

Solvent Effect on the Photochemistry of Anthraquinones[†]

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The spectral properties and the photochemical reactions of anthraquinone in ethanol, aqueous ethanol, formic acid, sulphuric acid, sulphuric acid-ethanol and formic acid have been studied. In ethanol, aqueous ethanol and formic acid, the lowest excited state of the quinone is $n-\pi^*$ and the only photochemical reaction that can be detected is photoreduction to semiquinone while in concentrated (98%) to aqueous 60% H_2SO_4 , as well as ethanol- H_2SO_4 , the lowest state has more $\pi-\pi^*$ character and the sole photochemical reaction is photo-substitution to produce hydroxyanthraquinone.

EXTENSIVE studies have been made on the photochemical reactions of *p*-quinones^{1,2}, particularly in alcoholic solution, because of their relevance to some important photosensitising effect, phototendering of cellulosic materials and photosensitised oxidation of various substrates. Recently, further interest has been aroused through the use of quinones in the field of solar energy storage as sensitisers as well as electron acceptors in photogalvanic cells³ or as a photocatalyst in photo-oxidation of chloride ion to chlorine⁴ or splitting of water⁴. Some quinones, such as 1,4-benzoquinone, 1,4-naphthaquinone, 9,10-anthraquinone, anthraquinone-2-sulphonate *etc.*, are photoreduced under appropriate conditions with unit efficiency, independent of wavelength of the exciting light. The excited state responsible for the reaction is proposed⁵ to be the lowest triplet $n-\pi^*$ state of the quinone, which in presence of H-donors, such as alcohols undergoes photoreduction to produce semiquinone radical and a hydroxyalkyl radical (from alcohol) which may disproportionate or further be oxidised to the corresponding aldehyde or ketone by the ground state quinone.

It was initially proposed⁶ that photoreduction of carbonyls always proceeds through abstraction of hydrogen atom. Subsequent studies⁷ have shown that at least with amines, sulphides *etc.* having low ionisation potentials, the photoreduction occurs through transfer of electron. However, some recent studies⁸ have shown that even with alcohol, water and carboxylic acids, electron transfer is the primary step followed by proton depending on the equilibrium of semiquinone/semiquinolate ion.

Though photoreduction is a more common photochemical reactions with quinones, substitution products are also often obtained, in some cases as the only photochemical product. Thus, anthraquinone-2-sulphonate in aqueous medium, on irradiation, produces both the semiquinone and hydroxy derivatives⁹, while 9,10-anthraquinone in concentrated sulphuric acid medium gives hydroxy deriva-

tive as the only photo-product¹⁰. Similarly, 1-methoxy-9,10-anthraquinone in aqueous acetonitrile containing ammonia gives 96% yield of 1-amino-9,10-anthraquinone, and 2-methoxy derivative gives 70% 1-amino-2-methoxyanthraquinone¹¹. It is not clearly known whether the photoreduction and substitution occur from the same excited state or that substitution proceed through the initial step of photoreduction or not.

The present work has been carried out with anthraquinones to study its photoreduction and photo-substitution processes in different solvents with a view to correlating the different processes with the excited state precursors.

Experimental

Anthraquinone (U.S.S.R.) was recrystallised from benzene in dark and dried in a vacuum desiccator.

The light sources used were a medium pressure mercury vapour lamp T/MS/577, 80 W (Thermal Syndicate, U.K.) and a 100 W HBO lamp (Osram GmbH) mounted vertically on an optical bench. Monochromatic light of different wave-lengths were obtained by using a high radiance monochromator (Applied Photophysics). The solutions were photolysed in a 3 ml quartz cell, the temperature being maintained at $29 \pm 0.1^\circ$ by a thermostatic arrangement. The intensity of light incident on the cell was determined by ferrioxalate actinometry. Other experimental details are given elsewhere⁹.

Anthrasemiquinone was detected and estimated from the absorption spectra, with absorption maximum at 380 nm ($\epsilon = 1.2 \times 10^4 M^{-1} \text{ cm}^{-1}$). Semiquinone readily oxidised in presence of oxygen. The spectra of the photolysed solution under anaerobic medium and that after subsequent oxygenation was recorded with a Beckman DB spectrophotometer. The difference of the two after normalisation gave the spectra of the reduced

[†] Dedicated to Professor Sadhan Basu on the occasion of his 65th birthday.

