The Photo-oxidation of Aliphatic Alcohols as Monolayers on Aqueous Solutions of 1,1'-Dimethyl-4,4'-Bipyridylium (Paraquat) Dichloride

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The oxidation of monomolecular films of primary and secondary long-chain aliphatic alcohols on aqueous solutions of paraquat dichloride when irradiated with light of 254 nm wavelength has been studied kinetically. The primary alcohols (C_{14}, C_{16}, C_{20}, C_{24}) are oxidised smoothly and completely and obey pseudo-zero-order kinetics. The rate of reaction is related to the concentration of chloride ions at the interface. Electronic energy transfer from molecules excited in the bulk solution to those at the interface was shown to be important. The secondary alcohols investigated (cyclododecanol, hexadecan-2-ol, octadecan-2-ol) behaved differently, in that oxidation only proceeds to 30—70% completion. Mixed film experiments with octadecan-2-ol and octadecan-2-one have been performed.

PHOTOCHEMICAL reactions of molecules within insoluble monolayers at a gas–liquid interface [1,2] have received little attention, despite the potential advantages of studying the reactions of species under controllable conditions of molecular order, alignment, mobility, and close proximity. Of especial photochemical interest are the efficiency of electronic energy transfer and the interaction of reactive intermediates at high effective molecular concentrations.

We report here initial explorations in this general area. Since the fraction of incident light absorbed by one complete monolayer containing even strong chromophores is extremely small ($\leq 0.1\%$), experimentally it was advantageous to examine the reaction of an insoluble monomolecular film with photo-excited molecules produced in or proximate to the film *via* direct excitation *and* by energy transfer from an underlying, strongly light absorbing, solution.

In homogeneous aqueous solution 1,1'-dimethyl-4,4'-bipyridylium (paraquat, PQ^{2+}) dichloride photo-oxidises [3] primary and secondary, but not tertiary, alcohols cleanly [reaction (1)] when irradiated with light of wavelength

$$R^1R^2CHOH + 2PQ^{2+} \longrightarrow R^1R^2C{=}O + 2PQ^{+\bullet} + 2H^+ \qquad (1)$$

shorter than *ca.* 340 nm; the paraquat cation radical produced is stable only in the absence of oxygen. Ion-pair, solvation, and steric effects appear to be significant.[4,5] Since long-chain aliphatic alcohols form readily characterised monomolecular films and paraquat dichloride ($\lambda_{max.}$ 265 nm) strongly absorbs the u.v. light of 254 nm wavelength emitted by a low pressure mercury arc, this combination of reagents and irradiation source was chosen for the detailed study reported herein.

A preliminary account of this work has appeared.[6]

EXPERIMENTAL

Materials.—Paraquat dichloride was prepared from commercial 4,4'-bipyridyl and methyl chloride, recrystallised twice from aqueous acetone, and dried at 120°. The product was found to be >99.9% pure by analysis for PQ^{2+} and chloride ion using standard methods.[7] The aliphatic alcohols (Fluka) were of high purity, $\geqslant$99%, checked by g.l.c., and by comparison of their surface characteristics on water with those reported in the literature.[8]

Octadecan-2-one was purified by preparative g.l.c. (Perkin-Elmer F-21; 9 ft × $\frac{1}{4}$ in diameter OV-1 glass column; 150 °C). Solvents carbon disulphide and pentane were redistilled and the absence of interfering impurities checked by g.l.c.

Paraquat solutions were made up using distilled deionised water.

Photochemical Experiments.—Petri dishes (7×10^{-3} m^2 in area) were boiled in Decon 75 for 24 h, rinsed in concentrated sulphuric acid, and boiled in deionised water for three days with periodic change of the water. The dishes were then washed with redistilled methanol, dried in air, washed with redistilled pentane and finally dried in warm air.

The irradiation source used was a Shandon 100 W low pressure mercury arc whose lowest coil (of four) was *ca.* 0.10 m from the Petri dish under irradiation. This configuration was identical for all experiments. Light could be excluded by a manually operated metal shutter. The light output was monitored by a calibrated u.v. meter (model J225, UV Products Inc.) as W m^{-2} direct, and found to be $7.2 \pm 0.4 \times 10^{18}$ quanta m^{-2} (254 nm) in all experiments. Control experiments showed that the lamp had negligible output below *ca.* 220 nm (impure silica plate filter) and that reaction rates were reduced ten-fold on interposing a Pyrex glass filter. The radiation is thus predominantly that of 254 nm wavelength.

