# Cation-radicals: Oxidation of Propan-2-ol by Paraquat Dichloride, photocatalysed by Benzophenone and Other Ketones

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Photoreduction of paraquat salts by aqueous propan-2-ol is very efficient with light of wavelength 366 nm in the presence of typical triplet sensitisers such as benzophenone, decafluorobenzophenone, and xanthone. Quantum yields for production of paraquat cation-radical are very similar to those for photoreduction of the ketone sensitiser under identical conditions. In contrast to the direct irradiation of paraquat in aqueous alcohols, the yield of radical which may be obtained is not limited by a reversible electron transfer, and the reactions are further complicated by a highly efficient process in which all the cation-radical produced is subsequently destroyed (photobleaching phenomenon) by an apparent chain reaction initiated by hydrogen transfer from intermediate semipinacol radicals. The reactions illustrate further the electron transfer capabilities of semipinacol radicals and paraquat. Photoreduction of xanthone (but not benzophenone) by aqueous propan-2-ol is efficiently quenched by iodide ion.

BIPYRIDYLIUM salts are chiefly of interest from the point of view of their herbicidal properties.[1] Paraquat dichloride (I), the most important and best characterised of these compounds, easily undergoes one-electron reduction to form the stable but air-sensitive cation-radical (II).


(I) (PQ⁺⁺)   (II) (PQ⁺·)

(III)
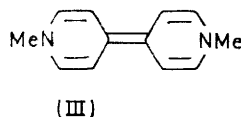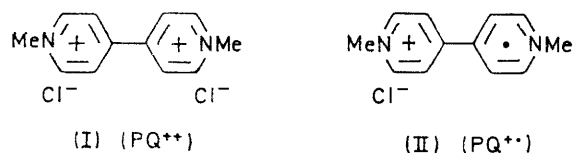
This one-electron reduction is accomplished electrochemically,[2] with chemical reducing agents,[3] or photolytically in the presence of primary or secondary alcohols.[4] In the last method, the reaction is thought to proceed via the singlet excited state of paraquat and

yields corresponding aldehydes or ketones in accordance with stoicheiometry (i).

$$2\ PQ^{++} + R^1R^2CHOH \xrightarrow{h\nu} 2\ PQ^{+\cdot} + R^1R^2C=O + 2\ H^+ \quad (i)$$
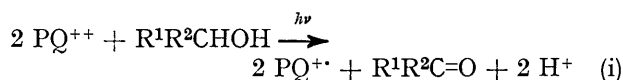
A highly significant feature of the photo-oxidation of alcohols by paraquat is the limiting yield of paraquat cation-radical ($PQ^{+\cdot}$) which may be achieved.[4] The limiting yield varies according to the nature of the alcohol being oxidised but is independent of the paraquat concentration and appears to result from a competing thermal reaction between $PQ^{+\cdot}$ and alkoxyl radicals formed in the primary photochemical processes,[5] e.g. reaction (ii).

$$R^1R^2R^3C-O\cdot + PQ^{+\cdot} \longrightarrow R^1R^2R^3C-O^- + PQ^{++} \quad (ii)$$

This paper reports the results of a study of the effects of various triplet state sensitisers, chiefly benzophenone, on the photochemical reaction between paraquat and propan-2-ol where conditions of limiting yield for $PQ^{+\cdot}$ are not obtained.

[1] W. R. Boon, Chem. and Ind., 1965, 782; A. A. Akhavein and D. L. Linscott, Residue Rev., 1968, 23, 97.

[2] R. M. Elofson and R. L. Edsberg, Canad. J. Chem., 1957, 35, 646; J. Volke, Coll. Czech. Chem. Comm., 1968, 33, 3044; S. Hunig and J. Grob, Tetrahedron Letters, 1968, 2599.

[3] E. M. Kosower and J. L. Cotter, J. Amer. Chem. Soc., 1964, 86, 5524; S. H. Yuen, J. E. Bagner, and D. Myles, Analyst, 1967, 92, 375; L. Michaelis, Chem. Rev., 1935, 16, 243.

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

[5] A. S. Hopkins and A. Ledwith, Chem. Comm., 1971, 830.

