Study of Bipyridyl Radical Cations. Part III.[1] Reaction of Paraquat Radical Cation with Oxygen and with Chromic Ions in Methanol

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We have studied methanol solutions of the radical cation of paraquat, 1,1'-dimethyl-4,4'-bipyridylium dichloride. The u.v.–visible spectrum changes with temperature in a very similar way to that for the corresponding morphamquat system. E.s.r. experiments show that, although above −20 °C in methanol solution, there is only one paramagnetic species (the paraquat radical cation, $PQ^{+\cdot}$), a second paramagnetic species develops at lower temperatures, in contrast to the behaviour of the morphamquat system. The reaction of methanol–paraquat radical cation solutions with oxygen has been followed by the stopped-flow technique over a range of temperature from +40 to −80 °C. At +40 °C the reaction is second-order in radical cation, with a velocity constant $8.0 \times 10^8\ l^2\ mol^{-2}\ s^{-1}$. The mechanism of this reaction is discussed. We have also studied the reaction of paraquat radical cation with Cr^{3+} ions in methanol over the temperature range 0—40 °C. The reaction is first order both in Cr^{3+} and in $PQ^{+\cdot}$ It does not go to completion but reaches an equilibrium position. The thermodynamic constants for this equilibrium have been determined and also the thermodynamic constants of activation for the reaction of Cr^{3+} with $PQ^{+\cdot}$ in methanol at +25 °C.

THERE has been much discussion of the herbicidal action of paraquat, 1,1'-dimethyl-4,4'-bipyridylium dichloride, and of the part played in this action by the oxidation of the paraquat radical cation.[2] It is reported that the reaction between oxygen and the radical cation is extremely fast at room temperature in aqueous solution.[3,4] By using methanol as solvent and our anaerobic, accurately thermostatted, stopped-flow apparatus,[5] we have studied the oxidation of the radical cation by O_2 and by Cr^{3+} ions.

EXPERIMENTAL

Materials.—The paraquat radical cation was prepared in methanol from paraquat (I.C.I. Ltd.) by the electrolysis of a solution of paraquat under an atmosphere of argon at a fixed voltage, controlled by a Beckman Electroscan 30 potentiostat to 0.5 ± 0.002 5 V. The solution was freed from oxygen initially by using a stream of argon, and throughout the electrolysis the argon pressure was kept in excess of atmospheric. Methanol solutions of $CrCl_3$ (Pure Grade; Koch–Light) were made up and vacuum degassed. Methanol was purified as described previously [6] and oxygen and argon were obtained from Air Products.

Procedure.—*Spectroscopic measurements.* The u.v.–visible spectrum of the reduced paraquat solution was measured by a Unicam SP 800 spectrophotometer with an E-4557-9 Varian temperature control system. The temperature could be held to ±2° over a temperature range of +40 to −130 °C.

Kinetics. The apparatus used has been described earlier.[5]

Oxygen electrode. The technique of mixing the solutions was the same as in Part II,[1] except that the concentration of oxygen in the methanol solution, just prior to its entering the syringe was determined by an oxygen electrode. A Beckman 39550 steam sterilisable oxygen sensor was used, which was modified by replacing the polytetrafluoroethylene membrane supplied with the electrode by a fluorinated ethylene–propylene copolymer membrane supplied by I.C.I. This change of membrane enabled us to use the electrode in non-aqueous solvents. Without this modification this instrument could not give reproducible results in methanol.

The electrode was introduced into a vessel (provided with a magnetically operated stirrer) just before the syringe. In this way the oxygen concentration of the methanol solution could be monitored just before it entered the syringe. The voltage of the electrode was measured on a simple potentiometer circuit and recorded on a flat bed recorder. The sensor was calibrated by stirring methanol under a given oxygen pressure and at a given temperature, until no further change in reading was recorded, and using the published values for the solubility of oxygen in methanol at that temperature.[7] An excellent straight line calibration graph was obtained by plotting oxygen pressure against electrode voltage over a pressure range of 0—120 cmHg; the range within which we worked during our kinetic experiments was 30—120 cmHg.

The two syringes were filled, one with reduced paraquat–methanol and the other with O_2–methanol, or Cr^{3+}–methanol, and the reaction between the reduced paraquat and the oxidising agent followed by monitoring with light of wavelength 605 nm (a $\lambda_{max.}$ of reduced paraquat). Paraquat does not absorb at this wavelength ($\lambda_{max.}$ for paraquat is 270 nm in methanol).

