Kinetic Studies of the Photoreduction of 4,4′-Di-n-alkylbipyridylium Salts by Alkanols in Aqueous Solution

By **Norman M. D. Brown, David J. Cowley,* and Mahoud Hashmi,** School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland

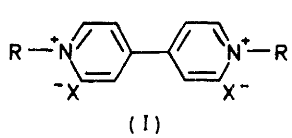
The photoreduction of dilute ($\leq 10^{-3}$M) aqueous solutions of bipyridylium salts $R\overset{+}{N}C_5H_4-C_5H_4\overset{+}{N}R$ (R = Me, Et, Pr^n, Bu^n, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}) by alcohols R^1R^2CHOH (R^1 = H, R^2 = Me, Et, Pr^n, Bu^n, and $R^1 = R^2$ = Me) on irradiation with light of 254 nm wavelength is investigated. Triplet excited bipyridylium dication reacts initially with the alcohol to give an exciplex, which subsequently leads to cation radical formation *via* hydrogen atom transfer. Halide ions exert a strong quenching effect. The lengths of the substituent alkyl chains R (in the salt), and R^2 (in the alcohol) greatly influence the net quantum yield of photoreduction.

Bipyridylium salts are chiefly of interest in view of their herbicidal properties,[1] which arise from their relative ease of reduction. For many years they have been utilised in the characterisation of redox potentials of biological systems. Photochemical reactions, generally involving bipyridylium salts in a chemical role of electron acceptor, have been reported [2-7] from time to time but detailed mechanistic studies are scarce. The broad features of the photoreduction of paraquat dihalides $PQ^{2+}X_2^-$ (1,1′-dimethyl-4,4′-bipyridylium dihalide) *per se* in aqueous alcoholic solutions have been established by Ledwith and his co-workers.[8,9] The stable, but oxygen sensitive, cation radical [10] $PQ^{+\cdot}$ is formed on photolysis of PQ^{2+} in the presence of primary and secondary, but not tertiary, alcohols [equation (1)].

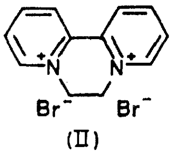
$$2PQ^{2+} + R^1R^2CHOH \xrightarrow{h\nu} 2PQ^{+\cdot} + R^1R^2C{=}O + 2H^+ \quad (1)$$

Some evidence was adduced regarding the intermediacy [11] of alkoxyl radicals $R^1R^2CHO\cdot$ and a rate-determining electron-transfer step involving singlet excited paraquat species and alcohol.

We report here more extensive kinetic data on the photoreduction of 1,1′-di-n-alkyl-4,4′-bipyridylium halides and diquat dibromide, hereafter referred to as (I), $RQ^{2+}X_2^-$, and (II), $DQ^{2+}Br_2^-$, respectively. Photoreduction of the salts in dilute solutions ($<10^{-3}$M) by n-alkanols and propan-2-ol was examined originally to explore possible micellar effects as the n-alkyl chains are lengthened. While we are able to substantiate some of the ideas advanced by Ledwith *et al.*[8] (on which also an early communication [12] by us was based) from a study of more concentrated paraquat solutions, we have cause to favour a different spin multiplicity for the excited precursor in the case of dilute solutions considered here.



(I)



(II)

R = n-alkyl , X = halogen

The relative reactivity of (triplet) excited bipyridylium salts towards alcohols is of some interest for comparison with that of triplet excited ketones and also inorganic species such as uranyl ion UO_2^{2+} whose reactivity patterns have generated discussion [13,14] regarding the factors influencing the extent of charge-transfer in reactions involving formal hydrogen abstraction.

EXPERIMENTAL

Materials.—The alcohols were of AnalaR grade and used as received. The 1,1′-di-n-alkyl-4,4′-bipyridylium dibromides were prepared by reaction of 4,4′-bipyridyl with the appropriate n-alkyl bromide (1 : 2 molar ratio) in diethylene glycol at 60—130 °C for 16—42 h. The salts were purified by recrystallisation from aqueous acetone, dried at 110 °C, and stored in sealed jars in the dark.

1,1′-Dimethyl-4,4′-bipyridylium (paraquat) dichloride dihydrate and diquat dibromide were kindly provided by I.C.I. Plant Protection as 100% pure and were used without further purification.

Paraquat di-iodide dihydrate was prepared by reaction of 4,4′-bipyridyl with methyl iodide under reflux.

Satisfactory ^{13}C and ^1H n.m.r. spectra of the salts dissolved in D_2O and i.r. spectra (KBr disc) were obtained and are to be reported elsewhere.