EXPERIMENTAL

Materials.—Paraquat (1,1'-dimethyl-4,4'-dipyridylium) (I.C.I. Mond) was purified by several recrystallisations from concentrated solution in water–acetone, dried *in vacuo*, and left in air for three days to equilibrate with atmospheric moisture, forming the trihydrate. AnalaR propan-2-ol was purified by refluxing overnight over freshly ground calcium hydride, followed by fractional distillation. Benzophenone was recrystallised twice from absolute ethanol and dried *in vacuo*, m.p. 47—48°. Deionised water was used in all solvent mixtures. The solvent composition was 9 : 1 v/v propan-2-ol–water in all runs except those involving paraquat di-iodide, where a larger percentage of water (85 : 15) is required to overcome the lower solubility of this salt in propan-2-ol.

Photolyses.—Photolyses were carried out in a 1 cm silica cell, with reaction mixtures outgassed by the usual high vacuum techniques, at ambient temperature by means of a 250 W medium pressure mercury lamp and a 366 nm interference filter. The formation of $PQ^{+\bullet}$ was monitored by measuring the optical density of the solution at 603 nm (ε $1\cdot20 \times 10^4$ l mol^{-1} cm^{-1}) at convenient intervals, using a Unicam SP 1800 spectrophotometer. The initial paraquat dichloride concentration was *ca.* 10^{-4}M in all the kinetic experiments.

Quantum yield measurements were carried out using the ferrioxalate actinometry procedure developed by Kurien [6] which was described earlier.[7] The quantum yield for xanthone disappearance in 9 : 1 v/v propan-2-ol–water was measured by observing the rate of disappearance of the absorption at 338 nm during photolysis, both in the presence and absence of iodide ion (initial [xanthone] = $1\cdot1 \times 10^{-3}$M in both cases; added [potassium iodide] = $1\cdot95 \times 10^{-3}$M to approximate the concentration present during photolyses in the presence of paraquat di-iodide).

Product Determination.—Acetone was determined spectrophotometrically using a modification of the method given by Milton and Waters.[8] To 5 cm³ of sample were added 40% aqueous sodium hydroxide (4 cm³), 20% salicylaldehyde in ethanol (1 cm³), and deionised water (15 cm³) to keep the solution homogeneous. After heating at 50° for 50 min the mixture was allowed to cool for 30 min. The product, dihydroxydibenzylideneacetone, was determined colorimetrically at 474 nm. The procedure was calibrated using known mixtures of AnalaR acetone in AristaR propan-2-ol; AristaR propan-2-ol–water (9 : 1 v/v) was used as solvent for the runs in which acetone was determined.

Benzophenone was determined by g.l.c. using *p*-chlorobenzophenone as described previously.[7]

The product of the photobleaching reaction was determined as follows: paraquat (0·5 g) and benzophenone (1·84 g) were dissolved in propan-2-ol–water, the solution was flushed with nitrogen, and irradiated using the 366 nm broad band lamps of a Hanovia Reading photoreactor. On completion of the reaction, the solution was evaporated to a yellow oil which was extracted several times with ether to remove benzophenone and any benzpinacol formed. The residue was dissolved in a small amount of methanol, and precipitated as a pale yellow compound by addition of acetone. This product, although stable under acetone, rapidly absorbed water and darkened in colour when exposed to air.

[6] K. C. Kurien, *J. Chem. Soc. (B)*, 1971, 2081.
[7] J. R. Barnett, A. S. Hopkins, and A. Ledwith, *J.C.S. Perkin II*, 1973, 80.

No $PQ^{+\bullet}$ was obtained in an attempted re-reduction of this product by zinc under vacuum, showing that the final product of the photobleaching reaction had not undergone atmospheric oxidation back to paraquat.

The n.m.r. spectrum (solvent CD_3OD) showed only broad resonances at low field and was conclusive only in showing the absence of significant benzophenone residues. The i.r. spectrum, even when obtained from a KBr disc prepared under nitrogen, was also inconclusive. The mass spectrum of the product showed some peaks of high molecular weight (m/e >500) but these were shown up only at very high amplitude, the remainder of the spectrum being that of the more volatile benzophenone, which from the i.r. and n.m.r. data could only be present as a trace impurity.

