

Anodic Oxidation of Anthracenes and Related Compounds

Part III. Hydroxylation of Haloanthracenes

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The 9,10-dihaloanthracenes undergo initial one electron transfer upon anodic oxidation in acetonitrile. The resulting cation-radicals are moderately stable during the time-scale of cyclic voltammetry. The major reaction pathway followed by the intermediate cation-radicals is reaction with residual water and further electron transfer. The oxidations are accompanied by the consumption of 2.0 Faradays per mole of substrate and proceed through intermediate formation of the bis-halohydrin which loses H-X in a chemical step to form anthraquinone in high yield.

Anthracene derivatives substituted in the 9 and 10 positions with substituents such as phenyl,¹ methyl,² and methoxy³ form cation-radicals upon electro-oxidation which are stable or moderately stable in acetonitrile. The electrochemistry of these systems has been thoroughly characterized. Compounds in which the 9 and 10 positions are not occupied by such "blocking" groups form very reactive cation-radicals which cannot be detected by ordinary electrochemical techniques and are very prone to reaction with trace amounts of water always present even in carefully purified acetonitrile. The most conclusive evidence for the nature of these reactions has emerged from consideration of the structures of the products obtained. For example, bianthrone was found to be the major product of the anodic oxidation of anthracene in acetonitrile.^{4,5} We have recently shown that bianthrone is the result of 3e anodic oxidation of anthracene⁶ and is the product at moderate water concentrations. At lower water content anthraquinone is a major product.⁷ At water concentrations of 3 M or greater, a trimer with an anthracene moiety inserted between two 9-anthronyl groups is a major product of the anodic oxidation of anthracene in acetonitrile.⁷

Anodic hydroxylation of aromatic compounds has recently been reported to take place under voltammetric conditions. For example, 1,5-dihydroxy-

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naphthalene yields 5-hydroxy-1,4-naphthoquinone upon anodic oxidation in aqueous perchloric acid. The mechanism of this reaction was shown to involve 1,4-addition of water to the initially formed quinone followed by further oxidation. Anodic hydroxylation of a number of aromatic compounds has been observed under noncontrolled conditions.⁹

Very little is known about the anodic oxidation pathways of 9,10-dihaloanthracenes. Lund isolated the monopyridinium salt arising from the anodic oxidation of 9,10-dibromoanthracene in the presence of pyridine.¹⁰ A mechanism was proposed involving a two electron transfer from the substrate followed by reaction with pyridine and decomposition of the dipyridinium adduct during work-up. We have recently found that the dilutidinium salt from 9,10-dibromoanthracene is not an intermediate in the formation of the monolutidinium salt.¹¹

A rotating disk electrode study recently provided conclusive evidence that anodic pyridination of anthracene derivatives, long believed to involve a two electron transfer, is actually an ECE process involving the cation-radical as an intermediate.¹² EEC mechanisms, involving reactions of organic dications have also been demonstrated for anodic substitution and addition reactions of aromatic compounds.^{13,14}

This investigation was undertaken in order to establish the nature of the anode processes that occur during anodic oxidation and the products produced from 9,10-dihaloanthracenes. Previous work under voltammetric conditions pointed to an EEC mechanism but no cyclic voltammetric or other evidence was available which could verify this mechanism.¹⁵

RESULTS AND DISCUSSION

Voltammetry. The early investigation of 9,10-dibromoanthracene led to the conclusion that the anodic oxidation involves a two electron transfer.¹⁰ In this study, cyclic voltammetry was used as the diagnostic tool to determine the number of electrons involved in the primary oxidation step. The peak potentials (E_p) and peak currents (i_p) for 9,10-dihaloanthracenes are summarized in Table 1. 9,10-Diphenylanthracene (9,10-DPA) was included as a standard one electron oxidation compound. At a voltage sweep rate of 10 V/min, a 1.0 mM solution of 9,10-dichloroanthracene (9,10-DCA) exhibits an i_p of 117 μ A as compared to 90 μ A for a similar solution of 9,10-DPA under

Table 1. Voltammetry of haloanthracenes.