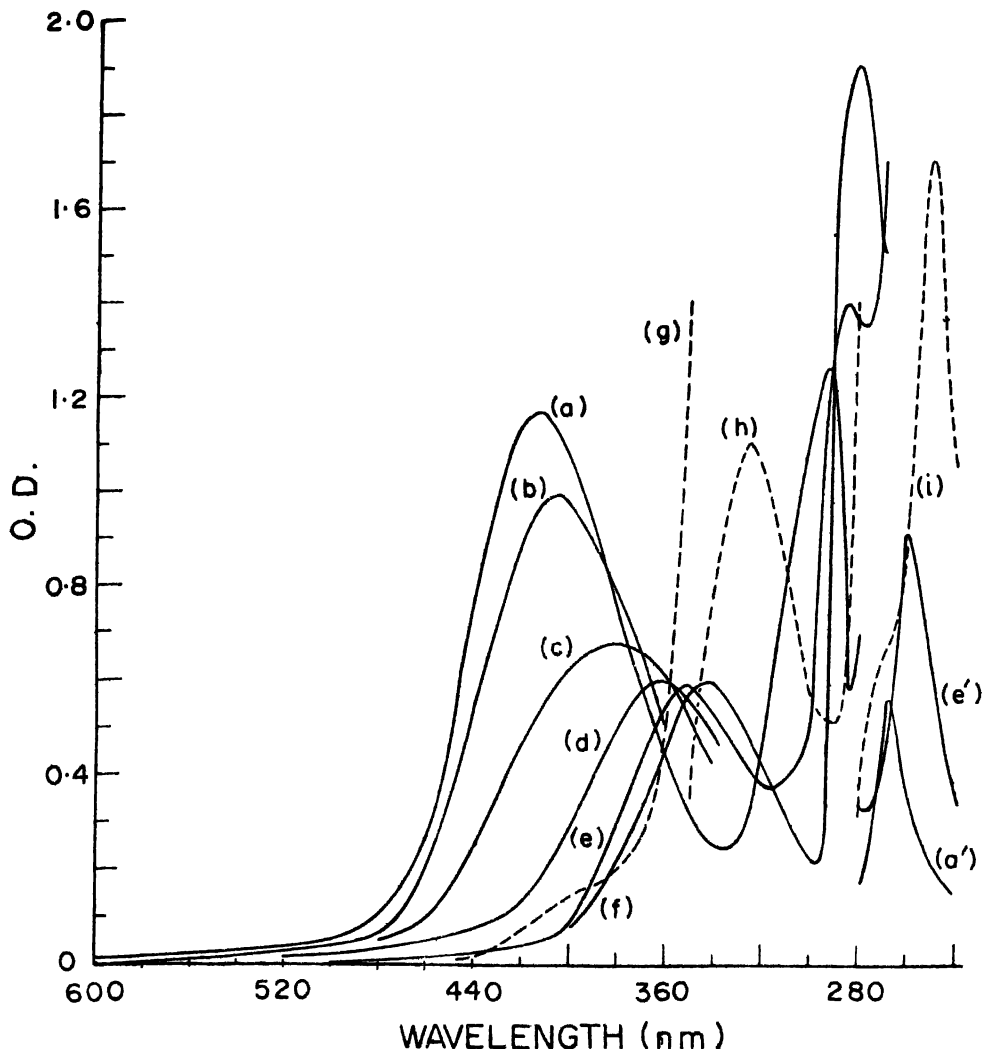


Fig. 1. Absorption spectra of anthraquinone in ethanol (---) and (—) aqueous sulphuric acid of different compositions (% v/v): (a) (a') 98.0, (b) 88.2, (c) 78.4, (d) 68.6, (e) (e') 58.8 and (f) 49.0% H_2SO_4 , and [AQ] from (a) to (f) = 1×10^{-4} and (a') to (e') = 2.5×10^{-5} M; (g) (h) (i) ethanol, and [AQ] for (g) = 1.3×10^{-5} , (h) = 2.6×10^{-4} and (i) = 4.0×10^{-4} M.

products. Hydroxy derivative was identified by the method described earlier¹⁰.

