Electron Spin Resonance Study of the Dimerization Equilibrium of the Radical Cation of 1,1′-Diethyl-4,4′-bipyridylium Diiodide in Methanol

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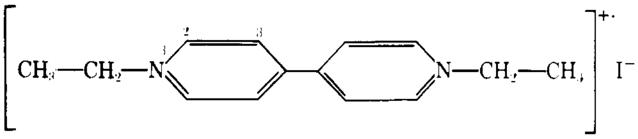
Abstract: We have studied the ESR spectra of methanol solutions of the radical cation (I) of ethylquat (1,1′-diethyl-4,4′-bipyridylium diiodide) from +30 to −90 °C. The values of the splitting constants obtained at −80 °C are A(pyridyl N) 0.414, A(pyridyl H(3)) 0.164, A(pyridyl H(2)) 0.136, $A(NCH_2)$ 0.232, and $A(CH_3)$ 0.007 mT. Proton hyperfine splitting constants have been determined using electron-nuclear double-resonance (ENDOR) spectroscopy. Assignments of the splitting constants were made by reference to the paraquat radical cation and computer simulation showed excellent agreement. On decreasing the temperature the concentration of the radical cation decreases until at −90 °C the ESR signal intensity is very low. This process is reversible and concentration studies indicate that the radical cation is in equilibrium with a diamagnetic dimer species. $\Delta H°$ for this equilibrium is found to be -8.19 ± 0.4 kJ mol^{-1}. The $\Delta G°$ and $\Delta S°$ values at 25 °C are -15.94 kJ mol^{-1} and $+26.01$ J mol^{-1} K^{-1}, respectively.

The bipyridylium salts have received a great deal of attention as they are now used as herbicides[1] as well as redox indicators.[2-4] These salts can be reduced in a variety of ways producing their respective radical cations. The reactivity of these radical cations plays a vital role in determining their herbicidal activity.[1] ESR studies of the paraquat radical cation have previously been reported.[5,6]

We have recently carried out an ESR study on methanol solutions of the radical cation of morphamquat.[7] Although a large number of lines were present in the spectrum, interpretation was achieved by deuterium substitution and computer analysis. It was found that the concentration of the radical cation decreases with decrease in temperature. This process is reversible and concentration experiments showed that the radical cation is in equilibrium with a diamagnetic species.

In this paper we describe the extension of this work to the radical cation of ethylquat (I). Johnson and Gutowsky[5] reported the preparation and the first ESR study of this radical cation but were unable to analyze the spectrum because of the low signal-to-noise ratio and the very large number of lines. They concluded that the gross features of the spectrum indicated splitting constants approximately equal to those for the paraquat radical cation. We have now analyzed the ESR spectrum of the radical cation of ethylquat by the ENDOR technique and checked the spectrum using computer simulation. We have also studied the temperature dependence of the radical cation concentration.



I

Experimental Section

Materials. Ethylquat was prepared by a similar method to that of Emmert and Stawitz,[8] mp 259.5–260.5 °C (lit.[9] mp 260 °C). Anal. Calcd: C, 35.90; H, 3.85; N, 5.98; I, 54.27. Found: C, 36.13; H, 3.78; N, 6.03; I, 54.18%.

Methanol (AnalaR) was left for 1 week over anhydrous calcium sulfate and then distilled under nitrogen and outgassed on a high-vacuum system.

Procedure. The radical cation was prepared from solutions of ethylquat in methanol (a) by reduction with a freshly prepared zinc film and (b) by treating with a sodium hydroxide–methanol solution. The radical cations obtained by both these methods gave identical ESR spectra, so we carried out our experiments on solutions prepared by method (a).

Samples of the ethylquat radical cation/methanol solution were sealed off in ESR tubes under high-vacuum conditions, and their spectra were measured as previously described[7,10] using a Varian E-3 spectrometer fitted with a Varian variable temperature unit.

The concentration of the radical cations was determined by a modification of the method used previously[11] by double integration using Weddle's method[12] and comparison with diphenylpicrylhydrazyl under similar conditions. ENDOR spectra were recorded on a Varian E-1700 high-power spectrometer at Varian Associates, Palo Alto, Calif. by Dr. D. S. Leniart.

Results and Discussion

ESR and ENDOR Spectra. The ESR spectrum of ethylquat radical cation at room temperature is shown in Figure 1. It was too complicated for reliable analysis, so ENDOR spectroscopy was used to elucidate it. The first ENDOR experiment on free radicals in liquids was performed by Hyde and Maki[13] and several reviews[14-17] cover the ENDOR literature in the intervening period.