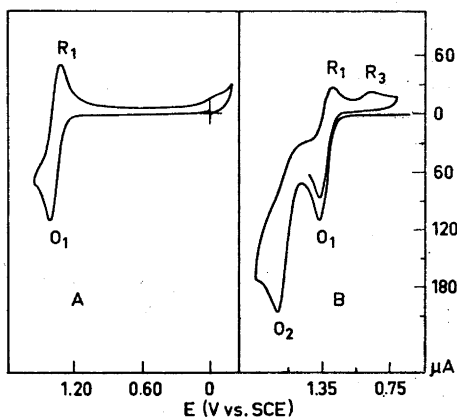
Substrate	E_{p1}	E_{p2}	i_{p1}	n_{p1}
9,10-DCA	+1.37	+1.75	117	1
9,10-DBA	+1.42	+1.76	108	1
9,10-DPA	+1.15	+1.55	90	1

Voltage sweep rate=10 V/min. (Substrate)=1.0 mM in acetonitrile ($(H_2O) \approx 8$ mM).

the same conditions. The first oxidation peak for 9,10-DCA, therefore, involves the transfer of much less than two electrons. The peak current for a similar solution of 9,10-dibromoanthracene (9,10-DBA) was determined to be equal to $109 \mu\text{A}$, close to the value expected for a one electron oxidation.

Fig. 1 shows the cyclic voltammogram of 9,10-DCA obtained at a voltage sweep rate of 10 V/min . An oxidation peak, O_1 , is observed at $+1.37 \text{ V}$. If the

Fig. 1. Cyclic voltammograms of 9,10-dichloroanthracene in acetonitrile containing lithium perchlorate (0.1 M). Voltage sweep rate = 10 V/min .



voltage scan is switched in the cathodic direction after O_1 , a cathodic peak, R_1 , is observed at $+1.28 \text{ V}$. The ratio of the cathodic to anodic peak current, i_{pc}/i_{pa} , is equal to 0.74. The baseline for the cathodic peak was established by the method of Adams and coworkers.¹⁶ When the anodic scan is continued beyond the first peak, a second anodic peak, O_2 , is observed at $+1.75 \text{ V}$. On

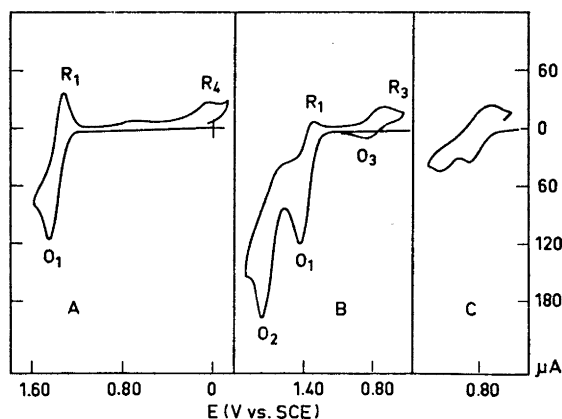


Fig. 2. Cyclic voltammograms of 9,10-dibromoanthracene (A, B) and tetraethylammonium bromide (C) in acetonitrile containing lithium perchlorate (0.1 M). Voltage sweep rate = 10 V/min .

the cathodic cycle, R_1 , is observed, smaller than before, and a new cathodic peak, R_3 , is observed at +0.99 V. (Fig. 1B). Since O_1 involves the transfer of one electron, the product of this reaction is the cation-radical. R_1 then is due to the reduction of the cation-radical and the ratio, i_{pc}/i_{pa} , a measure of the stability of the cation-radical, shows that the intermediate is moderately stable during the time-scale of cyclic voltammetry. Since the cation-radical is generated at O_1 and is moderately stable, it follows that O_2 involves the oxidation of the cation-radical to the dication. The voltammogram up to this point parallels that of 9,10-DPA which is known to form a stable cation-radical¹ and an unstable dication.¹⁷ The cathodic peak, R_3 , involves reduction of an oxidation product formed at O_2 since it does not appear when the direction of the voltage sweep is changed after O_1 . R_3 was found to match the reduction peak for chlorine obtained by the oxidation of chloride ion in acetonitrile.

