Cation Radicals: Photochemically Induced Electron-transfer Reactions Between Bipyridylium Dications and Formate, Oxalate, and Benzilate Anions

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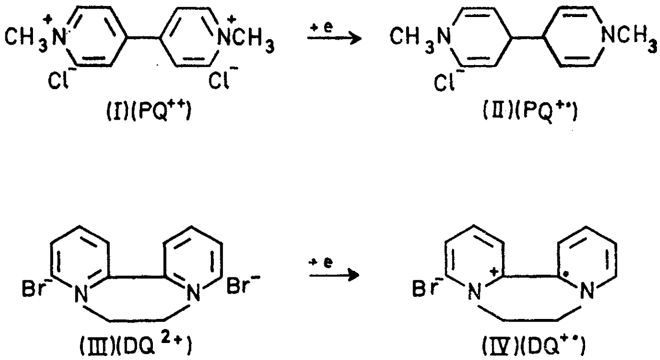
Aqueous solutions of the herbicidally active bipyridylium salts, paraquat dichloride and diquat dichloride, containing formate, oxalate, and benzilate anions undergo photoreduction to the bipyridylium cation radicals with high quantum efficiencies. Photoactivity occurs with light of wavelengths longer than can be absorbed by either oxidant or reductant, taken separately, and it is concluded that charge-transfer interaction between bipyridylium ion and carboxylate ion is the major activating influence. The three carboxylate anions are effective quenchers for the fluorescence of diquat suggesting a possible additional mechanism for photoreduction of the bipyridylium salts *via* interaction with their excited singlet states.

SEVERAL types of bipyridylium salts have been shown to have interesting herbicidal properties[1] and the most important of these are exemplified by paraquat dichloride (I) (1,1′-dimethyl-4,4′-bipyridylium dichloride) and diquat dibromide (III) (6,7-dihydrodipyrido[1,2-*a* : 2′,1′-*c*]pyrazinedi-ium dibromide). Herbicidal activity appears to depend, in part, on the ease of (reversible) one-electron reduction of (I) and (III) to form stable but air-sensitive cation-radicals (II) and (IV) respectively.[2] One-electron reduction of bipyridylium salts may be achieved electrochemically,[3] by a variety of chemical reducing agents,[4,5] and also, as we have recently shown,[6] by photolysis in the presence of primary and secondary alcohols. A particularly interesting observation from the latter type of reaction was that photoexcited bipyridylium dications react with alcohols by a primary electron-transfer process leading, in turn, to development of bipyridylium salts and their cation-radicals as new types of radical scavengers.[7,8]

In order to characterise further the nature and behaviour of electronically excited bipyridylium ions, photoinduced electron-transfer reactions with a range of reducing anions have been studied and the results are now presented.



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

[2] A. D. Dodge, *Endeavour*, 1971, **30**, 130; B. G. White, *Proc. 10th British Weed Control Conference*, 1970, 997.

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

[4] 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.

[5] J. A. Farrington, A. Ledwith, and M. F. Stam, *Chem. Comm.*, 1969, 259.

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

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

[8] A. Ledwith, *Accounts Chem. Res.*, 1972, **5**, 133.

EXPERIMENTAL

Materials.—Analytical Reagent Grade sodium oxalate, sodium formate, and sodium hydrogen carbonate were used without further purification. Benzilic Acid (B.D.H.) was washed with cyclohexane and dried *in vacuo*.

Diquat dichloride, diquat dibromide, and paraquat dichloride, kindly supplied by I.C.I. Mond Division, were crystallised at least three times from acetone–water or ethanol–water before being allowed to equilibrate with atmospheric moisture for approximately three days to stabilise the composition: $PQ^{2+}(Cl^-)_2,3H_2O$ (Found: C, 46·5; H, 6·5; N, 8·9. Calc. for $C_{12}H_{14}Cl_2N_2,3H_2O$: C, 46·3; H, 6·45; N, 9·0%); $DQ^{2+}(BR^-)_2,H_2O$ (Found: C, 39·9; H, 3·81; N, 7·80. Calc. for $C_{12}H_{12}Br_2N_2,H_2O$: C, 39·8; H, 3·9; N, 7·75%; $DQ^{2+}(Cl^-)_2,H_2O$ (Found: C, 56·3; H, 4·9; N, 10·6. Calc. for $C_{12}H_{12}Cl_2N_2,H_2O$: C, 56·5; H, 4·74; N, 10·98.

