Study of Bipyridyl Radical Cations. Part 5.[1] Effect of Structure on the Dimerisation Equilibrium

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We have studied the e.s.r. spectra of methanol solutions of radical cations of the form (1 : R = H. Me. Pr^n. Bu^n, or PhCH$_2$). over a range of temperature from +40 to −90 °C. and determined the values of the splitting constants. It is found that as the temperature decreases. the concentration of the radical cation decreases. until at −90 °C there is practically no e.s.r. spectrum. This process is reversible. Concentration experiments show that the radical cations are in equilibrium with a dimeric diamagnetic species. The thermodynamic constants for the dimerisation equilibrium were determined. and the results indicate that dimerisation involves desolvation. suggesting that in the dimer the radical cations are arranged in a plane to plane configuration. the two monomer molecules being linked together by a π–π' bond. For (1 : R=CH$_3$), *i.e.* for the radical cation of paraquat. reduction of the temperature is also accompanied by the production of a second paramagnetic species, the structure of which has not yet been determined.

E.S.R. experiments on morphamquat radical cation in methanol solution reported in Part 1[2] showed that the radical cation is in equilibrium with a dimeric diamagnetic species. In this paper we extend the work to a series of bipyridyl radical cations and discuss the effect of structure on the thermodynamic constants for this monomer–dimer equilibrium.

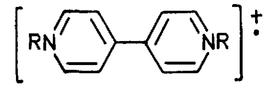
EXPERIMENTAL

Materials.—Methanol was purified as previously.[2] The radical cation was prepared (*a*) in methanol by reduction with a zinc film, (*b*) by using a solution of sodium propoxide in propanol, and (*c*) by using sodium hydroxide in methanol. The e.s.r. spectra of the radical cation prepared by these three methods were identical. 4,4′-Bipyridyl (B.D.H.) was used without further purification. 4,4′-Bipyridylium dibromide dihydrate was prepared as yellow needle-like crystals from 4,4′-bipyridyl in methanol by treatment with hydrogen bromide[3] (Found, for the anhydrous material: C, 37.9; H, 3.3; N, 8.4; Br, 51.0. Calc. for $C_{10}H_{10}Br_2N_2$: C, 37.75; H, 3.15; N, 8.8; Br, 51.35%). 1,1′-Dimethyl-4,4′-bipyridylium dichloride dihydrate was kindly given to us by I.C.I. Plant Protection as 100% pure and was used without further purification. 1,1′-Diethyl-4,4′-bipyridylium di-iodide dihydrate was prepared as red-orange needle-like crystals from an ethanol solution of 4,4′-bipyridyl by refluxing with 1-iodoethane,[3] m.p. 260.5° (lit.,[4] 260°) (Found, for the anhydrous material: C, 36.15; H, 3.8; N, 6.05; I, 54.2. Calc. for $C_{14}H_{18}I_2N_2$: C, 35.9; H, 3.85; N, 6.0; I, 54.25%). 1,1′-Dipropyl-4,4′-bipyridylium di-iodide dihydrate was prepared as red crystals by refluxing a propanol solution of 4,4′-bipyridyl with 1-iodopropane[3] (Found, for the anhydrous material: C, 37.95; H, 4.7; N, 5.75; I, 51.05. Calc. for $C_{16}H_{22}I_2N_2$: C, 38.7; H, 4.45; N, 5.65; I, 51.2%). 1,1′-Dibutyl-4,4′-bipyridylium dibromide dihydrate was prepared as yellow crystals by refluxing an ethanol solution of 4,4′-bipyridyl with 1-bromobutane[3] (Found, for the anhydrous material: C, 50.15; H, 6.0; N, 6.5; Br, 37.3. Calc. for $C_{18}H_{26}Br_2N_2$: C, 50.25; H, 6.05; N, 6.5; Br, 37.2%). 1,1′-Dibenzyl-4,4′-bipyridylium dichloride dihydrate was prepared as light greyish crystals by refluxing an ethanol solution of 4,4′-bipyridyl with benzyl chloride[3] (Found, for the anhydrous material: C, 70.15; H, 5.25; N, 6.95; Cl, 17.55. Calc. for $C_{24}H_{22}Cl_2N_2$: C, 70.4; H, 5.4; N, 6.85; Cl, 17.35%). Bis-1,1′-[(2,6-dimethylmorpholin-4-yl)-carbonylmethyl]-4,4′-bipyridylium dichloride dihydrate (morphamquat) was kindly given to us by I.C.I. Plant Protection and was used without further purification. Deuteriated morphamquat was prepared by deuteriation of the CH$_2$ group as previously.[2] The structure of all the salts were confirmed by mass spectrometry.