Elemental analyses were as follows for the anhydrous salts: (I; R = Et, X = Br) (Found: C, 44.7; H, 4.8; N, 7.35. Calc. for $C_{14}H_{18}Br_2N_2$: C, 44.95; H, 4.85; N, 7.5%); (I; R = Pr^n, X = Br) (Found: C, 47.75; H, 5.4; N, 6.85. Calc. for $C_{16}H_{22}Br_2N_2$: C, 47.8; H, 5.5; N, 6.95%); (I; R = Bu^n, X = Br) (Found: C, 49.6; H, 5.9; N, 6.15. Calc. for $C_{18}H_{26}Br_2N_2$: C, 50.25; H, 6.1; N, 6.5%); (I; R = n-C_5H_{11}, X = Br) (Found: C, 52.4; H, 6.6; N, 6.0. Calc. for $C_{20}H_{30}Br_2N_2$: C, 52.4; H, 6.6; N, 6.1%); (I; R = n-C_6H_{13}, X = Br) (Found: C, 53.65; H, 6.85; N, 5.85. Calc. for $C_{22}H_{34}Br_2N_2$: C, 54.35; H, 7.05; N, 5.75%); (I; R = n-C_7H_{15}, X = Br) (Found: C, 55.75; H, 7.25; N, 5.35. Calc. for $C_{24}H_{38}Br_2N_2$: C, 56.05; H, 7.45; N, 5.45%).

Potassium chloride, bromide, and iodide salts were B.D.H. AnalaR materials. Distilled de-ionised water was used in the preparation of the solutions.

Photolysis.—Aqueous solutions of the bipyridylium salt together with alcohol were introduced into a square, 10 mm path length, Spectrosil cell clear on all four faces joined *via* a graded seal to a degassing bulb and tap. The reaction mixture was degassed by repeated freeze–pump–thaw cycles and sealed. The sample was irradiated for known time intervals by a circular 25 W low pressure mercury arc emitting light predominantly at 254 nm wavelength. The solution optical density at this wavelength was always >1.2.

The formation of the radical cation RQ$^{+\cdot}$ was monitored in every case, by the light absorption at *ca.* 600 nm, using a Unicam SP 8000A spectrometer. Since the measurements were made at ambient temperatures (20 ± 2 °C) and the maximum concentration of radical cation was $\leq 8 \times 10^{-5}$M, we observed no evidence of radical dimerisation [10c] [except in the case of (I; R = n-C$_{10}$H$_{21}$, X = Br) which is not discussed here]. For all 4,4′-bipyridyl cation radicals the molar extinction coefficient [15,16] at the absorption maximum *ca.* 600 nm was taken to be 12 000 (±1 000) l mol^{-1} cm^{-1}. This was verified by titrations with molecular iodine in aqueous potassium iodide under a purified, oxygen-free nitrogen gas stream.[17]

The light flux was determined regularly by ferrioxalate actinometry after the procedure of Kurien,[18] and was found to be constant over long periods of time.

The quantum yield of photoreduction was taken to be the ratio of the rate of formation of radical cation (expressed as mol s^{-1}) and the flux of light absorbed.

Other Measurements.—Phosphorescence spectra at 77 K of *ca.* 10^{-3}M-bipyridylium salt solution in ethanol contained in 3 mm internal diameter silica tubes were recorded using a rotating can assembly with a Perkin-Elmer MPF-2A spectrofluorimeter.

Conductimetric measurements were made at 25.0 °C on aqueous solutions of the bipyridylium salts in the concentration range 10^{-4}—10^{-2}M (by the weight dilution method) using a conventional glass conductivity cell. The blackened platinum electrode had a surface area of *ca.* 1 cm^2.

Some difficulty in obtaining high reproducibility and long term stability was encountered, which could be attributed to the strong adsorption [19] of the bipyridylium dications on the glass and platinum surface and/or to ion exchange on the glass surface present. The general form of the results is not negated by such errors.

RESULTS AND DISCUSSION

(a) *Nature of Ground-state Reactants.*—The kinetic data reported here were obtained for solutions of RQ^{2+}X$_2^-$ below 10^{-3}M in concentration (*cf.* ref. 8 where much higher concentrations, *e.g.* 0.1M, were examined).

While it seems reasonable that a 2 : 1 electrolyte in aqueous solution at $\leq 10^{-3}$M concentration should exist as essentially free, hydrated ions, confirmatory evidence is desirable. Conductimetric and u.v. absorption studies on paraquat di-iodide (I; R = Me, X = I) considered as a prototype of the salts were carried out to investigate equilibrium (2). Typical measured conductances of