Photoreductions of the Bipyridylium Salts.—Aqueous solutions of either paraquat dichloride or diquat dichloride, together with sodium formate, sodium oxalate, or sodium benzilate (prepared *in situ* from equivalent amounts of benzilic acid and sodium hydrogen carbonate) were introduced into a Pyrex glass vessel joined to a 1-cm quartz spectrophotometer cell. After the reaction mixture had been degassed by repeated freeze–pump–thaw cycles, it was sealed off *in vacuo*, and irradiated by means of a 250 W medium-pressure mercury lamp through the spectrophotometer cell mounted on an optical bench. Appropriate interference filters were used to isolate the important mercury emission lines as required and the reaction mixture was shielded from heat and from light of wavelengths <310 nm by means of a 2-cm path-length water filter contained in a Pyrex glass vessel. Absorbance due to the cation-radicals formed was monitored at known time intervals on a Unicam SP 1800 spectrophotometer. Optical densities were measured at 603 nm (ε 12,000) for parquat cation-radical, and 760 nm (ε 3109) for diquat cation-radical. Plots of optical density *versus* time showed some curvature, thought to be due to absorption of light by the product cation-radical, but readily yielded reproducible ($\pm 10\%$) initial rates.

Ferrioxalate Actinometry.—The procedure of Kurien [9] was used whereby the ferrioxalate solution could be monitored by direct and immediate measurement of the optical density of the ferrioxalate-*o*-phenanthroline complex. A mixture (5 ml) of 0·1M-potassium ferrioxalate in 0·05M-sulphuric acid, 0·1% *o*-phenanthroline monohydrate in water, and the acetate buffer in the proportions 5 : 2 : 3 (final pH = 3·7) respectively was irradiated in the same vessel as had been used for the photoreduction (actinometry carried out as soon as possible after termination of the photoreduction). The optical density of the solution was measured using air as the blank at known time intervals at 510 nm (ε 11,100). Excellent straight-line plots were obtained for the actinometric experiments.

Fluorescence Quenching of Diquat Dibromide.—Fluorescence-quenching measurements were carried out with a Perkin-Elmer model 204 fluorescence spectrophotometer with xenon power supply. The fluorescence intensities at 350 nm (exciter wavelength 313 nm) of solutions of diquat dibromide and the various quenchers (6 different concentrations over a tenfold change in quencher concentration) were measured against a solution of diquat dibromide of the same concentration using deionized water as the zero blank. A plot of the ratio of the fluorescence intensities of the diquat dibromide solutions both in the absence and in the presence of quencher was made for the various concentrations of quencher; it yielded good straight-line plots from which the Stern–Volmer quenching constants were determined.

Quantitative G.l.c. Analysis for Benzophenone.—Mixtures of paraquat dichloride and sodium benzilate which had been photolysed for varying lengths of time were subjected to analysis. The aqueous solutions were washed out of the reaction vessel with water and chloroform and then extracted with chloroform. To the extract was added a known volume of a solution of *p*-chlorobenzophenone (B.D.H.) in chloroform and the mixture made up to a standard volume. G.l.c. (5% silicon oil column at 195 °C) of the mixture showed two non-solvent peaks attributable to benzophenone and *p*-chlorobenzophenone. A comparison of the relative areas of the two peaks gave a quantitative measure of the amount of benzophenone present in the reaction mixtures.

In several experiments using different concentrations of benzilate anion, the ratio [benzophenone]/$[PQ^{+\bullet}]$ was found to be 1·1 ± 0·1.

