Study of Bipyridyl Radical Cations. Part 4.[1] Reaction of Diquat Radical Cation with Oxygen and Copper(II)

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The radical cation (I) of diquat (6,7-dihydrodipyrido[1,2-*a*:1',2'-*c*]pyrazinium dibromide), differs from that of paraquat and morphamquat in that it does not dimerise to diamagnetic dimer molecules on lowering the temperature. The reaction of the radical cation of diquat with oxygen was studied by the stopped-flow technique over the temperature range +40 to −80 °C in methanol and +40 to −100 °C in ethanol. The reaction was second order in radical cation in both solvents at +40 °C, first order in radical cation in ethanol at −100 °C, and first order in oxygen under all conditions. At +40 °C the third-order rate constants are $(1.5 \pm 0.2) \times 10^9$ and $(8.8 \pm 0.7) \times 10^7$ $l^2\,mol^{-2}\,s^{-1}$ in methanol and ethanol respectively. The reaction of diquat radical cation with Cu^{II} in methanol at −80 °C is first order in radical cation and in Cu^{II}. The reaction of the radical cation of morphamquat with Cu^{II} in methanol at −80 °C is first order in radical cation dimer and second order in Cu^{II}.

WE have previously examined the reaction of the radical cation of morphamquat (MQ) [2] and of paraquat(PQ) [1] with oxygen, using methanol as solvent in our anaerobic accurately thermostatted stopped-flow apparatus.[3,4] These reactions were first order in oxygen, but the order in radical cation changed over the temperature range +40 to −80 °C. The results were considered in terms of various possible reaction mechanisms. We have now studied the reaction with oxygen of diquat (DQ) radical cation over a similar temperature range. This radical cation does not dimerise with decrease in temperature, as do morphamquat [2,5] and paraquat,[1,6] and the kinetic

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[1] Part 3, A. G. Evans, N. K. Dodson, and N. H. Rees, *J.C.S. Perkin II*, 1976, 859.

[2] A. G. Evans, R. E. Alford, and N. H. Rees, *J.C.S. Perkin II*, 1975, 1831.

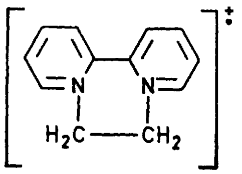
[3] A. G. Evans, N. H. Rees, and A. Walker, *J.C.S. Perkin II*, 1972, 1723.

[4] D. Michael, D. O'Donnell, and N. H. Rees, *Rev. Sci. Instr.* 1974, **45**, 256; D. O'Donnell, E. G. Phillips, and N. H. Rees, *ibid.*, p. 274.

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

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

study of its reaction clarifies our understanding of these electron transfer processes.



(I)

EXPERIMENTAL

Materials.—Diquat was prepared by quaternising 2,2′-bipyridyl with 1,2-dibromoethane as described by Ashley.[7] Solutions of diquat were reduced by a zinc film.[2] Morphamquat radical cation and methanol were prepared as described earlier.[2] AnalaR copper(II) chloride dihydrate was dehydrated on the high vacuum line to remove the water of crystallisation and then dissolved in out-gassed methanol.[2] AnalaR ethanol (James Burrough) was purified in two ways: (a) distilled from a diquat solution under nitrogen, allowed to stand over diquat overnight, refluxed for 1 h, and then distilled in nitrogen; (b) passed through a column of amberlite resin, IR-120(H) (B.D.H.) and distilled in nitrogen. Diquat–ethanol solutions made up using untreated AnalaR ethanol were yellow initially (and went almost colourless on standing), and did not obey Beer's law on dilution (although concentrating the solution on the high vacuum gave results which did obey Beer's law). Solutions made up using AnalaR ethanol treated in one of the two ways given above were colourless and did obey Beer's law on dilution. These results show the presence of a trace impurity in the AnalaR ethanol. Furthermore, similar results were found for morphamquat–ethanol solutions, *i.e.* purple solutions in AnalaR ethanol, and colourless solutions in purified AnalaR ethanol. This problem was not met with in our previous work using AnalaR methanol solutions (since presumably any impurity was too low in concentration).

