Photochemistry of Methoxyanthraquinones

By **Mahmood Ahmed, A. Keith Davies, Glyn O. Phillips, and John T. Richards,*** Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

The photochemical behaviour of 1- and 2-methoxyanthraquinones has been studied in a variety of solvents. No fluorescence or phosphorescence can be observed in deoxygenated fluid solutions, but phosphorescence is evident in rigid ethanol glasses at 77 K ($\phi_{T(1\text{-OMe})} = 0{\cdot}54$; $\phi_{T(2\text{-OMe})} = 0{\cdot}28$). Both derivatives can be photoreduced to the corresponding anthrahydroquinones in anaerobic benzene–propan-2-ol. In oxygenated, alkaline alcohol–water mixtures 1- and 2-hydroxyanthraquinones are formed. When oxygen is absent an intermediate is formed, which yields the same hydroxy-derivatives if oxygen is introduced after photolysis. The mechanisms of photolysis are discussed in terms of photosubstitution *via* the triplet states.

THE photochemistry of anthraquinone derivatives has been extensively studied because of their structural relationship to vat dyes, which can promote photo-tendering of textiles.[1] The derivatives which behave as strong sensitisers react with alcohols with high quantum efficiency, *via* the lowest n,π^* triplet state (A*) to give the corresponding semiquinone (AH$^{\cdot}$).[2] When oxygen

$$A^* + RCH_2OH \longrightarrow AH^{\cdot} + R\dot{C}HOH \qquad (1)$$

is absent anthrahydroquinones are formed.[2,3] At high

$$2AH^{\cdot} \longrightarrow AH_2 + A \qquad (2)$$

pH, the product of reaction (1) yields the radical ion ($A^{\cdot-}$), which is stable under these conditions. Weak

$$AH^{\cdot} + OH^- \longrightarrow A^{\cdot-} + H_2O \qquad (3)$$

sensitisers, such as the aminoanthraquinones, on the other hand have charge transfer lowest excited states,[4] and are considerably less reactive in the hydrogen abstraction reaction.[2,5] Here the radical anions can be

$$A^* + RO^- \longrightarrow A^{\cdot-} + RO^{\cdot} \qquad (4)$$

$$A^* + OH^- \longrightarrow A^{\cdot-} + OH^{\cdot} \qquad (5)$$

formed directly by electron transfer.[5] Reaction (5) also occurs with 2-sulphoanthraquinone.[6,7] The semiquinone radical anions formed by either route can be readily oxidised to the original quinones.

$$A^{\cdot-} + O_2 \longrightarrow A + O_2^{\cdot-} \qquad (6)$$

Our preliminary study showed that the absorption

[1] J. F. McKellar, *Radiation Res. Rev.*, 1971, **3**, 141.
[2] F. Wilkinson, *J. Phys. Chem.*, 1962, **66**, 2569.
[3] K. Tickle and F. Wilkinson, *Trans. Faraday Soc.*, 1965, **61**, 1981.
[4] G. Porter and P. Suppan, *Trans. Faraday Soc.*, 1965, **61**, 1664.
[5] A. K. Davies, J. F. McKellar, and G. O. Phillips, *Proc. Roy. Soc.*, 1971, *A*, **323**, 69.
[6] S. I. Sholina, *Zhur. fiz. Khim.*, 1969, **43**, 800.
[7] J. T. Richards and E. J. Land, unpublished results.

spectra of 1- and 2-methoxyanthraquinones are similar to those of certain yellow phototendering vat dyes. In this respect they resemble these dyes more closely than do the sulphoanthraquinones, which have previously been studied as 'models' for the more complex vat dyes.[8-10] It is for this reason that we have selected the 1- and 2-methoxyanthraquinones for a detailed study. We have found that in neutral alcoholic solution the photochemistry of the methoxyanthraquinones resembles that of strong sensitisers. However at high pH a completely different photochemical behaviour was observed.

EXPERIMENTAL

The μs flash photolysis equipment has already been described.[11] Solutions were flashed in a 200 mm long quartz cell having optically flat end windows. Photoflash energies of 450 J were employed. Spectra were recorded using Ilford HP 3 photographic plates.

Illumination for the continuous photolysis experiments was provided by a medium pressure mercury lamp (Hanovia UVS 220 W). Light of predominantly 365 nm wavelength was isolated using a Chance OX1 filter. Solutions were irradiated in a circular quartz cell (20 mm diam; 10 mm long) thermostatted in a water bath at 25°.

