Iodide Ion Quenching of the Photolysis of 1-Iodoanthraquinone Anion Radical: Evidence for an Aryl Radical–Nucleophile Reaction

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The photolysis of 1-iodoanthraquinone anion radical in acetonitrile containing tetrabutylammonium iodide(TBA^+I^-) is unaffected by changes in [TBA^+I^-] up to 0.2 mol dm^{-3}, confirming that the previously observed iodide ion quenching results from capture of photogenerated aryl radicals by the nucleophilic iodide, a process analogous to that in nucleophilic aromatic substitution by the $S_{RN}1$ mechanism.

Nucleophilic aromatic substitution ($ArX + Y^- \longrightarrow ArY + X^-$) initiated by electron transfer is formulated in terms of the $S_{RN}1$ chain mechanism [1] in which the key steps are unimolecular cleavage of the reactant anion radical ($ArX^{\bullet -}$) to generate an aryl radical and its reaction with the incoming nucleophile. In a survey of some of the evidence, this formulation has recently been strongly criticized by Denney and Denney [2] who focussed on the following aspects.

(i) Independent generation of aryl radicals gives different products and/or isomer distributions from reactions thought to proceed by the $S_{RN}1$ mechanism.

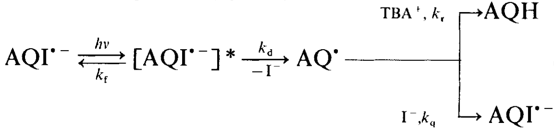
(ii) Product ratios, particularly the ratio of substitution to the competing reduction, vary with the method of initiating the chain process (chemical, electrochemical *etc.*).

(iii) Product ratios are subject to leaving group, counter ion and substituent effects that seem to suggest that the partitioned reactive intermediate is not an aryl radical.

Denney and Denney therefore propose that all these reactions should be formulated in terms of an alternative chain process involving bimolecular reactions of the reactant anion radical with nucleophiles, giving substitution, and with hydrogen donors, giving reduction products. Cleavage of the Ar–X bond is seen as occurring only by way of the dianion ArX^{2-}.

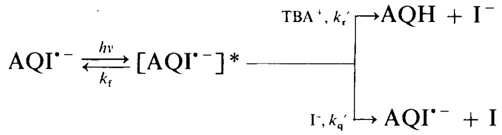
These criticisms of the $S_{RN}1$ mechanism may arise from an overly simplistic view of the product-determining situation in the diverse circumstances of the reactions cited as examples by Denney and Denney, and we present here evidence that, in one instance, the reduction/substitution ratio arises from competing reactions of an aryl radical and not of its precursor anion radical.

We have previously demonstrated that the anion radicals of 1-bromo- and 1-iodo-anthraquinone [$AQBr^{\bullet -}$ and $AQI^{\bullet -}$, generated electrochemically in CH_3CN containing tetrabutylammonium (TBA^+) perchlorate] undergo reduction to anthraquinone (AQH) on irradiation at their long wavelength absorption bands.[3] Since no reduction occurs in the presence of sodium as the counter ion, the source of the hydrogen is TBA^+. The AQH produced undergoes one-electron reduction under the reaction conditions, giving rise to observable photocurrents, kinetic analysis of which permits electrochemical mechanistic analysis, for example, for AQI a mixed ECE/DISPI process.[4] This photoreduction process is inhibited (quenched) by added iodide ion and experiments at constant [TBA^+] but variable [I^-] showed that this could be explained by partitioning of a reactive intermediate, which we believed to be the 1-anthraquinonyl radical, between reaction with TBA^+, forming AQH, and I^-, reforming ground state $AQI^{\bullet -}$ [eqn. (1)]. The mathematical expression (2) describing the rate coefficient for AQH formation (k_1) as a function of the concentrations of the ions and the light intensity absorbed I_{abs} is of the same form as eqn. (4) resulting from partitioning of a photoexcited 1-iodoanthraquinone anion radical [eqn. (3)] if fluorescence of [$AQI^{\bullet -}$]* is ignored ($k_f = 0$).