RESULTS

Spectroscopic Experiments.—The diquat radical cation in ethanol showed an absorption maximum at 380 nm (ε 25 900 l mol^{-1} cm^{-1}). In contrast to the behaviour of the radical cations of morphamquat [2] and paraquat,[1] there was no change in $\lambda_{max.}$ or ε at 380 nm with temperature. In addition, it was found that these solutions obeyed Beer's law. E.s.r. experiments [8] also confirmed that there was no change from paramagnetic monomer molecules to diamagnetic dimer molecules on lowering the temperature. Because of this there is no need to adopt the nomenclature ' reduced diquat ' which was done for the morphamquat and paraquat systems.[1,2]

Reaction of Diquat Radical Cation with Oxygen.—Ethanol as solvent. Reaction at +40 °C. The reaction curve obtained when diquat radical cation–ethanol solutions [ethanol purified by method (b)] were mixed at +40 °C with excess of oxygen as described previously [2] is shown in Figure 1. It was found that the optical density at the monitoring wavelength, 380 nm, decreases initially to a non-zero value, V_∞. Monitoring the system after this reaction is over shows that the absorption at 380 nm continues to decrease relatively slowly due to a subsequent reaction. The difference in rates of these two reactions is sufficiently great to enable an accurate V_∞ value for the first reaction to be determined.

The reaction of the radical cation of diquat with oxygen, therefore, gives initially a product which absorbs at the monitoring wavelength, and in this respect it differs from the reaction of the morphamquat and paraquat radical cations in methanol. The nature of this product is discussed later.

Analysis of the reaction curve shown in Figure 1 gives a second-order dependence on radical cation. The pseudo-second-order constants k'', vary with oxygen concentration as given in Table 1, and a plot of $\log_{10} k''$ against $\log_{10} [O_2]$ gives a line of slope 1.03 ± 0.04 showing that the order in oxygen is unity. The reaction is thus second order in $[DQ^{+\cdot}]$ and first order in oxygen. The third-order constant for the reaction at +40 °C is $(8.8 \pm 0.7) \times 10^7$ l^2 mol^{-2} s^{-1}.

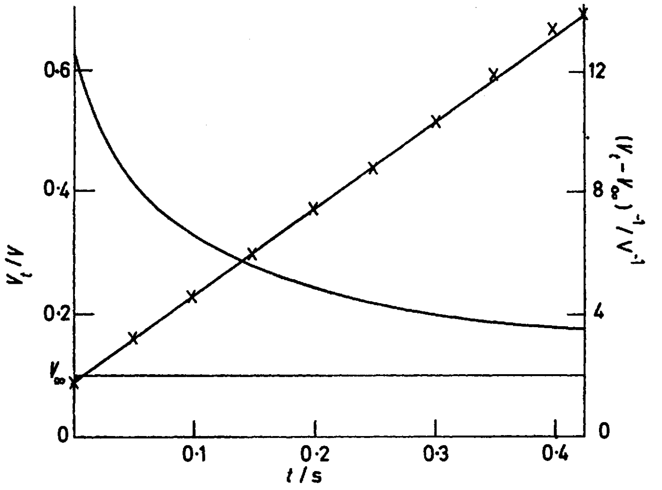


FIGURE 1 Rate curve and second-order analysis for reaction of $DQ^{+\cdot}$ with O_2 in ethanol at +40 °C: $[DQ^{+\cdot}]_i$ 1.13 × 10^{-4}M, $[O_2]$ 5.75 × 10^{-3}M

TABLE 1

Pseudo-second-order velocity constants for the reaction of diquat radical cation with oxygen in ethanol at +40 °C

$10^3[O_2]$/M	$10^3[DQ^{+\cdot}]$/M	$10^{-5}k''$/l mol^{-1} s^{-1}
5.75	0.113	4.66
4.05	0.113	3.71
2.79	0.113	2.73
1.69	0.113	1.47
0.858	0.113	0.69

The same kinetic results were obtained for diquat radical cation solutions in ethanol purified by method (a), or indeed, without any purification. It was necessary, however, to purify the solvent in order to determine accurate extinction coefficients.

Reaction over the range −70 to −100 °C. From −70 to −100 °C a first-order dependence of rate on radical cation was observed. A typical reaction curve is shown for −80 °C (Figure 2). The pseudo-first-order constants k' at −80 °C give a first-order dependence on $[O_2]$ (Table 2). The reaction is thus first order in both $DQ^{+\cdot}$ and in oxygen and the second-order constant is 4.4 ± 0.4 × 10^3 l mol^{-1} s^{-1} at −80 °C. Assuming that the first-order dependence on oxygen holds over the −70 to −100 °C range, we have plotted $\log_{10}$

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[7] M. G. Ashley, *Pesticide Sci.*, 1970, 1, 101.

[8] A. G. Evans, M. Baker, and J. C. Evans, unpublished results.