All absorption spectra were recorded with a Pye–Unicam SP 1800 spectrophotometer. Fluorescence and phosphorescence spectra, at room temperature and 77 K respectively, were measured with a Baird Atomic 'Fluorospec' spectrofluorimeter.

The oxygen absorption apparatus was based on the initial design of Bolland and Cooper.[8] The irradiation cell has been described.[12]

The methoxyanthraquinones were purified by solvent extraction and repeated recrystallisation from ethanol. Propan-2-ol was purified by repeated extraction with acidified 2,4-dinitrophenylhydrazine to remove carbonyl compounds, and subsequent fractional distillation. Deionised water for irradiation solutions was distilled from alkaline potassium permanganate. Solutions were deoxygenated by bubbling with B.O.C. 'white spot' nitrogen for 40 min. B.O.C. oxygen was used as received. Benzene and all other reagents were of AnalaR grade.

Initial rates of anthrahydroquinone formation were obtained from fluorescence measurements using the expression Rate $= S_F \times C/F_\infty$, where S_F is the initial slope of the fluorescence–time plot, C is the initial concentration of the methoxyanthraquinones, and F_∞ is the final fluorescence intensity corresponding to complete conversion to the anthrahydroquinone. Fluorescence intensity measurements were carried out at the emission maxima. Initial rates of formation of other products were obtained from absorption measurements using the expression Rate $= S_A \times C/(A_\infty - A_0)$, where S_A is the initial slope of the absorbance–time plot, and A_0 and A_∞ are the initial and final absorbances at the monitoring wavelength.

Quantum yields of formation of the hydroxyanthraquinones were measured using potassium ferrioxalate actinometry.[13] Quantum yields of anthrahydroquinone formation were determined by comparing the rates of formation with that for 2-methylanthraquinone, under conditions of equal absorption of the 365 nm light. A quantum yield of anthrahydroquinone formation of unity was assumed for 2-methylanthraquinone.[2]

Approximate quantum yields of phosphorescence in ethanol glass at 77 K, were obtained by comparison of the areas under the phosphorescence emission spectra of the methoxyanthraquinones with that for *p*-aminobenzophenone,[14] under conditions of equal light absorption.

RESULTS AND DISCUSSION

(a) *Spectroscopic Study*.—Maxima for the longest wavelength bands for the absorption spectra of 1- and 2-methoxyanthraquinones in propan-2-ol are at 382 and 369 nm, respectively. Linear Beer's law plots at these wavelengths were obtained over the concentration range 10^{-5}—3×10^{-4}M. The extinction coefficients calculated from these plots are ε(1-OMe; 382 nm) $5{\cdot}1 \times 10^3$ and ε(2-OMe; 369 nm) $3{\cdot}1 \times 10^3$ l mol^{-1} cm^{-1}. These extinction coefficients are considerably

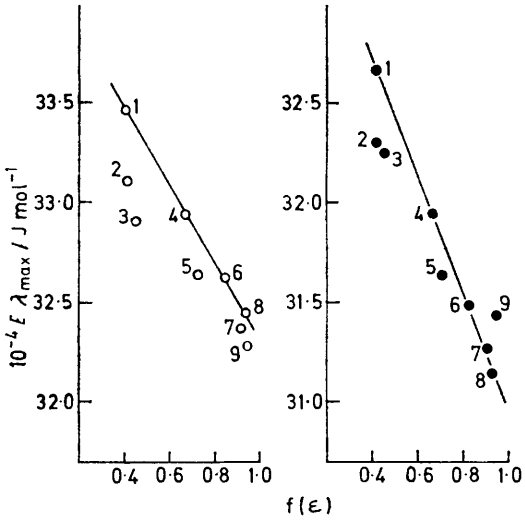

FIGURE 1 Solvent shift plots for 1-methoxyanthraquinone (●), and 2-methoxyanthraquinone (○). Solvents: (1) cyclohexane; (2) carbon tetrachloride; (3) benzene; (4) diethyl ether; (5) chloroform; (6) ethyl acetate; (7) acetone; (8) propan-2-ol; and (9) ethanol

greater than for the n–π^* band of anthraquinone (ε *ca.* 100).[5] Moreover in non-polar solvents the longest wavelength band of the methoxy-derivatives shows none of the vibrational structure evident in the n–π^* band of anthraquinone.