Results and Discussion

Fig. 1 shows the absorption spectra of anthraquinone in ethanol and in different concentrations of aqueous sulphuric acid medium. In ethanol the absorption bands at 250, 265-275, 325 and 400 nm have been assigned to allowed $\pi-\pi^*$, forbidden $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively¹². Addition of water to ethanol solution does not alter the band positions. But addition of sulphuric acid to ethanol (Fig. 1) or increase in sulphuric acid concentration in aqueous H_2SO_4 medium shifts all the bands to a considerable extent. Thus, the 250 nm band shifted to 268 nm, the 265-271 nm band to 310 nm and the

325 nm to 410 nm in concentrated sulphuric acid medium. The $n-\pi^*$ band at 400 nm in ethanol could not be detected at higher H_2SO_4 concentrations, probably due to superimposition of the lower band. Substituent or solvent often switches the electronic configuration of T_1 and T_2 states of aryl carbonyls, *i.e.* $n-\pi^*$ and $\pi-\pi^*$ may flip-flop energetically as a result of change in solvent polarity. In ethanol or aqueous ethanol the lowest excited state of anthraquinone is of $n-\pi^*$ character while with increasing H_2SO_4 proportion, the $\pi-\pi^*$ state gradually shifted to longer wavelength and lowest state assumes more of $\pi-\pi^*$ character. No thermal reaction occurs in concentrated sulphuric acid after keeping several hours in dark and even on heating¹⁰. Similar solvent dependent shift and switching of lowest excited state has been observed with acetophenone in cyclohexane and acetonitrile¹².

TABLE 1—QUANTUM YIELD OF SEMIQUINONE IN PHOTOLYSIS OF ANTHRAQUINONE IN ETHANOL AND AQUEOUS ETHANOL UNDER ANAEROBIC MEDIUM AT 313 nm

Anthraquinone concn. = 2.5×10^{-4} M, Time of irradiation = 10 min, Radiation source = Medium pressure Hg vapour lamp

Proportion of ethanol-water	Number of quanta absorbed at 313 nm	Number of molecules formed	Quantum yield
10 : 0	3.798×10^{17}	14.565×10^{16}	0.38
9 : 1	3.816×10^{17}	13.893×10^{16}	0.36
8 : 2	3.171×10^{17}	11.977×10^{16}	0.38
7 : 3	3.572×10^{17}	12.744×10^{16}	0.36
6 : 4	3.505×10^{17}	13.415×10^{16}	0.38

TABLE 2—QUANTUM YIELD OF SEMIQUINONE IN PHOTOLYSIS OF ANTHRAQUINONE IN ALKALINE ETHANOL UNDER ANAEROBIC MEDIUM AT 313 nm

Anthraquinone concn. = 2.5×10^{-4} M, Sodium hydroxide solution = 0.1 N, Time of irradiation = 10 min.

Proportions of ethanol-NaOH	Number of quanta absorbed at 313 nm	Number of molecules formed	Quantum yield
9 : 1	0.960×10^{17}	0.909×10^{17}	0.95
8 : 2	0.846×10^{17}	0.822×10^{17}	0.97
7 : 3	0.846×10^{17}	0.794×10^{17}	0.94
6 : 4	0.886×10^{17}	0.794×10^{17}	0.95

Photolysis of anthraquinone in ethanol under anaerobic medium produces semiquinone with oxidation of ethanol to aldehyde, as also reported earlier⁶. Table 1 shows the quantum yield values of semiquinone in ethanol and aqueous ethanol media. Addition of water upto 6 : 4 (ethanol-water) does not alter the quantum yield. Moreover, no other product could be observed. It may be mentioned here that with anthraquinone-2-sulphonate, photolysis in 1 : 1 aqueous ethanol medium produces semiquinone as well as hydroxy derivative of the quinone. In alkaline medium, with anthraquinone-2-sulphonate, the yield of semiquinone (semiquinolate ion) as well as hydroxy derivative increases sharply with the increase in alkali concentration⁶. With anthraquinone, the quantum yield of semiquinolate ion is higher in alkaline medium, but it does not increase with increase in alkali concentration (Table 2). No hydroxy product is observed even at highest alkali concentration.

