{|A|_P} = \frac{0.116}{0.054} = 2.15$$

assignments of the splitting constants were made by reference to the unsubstituted parent compound DPQ$^{\dot{+}}$ whose splitting constants have been assigned by deuteriation and Me substitution in the phenyl groups[9] with the pyridyl protons assigned as before.[3,4]

Monomer-dimer equilibrium

As the temperature of the system was reduced from +40°, the intensity of the ESR spectra decreased until at −90° the intensity was very small. However the ESR (and ENDOR) spectra showed no alternation in the radical species present. This change with temperature is completely reversible and suggests that an equilibrium is present involving paramagnetic and diamagnetic species. Experiments were carried out on solutions of differing concentrations to test if Beer's Law was obeyed, i.e. a two-fold dilution of the solution should reduce the optical density to one-half. This did not occur.

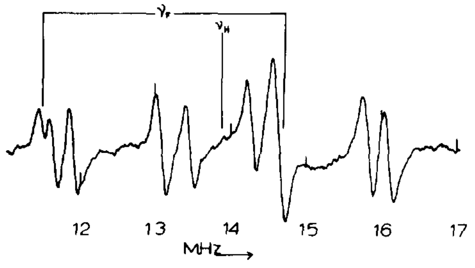


Fig. 2. ENDOR spectrum of radical cation of FPQ at −40°.

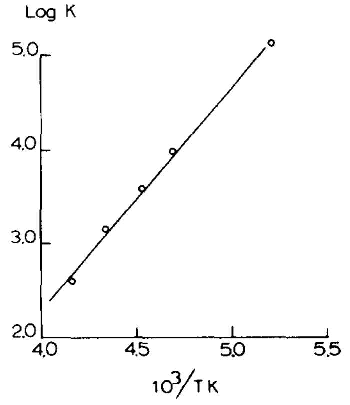
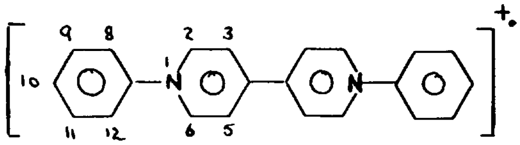


Fig. 3. Plot of $\log_{10} K$ vs $10^3/T$ K for equilibrium (1).

Table 1. The experimental splitting constants of the diquaternary 4,4'-bipyridylium radical cations, DPB and FPB (mT)



Compound	Position							
	1	2	3	8	9	10	11	12
DPB	0.380	0.140	0.159	0.050	0.031	0.054	0.031	0.050
FPB	0.380	0.141	0.161	0.050	0.030	0.116^{+}	0.030	0.050

+ fluorine

Table 2. Thermodynamic constants for the dimerisation of the radical cations DPB and FPB

Compound	ΔG^0 kJ mol^{-1}	ΔH^0 kJ mol^{-1}	ΔS^0 JK^{-1} mol^{-1}
DPB	-6.84	-34.84	-93.85
FPB	-5.44	-43.44	-127.51

We conclude from this that the equilibrium involved is not bimolecular in both directions and so therefore cannot be due to a disproportionation reaction in which two molecules of radical cations react to give a dication species together with a neutral molecule. The equilibrium could therefore be of the monomer-dimer type as postulated earlier by Evans *et al.*[3,4] for the paraquat and morphamquat radical cations (eqn 1).

$$(M)^{\dot{+}} + (M)^{\dot{+}} \rightleftharpoons (M)_2^{++}. \tag{1}$$

At temperatures above +40° there is no increase in the signal with temperature, therefore the concentration of radical cations at +40° gives the concentration of the total [FPQ$^{\dot{+}}$]. Thus at any other temperature knowing the concentration of [M] from the ESR spectrum, $[M]_2$ can be calculated and hence the value of $K = [(M)_2]/[(M)]^2$ for Eqn (1) determined. The values of K obtained are reasonably constant over a wide concentration range and this confirms the monomer-dimer type equilibrium proposed in Eqn (1).

Values of the equilibrium constant K calculated over the temperature range +40 to −90° gives a good straight line for a log K against 1/T plot (Fig. 3). The thermodynamic values obtained are given in Table 2, together with the thermodynamic parameters for the unsubstituted diphenyl bipyridylium DPQ radical cation. It is seen that F substitution in the *para* position of the phenyl group has little effect. The ΔG° values are very similar, the ΔH° values differ by 8.60 kJ mol^{-1}; the FPQ$^{\dot{+}}$ being the more exothermic.

The ΔS° values are negative as one would expect in a dimerisation reaction but the value for FPB$^{\dot{+}}$ is significantly more negative showing that the formation of the dimer is accompanied by a much greater ordering of the system.

Kosower and Cotter[10] from the examination of the electronic spectrum suggested that in the case of the radically cation of paraquat, PQ (N,N'-dimethyl-4,4'-bipyridylium dichloride) the dimer is a biradical. Itoh and Nagakura[11] however have found that 1-alkyl-4-carbomethoxy pyridyl radicals were in equilibrium with diamagnetic π type complex dimers consisting of two pyridinyl radicals one above the other. Fuhrhop[12] has also reported the formation of a $\pi - \pi'$ diamagnetic dimer of the zinc octaethyl porphyrin radical cation in methanol/chloroform solutions at low temperatures. He concludes that the two identical radical cations approach each other to give a face to face dimer of the porphyrin rings. We propose that the diamagnetic dimer of the DPQ$^{\dot{+}}$ and FPQ$^{\dot{+}}$ could also exist in a face to face configuration with a $\pi - \pi'$ bond linking the two monomer molecules.

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