The longest wavelength bands of the methoxyanthraquinones show red shifts on increasing the solvent polarity; the red shift is greater for the 1-derivative. Figure 1 shows plots of excitation energy *versus* $f(\varepsilon) = 2(\varepsilon - 1)/2\varepsilon + 1$,[15] where ε is the dielectric constant of the solvent. The slopes of these plots are much smaller

[8] J. L. Bolland and H. R. Cooper, *Proc. Roy. Soc.*, 1954, *A*, **225**, 405.
[9] C. F. Wells, *Trans. Faraday Soc.*, 1961, **57**, 1703, 1719.
[10] P. J. Baugh, N. W. Worthington, and G. O. Phillips, *J. Soc. Dyers and Colourists*, 1969, **85**, 241.
[11] J. H. Allen and J. F. McKellar, *Lab. Practice*, 1967, **16**, 991.
[12] G. O. Phillips, A. K. Davies, and J. F. McKellar, *Lab. Practice*, 1970, **19**, 1037.
[13] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.
[14] P. Suppan, personal communication.
[15] M. B. Ledger and P. Suppan, *Spectrochim. Acta*, 1967, **23A**, 641.

than those previously obtained for charge transfer bands of anthraquinones.[5,15] Thus we conclude that the first excited singlet states of the methoxyanthraquinones are mainly π–π^* in character. In Figure 1 the straight lines are given for cyclohexane, diethyl ether, ethyl acetate, and acetone, since Ledger and Suppan [15] have shown that these solvents, when used for spectroscopic studies of electron distribution, give linear results for energy of absorption maximum *versus* f(ε) plots, as compared with benzene which appears always to give anomalous results.

No fluorescence from either 1- or 2-methoxyanthraquinones was detected in fluid solution at room temperature. In rigid ethanol glass at 77 K both derivatives phosphoresce strongly. Unlike the n–π^* phosphorescence of anthraquinone, which has marked vibrational structure,[16] the phosphorescence bands of the methoxyanthraquinones are broad and featureless. In ethanol glass, at 77 K, the phosphorescence maxima are 532 and 522 nm for the 1- and 2-derivatives respectively. We have been unable to identify accurately the position of the O–O bands in the phosphorescence spectra, but the emission maxima correspond to triplet energies of 225 and 229 kJ mol^{-1}. The triplet level of anthraquinone has an energy [2] of 263 kJ mol^{-1}. The quantum yields of phosphorescence are ϕ(1-OMe) = 0·54 $\pm$ 0·05 and ϕ(2-OMe) = 0·28 $\pm$ 0·03. These phosphorescence characteristics indicate that the lowest triplet states of the methoxyanthraquinones like the corresponding singlet states are mainly π–π^* in nature.

(b) *Photochemistry*.—In neutral solution irradiation of the methoxyanthraquinones in anaerobic propan-2-ol with 365 nm light readily yields the corresponding anthrahydroquinones. These products characteristically exhibit brilliant green fluorescence; [17] the emission maxima are 482 and 500 nm for the 1- and 2-derivatives respectively. In anaerobic propan-2-ol the quantum yields of formation of the 1- and 2-methoxyanthrahydroquinones are *ca.* 0·53 and 0·22 respectively.

Flash photolysis of neutral anaerobic 1 : 1 propan-2-ol–water solutions of 2-methoxyanthraquinone leads to transient bands at *ca.* 480 and 360—400 nm. Similar transients were observed with 1-methoxyanthraquinone, but here the transient at 360—400 nm was somewhat obscured by the strong absorption band of the original compound. By comparison with earlier work,[18,19] we conclude that the broad transient at 360—400 nm is the semiquinone radical AH•, and the transient at 480 nm the radical anion A•$^-$. Photoreduction, therefore, in all probability occurs by hydrogen abstraction [8] from the alcohol by the triplet state of the methoxyanthraquinones [reaction (1)].

