A Study of Bipyridyl Radical Cations. Part II.[1] The Reaction of Morphamquat {Bis-*N*-[(2,6-dimethylmorpholin-4-yl)carbonylmethyl]-4,4′-bipyridylium} Radical Cation with Oxygen in Methanol

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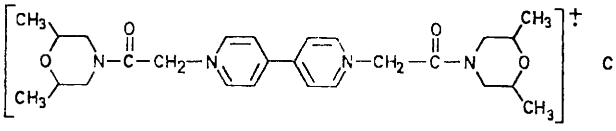
The equilibrium, $2MQ^{+\cdot} \rightleftharpoons (MQ^{+\cdot})_2$ between monomeric morphamquat radical cation, $MQ^{+\cdot}$, and diamagnetic dimer molecules, $(MQ^{+\cdot})_2$, has been examined by u.v. spectroscopy over the temperature range +81 to −88°, yielding $\Delta G°$ −13.4 kJ mol^{-1}, $\Delta H°$ −55.3 kJ mol^{-1}, and $\Delta S°$ −141 J K^{-1} mol^{-1}, which confirm data from our e.s.r. study. The reaction of the morphamquat radical cation with oxygen has been followed by the stopped-flow technique over a range of temperature from +40 to −80°. At +40° the reaction is second-order in monomer and first-order in oxygen with a velocity constant of 1.6×10^8 l^2 mol^{-2} s^{-1}, whereas at −80° it is first-order in dimer and first-order in oxygen with a velocity constant of 84 l mol^{-1} s^{-1}. The mechanism of these reactions is discussed.

E.S.R. studies of methanol solutions of morphamquat radical cation show the presence of a monomer–dimer equilibrium, which lies over to the monomer at +40° and to the dimer at −80°[1] at the low concentrations at which we are working. We have now used our anaerobic, accurately thermostatted, stopped-flow apparatus[2] to examine the oxidation of morphamquat radical cation to morphamquat by oxygen in methanol over this same temperature range.

Because methanol solutions of morphamquat radical cation involve an equilibrium mixture of monomer radical cations and diamagnetic dimer molecules, we adopt the following nomenclature in order to avoid confusion. The equilibrium system involving monomer and dimer at various temperatures is referred to as 'reduced morphamquat,' the monomeric radical cation as $MO^{+\cdot}$, the diamagnetic dimer molecule as $(MQ^{+\cdot})_2$, and the concentration of the equilibrium system containing monomer and dimer molecules as [total reduced morphamquat]. This latter concentration is expressed in terms of monomeric radical cation. Because of the marked change in volume of methanol with temperature this concentration is always given for a particular temperature.



$MQ^{+\cdot}$

EXPERIMENTAL

Materials.—Morphamquat {bis-*N*-[(2,6-dimethylmorpholin-4-yl)carbonylmethyl]4,4′-bipyridylium} dichloride dihydrate was kindly given to us by I.C.I. Plant Protection, Yalding. The reduced morphamquat was prepared in methanol from morphamquat by reduction with a zinc film under high vacuum conditions. Methanol was prepared as described previously[1] and the oxygen and argon used were Air Products commercial grades.

Procedure.—*Spectroscopic measurements*. The u.v.-visible spectrum of a methanol solution of reduced morphamquat was measured over the range +81 to −88° using a Unicam SP 800 spectrophotometer with an E-4557-9 Varian temperature control system. The temperature could be held to ±2° over this range.

Kinetics. The reduced morphamquat solution was transferred on the high vacuum line to an ampoule fitted with a greaseless P.T.F.E. joint and tap (Young Scientific Glassware, London), and then attached to the stopped-flow apparatus.[2] The solution of oxygen in methanol was made *in situ* by stirring methanol in contact with an argon–oxygen mixture, the pressure of which was always kept greater than atmospheric. Different oxygen–methanol concentrations were achieved by using different argon–oxygen mixtures containing 35, 60, 84, and 100% oxygen. These mixtures were made up by Air Products and the cylinders attached in turn to the stopped-flow apparatus. The oxygen concentration was determined from the pressure

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

[2] A. G. Evans, N. H. Rees, and A. Walker, *J.C.S. Perkin II*, 1972, 1723; D. Michael, D. O'Donnell, and N. H. Rees, *Rev. Sci. Instrc.*, 1974, **45**, 256; D. O'Donnell, E. G. Phillips, and N. H. Rees, *ibid.*, p. 274.

and the temperature of saturation.[3] The solutions of oxygen and reduced morphamquat were mixed and the reaction monitored by light of wavelength 495, 537.5, or 595 nm; morphamquat does not absorb at these wavelengths. These experiments were carried out over a temperature range of +40 to −80°.