(second-order constant) against $1/T$ and find an activation energy of 35.5 ± 4 kJ mol^{-1}.

Methanol as solvent. At +40 °C, the analysis of the reaction curve is similar to that for the ethanol system. The

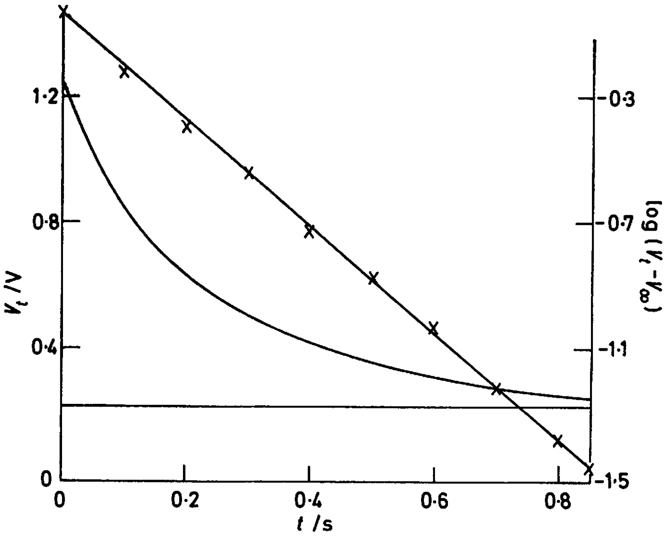

FIGURE 2 Rate curve and first-order analysis for reaction of $DQ^{+\cdot}$ with O_2 in ethanol at −80 °C: $[DQ^{+\cdot}]_i$ 1.84 × 10^{-4}M, $[O_2]$ 9.77 × 10^{-4}M

change of k'' with $[O_2]$ is given in Table 3, and a plot of $\log_{10} k''$ against $\log_{10} [O_2]$ gives a straight line of slope 0.98 ± 0.09. The third-order rate constant is (1.5 ± 0.2) × 10^9 l^2 mol^{-2} s^{-1} which is *ca.* 20-fold larger than the value in ethanol. The third-order rate constants for the reaction of $DQ^{+\cdot}$, $PQ^{+\cdot}$,[1] and $MQ^{+\cdot}$[2] with oxygen in methanol at +40 °C are, therefore, in the ratio 10 : 5 : 1.

TABLE 2

Pseudo-first-order velocity constants for the reaction of diquat radical cation with oxygen in ethanol at −80 °C

$10^3[O_2]$/M	$10^3[DQ^{+\cdot}]_i$/M	k'/s^{-1}
8.08	0.184	38.9
5.09	0.184	23.3
3.82	0.184	15.8
1.83	0.184	8.01
0.98	0.184	3.74

TABLE 3

Pseudo-second-order velocity constants for the reaction of diquat radical cation with oxygen in methanol at +40 °C

$10^3[O_2]$/M	$10^3[DQ^{+\cdot}]_i$/M	$10^{-6}k''$/l mol^{-1} s^{-1}
6.38	0.16	8.37
5.68	0.16	7.51
3.80	0.16	6.24
3.08	0.16	5.27
2.17	0.16	3.15
1.58	0.16	3.00
0.75	0.16	0.96

At low temperature the reaction is very much faster. We can only see a small portion of the total reaction, which makes analysis difficult.

Reaction of Diquat Radical Cation with Copper(II) *in Methanol*.—This reaction was too fast to study at room temperature. All the results were obtained at —80 °C. Typical results are given in Table 4. The optical density falls to a constant non-zero value which is due to the excess of $CuCl_2$. (We discount the possibility that this is due to a charge transfer complex, because the spectrum of the final solution shows a 100% regeneration of DQ^{2+}.) The analysis of the curve gives an excellent first order plot for $DQ^{+\cdot}$. The pseudo-first-order constants vary with $[Cu^{II}]$ as shown in Table 5. A plot of $\log_{10}k'$ against $\log_{10}[Cu^{II}]$ gives a good straight line of slope 0.98 ± 0.02. Thus the reaction is first order in both Cu^{II} and in $DQ^{+\cdot}$ and the second-order velocity constant at −80 °C is (99 ± 2) × 10^3 l mol^{-1} s^{-1}.

