PRIMARY PROCESS IN THE PHOTOCHEMISTRY OF AQUEOUS ANTHRAQUINONE-2-SULPHONATE BY FLASH PHOTOLYSIS

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Summary

The equilibrium between the semiquinone and semiquinolate ions in the photolysis of anthraquinone-2-sulphonate was studied. The pK value is 8.2. Evidence that the photoreduction of anthraquinone-2-sulphonate proceeds via the abstraction of an electron (and not a hydrogen atom) by excited quinone is reported.

1. Introduction

The reduction of quinones to the corresponding semiquinones is the most important step in the photochemistry of quinones. It has long been assumed that semiquinones are formed via the abstraction of a hydrogen atom or an electron from the solvent or some other substrate present in the system by the excited quinone molecule. Semiquinones exist in two forms, one protonated and the other ionic, depending on the pH of the medium. Hulme *et al.* [1] determined the pK values of the semiquinones produced by the pulse radiolysis of 1,2-substituted 9,10-anthraquinone sulphonate. The species were identified by their absorption spectra. They reported a pK value of 3.25 for the semiquinone derived from 9,10-anthraquinone-2-sulphonate. In previous investigations [2] of the long-range photolysis of aqueous anthraquinone-2-sulphonate (D) solutions under anaerobic conditions (where semiquinone is one of the photoproducts) we found no evidence for the formation of the semiquinolate ion $D^{\cdot-}$ at pH 7; only the protonated form $DH^{\cdot}$ was obtained. $D^{\cdot-}$ was detected at pH 8. This observation could not be explained on the basis of the data reported in ref. 1. Further, Gill and Stonehill [3], using a polarographic technique, found a value of 9.02 for the same equilibrium.

In the present paper we report an investigation of the flash photolysis of D under reducing conditions and also the determination of the pK value of the equilibrium $D^{\cdot-} + H^+ \rightleftharpoons DH^{\cdot}$ which were undertaken with a view to explaining the apparent anomaly in the above results.

The absorption spectrum of $D^{\bullet-}$ has maxima at 500 and 400 nm while the protonated form $DH^{\bullet}$ has a maximum at 385 nm and almost zero absorption at 500 nm [4]. Hulme *et al.* [1] measured the optical density at 500 nm, 20 μs after the pulse radiolysis of anthraquinones in the presence of formate, and obtained the pK value of the semiquinone from the plot of the optical density at 500 nm *versus* pH. They assumed that the radiolysis yield of semiquinone was constant all through the pH range studied (-2 to 11) and that the ionization equilibrium was attained within the 20 μs before the measurement. However, in a later report [5] it was shown that the yields of the hydroxy derivative of D in the radiolysis of the D solution are different in neutral and alkaline media (the yields of semiquinone were not reported). We have studied the mechanism of formation of the semiquinones and their subsequent equilibration in the system by flash photolysis.

As semiquinones are stable enough to be detected in the absence of oxygen, for the determination of the pK value of the equilibrium $D^{\bullet-} + H^+ \rightleftharpoons DH^{\bullet}$ they were produced by the photolysis and radiolysis of D under anaerobic conditions. To minimize the yields of photoproducts other than semiquinone, both the flash photolysis and the long-range photolysis of D were performed in the presence of high concentrations of formate where semiquinone is the only photoproduct. The detailed mechanism has been discussed elsewhere [2].

2. Experimental details

The sodium salt of anthraquinone-2-sulphonate (BDH) was recrystallized five times in the dark from doubly distilled water. The other reagents were BDH AnalaR grade. The solution pHs were adjusted by adding H_2SO_4 or NaOH solutions (the presence of the excess formate produced buffer action) and were measured before and after photolysis using an Elico model LI-10 pH meter.

The solutions were deaerated by bubbling high purity argon gas (Indian Oxygen Ltd., AR2 grade) through for 1 h.

The microsecond flash photolysis unit used in this study was fabricated in this laboratory. The details are given elsewhere [6]. Two xenon-filled quartz flash lamps (1/e time, 30 μs) were discharged in series at 150 - 400 J. The cylindrical quartz photolysis cell (capacity, 30 ml; path length, 10 cm) was located between two flash lamps. The analysing beam from an XBO 150 W xenon arc lamp was passed through the photolysis cell and a monochromator Rank Hilger (Monospec 600; 1200 lines mm^{-1}) and was detected using an IP28 photomultiplier tube. The output was recorded on a storage oscilloscope (Tektronix model DM64).