$$AQI^{\bullet -} \underset{k_f}{\overset{h\nu}{\rightleftharpoons}} [AQI^{\bullet -}]^* \xrightarrow[-I^-]{k_d} AQ^{\bullet} \begin{cases} \xrightarrow{TBA^+,\, k_r} AQH \\ \xrightarrow{I^-,\, k_q} AQI^{\bullet -} \end{cases} \qquad (1)$$

$$k_1 = \frac{I_{abs}k_d}{(k_d + k_f)} \frac{k_r[TBA^+]}{(k_r[TBA^+] + k_q[I^-])} \qquad (2)$$



$$AQI^{\bullet -} \underset{k_f}{\overset{h\nu}{\rightleftharpoons}} [AQI^{\bullet -}]^* \begin{cases} \xrightarrow{TBA^+,\, k_r'} AQH + I^- \\ \xrightarrow{I^-,\, k_q'} AQI^{\bullet -} + I^- \end{cases} \qquad (3)$$

$$k_1 = I_{abs} \frac{k_r'[TBA^+]}{k_f + k_r'[TBA^+] + k_q'[I^-]} \qquad (4)$$

The two reaction schemes can be distinguished, however, by examination of kinetic salt effects using the Brønsted–Bjerrum equation [5] given in eqn. (5) for reaction between reactants A and B of charge Z_A and Z_B respectively in solutions of ionic strength I assumed to behave in a Debye–Hückel limiting fashion. The

$$\log k_{AB} = \log k^{\circ}_{AB} + 2Z_AZ_BAI^{\frac{1}{2}} \qquad (5)$$

constant A for acetonitrile solution has a value of 1.405 at 25 °C, compared with 0.51 in water,[6] making the effect larger and more sensitive in the aprotic solvent; Debye–Hückel limiting behaviour is reported up to I = 0.019 mol dm^{-3}. For partitioning of $AQ^{\bullet}$ as in eqn. (1), $Z_AZ_B = 0$, so that k_1 should be invariant with salt concentration. On the other hand, reaction according to eqn. (3) would lead to k_r' decreasing and k_q' increasing as the salt concentration goes up and an overall decrease in k_1 would result.

Measurements were made of the photocurrents produced by irradiation of solutions of AQI in acetonitrile, containing varying concentrations of TBA^+I^- in the range 0.01–0.2 mol dm^{-3} flowing (flow rate V_f cm^3 s^{-1}) through a channel electrode assembly held at a potential corresponding to the transport-limited reduction of both AQI and AQH. The photocurrents were transformed into a normalised rate constant K_n by use of theoretical working curves computed on the basis of the channel electrode geometry and an optimised balance between ECE and DISP pathways (constant in all experiments).[4] On this basis K_n

takes the form of eqn. (6), where x_e is the electrode length, $2h$ is

$$K_n = k_1\left[\frac{4h^4d^2x_e^2}{9DV_f^2}\right]^{1/3} \qquad (6)$$

the channel depth, d its width and D is the diffusion coefficient of $AQI^{\bullet-}$. Values of k_1, the rate coefficient for the photochemical reduction were evaluated from the slopes of the linear plots of K_n *vs.* $V_f^{-2/3}$ as 0.076 ± 0.005 (at $[TBA^+I^-]$ = 0.01 mol dm^{-3}), 0.074 ± 0.005 (0.05 mol dm^{-3}), 0.075 ± 0.009 (0.1 mol dm^{-3}) and 0.070 ± 0.006 s^{-1} (0.2 mol dm^{-3}). Since $[TBA^+] = [I^-]$ in these experiments, a variation in k_1 only arises if the rate coefficients for the individual steps change with the salt concentration. Since no significant change is observed, it is evident that competition between photoreduction and quenching arises by the reactions in eqn. (1), confirming our earlier interpretation, and not as in eqn. (3).

The present results provide unequivocal proof that aromatic anion radicals carrying a potential leaving group can dissociate unimolecularly to give the σ-aryl radical and the anionic leaving group, albeit photochemically for the most part in this instance. The reaction of 1-anthraquinonyl radicals with nucleophiles is also proven. Since the same reaction proceeds slowly with thermal as well as photochemical stimulation,[3,4] we see no need radically to alter the present view of nucleophilic aromatic substitution initiated by electron transfer.

Acknowledgements

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References

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