Radicals and Excited States in the Pulse Radiolysis of 9,10-Anthraquinones

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Summary Semiquinones, OH adducts, and triplet states are formed on radiolysis of anthraquinone solutions.

MUCH information is available about intermediates involved in photo-reactions of anthraquinones from studies by flash photolysis,[1-3] steady-state photolysis,[4,5] and polarographic[6,7] and e.s.r.[8] techniques. We present evidence that several of the same intermediates are formed in the radiolysis of anthraquinone solutions, and show that pulse radiolysis can provide information about radicals and excited states derived from anthraquinones.

Pulse radiolysis of argon-flushed neutral aqueous solutions of 10^{-4}M-sodium 9,10-anthraquinone-2-sulphonate (A) gives rise to transient species due to the reactions of hydrated electrons (e_{aq}^-), OH radicals, and a small amount of H atoms. In the added presence of 10^{-1}M-HCO_2Na, where OH and H are converted into CO_2^- before reaction with A, only one radical derived from the anthraquinone is observed, having a spectrum (λ_{max} 500 and 390 nm.) identical with that of the radical anion ($A\cdot^-$).[1,2] The rates of formation of this absorption show the reduction of A to $A\cdot^-$ by e_{aq}^- and CO_2^- to proceed with rate constants of $2\cdot8 \times 10^{10}$ and $3\cdot1 \times 10^9$ M^{-1} sec.$^{-1}$, respectively.

In N_2O-saturated neutral aqueous solutions of 10^{-4}M-A, where e_{aq}^- is converted into OH before reaction with the anthraquinone, only one species again predominates, with an absorption maximum at 460 nm. Salt-effect studies of the second-order decay of this species indicate that it possesses unit charge, consistent with its being an OH adduct (AOH·). An absorption attributed to the semi-oxidised anthraquinone ($\mathrm{A}^{\cdot +}$) has been observed in the same spectral region.[2,3] The rate of formation of AOH· leads to a rate constant for the reaction of A + OH of $5{\cdot}6 \times 10^{9}\,\mathrm{M}^{-1}$ sec.$^{-1}$.

The spectrum of $\mathrm{A}^{\cdot -}$ is unaltered over the pH range 10—4. At lower pH, the 500 nm. absorption progressively decreases and almost disappears below pH 2. We attribute this to the protonation of $\mathrm{A}^{\cdot -}$ to form AH· ($\lambda_{\max}$ 390 nm.). Pulse radiolysis of an argon-flushed solution of A in the presence of $10^{-2}\mathrm{M}$-$\mathrm{H_2SO_4}$ and $10^{-1}\mathrm{M}$-$\mathrm{HCO_2H}$ results in the formation of $\mathrm{CO_2H}$ and H, which react at approximately the same rate ($\sim 2 \times 10^{9}\,\mathrm{M}^{-1}$ sec.$^{-1}$) with A to give AH·. The pK for equilibrium $\mathrm{A}^{\cdot -} + \mathrm{H}^{+} \rightleftharpoons \mathrm{AH}\cdot$ was measured by observing changes in the transient absorption at 500 nm. where only $\mathrm{A}^{\cdot -}$ absorbs, over the pH range 10 to -2. The pK of 3·25 found may be compared with an estimate[6] of 9·02 using a polarographic technique, and estimates of 4·0 and 5·7 for the corresponding semiquinones derived from benzoquinone[9] and duroquinone.[1]

The extinction coefficients of $\mathrm{A}^{\cdot -}$, AOH· and AH· were estimated using established primary radical yields for water radiolysis, $G(\mathrm{e_{aq}}^{-}) = 2{\cdot}6$, $G(\mathrm{OH}) = 2{\cdot}65$, and $G(\mathrm{H}) = 0{\cdot}55$.[10] The values in M^{-1} cm.$^{-1}$ thus obtained were 8200 (500 nm.) and 8200 (390 nm.) for $\mathrm{A}^{\cdot -}$; 3900 (460 nm.) and 18,000 (310 nm.) for AOH·; and 11,900 (390 nm.) for AH . The value at 500 nm. for $\mathrm{A}^{\cdot -}$ is in reasonable agreement with a previous estimate[11] of 8660.