RESULTS

Spectroscopic Experiments.—In Figure 1 we give the spectra of reduced paraquat–methanol solutions 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.) In the region 25—40 °C the $\lambda_{max.}$ values are 393 and 605 nm and there is no change in the spectrum with temperature. As the temperature is reduced below 0 °C, however, the spectrum changes, the $\lambda_{max.}$ values of 393 and 605 nm decreasing, and the $\lambda_{max.}$ values of 355 and 508 nm increasing. At −80 °C the spectrum is still

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

[2] A. Calderbank, Proc. 7th British Weed Control Conference, 1964, **1**, 312; A. Calderbank, *Adv. Pest. Control Res.*, 1968, **8**, 27.

[3] B. G. White, Proc. 10th British Weed Control Conference, 1970, **3**, 997.

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

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

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

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

changing with temperature in contrast to the case of the morphamquat radical cation [1] (see Discussion section).

Reaction of Reduced Paraquat with Oxygen.—On mixing methanol solutions of reduced paraquat and oxygen the characteristic colour of the former disappears very rapidly and the optical density at the monitoring wavelength, λ605 nm, falls to zero. The oxygen concentration was kept always well in excess of the reduced paraquat concentration to simplify the kinetic analysis.

Reactions in the −80 *to* −50 °C *range.* The reaction curves gave good first-order analyses (*e.g.* Figure 2) and the pseudo first-order constants, k', obtained from these reaction curves are given in Table 1 for different oxygen concentrations. A plot of $\log_{10}k'$ against $\log_{10}[O_2]$ (Figure 3) shows that the order of reaction in oxygen is 0.92 ± 0.06 by the least squares method. The half-lives of these reactions at $[O_2]$ 2.06×10^{-3}M are *ca.* 7 ms at −80 °C.

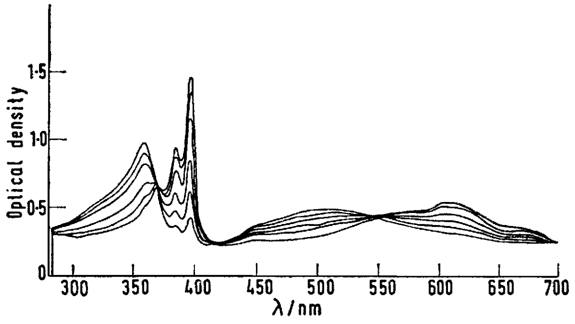

FIGURE 1 Effect of temperature on the spectrum of reduced paraquat in methanol over the range −100 to 25 °C; [Total Reduced Paraquat] = 2.07×10^{-4}M at 25 °C. The optical densities at λ 393 and 605 nm decrease with decreasing temperature, whilst at λ 355 and 508 nm an increase occurs

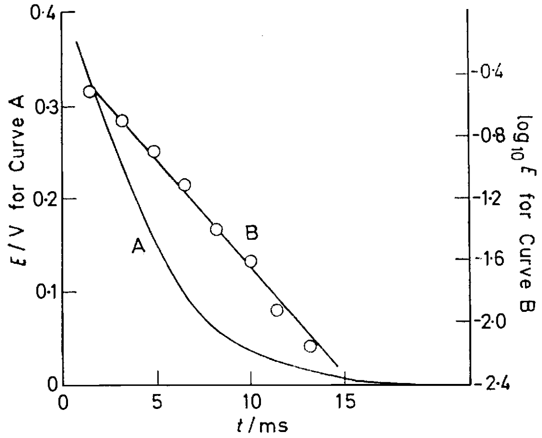

FIGURE 2 Rate curve and first-order plot for reaction of reduced paraquat with oxygen at −80 °C in methanol: $[O_2]$ 3.4×10^{-3}M; [Total Reduced Paraquat]$_i$ 4.2×10^{-4}M

TABLE 1

Pseudo-first-order constants for reaction of reduced paraquat with oxygen in methanol at −80 °C

10^4[Total Reduced Paraquat]$_i$/M	$10^3[O_2]$/M	k'/s^{-1}
4.2	2.06	185
4.2	3.47	308
4.2	5.10	388
4.2	6.00	485
4.2	6.50	535

The reaction is, therefore, first order in the absorbing species and first order in oxygen. The second-order velocity constants, k (second order), for these reactions are given in Table 2 for this temperature range. Plotting $\log_{10}k$ (second order) against $1/T$ gave a value of 12.6 ± 0.3 kJ mol^{-1} for the activation energy.

