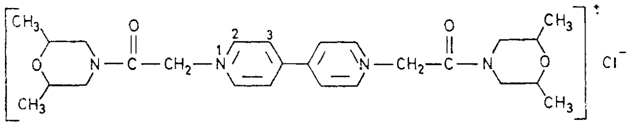
Bipyridyl Radical Cations. Part I. Electron Spin Resonance Study of the Dimerisation Equilibrium of Morphamquat Radical Cation in Methanol

By **Alwyn G. Evans,* Jeffrey C. Evans,** and **Michael W. Baker,** Department of Chemistry, University College, Cardiff

We have studied the e.s.r. spectra of methanol solutions of the morphamquat {bis-1,1′-[(2,6-dimethylmorpholin-4-yl)carbonylmethyl]bipyridyl} radical cation (I) from +40 to −80°. The value of the splitting constants obtained are A(pyridyl N) 0.400, A[pyridyl H(3)] 0.142, A[pyridyl H(2)] 0.048, $A(\mathrm{NC}H_2)$ 0.245, and A(morpholine N) 0.024 mT. It is found that as the temperature decreases the concentration of the radical cation decreases until at −80° there is no e.s.r. spectrum. This process is reversible. Concentration experiments show that the morphamquat radical cation is in equilibrium with a dimeric diamagnetic species. The ΔH° value for the equilibrium is found to be -45.05 ± 0.3 kJ mol^{-1}. The ΔG° and ΔS° values at 25 °C are -10.6 kJ mol^{-1} and -115.6 J mol^{-1} K^{-1} respectively.

THERE has been much discussion of the herbicidal action of bipyridyl radical cations. E.s.r. studies of paraquat radical cation have been made [1]. We have now investigated the morphamquat {bis-1,1′-[(2,6-dimethylmorpholin-4-yl)carbonylmethyl]bipyridyl} system and found that an equilibrium exists in methanol solution between the radical cation (I) and a diamagnetic dimeric species. The e.s.r. spectrum of the radical cation has been analysed and the thermodynamic constants for the equilibrium system evaluated.



(I)

EXPERIMENTAL

Materials.—Morphamquat was kindly given to us by I.C.I. Plant Protection. 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 spectra of the radical cation prepared by these three methods were identical, so the experiments were carried out using method (a).

Methanol (AnalaR) was left for one week over anhydrous calcium sulphate and then distilled under nitrogen and outgassed on a high vacuum.

Deuteriation of the CH_2 group was carried out by making a saturated solution of morphamquat in D_2O, leaving this for two days, recrystallising from [$^2H_4$]methanol and then making the radical cation in deuteriated methanol by method (a). The deuteriated material was checked by n.m.r. and mass spectrometry.

Procedure.—Samples of the morphamquat radical cation solution were taken off under high vacuum conditions and placed in the e.s.r. spectrometer. The spectrum was measured at varying temperatures by the method previously described.[2]

RESULTS

The e.s.r half spectrum for morphamquat radical cation is shown in Figure 1 and the splitting constants obtained from this spectrum are given in Table 1. The concentration of the radical cations was determined by a modification of the method used previously,[3] by double integration using Weddle's method [4] and comparison with diphenylpicrylhydrazyl under similar conditions.

As the temperature of the system was reduced from +40° the spectrum showed that the radical species remained the same, but decreased in concentration until at −80° no e.s.r. signal could be detected. This change with temperature is completely reversible and suggests that an equilibrium is present involving paramagnetic and diamagnetic species.

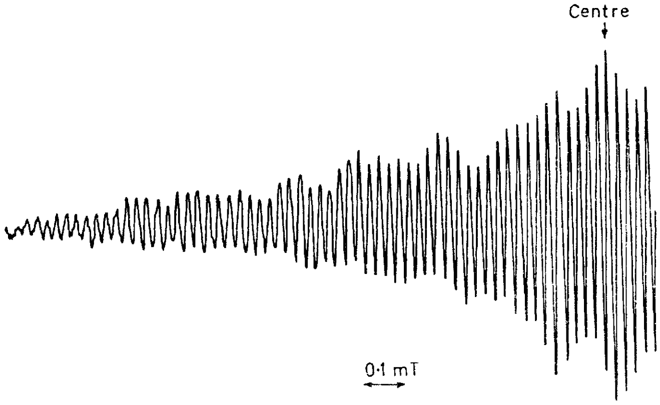


FIGURE 1 E.s.r. half spectrum of (morphamquat)$^{+\bullet}$ in methanol at 25°

TABLE 1

Splitting constants for (morphamquat)$^{+\bullet}$ (MQ$^{+\bullet}$) and (paraquat)$^{+\bullet}$ (PQ$^{+\bullet}$) in methanol at 25°

Position	Splitting constants for MQ$^{+\bullet}$ A/mT	Splitting constants for PQ$^{+\bullet}$ A/mT
Pyridyl N	0.40	0.423
Pyridyl H(3)	0.142	0.157
Pyridyl H(2)	0.048	0.133
$\mathrm{NC}H_2$ (MQ) or $\mathrm{NC}H_3$ (PQ)	0.245	0.399
Morpholine N	0.024	

When morphamquat was deuteriated the splitting given above for NCH_2 was markedly reduced.