The ENDOR spectrum of the radical cation of ethylquat at −80 °C given in Figure 2 shows that there are four proton splitting constants. These are given in Table I (although the nitrogen frequency is included the absorption is not shown in Figure 2). The improved resolution using frequency modulation (Figure 2b) over amplitude modulation (Figure 2a) enables the splitting constants, particularly the small one, to be obtained with greater accuracy.

Using the splitting constants obtained from the ENDOR analysis at −80 °C, computer simulation gave exact agreement with the ESR spectrum measured at the same temperature. The room-temperature ESR spectrum was analyzed using these ENDOR splitting constants as a guide, and computer simulation gave exact agreement with the observed ESR spectrum at room temperature. The splitting constants were assigned by analogy with those of the paraquat radical cation,[5] and are given in Table II (together with those for paraquat[5] and morphamquat[7] radical cations). The splitting constants at 25 and −80 °C are very similar, and the slight changes observed (which in some cases are within experimental error) could be due to the difference in the effect of the solvent at the two temperatures.

The small splitting in the ESR spectra due to the methyl protons was very difficult to resolve. (At −80 °C no splitting of this kind could be observed.) Maximum resolution was achieved at room temperature, but even so, the splitting con-

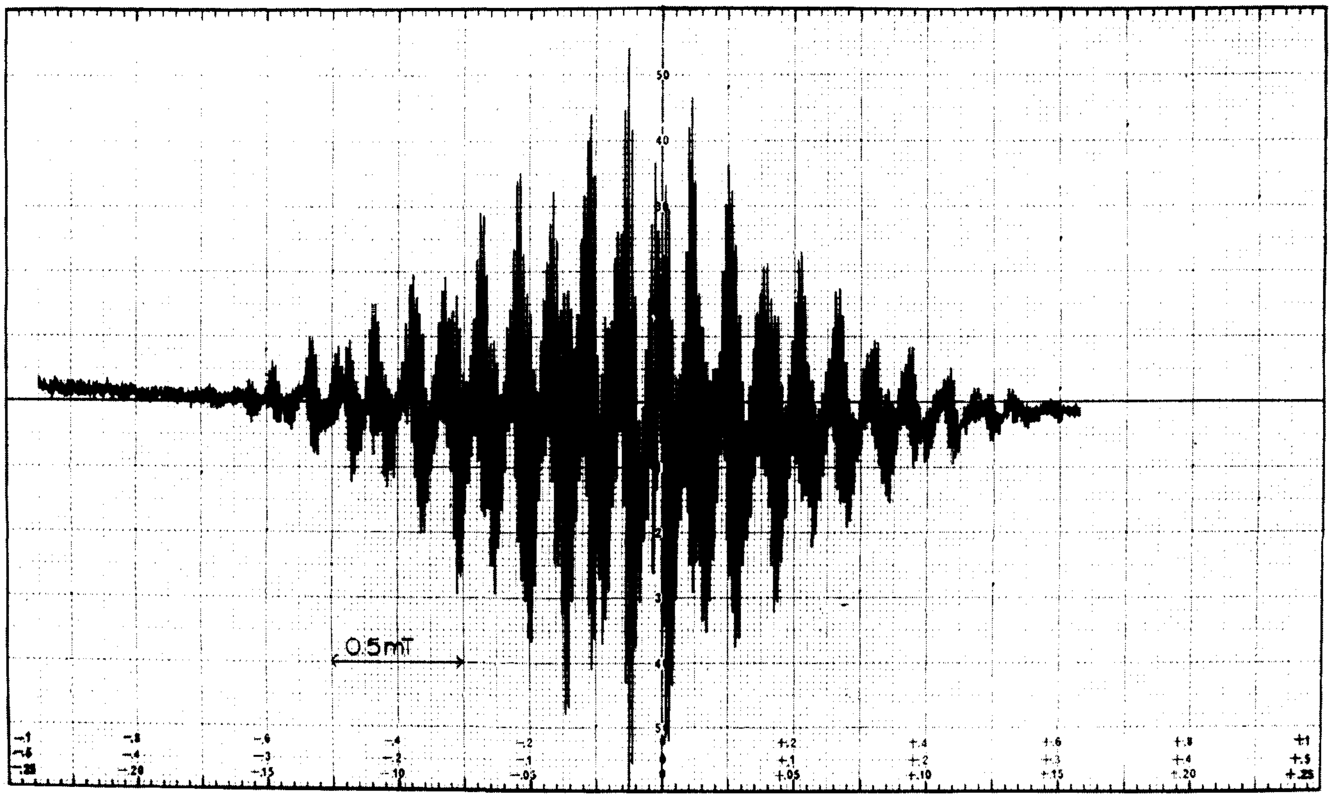


Figure 1. Electron spin resonance spectrum of ethylquat radical cation at 25 °C.