The pK of the semiquinone equilibrium was determined as follows. 3 ml of a 10^{-3} M anthraquinone-2-sulphonate solution containing 0.1 M sodium formate at a known pH was placed in a long-necked quartz cell (1 cm $\times$ 1 cm $\times$ 4 cm), deaerated by bubbling argon through and then photolysed

or radiolysed. The photolysis was performed using light of wavelength 366 nm and the radiolysis was performed using a ^{60}Co source (dose rate, 110 rad s^{-1}). The irradiation time was adjusted so that only about 10% of D was reduced. The spectra were recorded soon after the irradiation was complete. For the radiolysis a matched cell containing the same solution without D was simultaneously exposed to γ radiation, and this was used as a blank (γ radiolysis often produces a colour in the quartz cell itself, and to exclude this absorption by the cell material the blank was also radiolysed). Oxygen was bubbled through the irradiated solution for long enough to ensure complete oxidation of the reduced product and the spectra were again recorded. The difference between the two spectra gave that of the semiquinone. The concentrations of $D^{\cdot-}$ and $DH^{\cdot}$ were calculated from their optical densities (ODs) and extinction coefficients at 500 and 385 nm [2, 4]: $\epsilon^{D^{\cdot-}}{}_{500} = 6.8 \times 10^3$; $\epsilon^{D^{\cdot-}}{}_{385} = 5.37 \times 10^3$; $\epsilon^{DH^{\cdot}}{}_{385} = 5.55 \times 10^3$; $\epsilon^{D}{}_{385} = 3.0 \times 10^2$. The p$K$ was then calculated from the relation

$$pK = pH - \log\left(\frac{[D^{\cdot-}]}{[DH^{\cdot}]}\right)$$

3. Results and discussion

Figures 1 and 2 show the change in the absorbance at 500 nm with time after the flash photolysis of D solution containing formate at different pH values under anaerobic conditions. The spectrum of the transient species produced by the flash, which was recorded using the flash spectroscopic technique, showed an absorption maximum at 500 nm in agreement with the
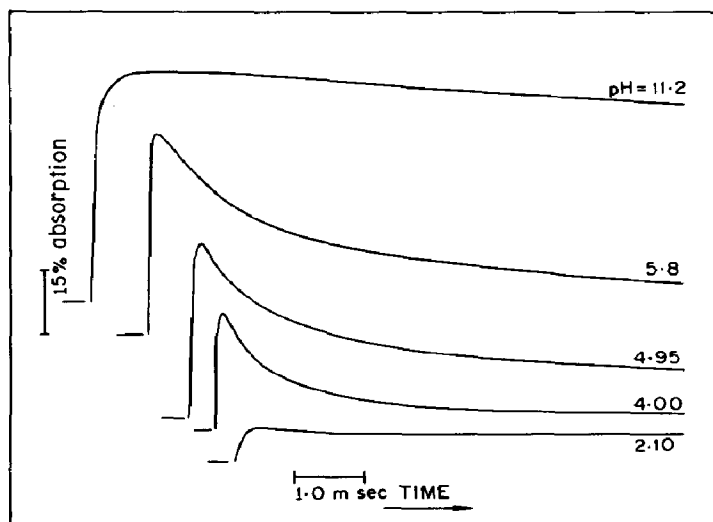

Fig. 1. Absorption spectra at 500 nm of the species formed by the flash photolysis of 5 × 10^{-4} M anthraquinone-2-sulphonate in the presence of 0.1 M formate at various pH values (flash energy, 144 J).
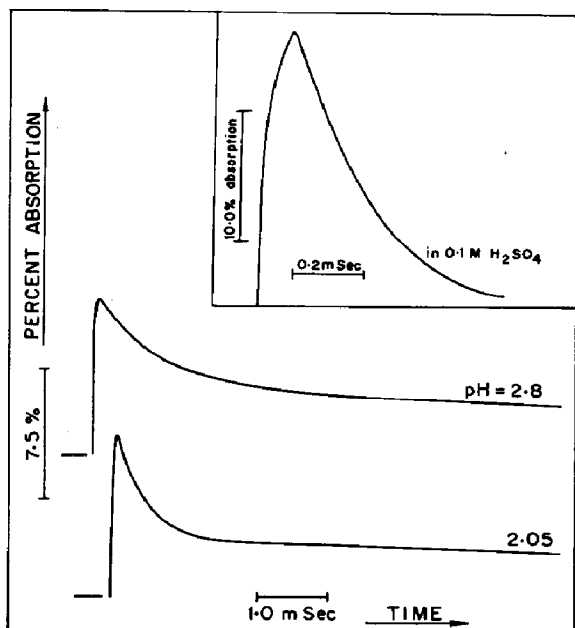
Fig. 2. Absorption spectra at 500 nm of the species formed by the flash photolysis of 2.5 × 10^{-3} M anthraquinone-2-sulphonate in the presence of 0.2 M formate (flash energy, 295 J).