In each experiment, to obtain the kinetic curves, portions (25 ml †) of the aqueous paraquat dichloride solution were placed in a Petri dish and an insoluble alcohol film formed on the liquid surface from 0.250 ml of a solution of the alcohol in pentane of an appropriate concentration. After evaporation of the spreading solvent and thermal equilibration for 5 min, the sample was moved into position and irradiated for a known period of time. The following internal standardisation procedure was then applied. A standard alcohol, differing from that under irradiation, was added to the previously irradiated film at a known surface concentration. The total film material was then extracted by dropping carbon disulphide (1.0 ml) on to the film and the

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† Trial experiments showed the reaction rate to be independent of the amount of liquid used providing the bottom of the dish was covered entirely by the solution.

[1] J. McPhee and S. S. Brody, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 50.

[2] D. G. Whitten, *J. Amer. Chem. Soc.*, 1974, **96**, 594.

[3] A. S. Hopkins, A. Ledwith, and M. F. Stam, *Chem. Comm.*, 1970, 494.

[4] N. M. D. Brown, D. J. Cowley, and W. L. Murphy, *J.C.S. Chem. Comm.*, 1973, 592.

[5] D. J. Cowley, unpublished data.

[6] N. M. D. Brown, D. J. Cowley, and W. L. Murphy, presented in part at the Vth I.U.P.A.C. Symposium on Photochemistry, Enschede, 1974.

[7] A. J. Macfarlane and R. J. P. Williams, *J. Chem. Soc. (A)*, 1969, 1517.

[8] G. L. Gaines, 'Insoluble Monolayers at Liquid–Gas Interfaces,' Interscience, New York, 1966.

liquid phases collected in a conical flask. Further CS_2 (1.0 ml) was used to collect the last traces of film from the Petri dish. (Film recovery efficiency was found to be >90% by this method but the exact value was not required using the internal calibration method.) The CS_2 layer was analysed by g.l.c. The temperature during reaction was 21 ± 1 °C in all cases.

G.l.c. Analysis.—The collected samples of the irradiated alcohol plus internal standard in CS_2 were analysed on a 12 ft × $\frac{1}{5}$ in bore silanised glass column, packed with 2% OV-1 on Diatomite CQ 90-100 mesh, at 180 for C_{12}–C_{16} alcohols and 200 °C for C_{18}–C_{24} alcohols. Cetyl alcohol $CH_3[CH_2]_{14}CH_2OH$ was used as the reference compound in most cases. For cetyl alcohol itself either n-eicosanol (C_{20}) or cyclododecanol (C_{12}) were used as internal reference and in the mixed film experiments, n-eicosanol. The linearity of detector response to the alcohols was verified and integrated (Infotronics CS-208) peak areas were used in determining concentrations relative to that of the standard alcohol chosen. In this way the amounts of alcohol remaining after various periods of irradiation were obtained to within ±2%.

Film evaporation losses were found to be negligible for the time scale of the above experiments.

RESULTS

Monolayers of hexadecan-1-ol were photolysed on 0.1M-paraquat dichloride solution at various initial surface concentrations. The variations of alcohol concentration with time are given in Table 1. Since the limiting area of the alcohol molecule from surface studies is *ca.* 0.20 nm², the nominal area per molecule of 0.10 nm² given in Table 1 corresponds to the presence of at least a bilayer or a complete monolayer with some multilayer regions. Further, paraquat dichloride is known from surface studies by us to be slightly surface-active and thus will compete for the surface with the alcohol. It is probable that, for the more dilute nominal alcohol concentrations, the interface is composed of islands of alcohol molecules compressed to the condensed, limiting area, state moving in a sea of paraquat dications (with their attendant anions).

TABLE 1

Photo-oxidation of hexadecan-1-ol

C_0	10.0	5.00	2.50	1.67	0.83
A_0	0.10	0.20	0.40	0.60	1.20
R_0	5.73	5.37	2.81	1.93	1.03
t			f		
0	1.00	1.00	1.00	1.00	1.00
15	0.94	0.91	0.86	0.80	0.75
30	0.88	0.68	0.84	0.59	0.58
45			0.54		
60	0.69	0.47	0.32	0.35	0.24
75				0.18	0.15
90		0.26	0.10	0.16	
105					0.04
135		0.10	0.02		
180	0.45	0.08	0.00	0.02	0.06

$C_0 = 10^{-18}$ × initial surface concentration of alcohol, molecules m^{-2}; A_0 = initial nominal surface area per alcohol molecule, nm²; t = irradiation time, s; f = fraction of initial alcohol remaining after time, t; $R_0 = 10^{-16}$ × pseudo-zero-order reaction rate, molecules m^{-2} s^{-1}; all data refer to reaction on 0.10M aqueous $PQ^{2+}(Cl^-)_2$ solution, unless otherwise specified; I_0 = incident light flux = 7.2 ± 0.4 × 10^{18} quanta (254 nm) m^{-2}.