Fig. 2 is the cyclic voltammogram of 9,10-DBA in acetonitrile. The same basic pattern as was observed with 9,10-DCA is seen. The ratio, i_{pc}/i_{pa} , for the redox couple, R_1-O_1 , is equal to 0.64 in this case. A very small bromine peak, * R_3 , is observed when the potential is switched between the two oxidation peaks (Fig. 2A) and is much larger when the switching potential is moved slightly anodic of O_2 (Fig. 2B). The small cathodic peak, R_4 , is due to reduction of protons.

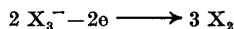
The current function ** for O_1 , $i_p/v^{1/2}$, plotted *versus* $v^{1/2}$, for the dihaloanthracenes along with that for the model compound 9,10-DPA, is shown in Fig. 3. The current function for 9,10-DPA is independent of v , the voltage sweep rate in V/min, and corresponds to the transfer of one electron at all values of v used. The current functions for both 9,10-DBA and 9,10-DCA are slightly greater than that for 9,10-DPA but clearly show one electron behavior with evidence of an ECE mechanism at the lower values of v . Therefore, 9,10-dihaloanthracenes are oxidized by an initial one electron transfer and undergo follow-up chemical reactions with solvent or residual water.

The voltammetric behavior of both 9,10-DBA and 9,10-DCA in acetonitrile containing water (150 mM) is markedly different from that in anhydrous solution. The height of O_1 is increased to correspond to the transfer of two electrons and R_1 cannot be seen. This observation is consistent with the ECE mechanism. The addition of water increases the rate of the chemical step to such an extent that all the cation-radical reacts during the time of the voltammetric experiment.

* Two anodic peaks are observed for the oxidation of halide ions in acetonitrile,¹⁸ the first corresponding to



and the second to



During the oxidation of the 9,10-dihaloanthracenes, the second peak was not detected, possibly due to the absence of excess halide ions. (The addition of perchloric acid to a solution of Br^- in acetonitrile eliminates the second peak in the voltammogram.). The voltammogram of Br^- is included in Fig. 2.

** The theoretical concepts of cyclic voltammetry have been developed by Nicholson and Shain.^{19,20}

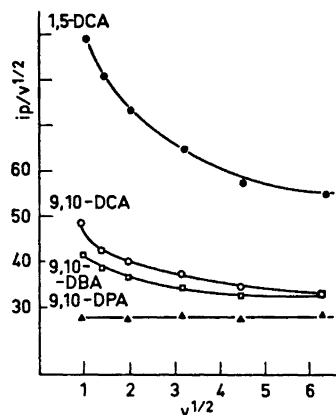


Fig. 3. Current functions for the halo-anthracenes. 1,5-Dichloroanthracene included as a typical example of ECE behavior.

Coulometry. Coulometric n values for the anodic hydroxylation of 9,10-DBA and 9,10-DCA were determined using the constant current techniques described in the previous paper (Table 2).²¹ The amperimetric end-point determination²¹ was used and thus the voltammetric characteristics of the electrolysis solutions were observed throughout the course of the electrolyses. The anodic oxidation of 9,10-DBA in acetonitrile containing water (150 mM) clearly involves the transfer of 2.0 electrons (Runs 1–7). Coulometric n values slightly greater than 2 were observed in dry acetonitrile (Runs 8–9). Precise 2 electron coulometry was observed for the oxidation of 9,10-DCA regardless of the water content of the acetonitrile (Runs 10–15).

Table 2. Coulometry of the anodic hydroxylation of 9,10-dibromo- and 9,10-dichloro-anthracene in acetonitrile.^a

Run	Substrate	(Substrate) mM	(H ₂ O) mM	E (vs. SCE) ^b	I mA	n ^c
1	DBA	0.625	150	1.20	25	1.96
2	DBA	0.625	150	1.18	25	1.98
3	DBA	0.625	150	1.18	25	2.03
4	DBA	1.25	150	1.19	25	2.00
5	DBA	1.25	150	1.20	25	2.01
6	DBA	1.25	150	1.20	50	1.95
7	DBA	1.25	150	1.20	50	1.96
8	DBA	1.25	8	1.21	25	2.09
9	DBA	1.25	8	1.18	25	2.15
10	DCA	0.625	150	1.19	25	1.93
11	DCA	0.625	150	1.17	25	1.92
12	DCA	1.25	8	1.17	25	2.01
13	DCA	1.25	8	1.18	25	1.98

^a The supporting electrolyte was LiClO₄ (0.1 M).