Before exposure to air photobleached solutions show a cut-off at *ca.* 350 nm, due to absorption by the benzophenone–propan-2-ol adduct. However, the simple two-electron reduction product, dihydroparaquat (III), having
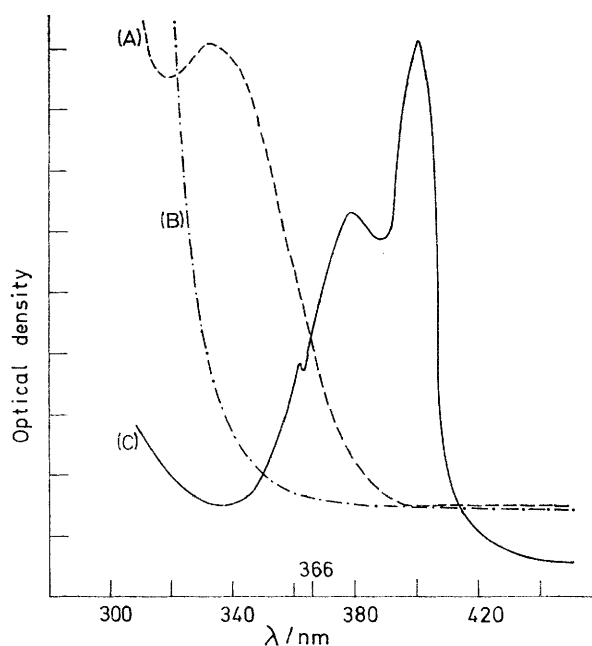

FIGURE 1   U.v. spectra of benzophenone (A), paraquat (B), and paraquat cation-radical (C)

a strong double absorption at longer wavelengths, $\lambda_{max.}$ 379 (ε 38,000 l mol^{-1} cm^{-1}) and 400 nm (46,000) [9] could not be detected.

RESULTS

Light of wavelength 366 nm was chosen for irradiation since, as shown in Figure 1, the triplet-state sensitisers have significant absorption, paraquat has no absorption, and paraquat cation-radical has a convenient ' window ' between two absorbances.

Figure 2 shows the variations in $PQ^{+\bullet}$ concentration with irradiation time for reactions sensitised by benzophenone, xanthone, and decafluorobenzophenone under typical conditions, all three ketones having rather similar light absorption characteristics at 366 nm. In contrast to the unsensitised reaction where a limiting yield of $PQ^{+\bullet}$ is

[8] R. F. Milton and W. A. Waters, ' Methods in Quantitative Microanalysis,' Arnold, New York, 1955, 2nd edn., p. 338.
[9] J. G. Carey, J. F. Cairns, and J. E. Colchester, *Chem. Comm.*, 1969, 1288.

obtained,[4] the yield of $PQ^{+\cdot}$ in these experiments reaches a maximum and then diminishes, with the radical being completely destroyed in the benzophenone- and xanthone-sensitised reactions.
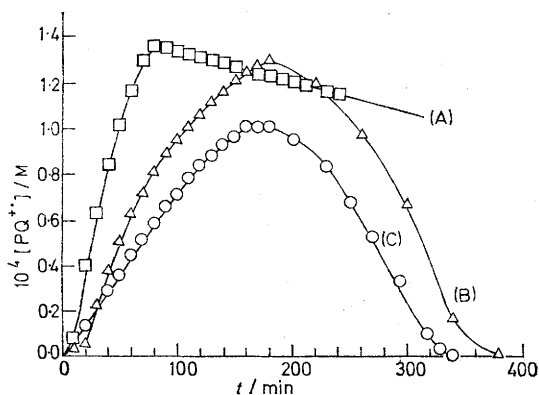

FIGURE 2 Typical curves showing variation of $[PQ^{++}]$ with irradiation time t in 9 : 1 v/v propan-2-ol–water at 25°: (A) [decafluorobenzophenone] $1\cdot34 \times 10^{-4}$M; $[PQ^{++}]\,1\cdot36 \times 10^{-4}$M; (B) [xanthone] $5\cdot32 \times 10^{-4}$M; $[PQ^{++}]\ 1\cdot28 \times 10^{-4}$M; (C) [benzophenone] $1\cdot01 \times 10^{-4}$M; $[PQ^{++}]\ 1\cdot01 \times 10^{-4}$M