D$^{\cdot-}$ spectra reported in the literature. Figure 1 shows the results obtained when a 5 × 10^{-4} M solution of D containing 0.2 M formate was photolysed at a flash energy of 144 J. The species D$^{\cdot-}$ produced immediately after the flash is stable at pH = 11.2. However, at pHs below 5.9 the initial D$^{\cdot-}$ species is transient with a lifetime of the order of milliseconds, and at pH 2.1 no species absorbing at 500 nm could be detected. Figure 2 shows the results obtained after the flash photolysis of a 2.5 × 10^{-3} M solution of D containing 0.2 M formate. The flash energy was 295 J and the sensitivity of the photomultiplier was increased by a factor of 4. At this increased flash energy, higher detector sensitivity and higher initial concentration of D (earlier observations showed that the quantum yield of semiquinone formation increased with increasing initial concentration of D in conventional photolysis) a transient species absorbing at 500 nm was observed even at pH 2.1. Comparison of the pulse amplitude with the flash energy and the detector sensitivity indicated that the yield of D$^{\cdot-}$ at pHs below 2.8 was about a factor of 8 less than that at pHs above 5. Conventional (long-range) photolysis results [2] indicate that the quantum yield of semiquinone at pHs below 2.75 is about one-tenth of that at pHs above 5, and this has been explained in terms of the higher reactivity of HCOO$^-$ towards the precursor of semiquinone than that of the undissociated HCOOH (the pK value of formate is 3.75). The above results suggest that the photoreduction of D always proceeds via the formation of D$^{\cdot-}$ rather than DH$^{\cdot}$ regardless of pH. D$^{\cdot-}$ is stable at pH 11 while at pHs below 6 it is transient. The steady state spectra recorded
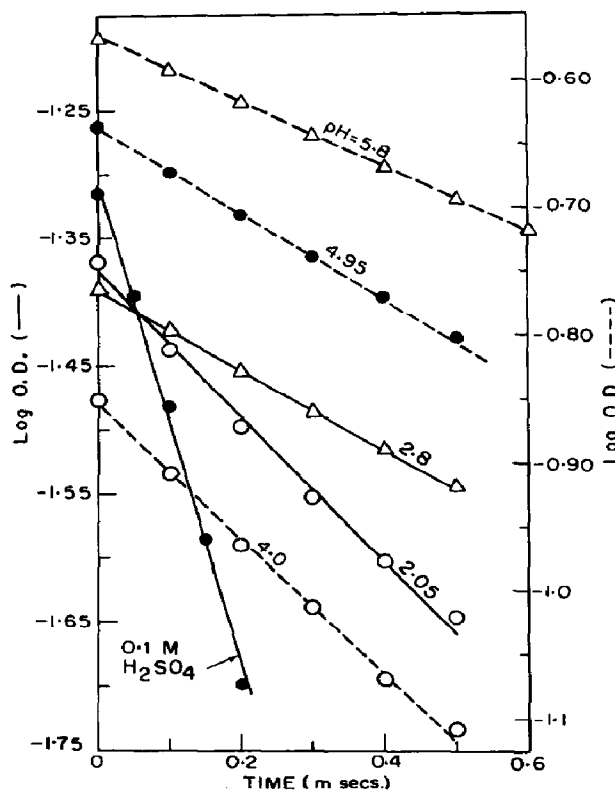
Fig. 3. Plot of log OD_{500} vs. time after flash photolysis of anthraquinone-2-sulphonate in the presence of formate at various pH values.
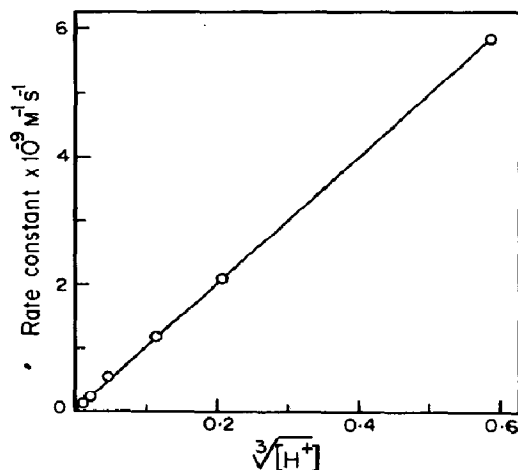
Fig. 4. Plot of the decay rate constant of the semiquinolate ion vs. the cube root of the hydrogen ion concentration.