TABLE 4

Reaction of $DQ^{+\cdot}$ with Cu^{II} in methanol at −80 °C

t/ms	V_t/V	V_∞/V
0	0.620	0.065
1	0.410	0.065
2	0.260	0.065
3	0.175	0.065
4	0.127	0.065
5	0.099	0.065
6	0.088	0.065
7	0.077	0.065
8	0.072	0.065

$[DQ^{+\cdot}]_i$ 1.68 × 10^{-4}M, $[Cu^{II}]$ = 4.93 × 10^{-3}M.

TABLE 5

Pseudo-first-order velocity constants for the reaction of diquat radical cation with Cu^{II} in methanol at −80 °C

$10^3[Cu^{II}]$/M	$10^3[DQ^{+\cdot}]$/M	k'/s^{-1}
2.45	0.168	244
4.93	0.168	493
7.90	0.168	794
12.1	0.168	1 159

Reaction of Reduced Morphamquat with Copper(II) *in Methanol*.—This reaction was also too fast to measure except at low temperature. The reaction was followed at −80 °C. Typical results are given in Table 6. This rate curve shows first-order dependence on optical density which, since the reduced morphamquat is practically completely in the form

TABLE 6

Reaction of reduced morphamquat with Cu^{II} in methanol at −80 °C

t/ms	V_t/V	V_∞/V
0	0.496	0
10	0.312	0
20	0.196	0
30	0.121	0
40	0.076	0
50	0.048	0
60	0.029	0
70	0.018	0

[Total reduced morphamquat]$_i$ 2.02 × 10^{-4}M, $[Cu^{II}]$ 2.49 × 10^{-3}M.

TABLE 7

Pseudo-first-order velocity constants for the reaction of reduced morphamquat with Cu^{II} in methanol at −80 °C

$10^3[Cu^{II}]$/M	10^3[Reduced morphamquat]/M	k'/s^{-1}
2.49	0.202	49.2
3.62	0.202	88.4
5.75	0.202	253
6.20	0.202	302
9.75	0.202	708

of dimer at this temperature and concentration,[2] means that the reaction is first order in $(MQ^{+\bullet})_2$. The pseudo-first-order constants vary with Cu^{II} as shown in Table 7, and a plot of $\log_{10}k''$ against $\log_{10}[Cu^{II}]$ gives a line of slope 2.00 ± 0.05. Thus the reaction of $(MQ^{+\bullet})_2$ with Cu^{II} is first order in dimer and second order in Cu^{II}.

DISCUSSION

Reaction of Diquat Radical Cation with Oxygen.—Ethanol as solvent. As the temperature is changed from +40 to −100 °C, the reaction of $DQ^{+\bullet}$ with oxygen changes from second order in radical cation and first order in oxygen to first order in radical cation and first order in oxygen. Over the intermediate temperatures, the order in radical cation varies between these two values.

We postulate reactions (1) and (2) to account for the observed reaction orders.

$$DQ^{+\bullet} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (DQ\,O_2)^{+\bullet} \qquad (1)$$

$$(DQ\,O_2)^{+\bullet} + DQ^{+\bullet} \xrightarrow{k_2} DQ^{2+} + DQ^{2+} + O_2{}^{2-} \qquad (2)$$

This system immediately proceeds to a product absorbing at 380 nm which is what we observe at V_∞. The rate of reaction is given in equation (3).

$$\begin{aligned}\text{Rate} &= k_2[(DQ\,O_2)^{+\bullet}][DQ^{+\bullet}]\\ &= \frac{k_2k_1[DQ^{+\bullet}]^2[O_2]}{k_{-1} + k_2[DQ^{+\bullet}]}\end{aligned} \qquad (3)$$

If at +40 °C, $k_2[DQ^{+\bullet}] < k_{-1}$ equation (4)

$$\text{Rate} = k_2k_1[DQ^{+\bullet}]^2[O_2]/k_{-1} \qquad (4)$$

applies. If at −100 °C $k_2[DQ^{+\bullet}] > k_{-1}$ equation (5) applies. This mechanism, which is the same as one of

$$\text{Rate} = k_1[DQ^{+\bullet}][O_2] \qquad (5)$$

those put forward previously for the morphamquat system [2] would thus explain the change of order in radical cation with temperature. As the temperature is reduced, we should expect the stability of $(DQ\,O_2)^{+\bullet}$ to increase, and hence the order of reaction to change.

Methanol as solvent. At +40 °C, the reaction is second order in radical cation, and first order in oxygen. At −80 °C the optical density–time plot is not a smooth curve (see later), and is impossible to analyse simply.