Figure 2 shows a typical plot of fluorescence intensity against irradiation time for the photoreduction of 1-methoxyanthraquinone in anaerobic benzene mixtures containing varying concentrations of propan-2-ol. Similar plots were obtained using the 2-derivative. The initial rates of anthrahydroquinone formation can

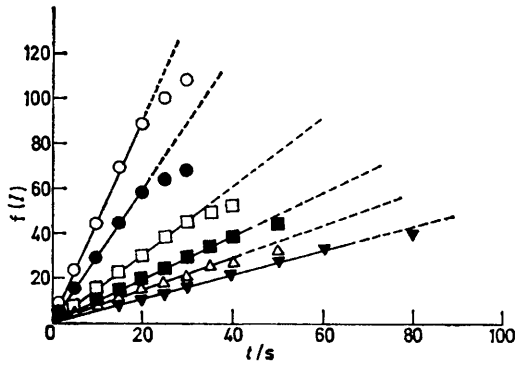

FIGURE 2 Increase in fluorescence intensity at 495 nm with time of irradiation for the photoreduction of 1-methoxyanthraquinone in nitrogen saturated benzene–propan-2-ol mixtures using 365 nm light. Propan-2-ol concentrations: ○, 3M; ●, 2M; □ 1M; ■, 0·65M; △, 0·5M; and ▼, 0·25M

be calculated from the slopes of these plots. Figure 3 shows plots of reciprocal rate of formation of the 1- and 2-methoxyanthrahydroquinones against reciprocal propan-2-ol concentration. Cooper [20] showed that for anaerobic aqueous alcoholic solutions of the 2- and 2,6-di-sulphoanthraquinones the formation of anthrahydroquinone can be represented by the kinetic equation $1/(d[AH_2]/dt) = (1 + k_0/k_1[RCH_2OH]) \times 1/I$. Here I is the rate of activation, proportional to the light intensity, k_0 is the rate constant for process (7), and k_1

$$(MeO - A)_T \longrightarrow (MeO - A) \qquad (7)$$

is the rate constant for reaction (1). The ratio k_0/k_1 is given by the slope/intercept of a plot of reciprocal

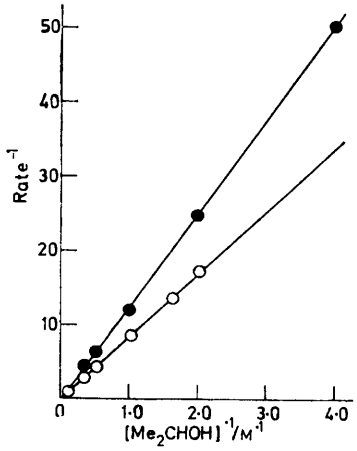

FIGURE 3 Plot of reciprocal rates of formation of 1-methoxyanthrahydroquinone (●) and 2-methoxyanthrahydroquinone (○), against reciprocal propan-2-ol concentration

rate *versus* reciprocal propan-2-ol concentration. Figure 3 shows that although the corresponding plots for the

[16] M. Kasha, *Radiation Res. Suppl.*, 1960, **2**, 243.
[17] G. S. Egerton, N. E. N. Assaad, and N. D. Uffindell, *J. Soc. Dyers and Colourists*, 1967, **83**, 45.
[18] N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, 1958, *A*, **244**, 259, 276.
[19] G. O. Phillips, N. W. Worthington, J. F. McKellar, and R. Sharp, *J. Chem. Soc.*, (*A*), 1969, p. 767.
[20] H. R. Cooper, *Trans. Faraday Soc.*, 1966, **62**, 2865.

species hydrogen bridging mechanism was obtained from a study on the hydrodimerisation of 2-acetylpyridine.[5] In this system, the intermediate ketyl radicals form strong intramolecular hydrogen bonds which greatly reduces the interspecies bonding and leads to a preponderance of the *meso*-product. In the case of acetophenone, the stereoselectivity was essentially the same for mercury, copper, or tin cathodes and was independent of electrode potential. It was concluded that coupling took place in the solution away from the electrode surface and not between adsorbed species. Two problems concerning the conclusions of Stocker and Jenevein have already been pointed out;[1] no account was taken of the effects of the strongly hydrogen-bonding solvent on the coupling process, and the evidence against surface coupling carries little weight since strong adsorption would be expected on each of the three cathodes employed. Evidence for the importance of a surface process has been provided by Puglisi *et al.*[6] for the hydrodimerisation of benzaldehyde. The addition of adsorbable ions such as tetra-alkylammonium and iodide altered the racemic : *meso* ratio although neutral adsorbed molecules such as amyl alcohol had no effect and none of these species affected the analogous photochemical process. It should be pointed out, however, that at the rather high cathodic potentials employed in the process, the adsorption of iodide ions and amyl alcohol would be slight. Further strong evidence for the importance of adsorbed intermediates is provided by the kinetic studies of Conway *et al.*[7,8] and Brown and Lister.[9]

The present study is an attempt to obtain further insight into the validity of the interspecies hydrogen-bonding mechanism and the way in which this is modified by adsorbed species. An aprotic solvent, anhydrous *NN*-dimethylformamide (DMF), was chosen as a starting point so that the effects of adding increasing amounts of water could be observed.