Table I. Analysis of ENDOR Spectrum of Ethylquat Radical Cation in Methanol at −80 °C

Frequency of ENDOR lines, MHz	Position	Splitting constant A, mT
6.78	Pyridyl N	0.414
10.35 and 16.85	NCH_2	0.232
11.30 and 15.90	Pyridyl H(3)[a]	0.164
11.75 and 15.55	Pyridyl H(2)[a]	0.136
13.50 and 13.70	CH_3	0.007

[a] Assignment based on the paraquat radical cation system.

Table II. Splitting Constants for (Ethylquat)$^{+\cdot}$ [(EQ)$^{+\cdot}$], (Paraquat)$^{+\cdot}$ [(PQ)$^{+\cdot}$], and (Morphamquat)$^{+\cdot}$ [(MQ)$^{+\cdot}$] in Methanol at 25 °C

Position	Splitting constants, A, for EQ$^{+\cdot}$, mT	Splitting constants, A, for PQ$^{+\cdot}$, mT	Splitting constants, A, for MQ$^{+\cdot}$, mT
Pyridyl N	0.415	0.423	0.400
Pyridyl H(3)	0.151	0.157	0.142
Pyridyl H(2)	0.132	0.133	0.048
NCH_2(MQ)			0.245
NCH_2(EQ)	0.235		
NCH_3(PQ)		0.399	
CH_3(EQ)	~0.01		
Morpholine N			0.024

stant could not be obtained with any degree of accuracy. Johnson and Gutowsky[5] tentatively assigned their smallest splitting constant of 0.013 mT to the methyl protons.

ENDOR spectra, at −80 °C (Figure 2) on the other hand, demonstrate this small splitting quite clearly, and the splitting constant which must be due to the methyl protons can be accurately measured as 0.007 mT. The use of ENDOR spectroscopy is, therefore, essential for the precise interpretation of the ESR spectra of the radical cation of ethylquat.

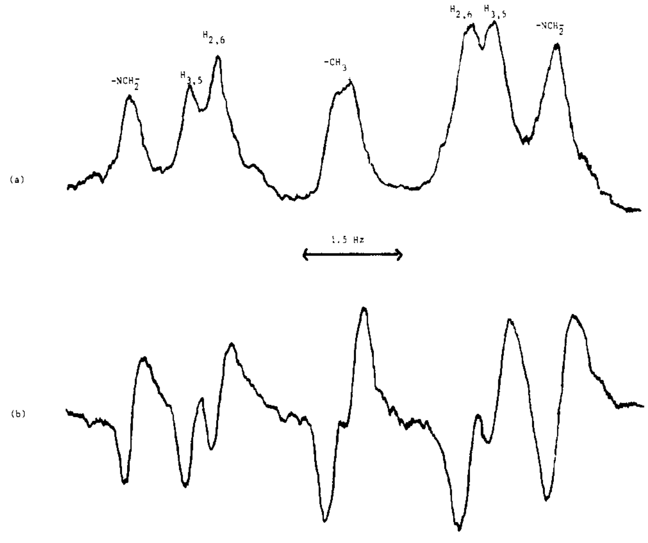


Figure 2. Proton ENDOR spectrum of ethylquat radical cation at −80 °C: (a) amplitude modulating the rf field at a 1 kHz rate; (b) frequency modulating the rf field at a 1 kHz rate using a frequency deviation of ±150 kHz. (Assignment based on the paraquat radical cation system.)

The results show that the unpaired electron is delocalized symmetrically over the ethylquat radical cation as a whole from the methyl group on one ethyl substituent to the corresponding position on the other, in a similar way as for the paraquat radical cation. This agrees with the findings of Johnson and Gutowsky[5] who, although unable to analyze the spectrum, concluded that the gross features were similar to those for paraquat radical cation, and hence that the splitting constants would be much the same. The morphamquat radical cation gave a much lower splitting constant at the 2 position[7] because of the drift of electron density toward the morpholinyl substituent group.

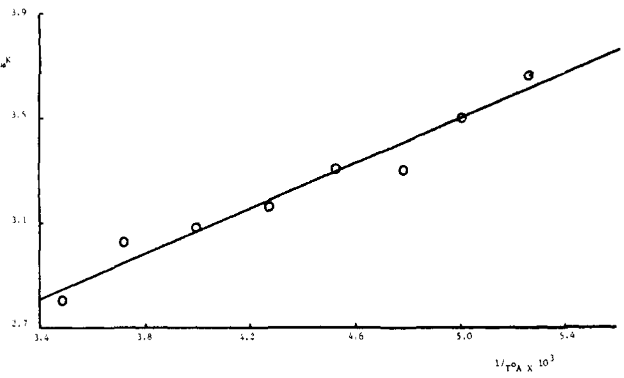


Figure 3. Plot of log K against $1/T$.