Fig. 2 shows the absorption spectra of anthraquinone in different proportion of H_2SO_4 -water after photolysis. The product formed has been identified to be a hydroxy derivative. Irradiation under anaerobic condition also produces hydroxy product but no semiquinone can be detected even in 6 : 4 H_2SO_4 -water medium. It is apparent from the spectra that the maximum yield of the hydroxy derivative is obtained at 4 : 1 H_2SO_4 -water medium.

While in 1 : 1 ethanol-water medium, the sole photochemical product is semiquinone (quantum yield 0.38) no semiquinone is photochemically produced even in 1 : 2 H_2SO_4 -ethanol medium, the only product being hydroxy derivative. The above results indicate that while in ethanol or aqueous ethanol the lowest $n-\pi^*$ state is responsible for photoreduction, in H_2SO_4 -water or H_2SO_4 -ethanol the $\pi-\pi^*$ state shifts to longer wavelength and becomes the lowest state and no photoreduction

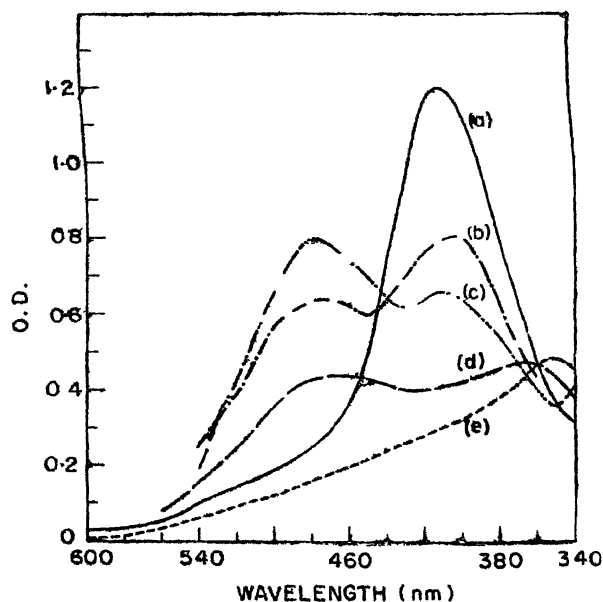


Fig. 2. Absorption spectra of anthraquinone in aqueous sulphuric acid of different compositions after irradiation at 366 nm for 1 h : (a) 98.0, (b) 88.2, (c) 78.4, (d) 68.6 and (e) 58.8% H_2SO_4 .

product is observed. It has also been noted that with anthraquinone-2-sodium sulphonate, similar shift in absorption bands occurs in H_2SO_4 medium compared to that in aqueous or aqueous ethanol media and photolysis in concentrated H_2SO_4 under anaerobic condition yields only hydroxy product, while in aqueous or aqueous ethanol medium (even upto 1 M H_2SO_4 solution), anaerobic irradiation produces both semiquinone and hydroxy derivative as stated earlier.

Use of formic acid instead of sulphuric acid, however, does not shift the band position from that

TABLE 3—QUANTUM YIELD OF SEMIQUINONE IN PHOTOLYSIS OF ANTHRAQUINONE IN FORMIC ACID-WATER UNDER ANAEROBIC MEDIUM AT 313 nm

Proportion of formic acid-water	Time of irradiation h	Number of quanta absorbed at 313 nm	Number of molecules formed	Quantum yield
10 : 0	2	14.168×10^{17}	0.888×10^{16}	0.0027
9 : 1	2	14.957×10^{17}	0.670×10^{16}	0.0046
8 : 2	2	13.496×10^{17}	1.724×10^{16}	0.018
7 : 3	2	14.169×10^{17}	2.688×10^{16}	0.019

in ethanol and photolysis under anaerobic medium produces semiquinone only, though with a lower yield. Increase in water proportion increases the semiquinone yield (Table 3).

Flash photolysis⁹ of anthraquinone in ethanol or aqueous ethanol produces a transient absorbing at 490 nm. The transient has been assigned to be the semiquinolate ion, formed by abstraction of electron by the excited quinone. No such transient is observed with anthraquinone in concentrated H_2SO_4 or aqueous H_2SO_4 , further confirming that in sulphuric acid medium the initial step is different from that in ethanol or aqueous ethanol media, where an electron is abstracted by the excited molecule.

Similar shift in absorption bands also occurs on the introduction of substituents, like hydroxy, methoxy or halogens, to quinones and in many cases photoreduction efficiency becomes extremely low¹⁴.

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