While the work was in progress, a note was published[10] on the pinacolisation of acetophenone in DMF and acetonitrile. However, slightly wet (unpurified commercial) solvents were employed and the effects of very aprotic conditions were not studied.

EXPERIMENTAL

Procedure.—Potentiostatic electroreduction of acetophenone was carried out at a mercury cathode (area *ca.* 7 cm^2) at 19 ± 1 °C in a cell with a separator between anolyte and catholyte. A solution containing acetophenone (1·3 ml) was made up to 100 ml with a solution that was approximately 10^{-1}M in supporting electrolyte. An electronic coulometer was attached to the potentiostat and current was passed until almost complete reduction (pinacol assumed) had occurred. Excess of solvent in the catholyte solution was then evaporated, and, in the case of DMF, the work-up involved treatment with *ca.* 10^{-1}M-hydrochloric acid (25 ml) and extracting at least three times with portions (20 ml) of diethyl ether. The ether was then dried (Na_2SO_4) and removed; the residue was analysed by n.m.r. spectroscopy following the procedure of ref. 3. This spectrum corresponded almost exactly with that given in the literature.[11] It was generally found unnecessary to neutralise any excess of acid which might have been introduced. For other solvents no hydrochloric acid was added.

Experiment	Potential w.r.t. s.c.e. (V)	Solvent–electrolyte system	Racemic : *meso* ratio	Tafel slope (mV)
1	−1·80	80% Ethanol–water, *ca.* 0·4M-HCl	1·1	
2	−2·49	Absolute ethanol, 0·1M-TBAP	1·8	127
3	−1·80	Absolute ethanol, 0·1M-LiCl	2·6	48
4	−2·22	DMF, 0·1M-TBAP	4·1	120
5	−2·28	DMF + 500 p.p.m. H_2O, 0·1M-TBAP	5·4	63
6	−2·31	DMF + 1500 p.p.m. H_2O, 0·1M-TBAP	6·2	70
7	−2·28	Commercial DMF, 0·1M-TBAP	7·6	23
8	−2·25	DMF + 1500 p.p.m. H_2O + 500 p.p.m. pyridine, 0·1M-TBAP	5·0	52
9	−2·16	DMF + 1500 p.p.m. H_2O + 2500 p.p.m. pyridine, 0·1M-TBAP	6·3	52
10	−2·22	DMF, 0·1M-$LiClO_4$	12·5	
11	−2·19	DMF + 1500 p.p.m. H_2O, 0·1M-$LiClO_4$	5·7	
12	−2·22	DMF + 1500 p.p.m. H_2O, 0·1M-tetrabutylammonium iodide	4·1	124

Materials.—Acetophenone was distilled under reduced pressure and stored in a dry-box before use. DMF was dried by using molecular sieves followed by distillation under reduced pressure and then stored in a dry-box. Absolute alcohol was reagent grade. Tetra-n-butylammonium perchlorate was dried in a vacuum oven before use at *ca.* 60 °C and lithium perchlorate was dried by the method described by Meibuhr.[12] No special precautions were taken in drying tetra-n-butylammonium iodide or lithium chloride, although the latter is known to be deliquescent.

RESULTS AND DISCUSSION

The results are given in the Table and they include values for the Tafel slopes which may be compared with those of Conway *et al.*[7,8] for varying water content in water–methanol mixtures.