RESULTS

In the early experiments, unfiltered light from a medium-pressure mercury lamp was used and the effects of varying concentrations (of bipyridylium salts and reducing anions) and of temperature on the rates of photoreductions were evaluated, as indicated in Table 1.

TABLE 1

Photoreduction of bipyridylium salts by carboxylate anions in water at 25 °C

Bipyridylium salt	Concentration 10^2 M	Carboxylate anion [a]	Concentration (10^2 M)	Rate of formation of cation radical (10^8 mol l^{-1} s^{-1})
$PQ^{2+}(Cl^-)$	10·0	Oxalate	20·0	68·0
,,	10·0	,,	5·01	29·0
,,	10·0	,,	1·01	7·9
,,	1·01	,,	5·04	16·7
,,	0·49	,,	5·04	9·7
,,	0·19	,,	5·04	5·1
,,	0·49	,,	5·04	8·2 [b]
,,	10·0	Formate	20·0	9·0
$DQ^{2+}(Cl^-)^2$	10·0	Oxalate	20·0	81·1
,,	10·1	,,	5·00	40·0
,,	10·0	Formate	20·0	8·7
,,	10·1	,,	5·1	2·3

[a] Added as sodium salts. [b] Temperature 40 °C.

For later work, appropriate interference filters were employed to isolate activating lines from the mercury emission spectrum, permitting determination of quantum yields (ferrioxalate actinometry) for formation of paraquat cation-radical as shown in Table 2.

Although paraquat salts do not luminesce at room temperature, diquat salts show a weak fluorescence ($\phi_F = 0·04$) and the dibromide was used to investigate apparent interactions between formate, oxalate, and benzilate ions with the photoexcited singlet states. Good Stern–Volmer plots were obtained as indicated in Figure 1, and the slopes yielded values of K_Q = 8·0, 47, and 17 l mol^{-1} for formate, oxalate, and benzilate respectively.

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[9] K. C. Kurien, *J. Chem. Soc.* (*B*), 1971, 2081.

The absorption spectra of aqueous solutions of paraquat and diquat containing reducing anions were found to be considerably extended to long wavelengths compared with the pure bipyridylium ions, leading to greatly increased wavelength sensitivity for the photoreduction processes. Representative u.v. absorption spectra for the paraquat–benzilate ion system are shown in Figure 2.

TABLE 2

Quantum yields for photoreduction of bipyridylium salts by carboxylate anions in water at 25 °C

Bipyridylium salt	Concentration (10^2 M)	Carboxylate anion [a]	Concentration (10^2 M)	Wavelength λ (nm)	Quantum yield [b]
$PQ^{2+}(Cl^-)_2$	2·50	Oxalate	10·2	313	0·29
,,	2·51	,,	10·1	313	0·26
,,	1·01	,,	5·0	313	0·25
,,	2·50	,,	10·2	366	0·21
,,	2·51	,,	10·1	366	0·26
,,	2·44	Formate	5·52	313	0·03
,,	2·40	Benzilate	10·0	313	1·21
,,	2·40	,,	10·0	313	1·20
,,	2·39	,,	5·10	313	1·12
,,	2·51	,,	1·00	313	0·62
,,	2·50	,,	0·50	313	0·38
,	2·40	,,	10·0	366	0·92
,,	2·40	,,	10·0	366	1·13
,,	2·39	,,	10·1	366	0·93
,,	2·39	,,	1·0	366	1·10
$PQ^{2+}(I^-)_2$	2·82	,,	9·77	313	0·65 [c]

[a] Added as sodium salt. [b] No. of moles cation-radical/no. of mol. equiv. of light quanta absorbed. [c] Typical value observed in presence of iodide ion. Actual fraction of light absorbed by PQ^{2+} (benzilate$^-$)$_2$ under these conditions is approximately 50% so that true value of quantum yield is similar to those determined in the absence of iodide ion.

