Anal. (mixture) Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09. Found: C, 62.46; H, 11.11; N, 8.30.

Methyl N-(4,4-dimethyl-2-pentane)carbamate was prepared from 4,4-dimethyl-2-pentene **21**. The INCO addition failed to go to completion as evidenced by the failure of the reaction mixture to decolorize. The iodocarbamate **22** was isolated prior to reduction: ir 3330, 2950, 1700, and 1530 cm^{-1}; nmr ($CDCl_3$) τ 5.1 (broad, 1, NH), 6.35 (s, 3, OMe), 6.17 (m, 1, CHN), and 9.05 (s, 9, $C(Me)_3$).

Anal. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09. Found: C, 62.19; H, 11.11; N, 8.25.

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Electrochemical Oxidation Pathways of Benzo[*a*]pyrene

Ljubomir Jeftić[1] and Ralph N. Adams

Contribution from the Department of Chemistry,
University of Kansas, Lawrence, Kansas 66044.
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Abstract: The electrochemical oxidation of benzo[*a*]pyrene (BP) at platinum electrodes in several nonaqueous solvents was studied. The initial oxidation of BP is a one-electron process to the cation radical. The latter is consumed in two pathways. One involves dimerization to 6,6′-bibenzo[*a*]pyrenyl, which is further oxidized, probably to polymeric products. The major portion of the cation radicals undergo several hydrolyses and oxidation steps ending with a mixture of BP quinones. All of the major steps in the overall process are substantiated by chemical and spectroscopic identification of intermediates and products which are consistent with the electrochemistry.

Most studies on the electrochemical oxidation of large aromatic hydrocarbons have been concerned with establishing the existence and stability of cation radicals produced in the initial electron transfer step.[2-6] Due to experimental difficulties, very little has been accomplished on detailed mechanisms of these oxidations. The electrooxidation of anthracene and several substituted anthracenes has been examined in considerable detail.[3,7]

This work describes the detailed anodic oxidation pathways of benzo[*a*]pyrene (BP) in a variety of solvent systems. The BP molecule was chosen for two specific reasons. First, with its complexity, a thorough analysis should serve as a model for other large hydrocarbon systems. Second, similar aromatic hydrocarbons are known to be carcinogenic and oxidative pathways are prevalent in their metabolism. BP is one of the most powerful of these carcinogens and it is possible that parallelisms between the electrochemical oxidation and metabolic processes will prove valuable.[8a]

There have been no previous studies of the anodic oxidation of BP. The metabolism has been investigated thoroughly. Metabolic products of interest to the electrochemistry include the 1-, 3-, and 6-hydroxy-BP's[8b-11] and the 1,6-, 3,6-, and 6,12-BP quinones.[10] Under physiological conditions BP also undergoes glucuronide and sulfate conjugation. Position 3 of BP appears to be the main point of biological oxidative attack. In contrast, position 6 seems favored in ordinary chemical oxidation.[12]

Experimental Section

The electrochemical equipment and techniques (cyclic voltammetry, rotated disk electrodes, controlled potential coulometry, absorption, fluorescence, and EPR spectroscopy, etc.) were all conventional and have been well described in previous literature from this and other laboratories.[3-6]

Materials. Acetonitrile was dried overnight over calcium hydride and then distilled from calcium hydride. The middle fraction was redistilled from phosphorus pentoxide. Karl Fischer analysis of this acetonitrile showed about 10 mM H_2O present. Propylene carbonate and dimethylformamide were dried overnight over calcium hydride, vacuum distilled, and stored over molecular sieves. Nitrobenzene was first passed through an alumina column and then vacuum distilled. The solvent systems contained 0.1 M tetraethylammonium perchlorate as supporting electrolyte in all cases. All potentials are in volts referred to the aqueous SCE. All work was done at platinum electrodes. Benzo[*a*]pyrene from Aldrich Chemicals was recrystallized from benzene–methanol.

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[1] On leave from Rudjer Bošković Institute, Zagreb, Yugoslavia.

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[3] K. E. Friend and W. E. Ohnesorge, *J. Org. Chem.*, **28**, 2435 (1963).

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[8] (a) Since this manuscript was submitted, two sets of workers have discussed the possible role of BP cation radical in carcinogenicity. Wilk (report of the Israel Academy of Sciences symposium on chemical carcinogens reported in *Science*, **165**, 417 (1969)) discussed probable one-electron oxidations in covalent bonding of BP with various purines. Hoffmann, Lesko, and Ts'o (Abstracts, 158th National Meeting of the American Chemical Society, Division of Medicinal Chemistry, New York, N. Y., Sept 1969, No. 74) suggested cation radical interactions in the iodine-induced binding of BP to DNA. (b) I. Berenblum and R. Schoental, *Cancer Res.*, **6**, 699 (1946).