Dependence of Rate Constant on Solvent.—The change of solvent from methanol to ethanol at +40 °C does not result in a change of mechanism. The rate is second order in radical cation and first order in oxygen in both solvents, but the change from ethanol to methanol causes a marked increase in the third-order rate constant from $(8.8 \pm 0.7) \times 10^7$ to $(1.5 \pm 0.2) \times 10^9\ l^2\ mol^{-2}\ s^{-1}$. It is interesting to note that we have not been able to measure the rate of this reaction in water because it is much too rapid in that solvent. Thus the rate constant increases as the dielectric constant of the solvent increases. We believe that this change may be related to the hydrogen bonding ability of the solvent since it is known that the radical cation of paraquat is much more stable to air in acetonitrile as solvent [6] (the blue colour persisting for *ca.* 1 h for 10^{-3}M solutions), although this is a polar solvent (dielectric constant 37.5). It may be that the $(DQ\,O_2)^{+\bullet}$ ' sticky collision ' is stabilised by hydrogen bonding with the solvent. This would mean not only that the reaction would be faster the greater the hydrogen bonding power of the solvent, but that as we change from a poorer hydrogen bonding solvent to a better one, the order in radical cation would tend to change from second to first. This, as we suggested earlier,[2] may be the reason why Farrington *et al.*[9] found the order in radical cation to be unity for the reaction of paraquat radical cation with oxygen in water at room temperature.

Reaction of Diquat Radical Cations and Morphamquat Radical Cation Dimer with Copper(II).—At −80 °C the reaction of $DQ^{+\bullet}$ with Cu^{II} is first order in each reagent, and so must occur as in reaction (6). At the same temperature, however, the reaction of reduced morphamquat

$$DQ^{+\bullet} + Cu^{2+} \longrightarrow DQ^{2+} + Cu^{+} \qquad (6)$$

with Cu^{II} is first order in $(MQ^{+\bullet})_2$ and second order in Cu^{II}. These orders would be given by a reaction of the type (7). At this temperature and concentration although the bulk of the reduced morphamquat is present

$$(MQ^{+\bullet})_2 + 2Cu^{2+} \longrightarrow 2Cu^{+} + 2MQ^{2+} \qquad (7)$$

as dimer $(MQ^{+\bullet})_2$ there is a small concentration of monomer radical cations $MQ^{+\bullet}$ present according to equilibrium (8). If the Cu^{II} were reacting with this small

$$MQ^{+\bullet} + MQ^{+\bullet} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} (MQ^{+\bullet})_2 \qquad (8)$$

amount of monomeric radical cation, the observed order of reaction could be obtained by reaction (9) with the

$$\begin{aligned}MQ^{+\bullet} + MQ^{+\bullet} + Cu^{2+} + Cu^{2+} &\xrightarrow{k_9}\\ MQ^{2+} + MQ^{2+} + Cu^{+} + Cu^{+}\end{aligned} \qquad (9)$$

rate give by (10) but it is inconceivable that a reaction

$$\begin{aligned}\text{Rate} &= k_9[MQ^{+\bullet}]^2[Cu^{2+}]^2\\ &= \frac{k_9k_{-8}[(MQ^{+\bullet})_2][Cu^{2+}]^2}{k_8}\end{aligned} \qquad (10)$$

of this type would occur. Reaction (11), with the rate

$$MQ^{+\bullet} + Cu^{2+} \xrightarrow{k_{11}} MQ^{2+} + Cu^{+} \qquad (11)$$

given by (12), would result in a reaction which was one-

$$\begin{aligned}\text{Rate} &= k_{11}[MQ^{+\bullet}][Cu^{2+}]\\ &= k_{11}\left(\frac{k_{-8}[(MQ^{+\bullet})_2]}{k_8}\right)^{\frac{1}{2}}[Cu^{2+}]\end{aligned} \qquad (12)$$

half order in $(MQ^{+\bullet})_2$ and first order in Cu^{II} which is not observed. This result clearly establishes that in methanol at −80 °C, it is the dimer molecules $(MQ^{+\bullet})_2$ which are reacting with the Cu^{II} ions.

The Subsequent Reaction.—The reaction of diquat

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

radical cation with oxygen in methanol, or ethanol at room temperature yields a product which absorbs at the monitoring wavelength of 380 nm, V_∞. This residual absorption gradually decreases to a smaller absorption which remains constant over a long period of time.

