Photohydroxylation of Anthraquinone in Concentrated Sulphuric Acid

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In concentrated sulphuric acid 9,10-anthraquinone gave solutions exhibiting absorption in the visible range which remained stable indefinitely in the absence of light. Treatment of such solutions with near-u.v. or visible radiation caused an efficient and clean phototransformation into a product, which was recovered and proved to be 2-hydroxyanthraquinone. Because of the remarkable photostability of the product and the relatively high efficiency of conversion, the reaction readily approaches completion. The reaction was carried out in dilute solutions for time-lapse spectroscopic measurements and in concentrated solutions for preparative purposes. The mechanism is discussed.

WHEN dissolved in strong acids, many unsaturated compounds tend to undergo photoreactions markedly different from those taking place in neutral solvents.[1] This is particularly true for substances having heteroatoms with non-bonding electrons involved in π-delocalization, since attachment of a Lewis acid to the unshared electrons frequently changes the nature of the lowest excited state. Numerous aromatic carbonyl compounds dissolve readily in concentrated sulphuric acid to form remarkably stable solutions of hydroxy-carbocations exhibiting characteristic absorption and emission spectra.[2] In most instances, the lowest excited singlet and triplet levels of these molecules are changed from n,π^* to π,π^* states by formation of the hydroxy-carbocation.

9,10-Anthraquinone also forms stable, golden-yellow solutions in concentrated sulphuric acid while undergoing complete monoprotonation. Unlike the previously reported aromatic ketones,[3] however, its corresponding hydroxy-carbocation does not show intense molecular luminescence. Instead, it undergoes an efficient and clean photoreaction when subjected to visible or near-u.v. radiation, to give 2-hydroxy-9,10-anthraquinone (1).

RESULTS

Solutions of 9,10-anthraquinone in sulphuric acid exhibit $\lambda_{max.}$ 270, 310, and 410 nm (Figure, curve 1). The u.v.–visible spectra of such dilute solutions remained unchanged even after months of storage in the dark without any precautions to exclude atmospheric oxygen. This remarkable stability was also shown by the quantitative recovery of unchanged anthraquinone after heating in 100% sulphuric acid for several hours in an open container.

The Figure shows the progressive spectral changes taking place after consecutive irradiations of a dilute acid solution of the quinone with a medium pressure 450 W Hanovia lamp. All three original peaks diminish rapidly and are replaced by new absorptions centered at 250, 295, and 485 nm. The curves in the Figure form clearly defined isosbestic points at 248, 275, 358, and 433 nm. If the irradiation was interrupted at any stage, the spectrum of the solution remained unchanged for at least several days in the dark. This suggests that there is no substantial dark side-reaction and that the photoproduct itself is stable indefinitely in acid solution.

[1] See for example, N. Filipescu and J. W. Pavlik, *J. Amer. Chem. Soc.*, 1970, **92**, 6062.

[2] N. Filipescu, S. K. Chakrabarti, and P. G. Tarassoff, *J. Phys. Chem.*, 1973, **77**, 2276.

[3] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

Preparative-scale photochemical reactions were carried out by irradiating 10^{-2}M-solutions of the quinone with a 450
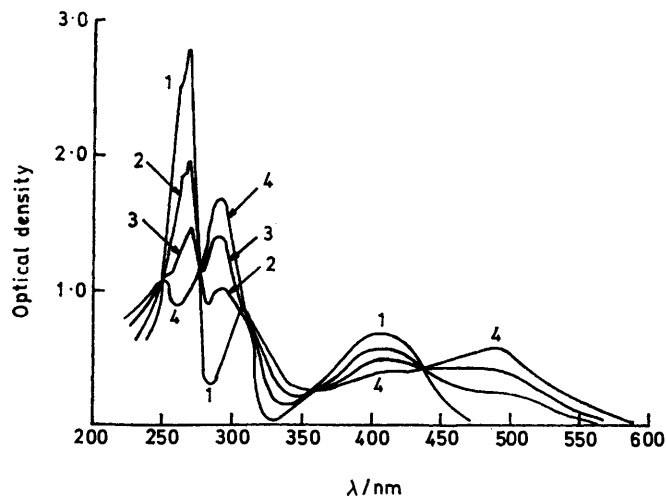
U.v.–visible absorption spectrum of a 5×10^{-5}M-anthraquinone solution in 100% sulphuric acid: 1, before irradiation; 2, after 10 min exposure to 9 W handlamp; 3, after an additional 12 min irradiation; 4, after another 163 min (total 185 min)

W mercury arc lamp for 1—3 days either in the presence of air or under nitrogen. The extent of reaction was estimated from the u.v.–visible spectra of diluted samples. The product was isolated by pouring the mixture onto ice and filtration. Yields varied from 40 to >80% depending on the irradiation time.

region corresponding to the remaining eleven aromatic carbon atoms. The u.v.–visible spectrum of a dilute solution of isolated photoproduct in concentrated sulphuric acid was essentially the same as that of the final irradiated solution of the starting quinone (curve 4, Figure). This observation tends to rule out any irreversible change that might have occurred during recovery of the photoproduct.