$$\mathrm{PQ^{2+} + I^- \rightleftharpoons (PQ^{2+} \cdots I^-)} \qquad (2)$$

PQ^{2+}I$_2^-$ in water and water containing 1.0M-propan-2-ol are given in Figure 1, and are similar to the values obtained for other 2 : 1 electrolytes, *e.g.* CaCl$_2$. Above *ca.* 10^{-3}M concentration, and independent of propan-2-ol concentration in the range 0—1.0M the conductivity falls more rapidly than expected from the calculated Onsager gradient for a 2 : 1 electrolyte in water at 25 °C. A simple Arrhenius-type analysis based on an equilibrium given by (2) and assuming that the molar conductance of PQ^{2+} is twice that of the ion pair (PQ$^{2+} \cdots$ I$^-$) yields a value of *ca.* 6 l mol^{-1} for the association constant, K_a. In aqueous or aqueous propan-2-ol solution, a well defined shoulder around 350 nm is detectable in the u.v. absorption spectra of PQ^{2+}I$_2^-$ when the bipyridylium salt concentration is increased above *ca.* 10^{-3}M. The optical density at 350 nm of such solutions increases non-linearly with increase in the PQ^{2+}I$_2^-$ concentration (Figure 1) and is enhanced upon addition of potassium iodide. We attribute this new absorption shoulder to a charge-transfer excitation from iodide ion to paraquat dication [20,21] within an intimate ion-pair. Such an absorption is not detectable for the chloride and bromide salts of paraquat presumably because the transition is to higher energy and is swamped by the nearby intense $\pi^* \longleftarrow \pi$ absorption of PQ^{2+} itself.

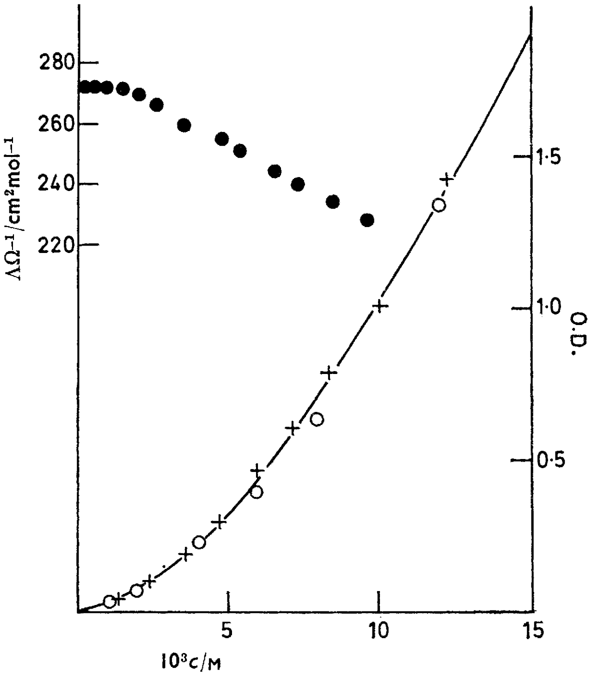
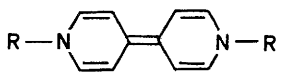


FIGURE 1 Molar conductance in water(●) and optical densities at 350 nm; (+) in water and (○) in 1.0M-propan-2-ol in water with change in the concentration of paraquat di-iodide PQ^{2+}I$_2^-$

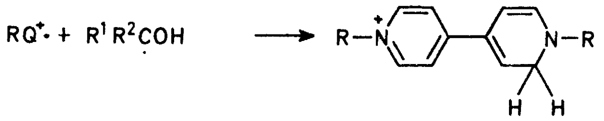
For the concentration range investigated (10^{-3}—10^{-2}M) the ion pair equilibrium (2) is assumed to lie over to the left and it can be shown that $D \approx 2K\varepsilon a_0^2$, where D is the solution optical density at 350 nm wavelength, ε is the molar extinction coefficient for the ion-pair at 350 nm, and a_0 is the activity of the paraquat salt. Debye–Hückel theory was used to compute the mean activity coefficient of the ions, and hence a_0, knowing the stoicheiometric concentration of the salt. From a plot of D against a_0^2, $K\varepsilon$ was determined to be 12 500 l^2 mol^{-1} cm^{-1}. The Benesi–Hildebrand method could not be applied directly to the data for the addition of potassium iodide to a constant concentration of PQ^{2+}I$_2^-$ since then the ionic strength of the solution unavoidably varied. However, extrapolation of the optical density data to a concentration of potassium iodide where all PQ^{2+} ions can be considered to be associated, enables a value of 1 800 l mol^{-1} cm^{-1} to be estimated for ε. In turn K_a is computed to be 12 500/1 800 $\approx$ 7 l mol^{-1}, in broad agreement with the estimate from the conductimetric data.