We believe that this effect can be explained as follows. The system $DQ^{2+} + DQ^{2+} + O_2^{2-}$, which is first formed by the reaction of $DQ^{+\cdot}$ with O_2, reacts further to produce pyridones and other oxidation products through a coloured intermediate. Under the conditions we have used in this paper, the coloured intermediate is produced immediately (giving the V_∞ reading) and then it reacts further, relatively slowly, to yield the final products (giving the final absorption value).

In this respect diquat is not in a different class from morphamquat and paraquat, since for these latter systems, too, although the absorption decreases initially to zero at the monitoring wavelength, it rises again on long standing to a final non-zero value when the final products are formed. Furthermore, preliminary results using diquat in water as solvent, show that absorption falls to zero initially as in the case of morphamquat and paraquat.

Additional evidence to show that the system formed by reaction of the radical cation with oxygen passes through a coloured intermediate on its way to the final products comes from the fact that for diquat radical cation in methanol at −80 °C the reaction curve decreases initially and then rises slightly before it falls off to the final absorption value. In this case, then, the intermediate is not formed fast enough to give a smooth absorption curve falling to a V_∞ value, and neither is it formed slowly enough to give a smooth absorption curve falling to zero which later rises to the final absorption value.

Evidence that in the case of paraquat and diquat O_2^{2-} and the dication initially produced lead further to a complex mixture of fluorescent products consisting mainly of mono- and di-ketones, comes from the work of Farrington *et al.*[10]

Conclusions.—(a) If the bipyridylium radical cation is monomeric, *e.g.* diquat, its reaction with a one-electron acceptor will be first-order in each reagent as in reaction (6). With oxygen the reaction will be (1) followed by (2). This system may or may not immediately give a coloured product, depending on the nature of the bipyridylium radical cation and of the solvent used.

The order of this reaction in $DQ^{+\cdot}$ will be second, or first, depending on the stability of the ' sticky collision ' $(DQ\ O_2)^{+\cdot}$.

The factors which will tend to change the order from second to first could be (i) an increase in hydrogen-bonding, *e.g.* a change in solvent from methanol to water, (ii) a decrease in temperature, *e.g.* the reaction of diquat radical cation with oxygen in ethanol is second order in $DQ^{+\cdot}$ at +40 °C and decreases to unity at −70 °C.

(b) If the reduced bipyridylium salt exists as a monomer–dimer equilibrium, *e.g.* morphamquat, then the monomer will react with a one-electron acceptor as in reaction (11), *i.e.*, it will be first-order in each reagent. With oxygen the reaction will be (13) followed by (14), *i.e.*, it will be second order in $MQ^{+\cdot}$ when $(MQ\ O_2)^{+\cdot}$ is

$$MQ^{+\cdot} + O_2 \rightleftharpoons (MQ\ O_2)^{+\cdot} \qquad (13)$$

$$(MQ\ O_2)^{+\cdot} + MQ^{+\cdot} \longrightarrow MQ^{2+} + MQ^{2+} + O_2^{2-} \qquad (14)$$

less stable, *e.g.* at high temperatures and in solvents of low hydrogen-bonding ability, and first order when $(MQ\ O_2)^{+\cdot}$ is more stable, *i.e.* at low temperatures and in solvents of high hydrogen-bonding ability.

The reaction of dimer with a one-electron acceptor is first order in dimer and second order in 1-electron acceptor. These orders would result from a reaction of the type (7). We do not believe that this three-body reaction represents the actual mechanism by which the electron transfer process takes place. It will probably proceed through two-body reactions involving an intermediate complex. Further work is being carried out to elucidate this point. With oxygen the reaction will be (15) *i.e.* first order in dimer and in oxygen.

$$(MQ^{+\cdot})_2 + O_2 \longrightarrow MQ^{2+} + MQ^{2+} + O_2^{2-} \qquad (15)$$

We have considered whether the existence of free ion–ion pair equilibria could be used to explain our observed reaction kinetics. The fact that there are no spectral changes with temperature for the diquat radical cation–methanol system is strong evidence that such equilibria do not play an important part in these reactions.

Thus by using both dimerising and non-dimerising bipyridylium radical cations (such as $MQ^{+\cdot}$ and $DQ^{+\cdot}$) together with one- and two-electron accepting oxidising agents (such as Cu^{II} and O_2), we have been able to select from among the possible reaction mechanisms put forward earlier[2] those by which these electron transfer reactions probably proceed.

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[6/699 *Received*, 9*th April*, 1976]

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[10] A. Calderbank, D. F. Charlton, J. A. Farrington, and R. James, *J.C.S. Perkin II*, 1972, 138.