The hydroxy-carbocation derived from the starting quinone did not exhibit intense luminescence. A 10^{-4}M-solution of anthraquinone in concentrated acid showed only a very weak fluorescence in the 460—490 nm range with $\lambda_{max.}$ 466 nm both in liquid sulphuric acid solution at ambient temperature and in a rigid matrix (sulphuric acid–glacial acetic acid) at 77 K. This emission showed an appropriate mirror-image relation with the absorption band at longest wavelength ($\lambda_{max.}$ 410 nm) and its excitation spectrum paralleled the absorption shown in the Figure.

The photoproduct, when dissolved in acid, behaved similarly. It exhibited only a faint fluorescence in the 540—630 nm range, centred at 580 nm, but showed no detectable phosphorescence at room or liquid nitrogen temperature.

DISCUSSION

The presence of four isosbestic points in the Figure testifies to the clean quality of the reaction. Absence of deviation from isosbestic behaviour even after several hours of irradiation (curve 4) suggests both lack of significant side reactions and high photostability of product. Although actual quantum yield measurements have not been made, the relatively high efficiency of the
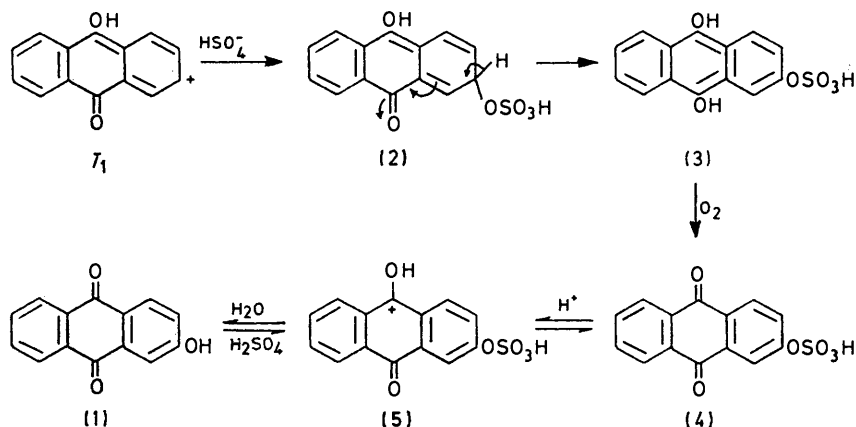
SCHEME

The identity of the product (1) was established by elemental analysis and mass, u.v.–visible, i.r., and ^{13}C n.m.r. spectrometry. ^{13}C N.m.r. spectrum (solvent 100% sulphuric acid) (see Experimental section) shows three low-field resonances attributed to the two original carbonyl carbon atoms and the carbon atom to which the new substituent is attached. Although the exact assignment of the two signals at 181.9 and 179.8 p.p.m. to each individual C:O cannot be made, the isolated peak at 165.6 p.p.m. is readily attributed to C·OSO$_3$H. The loss of molecular symmetry brought about by substitution at C-2 is also reflected by the complexity of the decoupled signals in the 115—135 p.p.m.

photoreaction can be estimated by comparing curves 1 and 3. Inspection of the decrease in absorbance at 270 nm shows that the phototransformation was more than half complete after 22 min irradiation. In view of the low solute concentration and the modest output of the 9 W handlamp, the reaction seems quite efficient. Absence of detectable phosphorescence in the visible range for protonated anthraquinone precludes adequate identification of the reactive excited state. The low fluorescence emission ($\phi_f < 10^{-3}$) is undoubtedly due to a high intersystem crossing rate to the triplet manifold.

Theoretically, since anthraquinone has been shown to be monoprotonated in concentrated sulphuric acid,[3] its lowest triplet level should be an n,π * state associated with the other, unprotonated, carbonyl group. However, there is uncertainty regarding the relative energies of the n,π * and π,π * states in strongly acidic media. Therefore, in the absence of $T_1 \longrightarrow S_0$ emission, the excited state responsible for the photochemical reaction can be only tentatively assumed to be the lowest triplet.

A reasonable mechanism is offered in the Scheme. The reacting excited state T_1 is arbitrarily represented by a valence-bond resonance structure of the ground state. The suggested enhanced decrease in electron density in the 2-position on electronic excitation was substantiated by an MO-SCF-CI calculation,[2] which showed a decline in electron density from 0.941 to 0.900 in the first electronic excited state. The reaction of the excited cation with the hydrogen sulphate nucleophile is acceptable not only on simple mechanistic grounds but also because such an attack by hydrogen sulphate on certain aromatic structures seems to take place under non-photochemical conditions as well, with eventual formation of the corresponding phenol.[4,5] The natural tautomerisation of the species (2) yields the hydrogen sulphate ester of 2,9,10-trihydroxyanthracene (3) which, like all anthrahydroquinones, is very susceptible to any oxidizing agent including air or concentrated sulphuric acid.[6] Oxidation † of (3) would yield anthraquinone sulphate (4) which in concentrated acid most probably exists in protonated form (5). Hydrolysis would then naturally liberate the identified product (1). Redissolving the pure photoproduct (1) in concentrated sulphuric acid to give a solution with the same u.v.–visible absorption as that seen at the completion of the photoreaction (Figure, curve 4) is consistent with re-esterification to give the cation (5).