Thus we conclude that the photochemistry reported subsequently involves free ions and not ion pairs. Thus the arguments advanced here do not necessarily negate those of Ledwith *et al.*[8]

(b) *Photoreduction Quantum Yields.*—Most measurements were made on $RQ^{2+}Br_2^-$ solutions in the concentration range 10^{-4}—10^{-3}M with typically 1.0M-alcohol present, and for low conversions of RQ^{2+} to the cation radical $RQ^{+\cdot}$. Above 10^{-3}M the quantum yield of photoreduction was very low due to strong bromide ion quenching. Below 10^{-4}M the intrinsic quantum yield is probably very high but determinations were subject to various corrections and sources of error, namely (i) incomplete and changing absorption of the incident radiation and (ii) competitive light absorption by the radical and parent dication. Indeed, prolonged photolysis of RQ^{2+} solutions at 1×10^{-4}M concentration or less, leads to an eventual decline in the cation radical concentration. An interesting phenomenon is present once the maximum in the radical concentration is passed thus. If the previously irradiated solution is kept in the dark for several minutes, the concentration of radical rises above the value pertaining immediately after irradiation. The subsequent dark period recovery is 50—75% of any destruction induced by a previous irradiation. Many such cycles can be performed. For these solutions, irradiation of the cation radical in its visible absorption bands (*ca.* 390 and 600 nm) did not lead to its removal, unlike irradiation at 254 nm. Photoreduction of the cation radical by alcohol is thus unlikely. The u.v. absorption spectrum of the solution after sufficient photolysis to produce and then destroy $RQ^{+\cdot}$, excluded the presence of dihydroparaquat (III). A similar phenomenon has been reported for paraquat photolysed in the presence of benzophenone[9] and the explanation offered there also seems reasonable in this case, namely, that $RQ^{+\cdot}$ species are chemically reduced by ketyl radicals to dihydropyridylpyridylium salt (IV).



(III)



(IV)

The dark production of the cation radical could then be *via* reaction (3), with (IV) also undergoing polymerisation or oligomerisation.

$$RQ^{2+} + (IV) \longrightarrow 2RQ^{+\cdot} + H^+ \qquad (3)$$

Table 1 gives values of $\phi_{RQ^{+\cdot}}$ for the series of $RQ^{2+}Br_2^-$ salts (R = Me, Et, Pr^n *etc.*) as a function of the total bipyridylium salt concentration at 1.0M-propan-2-ol.

TABLE 1

Quantum yields of cation radical formation ϕ for various (I; R = n-alkyl, X = Br); [propan-2-ol] = 1.00M; $c = 10^4[RQ^{2+}]$/M

R = Me		R = Et		R = Pr^n		R = Bu^n		R = n-C_5H_{11}		R = n-C_6H_{13}		R = n-C_7H_{15}	
c	ϕ	*c*	ϕ	*c*	ϕ	*c*	ϕ	*c*	ϕ	*c*	ϕ	*c*	ϕ
1.0	0.275	1.0	0.50	0.80	0.81	1.0	1.76	1.0	0.60	1.0	0.14	1.0	0.10
		2.0	0.27	1.0	0.69	2.0	1.32	2.0	0.35	2.0	0.10	2.0	0.10
3.0	0.126	3.0	0.16	1.5	0.39	3.0	0.94					2.5	0.10
		4.0	0.11	3.0	0.26	4.0	0.69	4.0	0.21	4.0	0.055	3.0	0.085
5.0	0.050	5.0	0.094	5.0	0.16	5.0	0.48					3.5	0.060
		6.0	0.082	6.0	0.11	6.0	0.30	6.0	0.11	6.0	0.020	4.0	0.054
7.0	0.026	7.0	0.047	8.0	0.028	7.0	0.25					5.0	0.020
8.0	0.017	8.0	0.028										
10.0	0.007	10.0	0.009	10.0	0.020	8.0	0.15	8.0	0.028	8.0	0.010	7.0	0.0076
				60.0	0.014	10.0	0.12	10.0	0.021	10.0	0.007	8.0	0.0050
				80.0	0.012	20.0	0.033					10.0	0.0033
						40.0	0.012						
0 *	0.4	0	1.0	0	1.6	0	2.0	0	1.7	0	0.9	0	0.1

* Estimated limit for ϕ by extrapolation.

The quenching effects of halide ions can be clearly seen from the data in Tables 2 and 3 as well as in Table 1.

