Complex Formation and the Photochemical Oxidation of Alcohols by Bipyridylium Salts in Homogeneous Solution and at an Air–Water Interface

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Summary Differences in the rates of oxidation of primary and secondary aliphatic alcohols in aqueous solution and at an air–water interface by paraquat salts are reported; evidence for a paraquat–alcohol–counteranion complex is discussed.

Investigation of the photochemical oxidation of alcohols[1] and certain carboxylate anions[2] with 1,1′-dimethyl-4,4′-bipyridylium (paraquat) salts in deoxygenated aqueous solution by Ledwith and his co-workers has demonstrated the intermediacy of the paraquat cation radical ($PQ^{+\cdot}$) and alkoxy–carboxyl-radicals. The proposed mechanism contains as an important primary step, electron transfer from the substrate to excited singlet-state photo-oxidant. However, the reaction kinetics have not been investigated in sufficient detail to define the species involved in the primary processes. U.v. spectroscopic and quantum yield data for the paraquat–carboxylate systems[2] do indicate the possible importance of charge-transfer complex formation.

We have examined in some detail the oxidation kinetics exhibited by aliphatic alcohols in aqueous solution and as monomolecular films over aqueous solutions of paraquat salts.†

We have confirmed, for C_1–C_5 aliphatic alcohols using light of 254 nm wavelength, the conclusion of Ledwith (based on limited data) that secondary alcohols undergo oxidation more readily than the corresponding primary alcohols in degassed homogeneous solution, under the limiting conditions of excess of alcohol.

The initial rate of formation of the paraquat cation radical, $d[PQ^{+\cdot}]/dt$, has been measured spectrophotometrically as a function of alcohol and paraquat methosulphate concentrations for propan-1-ol and propan-2-ol. Deoxygenated aqueous solutions were irradiated using light of

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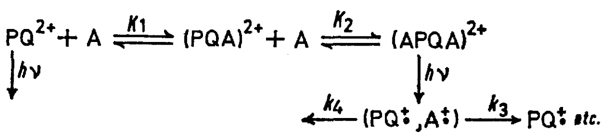
† A detailed kinetic analysis was submitted to a Referee, and is available on application to the authors.

254 nm wavelength to less than 1% conversion of PQ^{2+} into $\mathrm{PQ}^{\dot{+}}$, based on the reactant present in lower concentration. Thus the limiting rates described below are not a manifestation of the inhibition of the reaction by high $[\mathrm{PQ}^{\dot{+}}]$ previously[1] reported. It was found that: (i) for a given alcohol, the initial rate of $\mathrm{PQ}^{\dot{+}}$ formation is essentially independent of $[\mathrm{PQ}^{2+}]$ for parent cation concentrations in the range 0·01—0·10M; (ii) the initial rate increases with increasing concentration of the alcohol but reaches a limiting value (alcohol concentration range studied 0·01—0·33M); and (iii) the initial rate, in the limit, is characteristic of the alcohol. The Scheme, in which only excitation of an alcohol-complexed paraquat cation $(\mathrm{APQA})^{2+}$ leads to the production of cation radicals, $\mathrm{PQ}^{\dot{+}}$, can accommodate the kinetic data.



SCHEME. A ≡ *alcohol; k_4 includes all quenching reactions which do not lead to the formation of* $\mathrm{PQ}^{\dot{+}}$.

On this basis we have estimated values for K_2 of *ca.* 33 and 14 M^{-1} for propan-1-ol and propan-2-ol respectively. The uncertainties arise from the lack of knowledge of the molar extinction coefficients of the complexes. From a study of the small u.v. spectral shifts on addition of alcohols to aqueous paraquat solutions it seems likely that these are slightly less than that of paraquat itself (measured at 254 nm). The values of K_2 compare favourably with that of 88 M^{-1} reported[3] for the paraquat–*N*-phenyl-2-naphthylamine complex.

Stern–Volmer constants of *ca.* 3·5 M^{-1} are obtained for alcohol[4] quenching of the related diquat di-cation fluorescence in aqueous solution. The intrinsic radiative lifetime of diquat is 1·6 ns, estimated from absorption spectra, and since the quantum yield of fluorescence is 0·04, the actual singlet-state lifetime in the absence of bimolecular quenching is *ca.* $6{\cdot}7 \times 10^{-11}$ s. Thus a recalculation of the data[1] of Ledwith yields bimolecular quenching constants of 5·2, 13·6, 22·6, 71·4, and $9{\cdot}4 \times 10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for alcohols, Cl^-, Br^-, I^-, and phenol respectively. These are appreciably higher than the expected diffusion-controlled rate constant (water, 298 K, k_d *ca.* $1 \times 10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$). We infer that quenching occurs, at least in part, *via* species in intimate contact *before* photo-excitation, as has been found to be the case for *N*-methylacridinium ion.[5] The reactive complex in the oxidation of alcohols would appear to be an alcohol-separated paraquat cation–counteranion pair or a free alcoholated paraquat dication.

Further evidence for complex formation arises from a rather different source. We have noted unexpected deviations in the surface pressure (π)–surface area (A) characteristics of long-chain primary and secondary aliphatic alcohols (C_{12}–C_{24}) spread as monomolecular films on aqueous solutions of paraquat dichloride. The deviations have been ascribed[6] to specific association of components in monomolecular films in other systems. Furthermore, without exception, a primary alcohol is photochemically oxidised at an *air*–water interface more rapidly than the secondary alcohol of equivalent carbon number, under identical conditions. This is in marked contrast with the homogeneous situation.

In conclusion, the rate of oxidation of an alcohol by paraquat salts in dilute solution may be controlled more by the ability of the particular alcohol to penetrate the paraquat cation-counteranion pair in a ground-state equilibrium than by the oxidation potential of the alcohol; the latter obviously determines the feasibility of electron transfer within the photo-excited complex.

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