The data in Table 1 show that, in the benzophenone-sensitised reaction, the maximum yield of radical varies with initial benzophenone concentration, reaching 100% of theoretical for initial benzophenone concentrations of $\leqslant 5 \times 10^{-4}$M and that the total time taken to form this quantity of $PQ^{+\cdot}$ is generally equal to the total time necessary to destroy it.

TABLE 1

Photolysis of paraquat dichloride in 9 : 1 (v/v) propan-2-ol–water at 25°

Initially $[PQ^{++}] = 0\cdot988 \times 10^{-4}$M

10^4 Initial [benzo-phenone] (M)	10^8 Initial rate of $PQ^{+\cdot}$ formation (mol l^{-1} s^{-1})	Maximum yield of $PQ^{+\cdot}$ (%)	Time to reach maximum yield (min)	Total time to bleach solution (min)
10·0	14·40	75	13	26
6·70	9·92	96	29	58
5·06	7·70	100	38	76
1·01	1·22	100	170	330
0·506	0·78	100	325	640
0·202	0·29	100	820	1640

It is to be noticed (Table 3) that only 20 mole % benzophenone is apparently sufficient to form 100% of theoretical $PQ^{+\cdot}$ and then to destroy it on further irradiation, indicating that some form of chain or sensitisation mechanism is operative.

Initially, the increase in $PQ^{+\cdot}$ concentration is linear with time and enables good estimates of rates of reaction and quantum yields to be made. Figure 3 shows the variation in initial rate of $PQ^{+\cdot}$ formation with initial benzophenone concentration. The straight line obtained indicates an overall first-order dependence on benzophenone concentration in the range employed ($\leqslant 10^{-3}$M). Rate measurements for the radical destruction reaction were less useful since the rate appears to accelerate until nearly all the $PQ^{+\cdot}$ has been consumed.

Table 2 shows the results of quantum yield measurements on systems involving a variety of sensitisers and it is interesting to note the differing effects of iodide ion on the photolyses sensitised by benzophenone and by xanthone.

Table 3 shows typical results of determinations for acetone and benzophenone, carried out during a kinetic

TABLE 2

Quantum yields for sensitised reactions of paraquat salts in 9 : 1 (v/v) propan-2-ol–water at 25°

Cl or I in parentheses indicate the use of paraquat dichloride or di-iodide respectively; $[PQ^{++}]\ 10^{-4}$M, [Sensitiser] $1\cdot5 \times 10^{-3}$— $0\cdot5 \times 10^{-3}$M

Sensitiser	E_T (kcal mol^{-1})	λ (nm)	Quantum yield for $PQ^{+\cdot}$ formation
None		313	0·32 (Cl)
			0·00 (I) [a]
None		366	0·03 (Cl)
			0·00 (I) [a]
Benzophenone	69·5 [e]	366	0·57 (Cl)
			0·61 (I) [a]
Michler's ketone	61·3 [f]	366	0·00 (Cl)
Decafluorobenzophenone	70·0 [g]	366	0·74 (Cl)
Carbazole	70·5 [f]	366	0·00 (Cl)
Xanthone	74·5 [f]	366	0·42 (Cl)
			0·09 (I)
		366	0·43 [b,c]
			0·00 [b,d]

[a] Solvent mixture 85 : 15 v/v for reactions of paraquat di-iodide. [b] Quantum yield for disappearance of xanthone in 9 : 1 v/v propan-2-ol–water. [c] [Xanthone] $1\cdot1 \times 10^{-3}$M. [d] [Xanthone] $1\cdot1 \times 10^{-3}$M; [KI] $1\cdot95 \times 10^{-3}$M. [e] J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, p. 298. [f] W. O. Hoekstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 4537. [g] J. Simpson and H. Offen, *J. Chem. Phys.*, 1971, **55**, 4832.