The major features of the results are the very high value for the racemic : *meso* ratio for dry DMF containing

[6] V. J. Puglisi, G. L. Clapper, and D. H. Evans, *Analyt. Chem.*, 1969, **41**, 279.
[7] B. E. Conway, E. J. Rudd, and L. G. M. Gordon, *Discuss. Faraday Soc.*, 1968, **45**, 87.
[8] E. J. Rudd and B. E. Conway, *Trans. Faraday Soc.*, 1971, **67**, 440.
[9] O. R. Brown and K. Lister, *Discuss. Faraday Soc.*, 1968, **45**, 106.
[10] J. H. Stocker and R. M. Jenevein, *Coll. Czech. Chem. Comm.*, 1971, **36**, 925.
[11] H. Agahigian, J. F. Maraveck, and H. Gauthier, *Canad. J. Chem.*, 1963, **41**, 194.
[12] S. G. Meibuhr, *J. Electrochem. Soc.*, 1970, **117**, 56.

triplet state leads to the formation of $(MeO-A^{\cdot})^-$ either by hydrogen abstraction followed by deprotonation [reactions (12) and (13)] or direct electron transfer

$$(MeO-A)_T^* + Me_2CHOH \longrightarrow MeO-AH^{\cdot} + Me_2\dot{C}OH \quad (12)$$

$$MeO-AH^{\cdot} + OH^- \longrightarrow (MeO-A^{\cdot})^- + H_2O \quad (13)$$

[reaction (14)]. Hydroxyl radicals formed by this

$$(MeO-A)_T^* + OH^- \longrightarrow (MeO-A^{\cdot})^- + OH^{\cdot} \quad (14)$$

reaction react rapidly with the alcohol [reaction (15); $k_{15} = 9{\cdot}6 \times 10^8$ l mol^{-1} s^{-1}] [23] and cannot therefore be the agents leading to direct hydroxylation. Radical

$$Me_2CHOH + OH^{\cdot} \longrightarrow H_2O + Me_2\dot{C}OH \quad (15)$$

anions are known intermediates in certain substitution reactions,[24] therefore substitution of OMe by OH could result from OH^- attack on the radical anion $(MeO-A^{\cdot})^-$ [reaction (16)]. The product $HO-A^{\cdot -}$,

$$(MeO-A^{\cdot})^- + OH^- \longrightarrow HO-A^{\cdot -} + MeO^- \quad (16)$$

$$HO-A^{\cdot -} + OH^- \longrightarrow \bar{O}-A^{\cdot -} + H_2O \quad (17)$$

under alkaline conditions would ionise [reaction (17)]. Addition of oxygen, at this stage would oxidise the semiquinone radical anion intermediate to the hydroxyanthraquinone in its ionised form [reaction (18)].

$$\bar{O}-A^{\cdot -} + O_2 \longrightarrow \bar{O}-A + O_2^{\cdot -} \quad (18)$$

Addition of acid produces the yellow un-ionised form of the hydroxy-derivatives [reaction (19)].

$$\underset{\substack{\text{red}\\ \text{(high pH)}}}{\bar{O}-A} + H^+ \rightleftharpoons \underset{\substack{\text{yellow}\\ \text{(low pH)}}}{HO-A} \quad (19)$$

Mechanism in Oxygen Saturated Alkaline Propan-2-ol -Water Solutions.—The same final products are observed in oxygenated solutions. The triplet state will react preferentially with the alcohol under these conditions since $[ROH] \gg [O_2]$ and hence the oxygen will not cause any deactivation. However under these conditions additional reactions (20)—(24) might be

$$(MeO-A^{\cdot})^- + O_2 \longrightarrow MeO-A + O_2^{\cdot -} \quad (20)$$

$$O_2^{\cdot -} + O_2^{\cdot -} \longrightarrow O_2^{2-} + O_2 \quad (21)$$

$$Me_2\dot{C}OH + O_2 \longrightarrow Me_2\underset{O_2}{COH} \quad (22)$$

$$Me_2\underset{O_2}{COH} \longrightarrow {}^{\cdot}HO_2 + Me_2CO \quad (23)$$

$${}^{\cdot}HO_2 + {}^{\cdot}HO_2 \longrightarrow H_2O_2 + O_2 \quad (24)$$

anticipated. The three essential steps in the formation of the hydroxyanthraquinone by this mechanism are, therefore, (i) photoreaction to produce the methoxyanthrasemiquinone radical anion, (ii) substitution of the OMe group by OH, and (iii) oxidation of the hydroxyanthrasemiquinone radical anion, so formed to produce the hydroxyanthraquinone in its ionised form.