Under conditions similar to those described above, attempts to induce photoreduction of paraquat dichloride in water by azide ion, toluene-*p*-sulphinate ion, acetate ion, and ethyl malonate ion were completely unsuccessful, even after prolonged photolysis, although both azide and toluene-*p*-sulphinate, but not acetate and ethyl malonate, ions increased to longer wavelengths the absorption spectra of paraquat solutions.

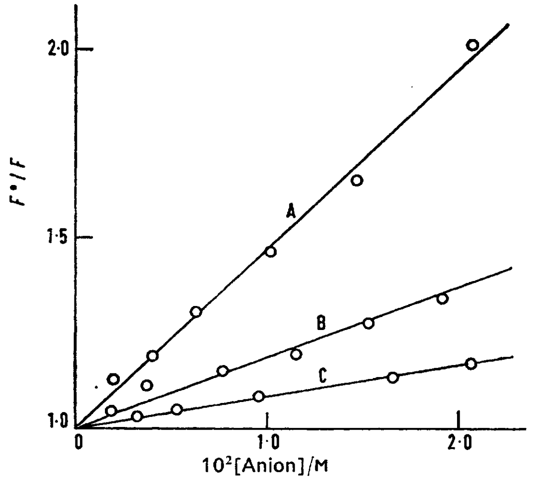


FIGURE 1 Fluorescence quenching of diquat dichloride in water at 25 °C by carboxylate anions; A, oxalate ion; B, benzilate ion; C, formate ion

A notable feature of the photoreductions by benzilate and oxalate anions was the apparent insensitivity to quenching by added iodide ion (Table 2).

DISCUSSION

Formate, oxalate, and benzilate anions were shown to be effective reductants, in aqueous solution, for the bipyridylium ions paraquat and diquat. Quantum yield determinations for production of paraquat cation-radical ($PQ^{+\bullet}$) were respectively 1·2 and 0·26 for benzilate and oxalate anions; formate ion was somewhat less reactive (Table 1) and the reactions are assumed to proceed as indicated below for oxalate and formate although the oxidation product (CO_2) was not identified:

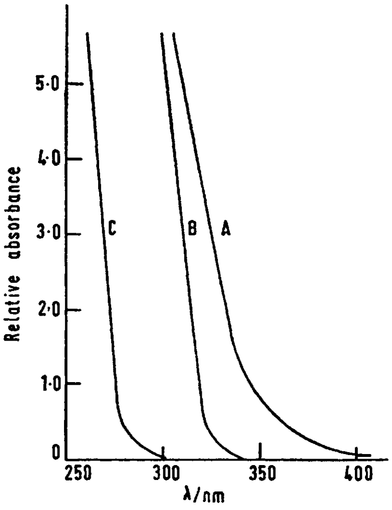
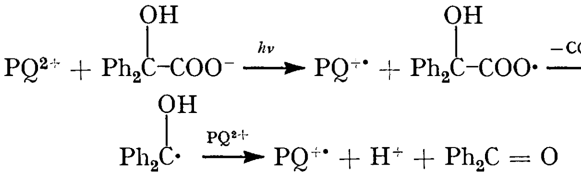


FIGURE 2 Absorption spectra of aqueous solutions A, [Na benzilate] = 0·10M, [$PQ^{2+}2Cl^-$] = 0·025M; B, [$PQ^{2+}2Cl^-$] = 0·025M; C, [Na benzilate] = 0·10M

$$PQ^{2+} + RCOO^- \xrightarrow{h\nu} PQ^{+\bullet} + RCOO\cdot \xrightarrow{PQ^{2+}} PQ^{+\bullet} + CO_2 + (H^+ \text{ or } CO_2) \quad (1)$$

In the photoreduction by benzilate anion the oxidation product was shown to be benzophenone, formed according to the following stoicheiometry:



$$PQ^{2+} + Ph_2C(OH){-}COO^- \xrightarrow{h\nu} PQ^{+\bullet} + Ph_2C(OH){-}COO\cdot \xrightarrow{-CO_2} Ph_2\dot{C}(OH) \xrightarrow{PQ^{2+}} PQ^{+\bullet} + H^+ + Ph_2C=O \quad (2)$$