run. Very little benzophenone is lost during the initial stages of the reaction, in accordance with a sensitisation
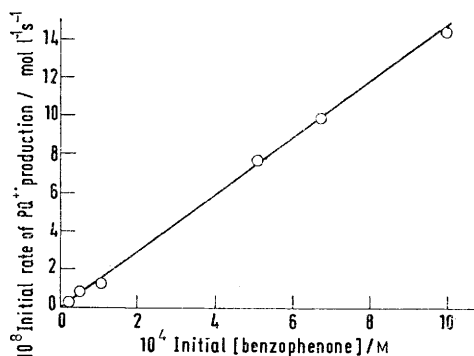

FIGURE 3 Variation of initial rate of formation of $PQ^{+\cdot}$ with benzophenone concentration in 9 : 1 v/v propan-2-ol–water at 25°. Initial $[PQ^{++}]\ 0\cdot988 \times 10^{-4}$M

mechanism, but rather more is lost during the radical destruction reaction.

TABLE 3

Products of a typical kinetic run

$[PQ^{++}]\ 10^{-3}$M; solvent 9 : 1 v/v propan-2-ol–water

$10^3[PQ^{+\cdot}]$ (M)	10^3[Acetone] (M)	10^3[benzophenone] (added or remaining) (M)
0·0	0·0	2·22
0·7	0·8	2·12
Bleached	3·0	1·54

The dependence of the photobleaching reaction on the presence of benzophenone was shown as follows. A solution of $PQ^{+\cdot}$, formed by chemical reduction of paraquat with zinc powder, was mixed with a solution of benzo-

phenone. On irradiation of the mixture the radical was destroyed in the normal fashion. In a second experiment, the benzophenone solution was irradiated to remove benzophenone by formation of the adduct with propan-2-ol [10] before mixing with the $PQ^{+\cdot}$ solution. When this mixture was irradiated no loss of radical occurred.

The semipinacol radicals ($Ph_2\overset{\bullet}{C}OH$) formed by thermolysis of benzpinacol are known to reduce paraquat to its cation-radical, and when in excess, to react further, destroying this radical.[11] As a test, a methanol solution containing preformed $PQ^{+\cdot}$ ($2\cdot46 \times 10^{-2}M$) and benzpinacol ($1\cdot86 \times 10^{-3}M$) was heated at 80°. After 21 h, less than two half-lives of benzpinacol at this temperature, all the $PQ^{+\cdot}$ had been destroyed. The number of $Ph_2\overset{\bullet}{C}OH$ radicals generated in this time have therefore destroyed more than five times the number of cation-radicals.

DISCUSSION

The data of Table 2 indicate that photoreduction of paraquat in propan-2-ol–water occurs in systems involving sensitisers which are photoreduced in propan-2-ol (benzophenone, xanthone, decafluorobenzophenone), but does not occur for those sensitisers which are not photoreduced in propan-2-ol (carbazole, Michler's ketone).

Paraquat di-iodide is not photoreduced in alcohols owing to quenching of singlet excited paraquat by iodide ion. However, changing the substrate from paraquat dichloride to the di-iodide produces no significant change in quantum yield of $PQ^{+\cdot}$ formation in the benzophenone system (Table 2); it is unlikely therefore that a singlet excited state of paraquat is involved. Paraquat has a triplet state energy of $71\cdot5$ kcal mol^{-1}, determined from its phosphorescence emission spectrum,[12] which is very close to those of the three ketones found to be effective in catalysing its photoreduction (Table 2). Triplet–triplet sensitisation would, therefore, appear to be unlikely or, at best, highly inefficient and may be ruled out because of the comparatively high values of the observed quantum yields. This follows since the observed quantum yields for sensitised photoreduction of paraquat are very similar to those observed for photoreduction of the sensitiser ketone under identical conditions. Of the ketones employed, xanthone (E_T $74\cdot5$ kcal mol^{-1}) might conceivably be an efficient triplet sensitiser for paraquat (E_T $71\cdot5$ kcal mol^{-1}). However, the photoreduction of paraquat sensitised by xanthone is strongly quenched by iodide ion in contrast to the corresponding reaction sensitised by benzophenone. Independent control experiments (Table 2) showed conclusively that photoreduction of xanthone in propan-2-ol is completely quenched by an amount of iodide ion equivalent to that involved in the paraquat reactions. Quenching of the photoreduction of aryl ketones by iodide ions does not appear to have been reported previously and possibly indicates a substantial degree