TABLE 2

Bromide ion quenching of cation radical formation; [propan-2-ol] = 1.00M; $[RQ^{2+}Br_2^-$ (R = Et)] = 1.00×10^{-4}M

10^4[KBr]M	0	4.0	10.0	18.0
$\phi RQ^{+\cdot}$	0.50	0.091	0.067	0.022

TABLE 3

Quenching effects of the counterion on the quantum yield of cation radical ϕ for paraquat salts (I; R = Me); [propan-2-ol] = 1.00M; $c = 10^4[RQ^{2+}]$/M

Counterion X^-					
Cl^-		Br^-		I^-	
c	ϕ	*c*	ϕ	*c*	ϕ
1.0	0.33	1.0	0.275	1.0	0.23
2.0	0.25			2.0	0.13
3.0	0.14	3.0	0.126	3.0	0.050
				4.0	0.022
5.0	0.055	5.0	0.050		
				6.0	0.0105
		7.0	0.026		
8.0	0.025	8.0	0.017	8.0	0.0055
10.0	0.012	10.0	0.007	10.0	0.004

Diquat dibromide, important because of the information provided by studies of its weak fluorescence in aqueous media, behaved similarly to the $RQ^{2+}Br_2^-$ salts (Table 4). The effect of alcohol concentration on the photoreduction quantum yield at constant, low concentrations of bipyridylium salts is typical of competitive scavenging of an excited intermediate (Table 5).

TABLE 4

Quantum yields for the formation of $DQ^{+\cdot}$ from diquat dibromide in the presence of alcohol; [propan-2-ol] = 1.00M

$10^4[DQ^{2+}]$/M	1	2	4	6	8	10
$\phi_{DQ^{+\cdot}}$	0.96	0.53	0.23	0.088	0.056	0.025

TABLE 5

Quantum yields of cation radical formation from (I; R = Et), $RQ^{2+}Br_2^-$, and (II), $DQ^{2+}Br_2^-$, with varying concentrations of propan-2-ol

$[DQ^{2+}Br_2^-]$ 1.0×10^{-4}M		$[RQ^{2+}Br_2^-]$ 1.0×10^{-4}M		$[RQ^{2+}Br_3^-]$ 5×10^{-4}M	
[Propan-2-ol]/M	ϕ	[Propan-2-ol]/M	ϕ	[Propan-2-ol]/M	ϕ
0.10	0.42	0.05	0.023	0.10	0.003
0.25	0.82	0.10	0.11	0.20	0.0215
0.50	1.20	0.20	0.21	0.40	0.033
1.00	1.20	0.40	0.30	1.00	0.094
2.00	1.08	0.70	0.43	2.00	0.195
3.00	1.20	1.00	0.50	3.00	0.191
4.00	1.28	2.00	0.50		

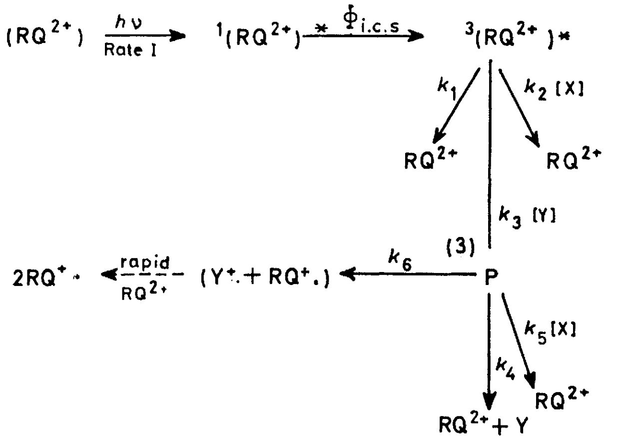
Stern–Volmer plots of reciprocal $\phi_{RQ^{+\cdot}}$ against quencher (halide) concentration using the data of Tables 1—3 enable estimates of $\phi_{RQ^{+\cdot}}$ at zero quencher concentration to be made by extrapolation, *i.e.* $\phi_{RQ^{+\cdot}}(0)$. These values differ for the various bipyridylium cations whereas, as expected, a given dication, *e.g.* paraquat, quenched by different counterions ($Cl^- < Br^- < I^-$) does yield identical limits within experimental error.

It is significant that in some cases the limiting yield approaches the anticipated maximum of 2, quite unlike the poor yields reported for high concentrations of $PQCl_2$.

In some cases the Stern–Volmer plots are reasonably linear in the lower concentration range (*e.g.* $<6 \times 10^{-4}$M) but curve upward sharply thereafter, while in other cases curvature is present at all concentrations of bipyridylium salts. However, in all the representative trial cases examined by us, the curvature of the Stern–Volmer plot can be eliminated by increase of the *alcohol* concentration. The behaviour suggests that halide ions, *inter alia*, can quench an excited species–intermediate in competition with the alcohol, and can also quench a second species on the path to the radical cation product.

(c) *Nature of the Reactive Excited State.*—The mechanism of the photoreduction can be clarified by some simple quantitative considerations. The lifetime of the fluorescent excited singlet state of diquat cation in the absence of quenching is estimated [8,12] to be 6.4×10^{-11} s in water (ϕ°_F 0.04, k^{-1}_F 1.6×10^{-9} s *via* the Strickler–Berg relationship). The fluorescence is quenched but weakly by alcohols, the Stern–Volmer constants being *ca.* 0.3M. Thus, at 0.25M-propan-2-ol, the fluorescence of DQ^{2+} is quenched * by *ca.* 7.5%. However, the photoreduction quantum yield is high (*ca.* 0.8, see Table 5) and changes dramatically with the concentration of the alcohol. The singlet excited state of the dication does not appear to be the species which reacts with alcohol to produce cation radicals under our conditions.