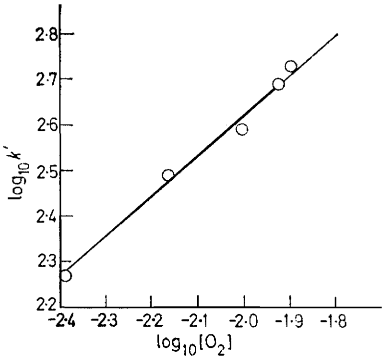

FIGURE 3 Plot of $\log_{10}k'$ against $\log_{10}$ $[O_2]$ at −80 °C in methanol at constant [Total Reduced Paraquat]$_i$ = 4.2×10^{-4}M

TABLE 2

Effect of temperature on the second-order rate constant in the −80 to −50 °C range

T/K	$10^{-4}k$ (second order)/ l mol^{-1} s^{-1}
193	7.94
198	9.62
203	11.5
208	14.5
213	16.8
218	18.9
223	21.8

Reactions at +40 °C. On raising the temperature above −50 °C the reaction curves could not be analysed. As +40 °C was approached the analysis of the reaction curves became more nearly second order and at +40 °C a very good second-order analysis was obtained (*e.g.* Figure 4), giving a pseudo-second-order constant of 2.78×10^6 l mol^{-1} s^{-1}. We have not obtained the order of the reaction in oxygen at +40 °C because a reasonable increase in oxygen concentration would make the reaction too fast to measure and a decrease would mean that pseudo-second-order kinetics would not hold. Neither have we studied the kinetics at temperatures above +40 °C because it is difficult to handle oxygen in solution at these temperatures on the stopped-flow apparatus.

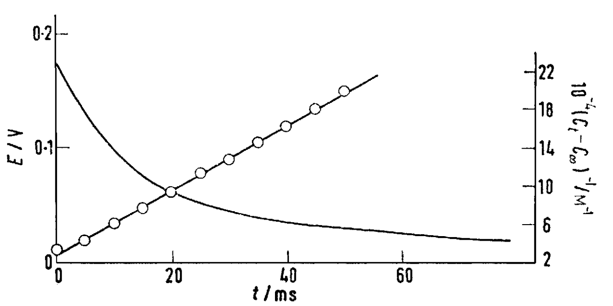

FIGURE 4 Rate curve and second-order analysis for reaction of O_2 with reduced paraquat at +40 °C in methanol: $[O_2]_i$ 3.47×10^{-3}M; [Total Reduced Paraquat]$_i$ 4.2×10^{-4}M

Reaction of Reduced Paraquat with Cr^{3+}.—These experiments were carried out from 0 to +40 °C. On mixing methanol solutions of reduced paraquat and Cr^{3+} the optical density at the monitoring wavelength, λ 605 nm, decreased to a non-zero steady value. This means that the oxidation reaction proceeds to an equilibrium position. For this reason we were not able to use the first-order analysis technique and had instead to measure the initial rates of reaction for systems having the same reduced paraquat concentration with various Cr^{3+} concentrations and *vice versa*. It was found that at 25 °C changing $[\mathrm{Cr}^{3+}]_i$ over the range 4.8×10^{-3}—$4.4 \times 10^{-2}\mathrm{M}$ at $[\mathrm{PQ}^{+\cdot}]_i$ $3.42 \times 10^{-4}\mathrm{M}$ gave an order for Cr^{3+} of 1.1 ± 0.1, and that changing $[\mathrm{PQ}^{+\cdot}]_i$ over the range 3×10^{-5}—$7 \times 10^{-4}\mathrm{M}$ at $[\mathrm{Cr}^{3+}]_i$ $5 \times 10^{-3}\mathrm{M}$ gave an order for $\mathrm{PQ}^{+\cdot}$ of 1.0 ± 0.1.