The 2-photohydroxylation of anthraquinone has synthetic value. Whereas 1-hydroxyanthraquinone is readily obtained by simple procedures,[7] its 2-hydroxy-isomer has been prepared only by more tedious methods.[8,9] The remarkable stability of the photoproduct to light allows virtually quantitative transformation, and recovery of the product is relatively simple.

EXPERIMENTAL

U.v. and i.r. spectra were recorded in double-beam mode with Cary 15 and Perkin-Elmer 457 spectrophotometers, respectively. Mass spectra were obtained with a Perkin-Elmer 270 spectrograph at 70 eV ionization energy. A

Varian XL-100 spectrometer was employed for the [13]C n.m.r. measurements.

Reagent grade anthraquinone (Fisher) was further purified by recrystallization from glacial acetic acid and vacuum sublimation. No difference was detected, however, if the compound was used without additional purification. Standard solutions of known concentrations in fluorometric grade 100% sulphuric acid (Matheson, Coleman, and Bell) were readily obtained by stirring the quinone with the acid. Attempts at partial exclusion of atmospheric oxygen did not qualitatively or spectroscopically affect the results. However, exposure to visible light was shown to cause photochemical reaction. Therefore, diluted samples designated for time-lapse spectrometry, either in the dark or by successive irradiations, were protected from inadvertent lengthy exposure to room light. Consecutive irradiations of short duration (minutes) were carried out with a 9 W long-wave u.v. handlamp (Ultraviolet Products) in 1 cm path square quartz cells which were transferred periodically to the Cary spectrophotometer for spectral recording.

Preparative-scale Photolysis of Anthraquinone in Sulphuric Acid.—Anthraquinone (3.69 g, 1.77×10^{-2} mol) was dissolved in 98% reagent-grade sulphuric acid (250 ml) to give a brilliant yellow solution which was placed in an immersion-well Hanovia photoreactor provided with a 450 W medium-pressure arc lamp. Passage of dry, high-purity nitrogen gas through the solution or magnetic stirring were adequate for agitation purposes. The solution and the lamp were cooled by circulating water. After 48 h of continuous irradiation, the colour of the solution had changed to a deep red. The acidic photolysate was cautiously poured onto crushed ice (300 g). A greenish-white suspension formed immediately. The solid material was collected by suction filtration and washed with water to give crude photoproduct (3.35 g, 91%). Vacuum sublimation at 5 mmHg followed by recrystallization from dry pyridine gave yellow crystals of 2-*hydroxy*-9,10-*anthraquinone* (52%), m.p. 302—303°. Substantially higher yields were obtained by irradiation for 80 h. In an alternative, more efficient procedure for purification of the product, the crude solid was dissolved in ether and extracted with 5% sodium hydroxide, from which pure hydroxylated product (68%) was recovered by acidification (Found: C, 74.95; H, 3.6. $C_{14}H_8O_3$ requires C, 75.0; H, 3.55%), $\nu_{max.}$ (KBr) 3 370 (OH), 1 680 (C=O), and 1 300 cm^{-1} (C–O); m/e 224 (M^+, most abundant), 196 (M – CO), 168, 139, 100, and 84; δ_C (from external Me$_4$Si; solvent 100% H$_2$SO$_4$) 181.9, 179.8, 165.7, 133.6, 133.4, 128.7, 127.6, 127.0, 124.2, 119.4, 116.2, and 115.8 p.p.m.

† An alternative route from (3) to (5) may involve an intramolecular redox reaction with loss of sulphur dioxide and water to give the hydroxyanthraquinone (1) which would then be re-protonated to give (5).

[4] W. Baker and N. C. Brown, *J. Chem. Soc.*, 1948, 2303.
[5] 'The Chemistry of the Hydroxyl Group,' ed. S. Patai, Interscience, New York, 1971, p. 1024.
[6] Rodd's 'Chemistry of Carbon Compounds,' vol. III, part B, Elsevier, New York, 1956, pp. 1382 *et seq.*
[7] See, for example, ref. 6, pp. 1400 *et seq.*
[8] A. R. Burnett and R. H. Thomson, *Phytochemistry*, 1968, 7(8), 1421.
[9] Badische Anilin & Soda Fabrik A.G. (K. Scherf and H. Nienburg), Ger. P., 1 160 124/1963.