From the data on the quenching affect of bromide ion on the photoreduction quantum yield, the Stern–Volmer constant in the case of (I; R = Et, X = Br), for example, is *ca.* 20 000 l mol^{-1}. If the quenching is diffusion controlled (k_d 1.0×10^{10} l mol^{-1} s^{-1}; water; 20 °C) then the lifetime of the reactive intermediate is *ca.* 2×10^{-6} s and is longer if the reaction is slower than diffusion controlled. The magnitude of the lifetimes thus estimated for all the excited bipyridylium salts suggests the involvement of the triplet excited state of the dication.



SCHEME 1 X = halide ion, Y = alcohol

(d) *Proposed Mechanism of Photoreduction.*—The mechanism shown in Scheme 1 appears to accommodate all the major features known for the photoreduction. Precise evaluation of individual rate constants is, however, difficult. Using the normal steady-state assumptions for $^3(RQ^{2+})^*$ and the intermediate P one may derive equation (4) where step 6 leads eventually to the production of two cation radicals (see later). The data can be seen to conform to the above mechanism by consideration of some limiting cases.

$$\phi_{RQ^{+\cdot}} = \frac{2k_6}{(k_6 + k_4 + k_5[X])} \cdot \frac{k_3[X]}{(k_1 + k_2[X] + k_3[Y])} \cdot \phi_{i.s.c.} \qquad (4)$$

(i) For a given alcohol Y and at a constant concentration of $RQ^{2+}X_2^-$ we obtain $1/(\phi_{RQ^{+\cdot}}) = a + b/[Y]$ where a and b are constants. As shown in Figure 2, this relationship is obeyed approximately by the data recorded in Table 5. The deviation from linearity noticeable at very high alcohol concentration and low salt concentration (1×10^{-4}M) is to be expected on the following grounds. Step 6 in the mechanistic scheme

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* An earlier communication [12] gave the Stern–Volmer quenching constant by alcohols as *ca.* 3.5 l mol^{-1}. This was given in error. The correct value is 1/3.5 = 0.285 l mol^{-1}, and leaves open the question of alcohol association with RQ^{2+} on this basis.

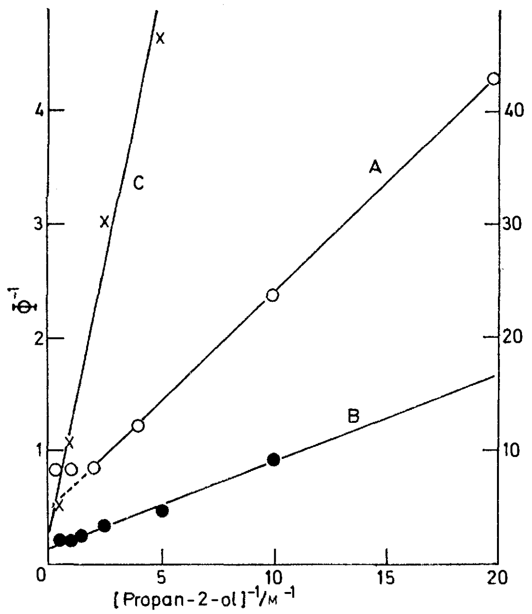


FIGURE 2 Plot of reciprocal quantum yield of cation radical formation against reciprocal propan-2-ol concentration: A, $DQ^{2+}Br_2^-$, 1.0×10^{-4}M; B, (I; R = Et, X = Br), 1.0×10^{-4}M; C, (I; R = Et, X = Br), 5.0×10^{-4}M

indicates that in order to produce two cation radicals $RQ^{+\cdot}$ from intermediate P, the radical species designated $Y^{+\cdot}$ must transfer an electron to a ground state RQ^{2+} in a bimolecular reaction. At very low concentrations of RQ^{2+} this second stage may become inefficient and $Y^{+\cdot}$ decays by other routes, possibly involving alcohol Y.

(ii) Under conditions of constant high alcohol concentration such that all $^3(RQ^{2+})^*$ are scavenged, $1/(\phi_{RQ^{+\cdot}}) = c + d[X]$ where c and d are constants.

Such a linear Stern–Volmer quenching law is obeyed by the bipyridylium salts (I; X = Br, R = Et, Pr^n, n-C_5H_{11}, and n-C_6H_{13}) at 1.0M-propan-2-ol with change in the salt concentration below *ca.* 6×10^{-4}M. However, such a limiting case does not appear to hold for (I; R = Me, X = Cl, Br, I) or for (I; R = Bu^n, X = Br).