of electron transfer in the reactions between photoexcited xanthone and propan-2-ol (iodide ion is a good electron donor) in contrast to the more usual hydrogen transfer processes. However it is perhaps worth noting that reactions of singlet excited xanthone are possible in protic solvents since the sensitiser is weakly fluorescent in such solvents;[13] furthermore the electronic nature of lowest energy triplet excited states of xanthone (*i.e.* n,π^* or π,π^*) differ in relative positions according to the nature of the solvent.[14]

Taken overall, the evidence suggests that photoreduction of paraquat in aqueous propan-2-ol, apparently sensitised by benzophenone, decafluorobenzophenone. and xanthone, does not involve triplet-excited paraquat. Rather, it is suggested that photoreduction of paraquat in these systems arises from thermal reactions of intermediates produced during conventional photoreduction of the sensitiser ketones, as exemplified for the case of benzophenone (Scheme).

$$[Ph_2C=O]_{S_0} \xrightarrow{h\nu} [Ph_2C=O]_{S_1} \longrightarrow [Ph_2C=O]_{T_1}$$

$$[Ph_2C=O]_{T_1} + Me_2CH(OH) \xrightarrow{(1)} Ph_2\overset{\bullet}{C}-OH + Me_2\overset{\bullet}{C}-OH$$

$$\downarrow (2)\ PQ^{++} \qquad \downarrow (3)\ PQ^{++}$$

$$Ph_2C=O + PQ^{+\cdot} + H^+ \qquad Me_2C=O + PQ^{+\cdot} + H^+$$

SCHEME

Reaction (1) is well known; reactions (2) and (3), resulting in the formation of benzophenone [7] and acetone [4] by rapid electron transfer from the respective radicals to ground state paraquat, have recently been characterised [11] and the net reaction is overall oxidation of one mole of propan-2-ol to acetone with production of two moles of paraquat cation-radical. The benzophenone which initially absorbs the light is eventually regenerated and the mechanism is therefore not a normal photosensitisation, but rather an example of what has been termed chemical sensitisation.[15]

Acetone determinations carried out on this system, gave results which typically were higher than theoretically possible according to the Scheme but, in addition to a possible contribution from the normal photooxidation of propan-2-ol by benzophenone not involving paraquat, this is likely to be due to catalytic peroxidation of the solvent during treatment of reaction mixtures in air during which peroxides are produced from paraquat cation-radical.

The Photobleaching Reaction.—That this novel photochemical destruction of paraquat cation-radical is a catalysed process is demonstrated by the thermolysis test with benzpinacol and by data presented in Table 1

[10] S. A. Weiner, *J. Amer. Chem. Soc.*, 1971, **93**, 425; N. Filipescu and F. L. Minn, *ibid.*, 1969, **90**, 1544.
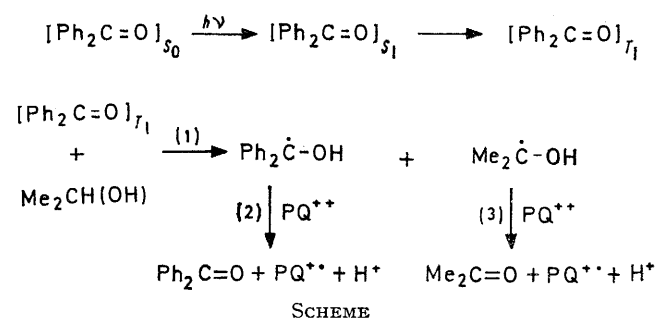[11] A. Ledwith, *Accounts Chem. Res.*, 1972, **5**, 133.
[12] D. G. Short, personal communication.
[13] J. F. Ireland and P. A. H. Wyatt, *J.C.S. Faraday I*, 1972, 1053.
[14] H. J. Pownall and J. R. Huber, *J. Amer. Chem. Soc.*, 1971, **93**, 6429.
[15] P. S. Engel and B. M. Monroe, *Adv. Photochem.*, 1971, **8**, 262; H. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, jun., IUPAC Div. Org. Chem. Photochem. IV, Baden-Baden, 1972, p. 269.

