Cation-radicals: Photochemical Oxidation of Alcohols by Bipyridylium Salts

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Summary Photochemical oxidation of primary and secondary alcohols occurs *via* singlet excited states of paraquat and diquat: deuterium kinetic isotope effects and fluorescence quenching suggest that electron-transfer reactions are rate determining.

ULTRAVIOLET irradiation of 1,1′-dimethyl-4,4′-bipyridylium dichloride (paraquat dichloride) (I, $2Cl^-$) in ethanol or isopropyl alcohol (but not t-butyl alcohol) has been reported[1] to give the blue cation radical $PQ^{\cdot+}$ (PQ = 1,1′-dimethyl-4,4′-bipyridyl) but no details were given. Previously we have shown[2] that paraquat is thermally reduced to $PQ^{\cdot+}$ by primary and secondary alcohols under alkaline conditions, and as part of a continuing interest in cation-radical chemistry[3] have studied in detail the corresponding photochemical processes (Table).

Paraquat dichloride was reduced to the cation radical $PQ^{\cdot+}$ by u.v. irradiation of aqueous solutions containing primary or secondary alcohols. There was no reaction on irradiation in pure water or when t-butyl alcohol was added. Reaction rates were retarded by added halide ion in the sequence of increasing quenching ability $Cl^- < Br^- \ll I^-$. Similar results were observed for diquat salts (II, $2Cl^-$) except that in this case halide ion quenching was so effective that the commercially important diquat dibromide could not be photoreduced in 0·1M-solutions. Photoreduction of paraquat dichloride in aqueous isopropyl alcohol was similarly retarded by addition of phenol and ferrocene. For all alcohols, stoicheiometric amounts (g.l.c.) of corresponding carbonyl compounds were produced according to the following overall equation:

Photochemical[a] *reduction of paraquat dichloride* (0·1M) *in aqueous solution at* 25°.

Reductant	Reductant (M)	Quencher	Quencher (M)	Rel. rate[b]
MeOH	0·65			0·22
EtOH	0·65			0·56
$\mathrm{Pr^iOH}$	0·65			1·00
$\mathrm{Pr^iOH}$	0·65	NaCl	1·0	0·75
$\mathrm{Pr^iOH}$	0·65	NaBr	0·1	0·25
$\mathrm{Pr^iOH}$	0·65	NaI	0·01	0·03
$\mathrm{Pr^iOH}$	0·65	Phenol	0·01	0·44
$\mathrm{Pr^iOH}$	0·65	Phenol	0·01	0·06
$\mathrm{Pr^iOH}$	0·65	Ferrocene	0·001	0·80
$\mathrm{Pr^iOH}$	0·65	Ferrocene	0·01	0·50
CH_3OH	0·50			1·0
CD_3OD	0·50			0·72
CH_3OH	0·50	(Solvent D_2O)		0·72

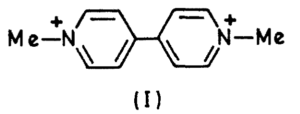
[a] Photolysis of vacuum outgassed solutions in glass vessels with 250 W medium-pressure mercury lamp.

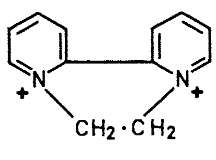
[b] Initial slope from plots of $[PQ^{\cdot+}]$ against time, $[PQ^{\cdot+}]$ determined spectrophotometrically (ref. 2). Reaction rates are normalised to overcome fluctuations in light intensity.

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

Reaction rates were proportional to the first power of the light intensity and could be activated using 313 or 334 nm (but not 366 nm) irradiation, consistent with excitation *via* the long-wavelength tail of the absorption spectrum of paraquat. For 334 nm irradiation in water at 25° ($[PQ^{2+}]$ = 0·1M, $[\mathrm{Pr^iOH}]$ = 0·65M) the quantum yield for formation of $PQ^{\cdot+}$ was initially 0·07 ± 0·02 (ferrioxalate actinometry[4]).

A striking feature of the photoreduction of (I) was the rapid decay in rate as reaction proceeds. Independent generation of $PQ^{\cdot+}$ by zinc reduction established that the decay in rate of photoreduction was caused entirely by this product although there is a convenient 'window' at 310—340 nm in its absorption spectrum.[5] Rate retardation by $PQ^{\cdot+}$ must therefore involve genuine quenching of excited states, or intermediates, although the mechanism is not clear. Because of retardation (or quenching) by the photoproduct, the amount of $PQ^{\cdot+}$ formed in any given system is limited, final limiting concentrations of $PQ^{\cdot+}$ varying with the initial $[PQ^{2+}]$ up to a maximum of *ca.* $1·6 \times 10^{-3}$M, at *ca.* 0·1M-$[PQ^{2+}]$. The limiting concentration was independent of the type or concentration, of alcohol reductant, and was unaffected by further increases in $[PQ^{2+}]$. Optimum yields of $PQ^{\cdot+}$ (*ca.* 7%) were obtained using 0·01M-$[PQ^{2+}]$ but considerably higher overall conversion of alcohol into carbonyl compound may be achieved by carrying out the photolysis in vessels exposed to the atmosphere, when the cation radical is continuously reconverted into (I) by reaction with oxygen. Very similar limiting yields and rate dependence have been noted for photoreduction of paraquat sensitised by illuminated chloroplasts.[6]