TABLE 1

Rate constants of the decay of the semiquinolate ion $D^{\cdot-}$ ($D^{\cdot-} + H^+ \rightleftharpoons DH^\cdot$) at various pH values

pH	Rate constant $(M^{-1}\,s^{-1})$
5.8	1.45×10^8
4.95	2.34×10^8
4.0	5.6×10^8
2.8	1.19×10^9
2.05	2.09×10^9
0.1 M H_2SO_4	5.84×10^9

after flash photolysis at pHs below 6 indicated the presence of $DH^\cdot$ suggesting that at these pHs the $D^{\cdot-}$ species produced initially decays to $DH^\cdot$ probably by the reaction $D^{\cdot-} + H^+ \rightleftharpoons DH^\cdot$. The plots of log OD_{trans} versus time at various pHs are linear (Fig. 3) indicating that the decay of $D^{\cdot-}$ at pHs below 6 is a pseudo-first-order process. The rate constants are given in Table 1. The plots of k versus $[H^+]^{1/3}$ are also linear (Fig. 4). The dependence of

the rate constants on the cube root of the hydrogen ion concentration can be explained by assuming a spherical distribution of hydrogen ions about $D^{\cdot-}$ where their average separation r is related to $[H^+]$ by

$$\frac{r_2}{r_1} = \frac{[H^+]_1^{1/3}}{[H^+]_2^{1/3}}$$

These results suggest a bimolecular diffusion-controlled reaction.

Weller [7] determined the rate constants for a similar reaction between the excited state β-naphthol anion and acid $(RO^{-*} + BH^+ \rightarrow ROH + B)$ from fluorescence quenching and reported values in the range of $10^{10} - 10^7$ depending on the acid reacting with the anion.

The second-order rate constant of the dismutation reaction of $D^{\cdot-}$ $(2D^{\cdot-} \rightarrow D^{2-} + D)$ has also been determined spectrophotometrically from the time dependence of the absorbance at 500 nm of the photolysed solution of D containing formate at pH 12.5 under anaerobic conditions. It was found to be 7.34 M^{-1} s^{-1}. This is a much slower process than the acid–base equilibration of $D^{\cdot-}$. It is therefore apparent that what Hulme *et al.* [1] noted 20 μs after the application of radiolysis pulses in their determination of the pK of $D^{\cdot-} + H^+ \rightleftharpoons DH^{\cdot}$ is the absorption of the transient $D^{\cdot-}$ at 500 nm. This does not correspond to the equilibrium concentration of $D^{\cdot-}$ in solution, and the reduction in absorbance between pH 4.5 and pH 2.0 is due not to the conversion of $D^{\cdot-}$ to $DH^{\cdot}$ but to the decrease in the quantum yield of the photoreduction of D to semiquinone in the presence of undissociated HCOOH compared with that in the presence of $HCOO^-$. Our plot of the quantum yield of semiquinone *versus* pH [2] is very similar to the plot of OD *versus* pH given by Hulme *et al.* [1]. The above results led us to determine the pK value of the semiquinone–semiquinolate equilibrium. As semiquinone is stable under anaerobic conditions the equilibrium concentration of the two forms was determined in the aqueous D solution after photolysis in the presence of formate (where semiquinone is the only product) at various pHs, and the pK was calculated using eqn. (3). It was also determined in a similar manner from the radiolysed solution of D.

Long-range photolysis and radiolysis studies gave pK values of 8.18 and 8.20 respectively for the semiquinone–semiquinolate equilibrium. These values are in good agreement with each other. The value of 9.02 reported from polarographic determinations may be due to the effect of ionic strength on the activities of charged $D^{\cdot-}$ and H^+. The pK value determined here is also in good agreement with the kinetics observed using flash photolysis. At pHs above 10 the $D^{\cdot-}$ species produced immediately after excitation is stable, whereas at pHs below 6 it decays to $DH^{\cdot}$ with a rate which is dependent on the hydrogen ion concentration in the medium. The fact that the semiquinolate ion and not semiquinone is the primary radical produced, regardless of the pH of the medium, suggests that the photoreduction of anthraquinone-2-sulphonate always proceeds via the abstraction of an electron rather than a hydrogen atom by the excited quinone molecules.

4. Conclusions

(1) The pK value of the semiquinone–semiquinolate equilibrium derived from anthraquinone-2-sulphonate is 8.2 and not 3.25 as reported earlier by Hulme *et al.* [1].

(2) The photoreduction of anthraquinone-2-sulphonate always proceeds via the abstraction of an electron rather than a hydrogen atom by the excited quinone, and the semiquinolate ion thus produced equilibrates to the ionic form $D^{\cdot-}$ or the protonated form $DH^{\cdot}$ depending on the pH of the medium. The reaction $D^{\cdot-} + H^+ \rightleftharpoons DH^{\cdot}$ is diffusion controlled and the rate constant is in the range $10^8 - 10^9 \ M^{-1} \ s^{-1}$.

Acknowledgment

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