Procedure.—The e.s.r. measurements were carried out on methanol solutions of the radical cations over a range of temperature using a Varian E-3 spectrometer. The concentrations of the radical cations were determined using the standard at each temperature as previously described.[2] The validity of experimentally obtained splitting constants was checked by computer simulation. The 'best-fit' results are tabulated.

RESULTS

The radical cations studied were of the form [1; R = H (hydrogenquat, HQ), Me (paraquat, PQ), Pr^n (propylquat, Pr^{n}Q), Bu^n(butylquat, Bu^{n}Q), PhCH$_2$ (benzylquat, BQ), and Et (ethylquat, EQ)]. The splitting constants for these radical cations are given in Table 1.



(1)

Effect of Temperature on the E.s.r. Spectrum.—For all these radical cations, with the exception of (1; R = Me), a decrease in temperature of the methanol solution from +40 to −90 °C did not affect the structure of the spectrum. In each case, however, there was a decrease in signal strength with decrease in temperature, and at −90 °C the intensity of the signal was practically zero.

Above +40 °C, there was no increase in signal strength with increase in temperature, and so the concentration of radical cation at this temperature is equal to the total radical cation present. Assuming a monomer–dimer equilibrium of type (1) the total concentration of monomer

$$\text{radical cation} + \text{radical cation} \rightleftharpoons \text{diamagnetic dimer} \qquad (1)$$

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[1] Part 4, A. G. Evans, N. H. Rees, and R. E. Alford, *J.C.S. Perkin II*, 1977, 445.

[2] A. G. Evans, J. C. Evans, and M. W. Baker, *J.C.S. Perkin II*, 1975, 1310.

[3] B. Emmert and J. Stawitz, *Ber.*, 1923, **56**, 83.

[4] C. S. Johnson, jun., and H. S. Gutowsky, *J. Chem. Phys.*, 1963, **39**, 58.

species could be calculated at any temperature from its e.s.r. spectrum, and hence the concentration of the diamagnetic dimer determined.

The equilibrium constant for the monomer–dimer equilibrium K = [Dimer]/[Monomer]^2 could thus be obtained. A plot of $\log_{10}K$ against $1/T$ gave a good straight line in each case confirming that the equilibrium is of the form (1). The thermodynamic values so obtained for the equilibrium are given in Table 2.

TABLE 1

Splitting constants (A/mT) for bipyridyl radical cations in methanol

Position	$HQ^{+\cdot}$ 25 °C	$PQ^{+\cdot}$ 25 °C	$EQ^{+\cdot}$ 25 °C	$Pr^nQ^{+\cdot}$ −80 °C	$BQ^{+\cdot}$ 25 °C	$MQ^{+\cdot}$ 25 °C
Pyridyl N	0.355	0.423 (0.423) *	0.415 †	~0.415	0.414	0.400
Pyridyl 2-H	0.163	0.133 (0.134) *	0.132 †		~0.150	0.048
Pyridyl 3-H	0.144	0.156 (0.164) *	0.151 †	~0.145	~0.150	0.142
NH	0.400					
NCH_3		0.400 (0.402) *	~0.01 †			
NCH_2			0.235 †		0.414	0.245
Morpholine N						0.024

* ENDOR results at −80 °C determined by Dr. Leniart, Varian Associates, Palo Alto. † E.s.r. results in A. G. Evans, J. C. Evans, and M. W. Baker, *J. Amer. Chem. Soc.*, in press.