---

[1] C. S. Johnson, J. R. Gutowsky, and H. S. Gutowsky, *J. Chem. Phys.*, 1963, **39**, 58; E. J. Poziomek and R. A. Mackay, Edgewood Arsenal Technical Report EATR 4567, November. 1971.

[2] A. G. Evans, J. C. Evans, and E. H. Moon, *J.C.S. Dalton*, 1974, 2390.

[3] A. G. Evans, J. C. Evans, and P. J. Pomery, *J.C.S. Perkin II*, 1974, 1385.

[4] Weddle's rule is a modified form of the sixth order Newton–Coates numerical integration technique. See ' Introduction to Numerical Methods and Fortran programming,' T. R. McCalla, Wiley, New York, 1967.

Experiments done at different concentrations show that Beer's law is not obeyed, *e.g.* a two-fold dilution of the system does not reduce the optical density to one-half. This means that the equilibrium involved is not bimolecular in both directions and so cannot be due to a disproportionation in which two molecules of radical cation give a neutral molecule and a dication.

We have tested the assumption that an equilibrium of the monomer-dimer type (1) exists (as has been suggested for the radical cation of paraquat[5]). Above +30° there is no

$$(\mathrm{I}) + (\mathrm{I}) \rightleftharpoons (\mathrm{I})_2 \qquad (1)$$

increase of signal with temperature. Thus the concentration of radical cations at this temperature gives us the concentration of the total morphamquat radical cation. At any other temperature, knowing $[(\mathrm{I})]$ from the e.s.r. spectrum, $[(\mathrm{I})_2]$ can be calculated. In this way we have calculated the value of $K = [(\mathrm{I})_2]/[(\mathrm{I})]^2$ for equation (1). The values so obtained are seen to be reasonably constant over a wide range of dilution (see Table 2) and this confirms that the equilibrium is of the monomer–dimer type shown in equation (1).

TABLE 2

Effect of dilution on K at $-11°$ in methanol

$[(\mathrm{I})]/10^{-4}$M	$[(\mathrm{I})_2]/10^{-4}$M	$K = [(\mathrm{I})_2]/[(\mathrm{I})]^2$ (l mol^{-1})
2.30	0.866	1 640
6.08	5.95	1 610
13.90	27.9	1 430
29.5	148.0	1 700

We have obtained values of K at different temperatures and in Figure 2 we plot $\log_{10} K$ against $1/T$. The fact that this plot gives a good straight line confirms the presence of the equilibrium shown in equation (1). From the plot a value of -45.05 ± 0.3 kJ mol^{-1} was obtained for $\Delta H°$. $\Delta G°$ and $\Delta S°$ at 25° are -10.6 kJ mol^{-1} and -115.6 J mol^{-1} K^{-1}, respectively.

DISCUSSION

E.s.r. Spectrum.—The results show that the odd electron is delocalised symmetrically over the morphamquat radical cation as a whole, from the morpholine N position on one morpholinyl substituent to the corresponding position on the other.

The splitting constants given in Table 1 are assigned by analogy with those of the paraquat radical cation.[1] To confirm this in more detail we have deuteriated the two hydrogen positions on the CH_2 group and find that the splitting constants assigned in Table 1 to the CH_2 group are markedly reduced. By comparison of the splitting constants for (morphamquat)$^{+\cdot}$ with those for (paraquat)$^{+\cdot}$ we see that the electron density on the CH_2 of the former is much less than on the CH_3 of the latter, the splitting constants of the hydrogen atoms on the rings (positions 2 and 3), have decreased and the electron density on the pyridyl N position has also decreased slightly. Thus the substitution of the morpholinyl group for the hydrogen atom of the methyl group in (paraquat)$^{+\cdot}$ results in a drift of electron density towards the morpholinyl substituent group.

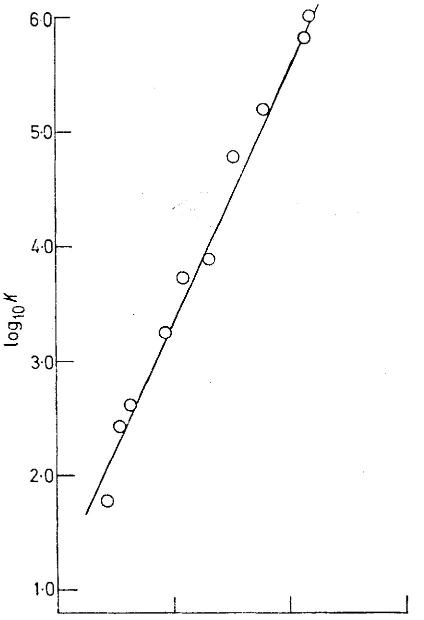


FIGURE 2 Plot of $\log_{10} K$ against $1/T$

Monomer–Dimer Equilibrium.—The effect of temperature and dilution on these systems shows that there is an equilibrium between paramagnetic monomer radical cations and a diamagnetic dimeric species. The formation of the dimer is exothermic to 45.05 kJ mol^{-1}. Further experiments are being carried out to determine the nature of the electron pairing in the dimer species.

We thank I.C.I. Ltd. Plant Protection, Yalding, Kent, for the gift of morphamquat.

[5/341 *Received*, 18*th February*, 1975]

---

[5] E. M. Kosower and J. C. Cotter, *J. Amer. Chem. Soc.*, 1964, **86**, 5524.