where it is seen that 20 mol % benzophenone is sufficient to reduce PQ^{++} to $PQ^{+\cdot}$ and then bleach the solution. If the primary step in this reaction is an electron transfer from $Ph_2\dot{C}OH$ to $PQ^{+\cdot}$ then the expected product would be dihydroparaquat (III); but this was not observed. A second, more likely, possibility is that a

$$PQ^{+\cdot} + Ph_2\dot{C}-OH \longrightarrow \text{(IV)} + Ph_2C=O \quad (4)$$
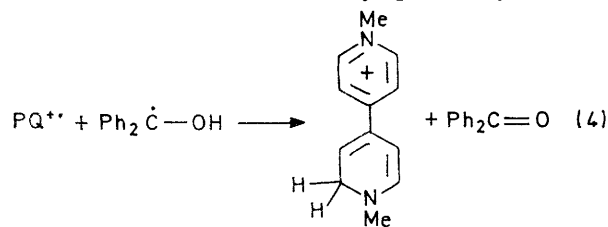
(IV)

hydrogen transfer occurs between the two radicals, regenerating benzophenone and producing the dihydropyridyl pyridinium salt (IV). By analogy with 4-vinylpyridinium salts which are known to polymerise spontaneously,[16] this species would also be expected to be highly reactive in polymerisation or oligomerisation.

In the photolytic system, benzophenone may react further to reform $Ph_2\dot{C}OH$ radicals which will eventually produce more of (IV) and all the $PQ^{+\cdot}$ could be removed by this reaction. In the thermal system, once reaction (4) has occurred, benzophenone can no longer regenerate $Ph_2\dot{C}OH$ radicals and it is necessary to postulate some form of addition reaction between $PQ^{+\cdot}$ and (IV) to account for the removal of $PQ^{+\cdot}$.

[16] J. C. Salamone, E. J. Ellis, and S. C. Israel, *Polymer Preprints*, 1972, **13**, 276; J. C. Salamone, B. Snider, W. L. Fitch, E. J. Ellis, and P. L. Dholakia, XXIII Internat. Congress Pure Appl. Chem., Boston, 1971, Macromol. Preprint, vol. II, p. 1177; I. Mielke and H. Ringsdorf, *Makromol Chem.*, 1971, **112**, 319.

Indirect evidence for involvement of a hydrogen transfer reaction comes from the decafluorobenzophenone system, which has the highest quantum yield of $PQ^{+\cdot}$ formation (0·74), but is anomalous in that the photobleaching reaction is both slow and linear with time (Figure 2).

It has been proposed [17] that the semipinacol radical (V) derived from decafluorobenzophenone on photolysis is highly resonance stabilised [*e.g.* (VI)], this feature leading to the production of the appropriate benzhydrol by disproportionation, rather than the more usual combination product, the benzpinacol derivative.

Extra stabilisation of semipinacol (V) would make the hydrogen transfer reaction to $PQ^{+\cdot}$ more difficult, so reducing its rate of removal.
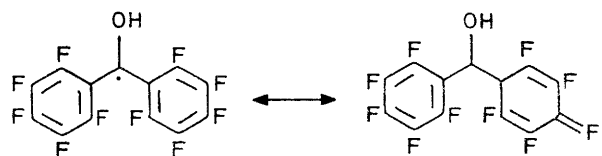
(V)   (VI)

The product of photobleaching has broad n.m.r. resonances, low volatility in the mass spectrometer, and is very hygroscopic. These characteristics seem to indicate that it is a low molecular weight polymer derived from the salt (IV) although mechanistic details of its formation remain obscure.

[17] N. Filipescu, J. P. Pinoin, and F. L. Minn, *Chem. Comm.*, 1970, 1413; but see also P. Margaretha, J. Gloor, and K. Schaffner, *J.C.S. Chem. Comm.*, 1974, 565.