DISCUSSION

Effect of Temperature on the Spectrum.—The change in u.v.–visible spectrum of methanol solutions of reduced paraquat with change in temperature shows very similar behaviour to that obtained for methanol solutions of reduced morphamquat.[1] In this latter system, it was found that monomer radical cations ($\lambda_{\text{max.}}$ 397 and 595 nm) were in equilibrium with diamagnetic dimer molecules ($\lambda_{\text{max.}}$ 354 and 494 nm) [reaction (1) where $\mathrm{MQ}^{+\cdot}$

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

represents the monomeric radical cation and $(\mathrm{MQ}^{+\cdot})_2$ the diamagnetic dimer molecule].

In methanol solutions of reduced paraquat, the $\lambda_{\text{max.}}$ values are very close indeed to those for reduced morphamquat, so we could by analogy postulate a similar monomer–dimer equilibrium (1) where· PQ^{+} represents

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

the monomer radical cation and $(\mathrm{PQ}^{+\cdot})_2$ the diamagnetic dimer molecule. An equilibrium of this kind has been postulated for aqueous solutions of reduced paraquat.[8]

There is, however, an important difference between the two systems. For reduced morphamquat–methanol solutions, e.s.r. experiments showed [6] that on reducing the temperature below 40 °C the nature of the paramagnetic species, $\mathrm{MQ}^{+\cdot}$, remained unchanged and its concentration decreased until at −80 °C it had all been converted into a diamagnetic species. In the case of reduced paraquat–methanol solutions, however, we find [9] that although above −20 °C the e.s.r. spectrum of the solution shows only one paramagnetic species (the splitting constants of which are identical with those determined for the paraquat radical cation, $\mathrm{PQ}^{+\cdot}$,[10] and the extinction coefficients of which are ε_{393} 48 000 ± 1 000 and ε_{605} 15 000 ± 1 000), as the temperature is reduced below −20 °C, a second paramagnetic species appears with a narrower e.s.r. spectrum and at higher field than the $\mathrm{PQ}^{+\cdot}$. As the concentration of total paramagnetic species decreases with decrease in temperature, this new paramagnetic species increases at the expense of the paraquat radical cation $\mathrm{PQ}^{+\cdot}$. We have not yet fully resolved the spectrum of this new paramagnetic species, so we cannot, as yet, discuss the effect of temperature on this system

There is another difference between the paraquat and morphamquat systems. The u.v.–visible spectroscopic work on reduced morphamquat solutions shows that, at the concentrations we are using, the system lies to the left of equation (1) at 40 °C, whereas at −80 °C, it is to the right. With reduced paraquat systems, however, absorption at 393 and 605 nm is more favoured, so that the system lies over to these wavelengths at the lower temperature of 25 °C, and at −80 °C there is still appreciable absorption at these $\lambda_{\text{max.}}$ values.

Mechanism of Reaction of Reduced Paraquat with Oxygen.—At the end of the reaction the optical density at $\lambda_{\text{max.}}$ for reduced paraquat (605 nm) has become zero and the optical density at $\lambda_{\text{max.}}$ 270 nm for paraquat has returned to its original value. This shows conclusively that we are studying the complete conversion of the reduced paraquat back into paraquat uncomplicated by side reactions. By using excess of oxygen we have ensured that the only reaction of the reduced paraquat is with oxygen.

Reaction at +40 °C. 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 $\mathrm{PQ}^{+\cdot}$. Thus, we interpret our results in the same way as discussed for the reaction of reduced morphamquat in Part II.[1] That is, the reaction could involve two $\mathrm{PQ}^{+\cdot}$ molecules and one oxygen molecule [reaction (2)]. It could also be that

$$\mathrm{PQ}^{+\cdot} + \mathrm{PQ}^{+\cdot} + \mathrm{O}_2 \xrightarrow{k_2} \mathrm{PQ}^{2+} + \mathrm{PQ}^{2+} + \mathrm{O}_2{}^{2-} \qquad (2)$$

the monomer and oxygen molecules combine to give an unstable complex [reaction (3)] which has a high probability of decomposing back into monomer and oxygen

$$\mathrm{PQ}^{+\cdot} + \mathrm{O}_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (\mathrm{PQO}_2)^{+\cdot} \qquad (3)$$

and only occasionally undergoing reaction with a second monomer molecule to complete a two-electron transfer (4).