The disappearance of the hexadecan-1-ol with time appears to obey pseudo-zero-order kinetics for at least 70% reaction in all cases.

This behaviour was also found for the other primary alcohols studied namely tetradecan-1-ol, eicosan-1-ol, and tetracosan-1-ol and Table 2 records the pseudo-zero-order rate for these alcohols at a nominal initial surface concentration of 2.5 × 10^{18} molecule m^{-2} on 0.10M³ aqueous paraquat dichloride. An obvious systematic decrease in the rate with increase in the carbon number of the primary alcohol is observed.

TABLE 2

Pseudo-zero-order reaction rates for C_n straight chain primary alcohols

A_0 = 0.40 molecule nm^{-2} in every case

n	14	16	20	24
R_0	3.17	2.81	2.33	1.60

TABLE 3

Photo-oxidation of cyclododecanol and hexadecan-2-ol

	Cyclododecanol				Hexadecan-2-ol	
C_0	4.165	2.50	1.48	0.862	2.78	1.00
A_0	0.24	0.40	0.675	1.16	0.36	1.00
t		f			f	
0	1.00	1.00	1.00	1.00	1.00	1.00
15	0.95	0.93	0.86	0.87	0.92	0.71
30	0.82	0.77	0.66	0.70	0.78	0.41
60	0.79	0.58		0.64	0.66	0.35
90					0.62	
120						
140					0.52	0.14
180	0.49	0.46	0.57	0.53		

TABLE 4

Mixed films of octadecan-2-ol and octadecan-2-one

(a)	t	0	6	10	30	40		
	c	2.50	2.40	2.375	2.11	2.16		
	k	0.50	0	0	0	0		
	Δ	0	0.10	0.125	0.39	0.34		
(b)	t	0	6	15	30	60		
	c	2.00	1.93	1.83	1.77	1.63		
	k	0.50	0.50	0.50	0.50	0.51		
	Δ	0	0.07	0.17	0.23	0.36		
(c)	t	0	3	15	30	40	60	90
	c	1.50	1.47	1.39	1.31	1.26	1.20	1.17
	k	1.00	1.01	0.99	0.99	0.99	1.00	1.02
	Δ	0	0.02	0.12	0.20	0.25	0.30	0.15
(d)	t	0	6	10	15	40	120	
	c	1.00	0.94	0.90	0.85	0.79	0.68	
	k	1.50	1.31	1.33	1.33	1.37	1.46	
	Δ	0	0.25	0.27	0.32	0.35	0.37	
(e)	t	0	3	15	30	60	90	120
	c	0.62	0.60	0.54	0.49	0.41		
	k	0.87	1.74	1.65	1.72		1.80	1.80
	Δ		0.15	0.34	0.28			
(f)	t	0	5	15	30	60	90	120
	c	0.50	0.47	0.44		0.32		0.30
	k	2.00	1.90	1.75	1.81		1.90	
	Δ	0	0.13	0.31				
(g)	t	0	5	20	40	100	120	
	c	0	0	0	0	0	0	
	k	2.50	2.48	2.50	2.49	2.49	2.50	

$c = 10^{-18}$ × surface concentration of alcohol (molecules m^{-2}); $k = 10^{-18}$ × surface concentration of ketone (molecules m^{-2}); $\Delta = (C_o - C) + (k_o - k)$ = calculated shortfall in the concentration of ketone at time t (see text also).

In the photolysis of the primary alcohols, only small concentrations of products (<10%) were detectable, all with g.l.c. retention times shorter than that of the alcohol present. One of the products, shown from its retention time behaviour to be the expected aldehyde, exhibited a build up and decay typical of that resulting from further reaction of this alkanal. In one experiment, a pure monolayer of hexadecan-1-al at a surface concentration of 2.5×10^{18} molecule m^{-2} (0.40 nm^2 per molecule, nominal) irradiated on 0.10M aqueous paraquat dichloride underwent >95% reaction in 5 s, thus confirming the photolability of the aldehyde under the photolytic conditions used. The other products can be presumed to be alkanes–alkenes resulting from molecular fragmentation but this feature was not pursued.