^b Initial value.

^c Expressed as Faradays per mole of substrate.

Coulometric experiments on 9,10-DBA at temperatures as high as the boiling point (80°C) of the electrolysis solution resulted in n values considerably higher than 2 and in some cases as high as 4. These values were difficult to reproduce but were consistently too high to be accounted for by a two electron process. Variation in n values with temperature was also observed for 9,10-DCA but was less pronounced.

Table 3. Hydroxylation of 9,10-dibromoanthracene in the presence of cyclohexene in acetonitrile.^a

Run	Substrate	Cyclohexene mM	i_p μA^b	n^d
(1-3) _{Ave}	9,10-DBA	0	69	1.99
21	9,10-DBA	12	102	3.24
22	9,10-DBA	24	123	3.49
23	9,10-DBA	48	129	3.68
24	9,10-DBA	84	156	4.35
24	9,10-DBA	120	158	4.29
26	TEAB ^c	120	—	1.18
27	TEAB	120	—	1.21

^a (H₂O)=150 mM, (LiClO₄)=0.1 M.

^b Peak current measured at 4 V/min on the solution before electrolysis was carried out.

^c Tetraethylammonium bromide.

^d Coulometric n value expressed in Faradays per mole of substrate.

Several experiments were carried out in which cyclohexene * was added to the solution of 9,10-DBA in acetonitrile (Table 3) in order to determine the effect of the presence of a bromine acceptor. A marked effect was observed on both the voltammetry and coulometry upon the addition of cyclohexene. The voltammetric peak current increased by more than a factor of 2 by the addition of cyclohexene (120 mM) and the coulometric n value increased from 2.0 to 4.3. At lower cyclohexene concentration the effect was proportional to the concentration. The maximum effect was observed at a concentration of 84 mM. Under the same conditions bromide ion was found to undergo 1.2e oxidation (Runs 26-27).** Coulometry for the anodic oxidation of 9,10-DCA was not effected by the presence of cyclohexene.

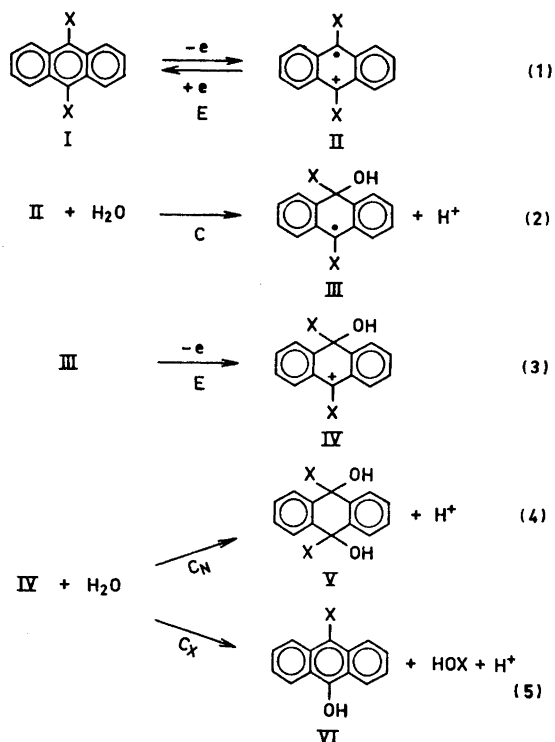
Products. Several electrolyses were conducted using greater amounts of substrate and the products were isolated. The preparative runs were carried out under the same conditions as the coulometric runs. The only product that could be detected from either 9,10-DBA or 9,10-DCA when exhaustively oxidized in acetonitrile containing water (150 mM) was anthraquinone. Direct analysis on the electrolytic solutions by GLC showed that the primary 2e oxidation product analyzed quantitatively as anthraquinone. Crude products

* Cyclohexene did not appreciable change the background current below +2.0 V (vs. SCE).