Rapid oxidation of semipinacol radicals ($Ph_2\dot{C}{-}OH$) by electron transfer to ground-state paraquat has been demonstrated previously,[8] and photodecomposition of benzilic acid–ferric complexes has been shown to occur by very similar one-electron steps.[10] For benzilate ion it is, of course, possible that the primary photo-oxidation

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[10] H. D. Burrows, D. Greatorex, and T. J. Kemp, *J. Amer. Chem. Soc.*, 1971, **93**, 2539.

involves the hydroxy-group rather than the carboxylate ion. However, the charge-transfer spectral data, and wavelength sensitivity (see below), argue strongly in favour of a primary carboxylate ion mechanism.

It appears therefore as if photoexcited paraquat and diquat can function as one-electron oxidants towards suitably activated carboxylate ions in a manner similar to that of many inorganic oxidants but without the complexities associated with ligand bonding to the metal oxidant.[11]

Although paraquat does not luminesce under normal laboratory conditions, diquat shows a weak fluorescence which may be used to monitor apparent interaction of the lowest singlet excited state with added anions. Previously we have shown [6] that added (electron donor) nucleophiles, including halide ions, are efficient quenchers for singlet excited diquat, and for photoreduction of paraquat and diquat by primary and secondary alcohols. Figure 1 shows conclusively that the reducing anions used in the present work are also effective quenchers of diquat fluorescence and values of apparent Stern–Volmer quenching constants (K_Q) and bimolecular rate coefficients for quenching (k_q) are estimated as $K_Q = 17$ l mol^{-1} $k_q = 10 \times 10^9$ l mol^{-1} s^{-1} (benzilate); $K_Q = 47$ l mol^{-1}, $k_q = 29 \times 10^9$ l mol^{-1} s^{-1} (oxalate); $K_Q = 8{\cdot}0$ l mol^{-1}, $k_q = 5 \times 10^9$ l mol^{-1} s^{-1} (formate). As in the case of quenching by halide ions, the rate coefficients approximate to the diffusion-controlled encounter values for aqueous solutions. Taken with the high quantum yields observed, especially for benzilate anion, these data suggest that oxidation of these anions by photoexcited diquat (and by inference, paraquat) could occur *via* the lowest excited *singlet* state. Several related examples of quenching of photoexcited singlet states by anions [12,13] and nucleophiles [14] have been reported, but it must be stressed that this kind of Stern–Volmer quenching behaviour might also be observed if ground-state ion pairs are involved.[13,15]

Paraquat does not absorb light of wavelengths greater than about 345 nm (Figure 2) but the data of Table 2 show clearly that photoreduction of paraquat by oxalate and benzilate anions occurs with equal facility at 313 and 366 nm; for paraquat–benzilate anion combinations photoactivity was observed at wavelengths greater than 400 nm. The absorption spectra of paraquat solutions containing any of the three anions used in the present work confirmed that absorption occurs to longer wavelengths than that from either the anion or paraquat alone and representative spectra for paraquat–benzilate anion solutions are shown in Figure 2.

Pyridinium [16] and bipyridylium [17] ions are known to give rise to charge-transfer spectra in combination with a variety of neutral and anionic donor species. It seems reasonable to conclude therefore, that photoactivity in the present work arises from charge-transfer interaction between the bipyridylium cation and formate, oxalate, and benzilate ions [*e.g.* equation (3). Represented in this way, the interaction between bipyridylium ions and carboxylate ions is strictly analogous to that between pyridinium ions and iodide ion [16] and photoactivity may result from absorption of a quantum of irradiation by the ground state of the charge-transfer pair (intimate or contact-ion pair) or, following absorption by a contact-pair formed on random collisional encounter.

$$\mathrm{PQ^{2+} + RCOO^- \rightleftharpoons [PQ^{2+}, {}^-OOCR \longleftrightarrow PQ^{+\bullet}, \dot{O}OCR] \xrightarrow{h\nu} PQ^{+\bullet} + \dot{O}OCR} \quad (3)$$