Secondary alcohols (in particular cyclododecanol was more fully investigated) showed a marked contrast in kinetic behaviour. The initial rates of alcohol disappearance were comparable with, and indeed faster than, those observed for the primary alcohols. In all cases, however, a substantial subsequent decline in rate took place with ultimately negligible reaction once *ca.* 30–70% reaction had occurred depending on the concentration of the alcohol initially present.

Despite the fact that the corresponding ketones, the expected initial product, were found to be stable under irradiation on aqueous paraquat dichloride solutions *in the absence of the alcohol*, it is significant that only low concentrations of ketonic product could be detected during photolysis of the alcohol, with no g.l.c. evidence for the presence of more volatile lower molecular weight alkane–alkene material.

To clarify this behaviour, experiments were performed on mixed films of octadecan-2-ol and octadecan-2-one in which the total insoluble film material was kept constant but the proportion of the two components varied over a substantial range. The results are given in Table 4. The symbol Δ represents the shortfall in ketone concentration at any stage of reaction calculated from the difference in the observed and the initial ketone concentrations together with the amount of ketone expected, on the basis of the 1 : 1 stoicheiometry, from the observed loss of alcohol at that stage of reaction. It should be noted that in some experiments the ketone concentration was actually found to drop in the early stages.

Table 5 records the results, for hexadecan-1-ol and cyclododecanol, of varying the concentration of the underlying paraquat dichloride solution. Tables 1 and 3 should be consulted for the results at 0.10M-$PQ^{2+}(Cl^-)_2$. The rate of reaction declines with decrease in $PQ^{2+}(Cl^-)_2$ concentration but from our limited data not in a simple manner.

TABLE 5

Effect of $PQ^{2+}(Cl^-)_2$ concentration on the photo-oxidation of hexadecan-1-ol and cyclododecanol

$A_o = 0.40$ nm^2 molecule^{-1}, in every case

$[PQ^{2+}(Cl^-)_2]/M$

	5×10^{-3}	2×10^{-2}	1×10^{-1}	5×10^{-3}	2×10^{-2}	1×10^{-1}
	Hexadecan-1-ol			Cyclododecanol		
t		f			f	
0	1.00	1.00	1.00	1.00	1.00	1.00
15	0.98	0.94	0.86	1.02	0.94	0.93
30	0.91	0.91	0.84	1.00	0.98	0.77
60	0.86	0.82	0.32	0.94	0.91	00.58
180	0.83	0.60	0.00		0.74	0.46

The effect of solution acidity was investigated for both hexadecan-1-ol and cyclododecanol. In the pH range 1.7—5.2 little change was noted; the experiments above were conducted at *ca.* pH 3.7. At pH 9.2 the reaction rates were slower by a factor of three.

DISCUSSION

Photochemical Aspects.—The results provide evidence for the flux of energy into the interfacial region from the bulk of the solution as well as by direct absorption *via* paraquat dications in the interface.

The cross-sectional, minimum packing, area of a PQ^{2+} ion has been found to be *ca.* 1.00 nm^2 from surface tension data.[9] Even assuming *complete* monomolecular film coverage of the surface of PQ^{2+}, a most unlikely event, from the molar u.v. absorption coefficient (ε 2×10^4 l mol^{-1} cm^{-1}) at 254 nm only $\leqslant 0.003$ of the incident 254 nm light would be absorbed by the interfacial PQ^{2+}.

From the data, the *apparent* quantum yield (rate of alcohol removal/total incident light flux) for the removal of hexadecan-1-ol, for example, can be as high as 0.005. Further, in the case of the aldehyde decomposition reaction, the apparent quantum yield is calculated to be $\geqslant 0.06$. For a 0.10M solution of $PQ^{2+}(Cl^-)_2$, >90% of the incident 254 nm light is absorbed in a layer 10^4 nm thick. Excited PQ^{2+} species in this bulk layer may produce interfacial reaction (i) after direct diffusion to the interface and (ii) by concerted electronic energy transfer involving (a) a Förster mechanism and/or (b) an emission–reabsorption mechanism.