** n values greater than 1.0 can occur due to reactions such as $2 Br^- \xrightarrow{-2e} Br_2 \xrightarrow{H_2O} HOBr + H^+ + Br^-$

obtained by extraction of the electrolysis mixture with water and methylene chloride and evaporation of the organic solvent contained only anthraquinone. Crystalline samples were obtained by partial evaporation of the methylene chloride and were shown to be identical to authentic anthraquinone by IR and mass spectrometry as well as by elemental analysis.

Mechanism. The voltammetric study clearly shows that the 9,10-dihaloanthracenes undergo initial one electron transfer in dry acetonitrile to form the corresponding cation-radicals which are moderately stable during the time-scale of cyclic voltammetry. Introduction of water into the system has the apparent effect of changing the overall anode process to a 2e transfer. The stepwise nature of the reaction (ECE) can be implied from other similar cases. Reactions of anodically generated cation-radicals with nucleophiles such as pyridine¹² and water²² have recently been demonstrated using the rotating disk electrode and cyclic voltammetry. The 2e oxidation product apparently retains the halogen atoms of the substrate during the time scale of cyclic voltammetry since the halogen-halide couple can barely be detected. An ECE process, accompanied by the formation of the bis-halohydrin (V) is consistent with these results (Scheme 1). The cationic intermediate (IV) has

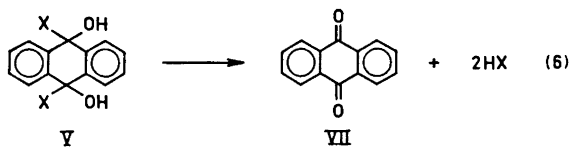


Scheme 1

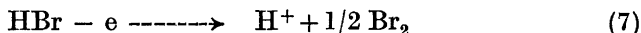
two possible reaction pathways; either (a) reaction with water (as a nucleophile toward carbon) to give (V) or (b) with water (as a nucleophile toward bromine) to give (VI) plus hypohalous acid. By virtue of the ease of oxidation of anthranols,^{23,24} VI would be expected to undergo further oxidation. Since halogen species such as HOX are detectable by cyclic voltammetry and only traces of such species are evident by the cyclic voltammetry of 9,10-dihaloanthracenes in acetonitrile containing water (150 mM), attack of water on halogen (eqn. 5) can be ruled out. However, halogen is detected during voltammetry in dry acetonitrile and reaction (5) may occur under these conditions. An intermediate similar to IV forms during anodic lutidination of 9,10-DBA and undergoes both reactions (4) and (5) (lutidine rather than water acting as the nucleophile).¹¹

Coulometry indicates that both 9,10-DBA and 9,10-DCA undergo 2.0e oxidation in acetonitrile containing water (150 mM). These results are consistent with the voltammetry and the formation of V.

Since the only product that is isolated from either of the dihaloanthracenes is anthraquinone, V must undergo decomposition during the isolation procedure. This reaction must also occur during GLC analysis and during electrolysis



when the temperature is increased. An indication of the stability of V (X is Br) in acetonitrile containing water (150 mM) was obtained by voltammetry on an electrolysis solution. 9,10-DBA (1.25 mM) in acetonitrile (40 ml) containing water (150 mM) and lithium perchlorate (0.1 M) was oxidized at a constant current of 50.0 mA to the amperimetric end-point which required 6.35 min. Only small amounts of inorganic halogen species could be detected by voltammetry. On standing the anodic peak at +0.9 V due to oxidation of HBr was observed to grow larger with time during