RESULTS

Spectroscopic Experiments.—In Figure 1 the spectrum of the reduced morphamquat–methanol solution is given for different temperatures. The system shows good isosbestic points, (methanol exhibits an appreciable change in volume with temperature and this accounts for the fact that these are not perfect). This suggests that an equilibrium between two species is involved. At +40° and above the equilibrium lies over to the species with $\lambda_{max.}$ values of 397 and 595 nm, whereas at −80° and below it lies over to the species with $\lambda_{max.}$ values of 354 and 494 nm at the low concentrations at which we are working. These results confirm the conclusion reached from an e.s.r. study of this system [1] that a monomer–dimer equilibrium exists of type

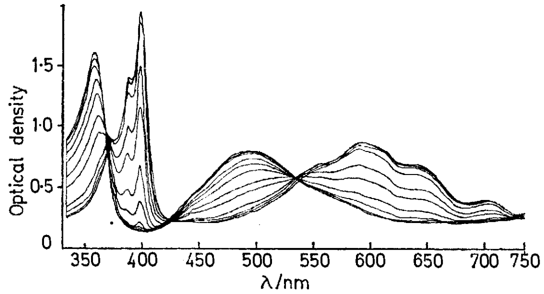

FIGURE 1 Effect of temperature on the spectrum of reduced morphamquat in methanol over the range +81 to −88°: [Total reduced morphamquat] = 1.99 × 10^{-4}M at 20°. The optical densities at λ 397 and 595 nm decrease with decreasing temperature, whilst at λ 354 and 494 nm an increase occurs

$$\mathrm{MQ^{+\cdot} + MQ^{+\cdot} \rightleftharpoons (MQ^{+\cdot})_2} \qquad (1)$$

(1) which lies over to the monomer at +40° and above and to the dimer at −80°. We have thus calculated the following extinction coefficients: monomer, $\varepsilon_{M,354nm}$ 11 000 ± 1 000, $\varepsilon_{M,397nm}$ 48 000 ± 1 000; dimer, $\varepsilon_{D\ 354nm}$ 68 000 ± 1 000, $\varepsilon_{D\ 397nm}$ 2 800 ± 700 cm^{-1} mol^{-1} l.

TABLE 1

Dilution experiments on the reduced morphamquat–methanol system at −28°

10^3[Monomer]/M	10^3[Dimer]/M	$10^{-3}K$/l mol^{-1}
0.104	0.327	29.9
0.0882	0.216	27.7
0.0718	0.118	23.0
0.0576	0.0791	23.8
0.0408	0.0411	24.7
0.0290	0.0190	22.5
0.00845	0.00156	21.9

Effect of dilution. By the method of simultaneous equations, using the extinction coefficients, we have calculated concentrations which have enabled us to determine the equilibrium constant $K = [(\mathrm{MQ^{+\cdot}})_2]/[\mathrm{MQ^{+\cdot}}]^2$, for equation (1) over a 65-fold range of concentration (Table 1). These values, which are constant to ±4 × 10^3 l mol^{-1}, confirm that the equilibrium involves the association of two species, and is not a simple disproportionation in which two molecules of radical cation give a neutral molecule and a dication.

Effect of temperature on K. Values of K have been obtained at various temperatures and the results are shown in Table 2. A plot of $\log_{10}K$ against $1/T$ gives an excellent straight line, thus supporting the type of equilibrium shown in equation (1). The value of $\Delta H°$ obtained from this plot is −55.3 ± 3.0 kJ mol^{-1}. $\Delta G°$ and $\Delta S°$ at 25° are −13.4 kJ mol^{-1} and −141 J mol^{-1} K^{-1} respectively. (These values agree adequately with those obtained from our e.s.r. study:[1] $\Delta H°$ −45.05 kJ mol^{-1}, $\Delta G°$ −10.6 kJ mol^{-1}, and $\Delta S°$ −115.6 J mol^{-1} K^{-1}, considering the difference in the techniques used.)