Direct diffusion (i) does not seem feasible in view of the extremely short lifetime of singlet electronically-excited PQ^{2+}, which by analogy with that of the related diquat dication [3,4] is certainly $\leqslant 10^{-9}$s.* Paraquat salts are known not to exhibit fluorescence and hence (iib) is unlikely to be a major factor in the explanation. Electronic energy transfer among PQ^{2+} species *via* a Förster mechanism appears reasonable if the critical distance is similar to those normally found, *e.g.* 3.0—7.0 nm. The observed decrease in the rate of oxidation of alcohol with decrease in the concentration of $PQ^{2+}(Cl^-)_2$ can then be attributed to (a) the increased interionic spacing on dilution reducing the efficiency of electronic energy transfer (5×10^{-3}M ≡ 6.2 nm spacing) and (b) the loss of PQ^{2+} ions from the actual interface, confirmed by surface-pressure–area curves for the alcohols on paraquat solutions reported elsewhere.[9]

It is of interest to note that, as a monolayer on $PQ^{2+}(Cl^-)_2$ solution, octadecan-2-one is stable to 254 nm radiation whereas hexadecan-1-al rapidly fragments under the same conditions. This parallels the general photolytic behaviour of simple ketones and aldehydes in the gas and liquid phases.

Oxidation of Primary Alcohols.—The prominent features are, first, the near zero-order decay kinetics and second, the variation of the zero-order decay rate with the initial alcohol monolayer coverage.

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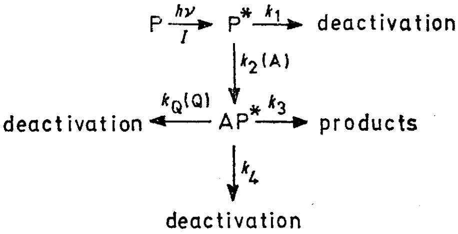
* 0.10M-$PQ^{2+}(Cl^-)_2$ is equivalent to a regular cubic array of dications 2.3 nm apart. The Einstein random-walk equation gives x 0.9 nm for D 4×10^{-10} m^2 s^{-1} and t 10^{-9} s.

[9] D. J. Cowley and W. J. Murphy, unpublished data.

Several mechanistic schemes were tried and found to be only partially successful models in accounting for the data. We present a simple Scheme which is compatible with all our data and is closely analogous to that proposed[3] for the photo-oxidation of alcohols by paraquat dication in homogeneous solution, yet accommodates the interfacial characteristics of the systems under study.



SCHEME P = Paraquat dication; A = alcohol; ( ) = activity (concentration); I = total energy flux into the interface *via* direct excitation and energy transfer from the bulk.

The k_1 step is internal deactivation, independent of surface phase concentration, and may include energy transfer back into the bulk solution. AP* is an alcohol–paraquat ' exciplex ' capable of dissociating into a pair of radicals following electron-transfer within the ' exciplex '. The k_4 step is analogous to k_1. The quencher Q refers to an *interfacial* species designated subsequently. On the basis of the Scheme it can be deduced, using stationary state assumptions for P* and AP* that equation (2) applies.

If $k_2(\mathrm{A}) \gg k_1$, and $k_\mathrm{Q}(\mathrm{Q}) \gg k_3$ and k_4 this expression reduces to (3). We propose that the rate =

$$-\mathrm{d(A)}/\mathrm{d}t = \frac{k_2(\mathrm{A})I}{[k_2(\mathrm{A}) + k_1]} \cdot \frac{k_3}{[k_3 + k_4 + k_\mathrm{Q}(\mathrm{Q})]} \qquad (2)$$

$$-\mathrm{d(A)}/\mathrm{d}t = Ik_3/k_\mathrm{Q}(\mathrm{Q}) \qquad (3)$$

quenching agent Q in the interface is chloride ion and thus stoicheiometrically related to the interfacial PQ^{2+} concentration, and hence dependent on the initial surface coverage by the alcohol.

Consider unit area of surface. Let E be the fraction of that area covered by the alcohol. If C_0 is the initial surface concentration of alcohol, in molecules m^{-2}, and S_A is the cross-sectional area of the alcohol, in m^2, then $E = C_0S_\mathrm{A}$. Let S_P be the cross sectional area of PQ^{2+} on the surface. Then (P) = concentration of PQ^{2+}, in molecules $m^{-2} = (1 - C_0S_\mathrm{A})/S_\mathrm{P} = (1 - E)/S_\mathrm{P} = (\mathrm{Q})/2$. If the interfacial PQ^{2+} ions squeeze the alcohol film into a condensed close-packed state, then E = limiting area of alcohol molecule/initial nominal area per molecule which is thus a constant throughout a given reaction if the alcohol gives rise to surface-active and non-volatile (at least relative to the reaction duration) products.