(iii) If the concentration of alcohol is kept constant but all triplet dications are not scavenged, then $1/(\phi_{RQ^{+\cdot}}) = (c + d[X])(e + f[X])$ where c—f are constants.

The exceptions noted in (ii) fall into this category. Unfortunately, curve fitting of the data was unsatisfactory in chemical interpretation since the relevant constants in the expression required evaluation from a too limited set of points and were highly susceptible to small errors in those points.

We conclude only that the proposed mechanistic scheme is fully compatible with the data. At higher concentrations of bipyridylium salt, *e.g.* above 7×10^{-4}M, the photoreduction is very inefficient due to the quenching processes outlined in the scheme and the increasing influence of static quenching *via* ion pairs. The inefficient photoreduction of $PQ^{2+}Cl_2^-$ at 0.1M ($\phi_{max.}$ *ca.* 0.07) must be attributed to the shortened lifetime of the triplet ion pair or intermediate P,X^- *via* the enhanced spin–orbit coupling (and possibly charge-transfer in the case of iodide). The small effect of ferrocene on the above system noted by Ledwith *et al.*[8] does not negate the intermediacy of triplet species in the photoreduction. A ferrocene concentration of 0.01M resulted in a two-fold decrease in $\phi_{PQ^{+\cdot}}$ when the propan-2-ol concentration was 0.65M. This implies that ferrocene is intrinsically two orders of magnitude more efficient than propan-2-ol in competing for the (triplet) excited state. Similarly, while triplet energy transfer to phenol is impossible, at the concentrations adopted[8] charge-transfer quenching by both static and dynamic mechanisms are possible.

(e) *Correlations of Quantum Yield with Alkyl Chain Lengths in* $RQ^{2+}Br_2^-$ *and Alcohol.*—At a constant low concentration of $RQ^{2+}Br_2^-$, *e.g.* 1.0×10^{-4}M in the presence of propan-2-ol in high concentration, *e.g.* 1.0M, the observed quantum yields of photoreduction vary considerably with the length of the n-alkyl chain R of the salt, reaching an obvious maximum for the C_4 system (see Table 1) and declining markedly on either side of this. On the proposed mechanism, the yield $\phi_{RQ^{+\cdot}}$ reflects the function $2\phi_{i.s.c.}k_6/(k_4 + k_6 + k_5[Br^-])$.

For a given salt, $RQ^{2+}Br_2^-$, $\phi_{RQ^{+\cdot}}$ measured for equimolar concentrations of different straight-chain primary alcohols varies noticeably with the number of carbon atoms in the alcohol, reaching a peak for every salt investigated with propan-1-ol (see Figure 3). The prominence of the peak is less for R = pentyl, hexyl, and heptyl in the salt (I; X = Br). Since $\phi_{i.s.c.}$ can be considered constant for a given salt in the largely

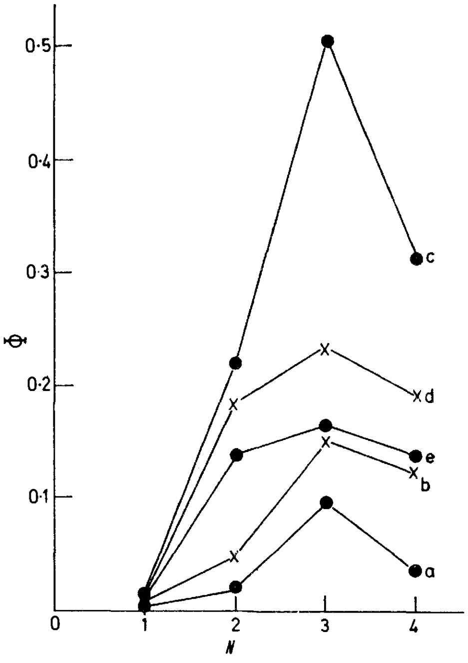


FIGURE 3 Variation of the quantum yield of cation radical formation with the number of carbon atoms, *N*, in the primary alcohol used to photoreduce the bipyridylium salt (I; X = Br, R = ethyl) (a), (R = n-propyl) (b), (R = n-butyl) (c), (R = n-hexyl) (d), or (R = n-heptyl) (e)

aqueous media, the yields reflect mainly the influence of the alcohol reductant on the rate constants k_4 and k_6, quenching by bromide ions being small under the conditions used.