(I)


(II)

Paraquat does not luminesce at room temperature whereas diquat dichloride fluorescesces in water ($\phi_F = 0·04 \pm 0·02$†) but not at all in alcohols (including t-butyl alcohol) or in *ca.* 20% aqueous alcoholic solutions. Fluorescence quenching of diquat dichloride (10^{-4}M) in water was observed

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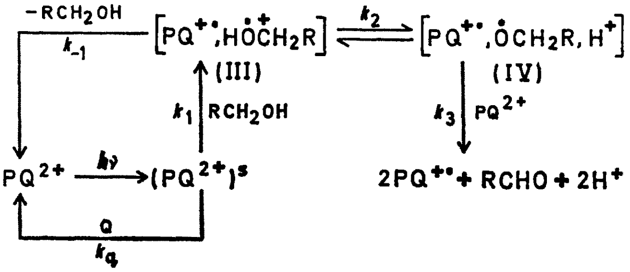
† Determined by reference to quinine bisulphate (see ref. 4.)

for Cl⁻, Br⁻, I⁻, and phenol. Very good Stern–Vollmer plots ($F_0/F = 1 + K_Q[Q]$) were obtained for all the quenchers yielding quenching constants (K_Q) and estimated‡ quenching rate coefficients (k_q) respectively, as follows:

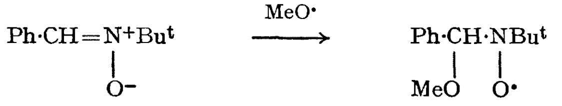
Cl⁻, 9·1 M, $5·6 \times 10^9$ $\text{M}^{-1}\,\text{sec}^{-1}$; Br⁻, 15·1 M^{-1}, $9·2 \times 10^9$ $\text{M}^{-1}\,\text{sec}^{-1}$; I⁻, 47·6 M^{-1}, 29×10^9 $\text{M}^{-1}\,\text{sec}^{-1}$; phenol, 6·3 M^{-1}, $4·5 \times 10^9$ $\text{M}^{-1}\,\text{sec}^{-1}$.

The values of k_q are reasonably close to the diffusion limiting rates for water solutions and parallel the observed quenching effects in photoreduction of paraquat, arguing strongly in favour of excited singlet paraquat as the major reactive intermediate. The observed quenching of photoreduction of paraquat ($E_T = 71·5$ kcal[7]) by phenol ($E_T = 82$ kcal[4]) could not involve triplet energy transfer and also the comparable, mild, quenching efficiency of ferrocene, normally a very efficient quencher for triplet states,[8] argues against triplet intermediates. k_H/k_D kinetic isotope effects for CH_3OH/CD_3OH and CH_3OH/CH_3OD are approximately 1·4 suggesting strongly that hydrogen abstraction is not a rate-determining process. In fact these isotope effects are similar to those reported[9] for electron transfer quenching of biacetyl fluorescence by amines, phenols, and alcohols supporting a similar mechanism for the present case. Electron-transfer quenching of fluorescence has also been reported for pyridinium ions.[10] The observed kinetic form and quenching phenomena could be explained as in the Scheme, assuming k_1 to be a slow step compared with k_{-1}, k_2, and k_3.

An important step in the suggested mechanism is the oxidation of alcohols to alkoxy-radicals by singlet excited paraquat. However only when the alkoxy-radical has an α-hydrogen atom is the product PQ·⁺ observed experimentally. Otherwise intermediate complexes (III) and (IV) revert back to ground-state reactants, with apparent fluorescence quenching in the case of diquat. According to this mechanism t-butyl alcohol should be effective as a quencher for diquat fluorescence, as observed experimentally, but cannot produce PQ·⁺. Unambiguous confirmation of the intermediacy of alkoxy-radicals in these processes was provided by spin trapping experiments with phenyl *N*-t-butyl nitrone (V).[11]



SCHEME



$$\text{Ph·CH=}\underset{\substack{|\\ \text{O}^-}}{\text{N}^+}\text{Bu}^t \xrightarrow{\text{MeO·}} \text{Ph·}\underset{\substack{|\\ \text{MeO}}}{\text{CH}}\text{·}\underset{\substack{|\\ \text{O·}}}{\text{N}}\text{Bu}^t$$

(V) (VI)

Continuous photolysis of paraquat in methanol containing (V) gives rise to a long-lived free radical having nitrogen and β-hydrogen hyperfine coupling constants identical with those of the nitroxide radical (VI) obtained independently.[12]

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‡ Calculated radiative lifetime of diquat $1·6 \times 10^{-9}$ sec., estimated as described in ref. 4.

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