TABLE 2

Dependence of K on temperature for monomer–dimer equilibrium

T/K	$10^{-3}K$/l mol^{-1}	T/K	$10^{-3}K$/l mol^{-1}
334	0.0187	261	4.80
318	0.0499	244	23.8
304	0.121	230	129.0
287	0.448	214	1 570.0
273	1.85		

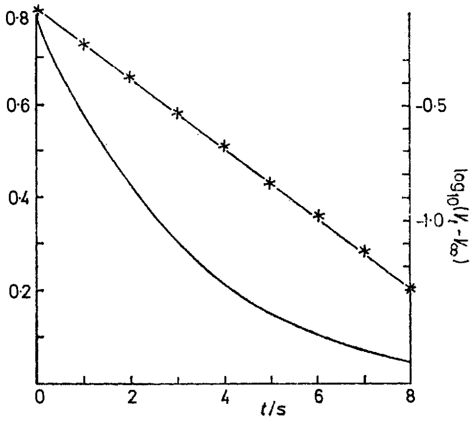

FIGURE 2 Rate curve and first-order analysis for reaction of O_2 with reduced morphamquat at −80° in methanol: [O_2] 4.15 × 10^{-3}M; [Total reduced morphamquat]$_i$ 0.295 × 10^{-3}M

Reaction of Reduced Morphamquat with Oxygen.—On mixing methanol solutions of reduced morphamquat and oxygen the characteristic colour of the reduced morphamquat disappears very rapidly and the optical density falls to zero at the monitoring wave length, λ 495, 537.5, or 595 nm (*i.e.* $\lambda_{max.}$ for dimer, λ for isosbestic point, and $\lambda_{max.}$ for monomer respectively). The oxygen concentration was

TABLE 3

Pseudo-first-order rate constants for reaction of reduced morphamquat with O_2 in methanol at −80°

$10^3[O_2]$/M	10^3[Total reduced morphamquat]$_i$/M	k'/s^{-1}
1.12	0.295	0.091
2.08	0.295	0.179
3.11	0.295	0.249
4.15	0.295	0.340
6.15	0.295	0.487
6.90	0.295	0.501

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[3] A. Seidell, ' Solubilities of Inorganic and Metal Organic Compounds,' Van Nostrand, New York, 1940, vol. I, p. 1353.

kept always well in excess of the reduced morphamquat concentration to simplify the kinetic analysis.

TABLE 4

Effect of temperature on the second-order rate constant in the -80 to $-40°$ range

T/K	$10^{-3}k$/l mol^{-1} s^{-1}	T/K	$10^{-3}k$/l mol^{-1} s^{-1}
233	3.50	208	0.418
228	2.96	203	0.220
223	1.81	198	0.135
218	1.07	193	0.084
213	0.585		

Reactions in the -80 *to* $-40°$ *range.* The reaction curves gave very good first-order analyses (*e.g.* Figure 2) and the pseudo-first-order constants, k', obtained from these reaction curves are given in Table 3 for different oxygen concentrations. A plot of $\log_{10}k'$, against $\log_{10}[O_2]$, shows very good linearity and gives an order of reaction in O_2 of 0.95 ± 0.03. The half-lives of these reactions at an $[O_2]$ of 2.24×10^{-3} mol l^{-1} are *ca.* 5 s at $-80°$. The reaction is, therefore, first order both in absorbing species and in oxygen, and the second-order velocity constants, k(second-order), are given in Table 4 for this temperature range.

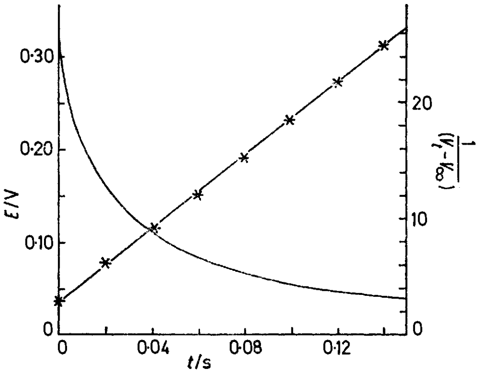

FIGURE 3 Rate curve and second-order analysis for reaction of O_2 with reduced morphamquat at $+40°$ in methanol: $[O_2]$ 3.57×10^{-3}M; [Total reduced morphamquat]$_i$ 0.258×10^{-3}M

Plotting $\log_{10}k$ (second order) against $1/T$ gave an excellent straight line and a value of 36.6 ± 0.5 kJ mol^{-1} for the activation energy.

Reactions at $+40°$. As the temperature was raised above $-40°$ the first-order analysis of the reaction curve gave a progressively poorer straight line, until at $+40°$ the reaction curve analysed to a very good second order (*e.g.* Figure 3). The pseudo-second-order constants, k'', obtained from these reaction curves are given in Table 5 for different oxygen concentrations, and the plot of $\log_{10} k''$ against $\log_{10} [O_2]$ gives a good straight line and an order in oxygen of 0.97 ± 0.06. The average third-order constant at $+40°$ for the reaction is $1.6 \pm 0.2 \times 10^8$ l^2 mol^{-2} s^{-1}. We have not studied the kinetics at temperatures above $+40°$ because it is difficult to handle oxygen in solution at these temperatures in the stopped-flow apparatus.