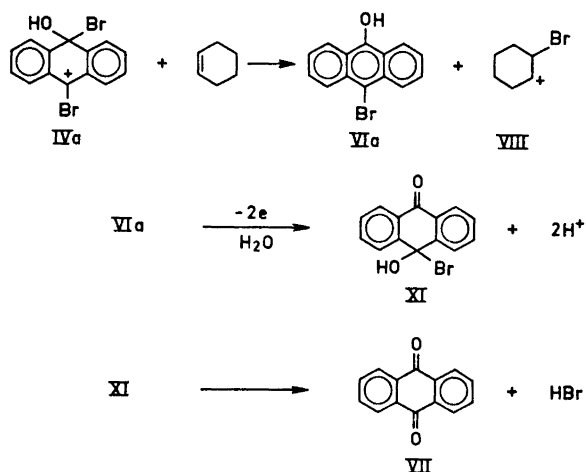


voltammetry of the solution and steadily increased in height and reached a maximum at about 30 min after the electrolysis was stopped. It was not possible to account for all the HBr required by eqn. 6; however, these results clearly show that V is not stable in acetonitrile and undergoes decomposition producing HBr (eqn. 6).

The effect of cyclohexene on the voltammetry of 9,10-DBA cannot be accounted for by the reaction with bromine liberated by oxidation of HBr. The presence of cyclohexene changes the nature of the anode processes from a 2e oxidation to a 4e oxidation during the time scale of voltammetry, indicating that the slow decomposition of V (eqn. 6) does not occur. An attractive rationalization is that the cation, IVa, acts as a brominating agent (Scheme II), reacting with cyclohexene to produce VIa and VIII. The anthrol, VIa, could

then undergo 2e oxidation (hence, an overall 4e process) to give IX, which on decomposition produces anthraquinone and HBr. The only product detected from 9,10-DBA in the presence of cyclohexane was anthraquinone. The nature of the products derived from cyclohexene during this reaction is being investigated.

Preliminary results of a rotating disk electrode study²⁵ support the conclusions of this study. Limiting current values corresponding to the transfer of one electron are observed during the anodic oxidation of 9,10-DBA in dry acetonitrile. At a water concentration of 150 mM, two electron behavior at low rotation rates and limiting one electron behavior at high rotation rates is observed. In the presence of cyclohexene (50 mM), limiting currents at low rotation rates correspond to the transfer of greater than three electrons and at higher rotation rates only slightly greater than one electron. Thus, the primary process corresponds to a one electron oxidation under all conditions studied.



Scheme 2

In summary, the anodic hydroxylation of 9,10-dihaloanthracenes in acetonitrile is best described by an ECEC process producing the bishalohydrin, V. At low water concentration, the rate of the reaction of the cation-radical, II, with water is sufficiently slow to allow its detection by cyclic voltammetry. Increasing the water concentration has the effect of making the primary process appear as a two electron oxidation when examined by slow sweep cyclic voltammetry, however, rotating disk electrode voltammetry suggests that the same process occurs with the rate of reaction between II and water taking place at a much greater rate.

EXPERIMENTAL

The apparatus for voltammetry, coulometry, and preparative electrolysis was described in the previous paper.²¹ All chemicals were reagent grade and used without further purification. The solvent was either Eastman anhydrous acetonitrile (<0.01 % H₂O) or practical grade purified by two distillations from phosphorus pentoxide in which only the middle 60 % fraction was collected. A bulk solvent-electrolyte (0.1 M lithium perchlorate) solution was prepared and used for most of the experiments. The water content of the dry solution was estimated at 8 mM by Karl Fischer titration. The solution was stored under an atmosphere of argon.

The products were isolated by pouring the entire electrolysis mixture into a separatory funnel and adding an equal portion of methylene chloride. This solution was extracted with several equal-volume portions of water to remove most of the acetonitrile and all of the supporting electrolyte. The methylene chloride solution was dried over anhydrous magnesium sulfate and evaporated to dryness under the aspirator. In order to avoid fractionation of products, the crude mixtures were analyzed by IR, NMR, and mass spectrometry. Crystalline samples of the pure products could be obtained by incomplete evaporation of the methylene chloride. The IR spectra of the crude and purified samples were nearly identical for both substrates and only one significant product could be detected. Verification of the identity of the product was obtained by comparison of the spectra with that of authentic anthraquinone and by elemental analysis.

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