Reaction (25) has been excluded from our reaction

$$(MeO-A)_T^* + OH^- \longrightarrow HO-A + MeO^- \quad (25)$$

mechanism for two reasons. This reaction cannot account for (*a*) semiquinone radical anion intermediates in nitrogen saturated solution or (*b*) the absorption of oxygen which accompanies the formation of the hydroxyanthraquinone in oxygen saturated solution. Experimentally R = mole of O_2 absorbed/mole of hydroxyanthraquinone formed was found to be 0·63, which is consistent with the mechanism we have proposed {assuming that most of the radical anion $(MeO-A^{\cdot})^-$ reacts *via* reaction (16) and not *via* reaction (20), *i.e.* $[OH^-] \gg [O_2]$}.

In nitrogen saturated solutions the rate-retarding reaction (20) does not occur, which accounts for our observation that the quantum yields of hydroxyanthraquinones formed indirectly by oxidation of the intermediates exceeds those obtained directly by irradiation of oxygen saturated solutions. The 1-methoxy-derivative shows not only a greater quantum yield of hydroxyanthraquinone in alkaline solution but also a greater quantum yield of anthrahydroquinone in neutral solution than the 2-methoxyanthraquinone. It would appear therefore that the yield of triplet is greater for the 1-derivative. A similar conclusion can be drawn from the phosphorescence data.

General Significance.—The photochemistry of the methoxyanthraquinones in neutral alcoholic solution is of interest in relation to the problem of phototendering. High quantum yields for the photoreduction of carbonyl compounds are usually associated with n–π^* triplet states.[25] In 1-methoxyanthraquinone we have an example of a derivative whose first excited singlet and triplet states appear to be mainly π–π^* in character. Nevertheless this compound undergoes quite efficient photoreduction by hydrogen atom abstraction. It is possible that these states are not pure π–π^* but have some n–π^* character. Since the spectral properties of 1-methoxyanthraquinone closely resemble those of certain yellow phototendering dyes, we consider that the observation of efficient hydrogen atom abstraction by the 1-methoxy-derivative supports the hydrogen abstraction theory of phototendering.[1]

The substitution reactions of methoxyanthraquinones, which occur in alkaline solution, are of more general photochemical interest, particularly in relation to the work of Havinga and his co-workers.[26,27] These workers have studied the photosubstitution of various electron-donating substituent groups such as methoxy; in

[23] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1965, **16**, 227.
[24] N. L. Holy and J. D. Marcum, *Angew. Chem. Internat. Edn.*, 1971, **10**, 115.
[25] G. Porter and P. Suppan, *Trans. Faraday Soc.*, 1966, 62, 3375.
[26] E. Havinga in 'Reactivity of Photoexcited Molecules,' Interscience, London, 1967, p. 201
[27] E. Havinga and R. O. de Jongh, *Bull. Soc. chim. belges*, 1962, **71**, 803.

particular they have studied the photosubstitution of *meta*-nitroanisole in alkaline solution. They concluded that the excited state responsible for these reactions are the π–π^* singlet states of the molecules, though this assignment has been refuted by Letsinger and Steller[28] who have shown that the reactions probably take place *via* the triplet state using benzophenone-sensitised reactions. Our anthracene quenching data would support the latter case. It is also of interest to contrast the photoreactions of the methoxyanthraquinones at high pH with the photohydroxylation reactions which were proposed for 2-sulphoanthraquinone.[19,29-32] Here attack by hydroxyl radicals is suggested to form hydroxy-derivatives and the sulpho-group remains intact. The reactions examined here, on the other hand, are clearly substitution reactions involving the hydroxide ion (see for example the ^{18}O work of Havinga[26]). Hydroxyl radicals produced in reaction (14), at the high concentration of propan-2-ol employed, would be efficiently removed by reaction (15) and cannot be involved in the observed photosubstitution reactions.

[3/505 *Received, 9th March,* 1973]

[28] R. L. Letsinger and K. E. Stellar, *Tetrahedron Letters*, 1969, **18**, 1401.
[29] B. Mooney and H. I. Stonehill, *Chem. and Ind.*, 1961, 1309.
[30] A. D. Broadbent, *Chem. Comm.*, 1967, 382.
[31] K. P. Clark and H. I. Stonehill, *J.C.S. Faraday I*, 1972, 577.
[32] K. P. Clark and H. I. Stonehill, *J.C.S. Faraday I*, 1972, 1676.