TABLE 5

Pseudo-second-order rate constants for reaction of reduced morphamquat with O_2 in methanol at $+40°$

$10^3[O_2]$/M	10^3[Total reduced morphamquat]$_i$/M	$10^{-5}k''$/l mol^{-1} s^{-1}
1.60	0.258	3.13
2.67	0.258	3.71
3.57	0.258	5.37
5.30	0.258	8.38
7.65	0.258	11.8

DISCUSSION

Effect of Temperature and Dilution on the Spectrum.—The effect of temperature and of dilution on the u.v.–visible spectrum of the reduced morphamquat–methanol system shows the presence of an equilibrium between the monomeric and dimeric species [equation (1)]. At concentrations of *ca.* 10^{-4} mol l^{-1} this equilibrium lies over to the dimer at $-80°$ and below, and to the monomer at $+40°$ and above. The values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for this equilibrium agree well with the corresponding values determined by e.s.r. technique.[1]

Mechanism of Reaction of Reduced Morphamquat with Oxygen.—When the optical density at the monitoring wavelength has been reduced to zero at the end of the reaction, the optical density at $\lambda_{max.}$ 264 nm for morphamquat has returned to its original value. This shows conclusively that we are studying the complete conversion of reduced morphamquat into morphamquat uncomplicated by side reactions. By using an excess of oxygen we have ensured that the only reaction of the reduced morphamquat is with oxygen.

Reactions at $+40°$. At this temperature equilibrium (1) lies over to the monomer. Thus, the fact that at this temperature the optical density at the monitoring wavelength shows a second-order fall off with time means that the reaction with oxygen is second-order in monomer. The order in oxygen at this temperature is unity. Thus the reaction we are following could be (2). If, however,

$$\underset{\sim}{MQ}^{+\bullet} + \underset{\sim}{MQ}^{+\bullet} + O_2 \xrightarrow{k_2} \underset{\sim}{MQ}^{2+} + \underset{\sim}{MQ}^{2+} + O_2{}^{2-} \quad (2)$$

the monomer–dimer equilibration is faster than the reaction with oxygen, another possibility could be that the oxygen is not reacting with $\underset{\sim}{MQ}^{+\bullet}$ but with $(\underset{\sim}{MQ}^{+\bullet})_2$ [reaction (3)]. The concentration of $(\underset{\sim}{MQ}^{+\bullet})_2$ would be

$$(\underset{\sim}{MQ}^{+\bullet})_2 + O_2 \xrightarrow{k_3} \underset{\sim}{MQ}^{2+} + \underset{\sim}{MQ}^{2+} + O_2{}^{2-} \quad (3)$$

very small at this temperature but since it would be equal to $K[\underset{\sim}{MQ}^{+\bullet}]^2$ reaction (3) would give the observed order of reaction: rate of reaction $= k_3[(\underset{\sim}{MQ}^{+\bullet})_2][O_2] = k_3K[\underset{\sim}{MQ}^{+\bullet}]^2[O_2]$.

At first sight it seems surprising that the orders of reaction found experimentally show that at $+40°$ a one-electron transfer from a monomer molecule to an oxygen molecule does not take place. It could be that the monomer and oxygen molecules combine to give an

$$\underset{\sim}{MQ}^{+\bullet} + O_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} (\underset{\sim}{MQ}\ O_2)^{+\bullet} \quad (4)$$

unstable complex [reaction (4)] which has a high probability of decomposing back into monomer and oxygen and only occasionally undergoing reaction with a second monomer molecule to complete a two-electron transfer [reaction (5)]. If $k_{-4} \gg k_5[\mathrm{MQ}^{+\bullet}]$ this scheme would give the observed reaction orders, *i.e.* second-order in $\mathrm{MQ}^{+\bullet}$

$$(\mathrm{MQ\ O_2})^{+\bullet} + \mathrm{MQ}^{+\bullet} \xrightarrow{k_5} \mathrm{MQ}^{2+} + \mathrm{MQ}^{2+} + \mathrm{O_2}^{2-} \quad (5)$$

and first-order in oxygen: rate of reaction $= k_5\ [(\mathrm{MQ\ O_2})^{+\bullet}][\mathrm{MQ}^{+\bullet}] = k_5\ k_4[\mathrm{MQ}^{+\bullet}]^2[\mathrm{O_2}]/k_{-4}$.