Monomer–Dimer Equilibrium. As the temperature of the system was reduced from +30 °C the spectrum showed that the radical species remained the same, but decreased in concentration until at −90 °C the ESR signal was very low.

Experiments carried out at widely different concentrations indicate that Beer's law is not obeyed, e.g., a twofold dilution of the system does not decrease the concentration of the radical cation species to one-half. This result means that the equilibrium involved cannot be bimolecular in both directions and is, therefore, not due to a disproportionation reaction in which two molecules of radical cation react producing a neutral molecule and a dicationic species.

We have tested the assumption that the equilibrium is of the monomer–dimer type shown in eq 1

$$EQ^{+}\cdot + EQ^{+}\cdot \rightleftarrows (EQ^{+}\cdot)_2 \qquad (1)$$

where $EQ^{+}\cdot$ represents the radical cation of ethylquat). This type of equilibrium has been suggested previously for the paraquat[18] and morphamquat[19] radical cations.

Above +30 °C, no increase in signal strength with temperature is observed, and, therefore, the concentration of radical cations at this temperature gives the total ethylquat radical cation concentration. At any other temperature, knowing the total concentration of radical cation species from its ESR spectrum, the concentration of the diamagnetic dimer can be calculated. Using this method we have determined the value of the equilibrium constant $K = [(EQ^{+}\cdot)_2]/[EQ^{+}\cdot]^2$ for eq 1.

The values obtained are reasonably constant over a range of dilution (see Table III) and this confirms that the equilibrium is of the monomer–dimer type shown in eq 1.

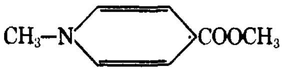
Values of the equilibrium constant K calculated over the temperature range +30 to −90 °C gives a good log K against $1/T$ plot (Figure 3), resulting in the thermodynamic values: $\Delta H° -8.19 \pm 0.4$ kJ mol^{-1}, $\Delta G°$ (25 °C) -15.94 kJ mol^{-1}, $\Delta S°$ (25 °C) $+26.01$ J mol^{-1} K^{-1}.

The corresponding values for morphamquat radical cations are: -45.05 ± 0.3 kJ mol^{-1}, -10.6 kJ mol^{-1}, and -115.6 J mol^{-1} K^{-1}. Thus, although the $\Delta G°$ value for this reaction does not change much from the radical cation of ethylquat to that of morphamquat, there is a great increase in exothermicity (~37 kJ mol^{-1}) and a marked decrease in entropy (~142 J mol^{-1} K^{-1}) showing that the formation of the dimer is accompanied by a much greater ordering of the system in the case of the morphamquat radical cation.

Table III. Effect of Dilution on K at −11 °C in Methanol

$[EQ^{+}\cdot]/10^{-4}$ M	$[(EQ^{+}\cdot)_2]/10^{-4}$ M	$K = [(EQ^{+}\cdot)_2]/[EQ^{+}\cdot]^2$
4.40	2.33	1203
8.71	8.55	1126
27.57	82.59	1086

In the paraquat system Kosower and Cotter[18] concluded, from examination of the electronic spectrum, that the dimer is a biradical. On the other hand, Itoh and Nagakura[20,21] have found that at low temperature in isopentane solution a pyridinyl radical of the type



was in equilibrium with a diamagnetic π-type complex consisting of two pyridinyl radicals one above the other. More recently Fuhrhop et al.[22] reported that a zinc porphyrin radical cation forms a diamagnetic dimer in methanol at low temperature. They attribute the stability of this dimer to a novel π–π' bond formed by overlap of the half-filled π orbitals in the face-to-face dimer of the porphyrin rings. It may be that a similar dimeric species is present in the morphamquat and ethylquat systems.

The fact that the change from ethylquat to morphamquat results in a more negative $\Delta S°$ for the dimerization of the radical cation may be due to a greater desolvation of the radical cations on dimerization in the former case or to the fact that the presence of the two morpholinyl substituent groups in the latter case imposes a more specific orientation on the two-radical cations with respect to each other in the dimer. Both of these factors may be operating simultaneously.

The greater exothermicity of the dimerization reaction of the radical cation of morphamquat compared to that of ethylquat may be related to the greater delocalization of the electron in the former radical cation which would make possible a better overlap between the π and π' molecular orbitals.

Further experiments are being carried out to determine the nature of the electron pairing in the dimer species of these bipyridylium systems.

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