$$(\mathrm{PQO}_2)^{+\cdot} + \mathrm{PQ}^{+\cdot} \xrightarrow{k_4} \mathrm{PQ}^{2+} + \mathrm{PQ}^{2+} + \mathrm{O}_2{}^{2-} \qquad (4)$$

If $k_{-3} \gg k_4[\mathrm{PQ}^{+\cdot}]$ this scheme would give the observed reaction orders, *i.e.* second order in $\mathrm{PQ}^{+\cdot}$ and first order in oxygen. From reactions (3) and (4) the rate equation (5) is obtained.

$$\begin{aligned}\text{Rate} &= k_4[(\mathrm{PQO}_2)^{+\cdot}][\mathrm{PQ}^{+\cdot}] \\ &= k_4k_3[\mathrm{PQ}^{+\cdot}]^2[\mathrm{O}_2]/k_{-3} \qquad (5)\end{aligned}$$

We cannot discuss the results obtained for the −80 to −50 °C region until we have elucidated the nature of

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

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

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

the second paramagnetic species which is present in this temperature range.

Effect of bipyridyl radical cation structure on its behaviour. Although the paraquat radical cation has a very similar u.v.–visible absorption spectrum to that of the morphamquat radical cation,[1] e.s.r. experiments show that the change from $PQ^{+\cdot}$ to $MQ^{+\cdot}$ increases the delocalisation of the odd electron.[6] Thus, it is not surprising that at 40 °C, at which temperature both systems are in the form of monomer, $PQ^{+\cdot}$ should be five times more reactive than $MQ^{+\cdot}$; the values of the third-order velocity constant for the reaction of the radical cations with oxygen being 8×10^8 and 1.6×10^8 l^2 mol^{-2} s^{-1} for paraquat and morphamquat radical cations respectively at 40 °C.

Using pulse radiolysis Farrington *et al.*[4] found that in aqueous solution and in the presence of excess of oxygen the decay of paraquat radical was first order at room temperature. One of the big differences between their results and ours lies in the fact that in water the reaction rate is very much greater than in methanol. We might expect that for these reactions the change from initial to transition state would be markedly affected by a change of solvent. It is known for example that in acetonitrile as solvent [8] reduced paraquat is extremely stable to air, and we have carried out preliminary experiments which confirm this. This extreme stability in acetonitrile is surprising at first sight since the dielectric constant is not very low, 37.5, and it may well be that a critical feature of the solvent is its power to hydrogen bond with the oxygen in the transition state. If this is the case then it is not at all surprising that a change from water to methanol should have such a marked effect on the reaction rate.

The other difference between our two sets of results is that Farrington *et al.* find the decay of paraquat radical in the presence of excess of oxygen to be first order at room temperature, whereas we find that at +40 °C the disappearance of paraquat radical is second order in radical cation.

It may be that this difference could be due to a difference in the radical cation concentration of the two sets of experiments. We do not know the concentration of radical cations in the experiments of Farrington *et al.*, but as the concentration decreases then the reaction which is first order in cation will become more favoured compared with the reaction which is second order in cation and it could be that the difference between our results is due to a difference in the radical cation concentration favouring the one step more than the other.

It could also be that in aqueous solution the complex formed between $PQ^{+\cdot}$ and O_2 [reaction (3)] is more stable (due to better hydrogen bonding) than in the case of methanol solutions. If this were the case then it could be that $k_{-3} \ll k_4[PQ^{+\cdot}]$ and in this case the rate of reaction would be first order in radical cation. The fact that these workers did not detect any $O_2^{-\cdot}$ as intermediate in their reactions supports this suggestion.

Experiments are being carried out to elucidate these problems. In particular we are investigating the nature of the second paramagnetic species of the paraquat radical cation and carrying out temperature-jump experiments on these systems.