Reactions at −80°. At this temperature equilibrium (1) lies over to the dimer. Thus the fact that at this temperature the optical density at the monitoring wavelength shows a first-order fall off with time means that the reaction with oxygen is first order in dimer. The order in oxygen at this temperature is unity, so that the reaction we are following could be reaction (3). If, however, the monomer–dimer equilibration is faster than the reaction with oxygen, another possibility could be that the oxygen is not reacting with $(\mathrm{MQ}^{+\bullet})_2$ but with $\mathrm{MQ}^{+\bullet}$ as in reaction (2). The concentration of $\mathrm{MQ}^{+\bullet}$ would be very small at this temperature but since it would equal $[(\mathrm{MQ}^{+\bullet})_2]^{\frac{1}{2}}/K^{\frac{1}{2}}$, reaction (2) would give the observed order of reaction: rate of reaction $= k_2[\mathrm{MQ}^{+\bullet}]^2[\mathrm{O_2}] = k_2[(\mathrm{MQ}^{+\bullet})_2][\mathrm{O_2}]/K$.

In the case of the dimer molecule it could be that

$$(\mathrm{MQ}^{+\bullet})_2 + \mathrm{O_2} \longrightarrow \mathrm{MQ}^{+\bullet} + \mathrm{MQ}^{2+} + \mathrm{O_2}^{-\bullet} \quad (6)$$

instead of a two-electron transfer [reaction (3)], the oxygen receives its two electrons one at a time [reaction (6)] followed by a more rapid reaction (7) since this scheme too would give the observed reaction orders.

$$(\mathrm{MQ}^{+\bullet})_2 + \mathrm{O_2}^{-\bullet} \longrightarrow \mathrm{MQ}^{+\bullet} + \mathrm{MQ}^{2+} + \mathrm{O_2}^{2-} \quad (7)$$

A possible alternative to reaction (7) [reaction(8)] is unlikely because at −80° $[\mathrm{MQ}^{+\bullet}]$ is much less than $[(\mathrm{MQ}^{+\bullet})_2]$. $\mathrm{MQ}^{+\bullet}$ would not be involved at this temperature unless on being formed in reaction (6) it was held to $\mathrm{O_2}^{-\bullet}$ by a

$$\mathrm{MQ}^{+\bullet} + \mathrm{O_2}^{-\bullet} \longrightarrow \mathrm{MQ}^{2+} + \mathrm{O_2}^{2-} \quad (8)$$

cage effect, and this would make the overall reaction virtually the same as reaction (3).

In a pulse radiolysis study of aqueous solutions of paraquat (*NN'*-dimethyl-4,4'-bipyridylium dichloride) containing an excess of oxygen at room temperature, Farrington *et al.*[4] found that the decay of paraquat radical was first order. The products of the reaction were assumed to be paraquat and $\mathrm{O_2}^{-\bullet}$. At first sight it might seem surprising that in water the electron transfer from $\mathrm{PQ}^{+\bullet}$ to $\mathrm{O_2}$ involves one radical cation, whereas in methanol at +40° we find that, if the electron transfer is from the radical cation, then two molecules of cation are involved.

In comparing these two sets of results we must remember that we are dealing with two different bipyridyls having different E^0 values, and with two different solvents. These differences could have a marked effect on the nature of the transition state for the electron transfer reaction.

In any case, in a competition between an electron transfer reaction which involves two radical cations and one which involves only one radical cation, as the concentration of the radical cation is reduced the latter is favoured at the expense of the former. We do not know the concentration which Farrington *et al.* used, but suggest this possibility as one explanation of the difference between our two sets of results.

The first-order decay which Farrington *et al.* find for the paraquat radical cation could also be interpreted in terms of reactions (4) and (5), where the condition, $k_{-4} \gg k_5[\mathrm{MQ}^{+\bullet}]$, leads to a reaction which is second order in radical cation, whereas $k_{-4} \ll k_5[\mathrm{PQ}^{+\bullet}]$ would lead to a reaction which is first order in radical cation. This could explain the difference between our results, and also the fact that no intermediate radical, *e.g.* $\mathrm{O_2}^{-\bullet}$ has been detected.[4]

Under conditions when the oxygen was not in excess, Farrington *et al.* interpret their results in terms of two successive one-electron transfer steps.

Experiments are being carried out to elucidate these problems. In particular, the rate of the monomer–dimer equilibration is being studied by the temperature-jump method to determine whether this is too slow to be involved in the oxidation reactions or whether it is so fast that the monomer–dimer equilibrium is maintained throughout. The monomer–dimer equilibration reactions cannot be rate-determining steps in our oxidation reactions because this would result in a zero order in oxygen which is not the case.

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[4] J. A. Farrington, M. Ebert, E. J. Land, and K. Fletcher, *Biochim. Biophys. Acta*, 1973, **314**, 372.