TABLE 2

Effect of bipyridyl structure on thermodynamic constants of monomer–dimer equilibrium at 25 °C in methanol

Radical cation	$\Delta H°$/ kJ mol^{-1}	$\Delta G°$/ kJ mol^{-1}	$\Delta S°$/ J K^{-1} mol^{-1}
$HQ^{+\cdot}$	−4.25	−16.16	+34.76
$PQ^{+\cdot}$	−6.77	−16.37	+32.21
$EQ^{+\cdot}$	−8.19 [a]	−15.94 [a]	+26.01 [a]
$Pr^nQ^{+\cdot}$	−10.46	−15.17	+15.80
$Bu^nQ^{+\cdot}$	−12.07	−15.15	+10.34
$BQ^{+\cdot}$	−22.97	−13.67	−31.19
$MQ^{+\cdot}$	−45.05 [b]	−10.60 [b]	−115.6 [b]

[a] Results in A. G. Evans, J. C. Evans, and M. W. Baker, *J. Amer. Chem. Soc.*, in press. [b] See ref. 2.

Dilution Studies.—Solutions of radical cations at various concentrations were made up and the equilibrium constants determined at constant temperature. The results are given in Table 3.

TABLE 3

Dilution studies for monomer–dimer equilibrium in methanol

Radical cation	10^4[Monomer]/M	K/l mol^{-1}
$HQ^{+\cdot}$ (−13.5 °C)	2.82	239
	12.7	226
	94.4	233
$Pr^nQ^{+\cdot}$ (−10 °C)	3.15	948
	12.9	982
	26.9	953
$Bu^nQ^{+\cdot}$ (−12.5 °C)	5.43	896
	12.1	881
	40.1	904
$BQ^{+\cdot}$ (−20 °C)	2.90	1 410
	5.39	1 380
	14.9	1 430

Radical Cation of Paraquat.—On decreasing the temperature of the paraquat radical cation solution, the spectrum altered considerably, until at *ca.* −40 °C a mixed spectrum was obtained showing two paramagnetic species. One of these was the paraquat radical cation which had been examined at room temperature, while the second was an unknown species which we shall call X.

Below −40 °C, species X increased in concentration at the expense of the paraquat radical cation, until at *ca.* −80 °C its proportion reached a maximum. Below this temperature, the concentration of both paraquat radical cation and X decreased, and finally a diamagnetic system was obtained.

Previous workers have reported that at 77 K a single featureless line is obtained in the e.s.r. spectrum.[5,6] We also find the same if we cool the system rapidly to liquid nitrogen temperature. If, however, the solution is cooled slowly so that the equilibrium can be attained at each temperature, there is no e.s.r. signal observable at liquid nitrogen temperature.

Above +40 °C no increase in signal strength with increase in temperature was observed, and, therefore, the concentration of paramagnetic material at this temperature represented the total paramagnetic species available. The plot of $\log_{10}K$ against $1/T$ gives a curve, due probably to the presence of the second radical cation species X. Drawing a straight line through the four high temperature data points gives the thermodynamic constants shown in Table 2.

DISCUSSION

E.s.r. Spectra.—The e.s.r. spectra of hydrogenquat and paraquat radical cations in methanol at room temperature gave the same splitting constants as found by Johnson and Gutowsky.[4]

For the radical cation of propylquat the e.s.r. spectrum at room temperature was poorly resolved. At −80 °C hyperfine structure was visible from which two approximate splitting constants were obtained (Table 1). The nitrogen splitting constant was assigned by its intensity ratio of 1 : 2 : 3 : 2 : 1 for two nitrogen atoms. The splitting constant of 0.145 mT corresponded to four protons, but the assignment could only be tentatively determined as being that of position 3 in the pyridylium rings.

For benzylquat radical cation, the spectrum is not

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[5] M. J. Blandamer, M. C. R. Symons, and G. S. P. Verma, *Chem. Comm.*, 1965, 624.

[6] E. J. Poziomek and R. A. McKay, Edgewood Arsenal Technical Report EATR 4567, 1971.

sufficiently well resolved for complete analysis (Table 1); the large line width of *ca.* 0.2 mT probably masks the phenyl proton splitting. The splitting constants were assigned by analogy with those obtained by Johnson and Gutowsky.[4]

For butylquat radical cation it was impossible to obtain a well resolved spectrum of the radical cation, and so experimental splitting constants could not be measured.