TABLE 6

Triplet state energies of $RQ^{2+}Br_2^-$ salts in ethanol glass at 77 K estimated from the position of the 0,0 phosphorescence band

R	Me	Et	Pr^n	Bu^n	Hex^n	DQ^{2+}
$E(T_1)$/kJ mol^{-1}	285	286	284	283	284	267 ± 2

Examination of the phosphorescence emission of the bipyridylium salts in ethanol at 77 K reveals that the n-alkyl chain length does not perturb the triplet state energy to any significant extent (Table 6), also the intrinsic triplet yields are comparable. Thus the assumption of a constant $\phi_{i.s.c.}$ in all the salts is supported. From the limiting yields of cation radical formation in the most favourable cases (close to 2.0), we may deduce that $\phi_{i.s.c.} \gtrsim 0.75$.

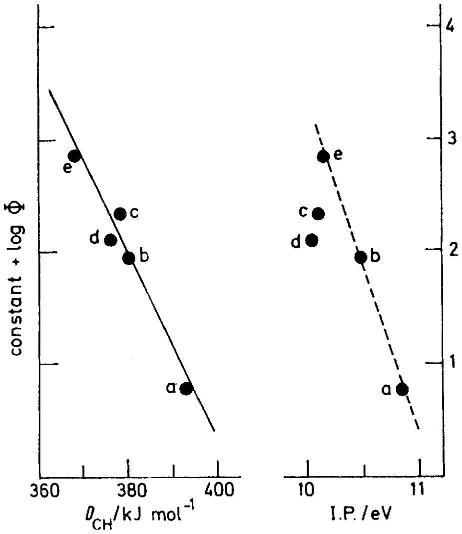
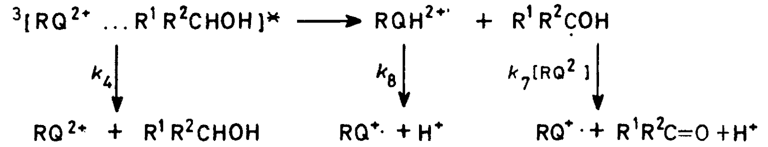


FIGURE 4 Possible correlation of log (quantum yield of cation radical formation) with the α-carbon–hydrogen bond dissociation energy and the ionisation potential of the alcohol. Salt (I; R = Bu^n, X = Br): a, methanol; b, ethanol; c, propan-1-ol; d, butan-1-ol; e, propan-2-ol



SCHEME 2

The above correlations converge to indicate that (for n-alkyl chains) the separation efficiency of the intermediate P yielding $RQ^{+\cdot}$ relative to collapse to ground-state reactants is greatest for C_3—C_4 chains.

(f) *Nature of the Intermediate* P.—Three extreme structures can be formulated: (i) a pair of cation radicals, arising from electron transfer from alcohol to triplet RQ^{2+}; (ii) a radical pair, arising from abstraction of an α-hydrogen atom from the alcohol by triplet RQ^{2+}; (iii) a 'solvent exciplex' consisting of triplet RQ^{2+} and an alcohol molecule in association.

Attempted correlations of the photoreduction quantum yield with C_α–H bond dissociation energy of the alcohol or ionisation potential (I.P.) of the alcohol, for a given bipyridylium salt are shown in Figure 4. The former shows a better correlation than the latter, especially with respect to propan-1-ol, propan-2-ol, and butan-1-ol.

Further, isotopic substitutions in the water–methanol–diquat dibromide system (Table 7) reveal the existence of a large isotope effect in connection with the C_α–H(D) replacement.

TABLE 7

Effects of isotopic replacement on the quantum yields of cation radical formation. [alcohol] = 1.0M, [DQ^{2+}-Br_2^-] 1.0×10^{-4}M

Solvent	Alcohol	$\phi_{DQ^{+\cdot}}$
H_2O	CH_3OH	0.17
D_2O	CH_3OH	0.15
H_2O	CD_3OD	0.025

Thus, the balance of the evidence suggests that the photoreduction yield is dominated by step 6 and that considerable C–H bond stretching occurs during this reaction step. For this reason we suggest that P is the triplet exciplex of (iii), and accordingly the ultimate reaction steps can be formulated as in Scheme 2. Step 7 is expected to be very fast, possibly diffusion controlled, from the known reducing properties of hydroxyalkyl radicals.

It is plausible, on grounds of electron distribution arguments to suggest that the species $RQH^{\cdot 2+}$ is formed by the addition of a hydrogen atom at the 2-position in the bipyridylium entity. Increase of the alkyl chain length R from Me to Et to Pr^n could be expected to provide stabilisation *via* electron release into the pyridyl system. A further increase in chain length would add nothing to such electronic stabilisation but could well hinder the addition of hydrogen at the adjacent position to nitrogen, as can be seen from molecular models if the alkyl tail doubles back over the pyridyl ring.

In conclusion, we have provided evidence that the photoreduction of bipyridylium salts by alcohols in aqueous media proceeds *via* the excited triplet state and that the rate-determining step in cation radical production involves a hydrogen atom transfer. Steric effects arising from the alkyl chains in the vicinity of the reaction sites are interesting.

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