Reactions with Cr^{3+} *Ions in the* 0—40 °C *Region.*—In this temperature range there is only one e.s.r. species, the monomer, $PQ^{+\cdot}$. Since the order is unity in both $PQ^{+\cdot}$ and in Cr^{3+} and the reaction proceeds to an equilibrium position, we postulate an equilibrium of the type (6).

$$PQ^{+\cdot} + Cr^{3+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} PQ^{2+} + Cr^{2+} \qquad (6)$$

The value of the velocity constant in the forward direction, k_f, can be calculated from the initial rate of reaction given by equation (7).

$$\text{initial rate} = k_f[PQ^{+\cdot}]_i[Cr^{3+}]_i \qquad (7)$$

The dependence of k_f on temperature (over a range of 40 °C) gives $\Delta H^\ddagger$ 55.8 ± 0.3 kJ mol^{-1} and the other thermodynamic constants of activation for the reaction are k_f 12.8 l mol^{-1} s^{-1}, $\Delta G^\ddagger$ 66.6 kJ mol^{-1}, $\Delta S^\ddagger$ − 36.2 J K^{-1} mol^{-1}.

The value of K' for this equilibrium was calculated from the initial concentrations of $PQ^{+\cdot}$ and Cr^{3+} and the equilibrium value of $[PQ^{+\cdot}]$ (this latter value being obtained from the equilibrium value of the optical density at λ 605 nm). Values of K' were also calculated for systems in which PQ^{2+} had been added to the equilibrium mixture. The average value of K' obtained in six experiments was 0.24 ± 0.15 at 25 °C.

The effect of temperature on K' is difficult to determine accurately because of the tendency of Cr^{2+} ions to react with the solvent. This reaction is too slow to have any effect on the kinetic experiments, but is sufficiently marked to introduce inaccuracies into the determination of the equilibrium constant, since in these experiments a solution is studied at different temperatures and is held at each temperature for a fair period of time. It is apparent, however, that the equilibrium is practically unaffected by temperature, and hence the value of ΔH° is zero to within this experimental accuracy. The values of ΔG° and ΔS° for this system are 3.5 kJ mol^{-1}, and −11.8 J K^{-1} mol^{-1}.

The rate of reaction with Cr^{3+} is much slower than with oxygen. This slower rate is associated with the fact that the reaction goes to an equilibrium position and that this equilibrium has the very small ΔG° value of 3.5 kJ mol^{-1} at 25 °C. This is not surprising in view of the fact that the E° values in water for PQ^{2+}–$PQ^{+\cdot}$ and Cr^{3+}–Cr^{2+} are very nearly equal *i.e.* −0.443 [3] and −0.410 V,[11] respectively. The difference in these E° values (−0.033 V) corresponds to a ΔG° value of −3 kJ mol^{-1} in water. The ΔG° value we find in methanol for this equilibrium has a value of +3.5 kJ mol^{-1}, which means that in methanol the difference between the E° values for PQ^{2+}–$PQ^{+\cdot}$ and Cr^{3+}–Cr^{2+} will be *ca.* +0.036 V.

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[11] 'Handbook of Chemistry and Physics,' Section D p. 111, Chemical Rubber Co., Cleveland, 1972, 53rd edn.

Change of oxidising agent. Our results show that the reaction of $PQ^{+\cdot}$ with Cr^{3+} must involve a one electron transfer; there is no possibility here of a two electron transfer step since only one Cr^{3+} ion is involved. It also shows that the donor molecule must be the monomeric $PQ^{+\cdot}$ radical cation. This situation differs strikingly from that found when oxygen is the oxidising agent, since in that case the reaction is second order in $PQ^{+\cdot}$ at +40 °C. This difference may well be due to the fact that oxygen can accept two electrons whereas Cr^{3+} can only accept one.

Preparation of Radical Cation by Treatment with Sodium Hydroxide.—The work described in this paper was carried out using reduced paraquat solutions prepared electrolytically. Solutions prepared using the sodium hydroxide technique (a high vacuum technique similar to that used by Farrington *et al.*[12]) gave a smaller rate of reaction with oxygen than the electrolytically prepared solutions. Although concentrations of $OH^- < 10^{-2}$M affect the rate constant, they have no effect on the u.v.–visible spectrum. This reduction in the rate constant is not due to the paraquat formed in the reaction with oxygen being converted back to reduced paraquat by OH^-, since our preliminary studies [13] on the reduction of paraquat by OH^- ions shows this process to be much slower than the reactions we report in this paper. Experiments are being carried out to elucidate the nature of the effect which OH^- ions have on this rate constant.

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[12] J. A. Farrington, A. Ledwith, and M. F. Stam, *Chem. Comm.*, 1969, 259.

[13] A. G. Evans, N. K. Dodson, and N. H. Rees, unpublished results.