Reference to Figure 2 shows that both paraquat and the paraquat benzilate ion-pairs absorb at 313 nm whereas only the latter absorb at 366 nm. Thus, whilst the total amount of light absorbed at 313 nm does not vary significantly with decreasing benzilate ion concentration, the fraction absorbed by the ion pair gets progressively smaller; further, there is an accompanying (apparent) reduction in quantum yield for photoreduction of paraquat. A similar ten-fold change in concentration of benzilate anion did not produce any effect in quantum yields measured with 366 nm irradiation, when the ground-state ion pairs and collisional contact pairs would be selectively activated. Further confirmation of these conclusions comes from the effect of added iodide ion on photoreduction of paraquat by benzilate anion. Iodide ion is a very efficient quencher for the singlet excited states of paraquat and diquat and effectively inhibits photoreductions of these ions occurring *via* their (uncomplexed) photoexcited states. In the present work, iodide ion competed with benzilate anion for ion-pair formation with paraquat as evidenced by the yellow-orange colour of the solutions but, after suitable correction for the appropriate fraction of light absorbed, did not have any significant effect on the quantum yield for photoreduction at 313 nm.

Values for ion-pair dissociation equilibrium constants (K_d) for salts of multiply charged ions are not readily available but rough values for paraquat dichloride ($K_d = 1{\cdot}0 \times 10^{-1}$ mol l^{-1}) and diquat bromide ($K_d = 6{\cdot}4 \times 10^{-2}$ mol l^{-1}) were estimated [18] from conductance measurements assuming only simple equilibria such as:

$$\mathrm{Cl^-PQ^{2+}Cl^- \rightleftharpoons Cl^-PQ^{2+} + Cl^-}$$

It seems likely therefore, that at the concentrations of

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[11] E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, 1971, **93**, 995; J. K. Kochi, 'XXIIIrd Internat. Congress of Pure and Applied Chemistry,' Butterworths, London, 1971, vol. 4, p. 377; N. J. Bunce and N. G. Murray, *Tetrahedron*, 1971, **27**, 5323.

[12] T. G. Beaumont and K. M. C. Davis, *J. Chem. Soc.* (*B*), 1970, 456.

[13] R. Beer, K. M. C. Davis, and R. Hodgson, *Chem. Comm.*, 1970, 840.

[14] D. G. Whitten, J. W. Happ, G. L. B. Carlson, and M. T. McCall, *J. Amer. Chem. Soc.*, 1970, **92**, 3500.

[15] C. A. Parker, 'Photoluminescence of Solutions,' Elsevier, Amsterdam, 1968, p. 73.

[16] E. M. Kosower, *Progr. Phys. Org. Chem.*, 1965, **3**, 81; 'An Introduction to Physical Organic Chemistry,' Wiley, New York, 1968.

[17] A. Ledwith and J. H. Woods, *J. Chem. Soc.* (*C*), 1970, 1422; B. G. White, *Trans. Faraday Soc.*, 1969, **65**, 2000.

[18] A. S. Hopkins, Ph.D. Thesis, University of Liverpool, 1972.

diquat dibromide used for measurement of fluorescence ($\leqslant 10^{-4}$ mol l^{-1}), the salts will be completely dissociated; the observed fluorescence quenching might then be a coincidence and should not be used as *a priori* evidence for the intervention of excited singlet states in the present work. Presumably the relatively more efficient photoreductions by benzilate and oxalate anions over formate anion represent a combination of increasing ion-pair dissociation constants, decreasing ease of oxidation, and relatively increasing stabilities of radicals and anion-radicals formed by one-electron oxidation of the carboxylate anions.

These experiments illustrate further the photo-oxidising capabilities of bipyridylium salts and provide an additional example of photochemical activation *via* charge-transfer spectra.[19]

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[19] D. H. Iles and A. Ledwith, *Chem. Comm.*, 1969, 364.