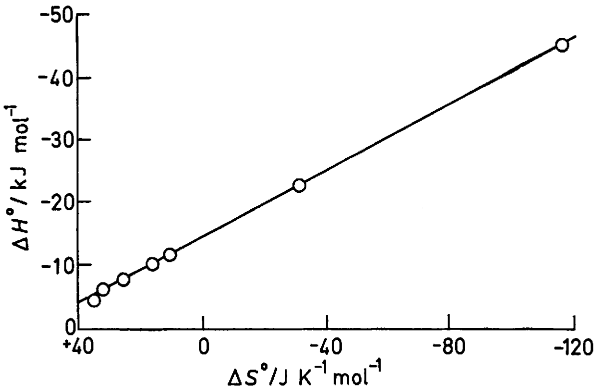

FIGURE 1 Relationship between ΔH° and ΔS° for monomer–dimer equilibria at 25 °C

The results in Table 1 show that the odd electron in the radical cation moves out into the substituent groups, at least as far as the CH_2 and CH_3 groups and the morpholine nitrogen.

Monomer–Dimer Equilibrium.—The effect of structure on the thermodynamic constants of the monomer–dimer equilibrium is seen in Table 2. As the radical cation increases in size, the dimerisation reaction increases in exothermicity and the entropy of dimerisation becomes increasingly more negative. At room temperature the entropy term wins over the enthalpy term so that an increase in size of the radical cation results in a movement of the equilibrium position from dimer towards monomer. In Figure 1 ΔH° is plotted against ΔS° and it is seen that there is a linear relationship between the two.

Although the ΔS° values for $BQ^{+\cdot}$ and $MQ^{+\cdot}$ are negative, as one would expect in a dimerisation reaction, the remaining ΔS° values are positive. This means that there is an opposing effect which causes an increase in entropy when two monomer radical cations dimerise. This effect must be the removal of solvent molecules from the solvation shell of the radical cation when dimerisation occurs. The greater the size of the radical cation the weaker the force holding the solvent molecules to the cation, and thus the smaller the increase in entropy which will occur when these solvent molecules are released on dimerisation. This result gives an indication as to how the radical cations are placed with respect to each other in the dimer. They must be plane to plane if there is to be an effective desolvation on dimerisation.

Recently Fuhrhop *et al.*[7] have reported the dimerisation of the radical cation of zinc octaethylporphin. The dimer is diamagnetic in methanol–chloroform solutions at low temperatures. He concludes that as the two identical radical cations approach one another, the electronic wave functions interact, to form a new π–π' bond.

In a similar way we propose that the diamagnetic dimer of the 4,4′-bipyridylium radical cation exists in a face to face structure with a π–π' bond linking the two monomer molecules.

Nature of the Unknown Paramagnetic Species X.—The second paramagnetic species has a smaller g value and a narrower e.s.r. spectrum than has $PQ^{+\cdot}$. We do not know what its structure is, but we can say that it is not a pseudo-base because zinc reduction in acetonitrile still produced the species X. It is not a π–π' dimer in the triplet state because, if it were, we would not observe a simple e.s.r. spectrum of a ' normal ' radical, but instead a signal at half field.

The results of ENDOR studies on methanol solutions of paraquat radical cation at −80 °C are given in Figure 2 and Table 1, and these agree reasonably well with e.s.r. values obtained at 25 °C. Further work is being carried out to determine the structure of the paramagnetic species X.

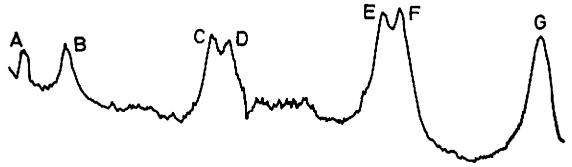

FIGURE 2 ENDOR Spectrum of methanol solution of paraquat radical cation at −80 °C: A, low frequency N; B, low frequency CH_3; C, low frequency 3-, 5-H; D, low frequency 2-, 6-H; E, high frequency 2-, 6-H; F, high frequency 3-, 5-H; G, high frequency CH_3

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[7/266 *Received*, 14*th February*, 1977]

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[7] J. H. Fuhrhop, P. Wasser, D. Reisner, and D. Mauzerall, *J. Amer. Chem. Soc.*, 1972, **94**, 7996.