Combining equations leads to (4). The apparent rate

$$\frac{-\mathrm{d(A)}}{\mathrm{d}t} = \frac{Ik_3}{k_\mathrm{Q}} \cdot S_\mathrm{P}/2(1 - E) \qquad (4)$$

should be a constant during a given reaction determined by E, *i.e.* by the initial nominal area per alcohol molecule.

This expression is not strictly obeyed quantitatively in relation to the zero-order rates for hexadecan-1-ol. (Better agreement is, however, given by the initial rates found for cyclododecanol!) In view of the drastic simplifications in the Scheme, in particular the neglect of k_3 and especially k_4, which may include quenching by chloride ions in the ' bulk ' immediately adjacent to the interfacial monolayer (and independent largely of the interfacial concentrations), the general features are well reproduced. The fall-off in rate beyond *ca.* 70—80% reaction can be accounted for by assuming that k_1 is small but not negligible. (The absolute precision of the data does not justify more accurate computer curve fitting but is held to be sufficient for the presented analysis.) Interestingly, it should be noted that in the case where the initial alcohol concentration greatly exceeds that required for monolayer coverage *e.g.* nominal 0.10 nm^2 $molecule^{-1}$ for hexadecan-1-ol, reaction proceeds only as far as the oxidation of one complete monolayer. This implies that unreacted alcohol not in the first monolayer in contact with the bulk solution cannot react with PQ^{2+} neither can it penetrate the oxidised first layer at any appreciable rate. This supports one of the earlier assumptions that products remain at the interface. On this model the decrease in rate of reaction, at constant initial nominal area per molecule, with increase in carbon number of the alcohol can be attributed, in part, to a decrease in E, i.e. the longer chain alcohols form more readily a more compact rigid film.

The photo-oxidation of alcohols proceeds with the photoreduction of the paraquat dication to the cation radical under anaerobic conditions.[3,4] When oxygen is present the radical cation is rapidly converted back to the parent dication according to the stoicheiometric equation (5). Thus, under our reaction conditions the parent

$$2PQ^{+\cdot} + O_2 + 2H^+ \longrightarrow 2PQ^{2+} + H_2O_2 \qquad (5)$$

dication would be reformed continuously. (Prolonged photolysis does in fact lead to the breakdown of homogeneous solutions of bipyridylium salts *via* complex processes.)

It is conceivable that the peroxide product participates in the interfacial photochemical reactions but we consider that diffusion from the interface into the bulk solution is more likely.

Oxidation of Secondary Alcohols.—The preceding model is applicable in broad terms to the secondary alcohols if initial rates only are considered. However, the main feature of these systems is the failure of the oxidation to go to completion. The mixed film experiments with octadecan-2-ol and octadecan-2-one reveal clearly (1) that there is a sudden consumption of ketone, but not of the alcohol, on irradiation if alcohol is present and (2) that thereafter ketone is produced slowly as the alcohol is oxidised.

The maximum shortfall in the ketone concentration in all the experiments with mixed films is *ca.* 0.35×10^{18}

molecules m^{-2}. This corresponds closely to the surface concentration of PQ^{2+} expected to be present.*

Primary alcohols do not show this phenomenon presumably because of the extreme photolability (fragmentation?) of the product aldehyde.

We have found it difficult to construct a chemically plausible mechanism which obeys the above requirements for essentially *catalytic* intervention of alcohol in a ketone–paraquat dication photoreduction, and thus refrain from speculation in the absence of the necessary analytical data.

In conclusion, the systems investigated have highlighted some of the features inherent in the progress of photochemical reactions occurring at an interface between surface-active materials.

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* If the alcohol + ketone, nominally at 0.40 nm^2 $molecule^{-1}$, 2.5×10^{18} molecules m^{-2}, is compressed to occupy 0.25 nm^2 $molecule^{-1}$, the available space can be filled with PQ^{2+} ions, S_p 1.00 nm^2, and the concentration of PQ^{2+} will be $2.5 \times 10^{18} \times (0.40 - 0.25)/1.00 = 0.375 \times 10^{18}$ molecules m^{-2}.