The corresponding radical species derived from sodium 9,10-anthraquinone-1-sulphonate appear to have very similar characteristics to those from the 2-sulphonate. This is in marked contrast with the widely differing photosensitising abilities of the two sulphonates.[4]

To account for the photolysis of A in aqueous solution the reaction

$$\mathrm{A\ (excited)} + \mathrm{A} \longrightarrow \mathrm{A}^{\cdot -} + \mathrm{A}^{\cdot +} \qquad (1)$$

has been postulated.[2,3] The excited state most likely to be involved is the lowest triplet.[4] However, neither the triplet state of anthraquinone itself, nor that of a derivative, has yet been observed in fluid solution. A broad weak absorption between 350 and 500 nm. attributed to the triplet, has been obtained on flash photolysis of anthraquinone in isopentane–methylcyclohexane glass at 77° K.[12]

To obtain additional information about reaction (1), and in particular the nature of the excited states involved, pulse radiolysis studies of anthraquinone in benzene were undertaken. Unlike water, benzene promotes the formation of solute excited states on radiolysis. Unsubstituted anthraquinone was used since the 2-sulphonate is insoluble in benzene. Using $10^{-3}\mathrm{M}$-anthraquinone, a broad weak transient was obtained, absorbing between 360 and 440 nm. and with an apparent peak at 380 nm. The transient decayed by first-order kinetics ($k \sim 4 \times 10^{6}$ sec.$^{-1}$). At $3 \times 10^{-3}\mathrm{M}$-anthraquinone, the decay constant increased to $\sim 8 \times 10^{6}$ sec.$^{-1}$. The intensity of the transient from $3 \times 10^{-3}\mathrm{M}$-anthraquinone was more than doubled in the presence of $10^{-1}\mathrm{M}$-benzophenone. Our results indicate that this transient absorption is due to anthraquinone triplet. The concentration dependence of the rate of decay is consistent with the participation of a reaction analogous to reaction (1). Observation of only weak absorptions in the region where the radical anion[1] and cation would be expected to appear indicates that in benzene considerable self-quenching occurs, to form two ground-state molecules. In addition, more efficient ion-recombination would be expected in benzene due to the lack of solvation. Addition of increasing amounts of propan-2-ol to $10^{-3}\mathrm{M}$-anthraquinone in benzene results in the formation of a very strong long-lived transient with a spectrum very similar to that of AH·. The production of the neutral semiquinone radical would be expected, by reaction of triplet anthraquinone with the alcohol.

We have examined a number of substituted anthraquinones in benzene to determine directly the effect of substitution upon triplet-state reactivities. Using $10^{-4}\mathrm{M}$-2-piperidinoanthraquinone, a nonsensitiser[14] with a strong charge-transfer longest-wavelength band,[15] a transient absorption was obtained with maximum at 530 nm., decaying by first-order kinetics ($k_{\mathrm{I}} = 6 \times 10^{4}$ sec.$^{-1}$). This absorption, which was enhanced four times in the presence of $10^{-1}\mathrm{M}$-naphthalene and removed completely in the presence of $10^{-4}\mathrm{M}$-anthracene, we tentatively assign to triplet 2-piperidinoanthraquinone. Since the decay rate was hardly altered by increasing the solute concentration to $10^{-3}\mathrm{M}$, the ground-state quenching reaction corresponding to reaction (1) is much less efficient here than for unsubstituted anthraquinone or A, which are both good photosensitisers.[3] Addition of 0·26M-propan-2-ol did not reduce the lifetime of the 2-piperidino-triplet absorption, which further demonstrates the poor sensitising properties of this anthraquinone.[14] Experiments with 1- and 2-aminoanthraquinone, and duroquinone,[16] also appear to support the generalisation that photosensitiser triplets undergo efficient ground-state quenching, whereas the triplets of poor sensitisers do not.

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