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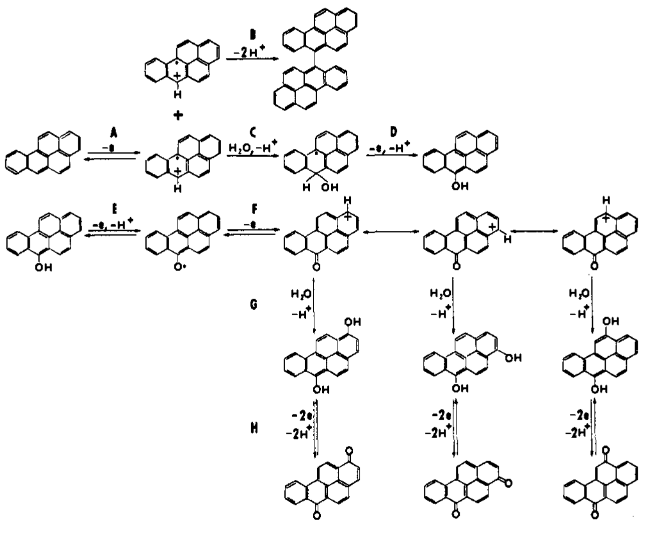

Figure 1. General reaction scheme for anodic oxidation of benzo[*a*]pyrene.

6-Acetoxybenzo[*a*]pyrene was synthesized from benzo[*a*]pyrene by glacial acetic acid oxidation.[13]

6-Hydroxybenzo[*a*]pyrene was prepared by Grignard reaction from 6-acetoxybenzo[*a*]pyrene.[12] 6,6′-Bibenzo[*a*]pyrenyl was made from benzo[*a*]pyrene by modifying a method published by Wilk, *et al.*,[14] as follows: a solution of benzo[*a*]pyrene in benzene was mixed with thin layer chromatography silica gel in a petri dish and dried in the vacuum oven. The dish was placed in a desiccator with another dish filled with iodine crystals, evacuated, and left under vacuum for 48 hr. The petri dish with silica gel was removed and iodine evaporated off on the hot plate. The silica gel was washed with hot benzene, and the solution evaporated to a small volume and chromatographed on alumina with benzene. The first fraction was unreacted benzo[*a*]pyrene and the second 6,6′-bibenzo[*a*]pyrenyl.

A mixture of 1,6-, 3,6-, and 6,12-benzo[*a*]pyrene quinones was prepared as published[15] and separated on alumina column, activity grade III, using benzene as solvent.[16]

Results and Discussion

To present the results as briefly and definitively as possible, we will anticipate the conclusions and depict the overall electrochemical reaction scheme in Figure 1. The experimental facts which substantiate each step in the scheme are discussed individually. The overall behavior of BP is identical in the solvent systems acetonitrile, dimethylformamide, propylene carbonate, and nitrobenzene. The individual solvents were used where advantageous for a particular facet of the experimental work.

BP oxidizes at a platinum electrode in all of the solvent systems at about +1.2 V. The cyclic voltammetry (CV) in any of the solvents is similar and Figure 2a in acetonitrile is representative. The initial oxidation step (peak I) at this slow scan rate (3.96 V/min) shows no indication of reverse cathodic current. This could be due to an irreversible electron transfer or to follow-up chemical reactions faster than the potential sweep. It is next shown that the initial oxidation is a simple one-electron transfer followed by a series of rapid chemical and additional electrochemical steps.

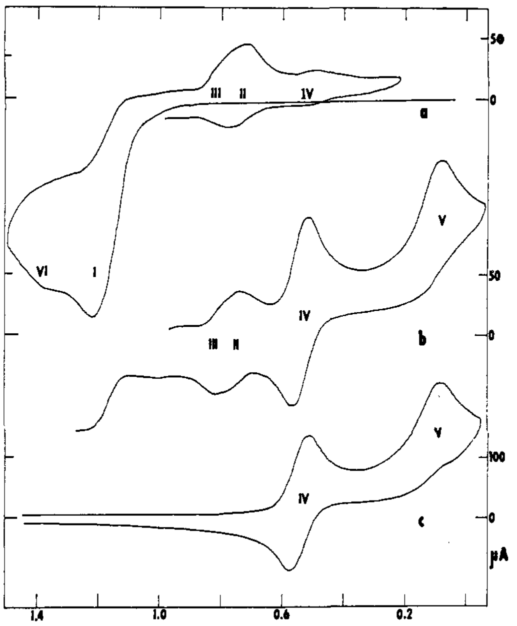

Figure 2. Cyclic voltammetry of benzo[*a*]pyrene in acetonitrile at various stages of electrolysis: (a) before electrolysis; (b) after approximately 3 electrons transferred; (c) end of electrolysis (approximately 5.2 electrons transferred). Controlled potential coulometry at +1.3 V in acetonitrile. BP concentration 9.9×10^{-4} *M*, 0.1 *M* tetraethylammonium perchlorate supporting electrolyte, cyclic voltammetry sweep rate 4 V/min in all cases.

Initial One-Electron Transfer. CV curves in nitrobenzene at sweep rates > 30 V/min and in acetonitrile at > 50 V/min indicate a reduction peak corresponding to the primary oxidation. The separation between anodic and cathodic peaks shows this to be a quasireversible process (corrections for uncompensated resistance were not made so this statement has only qualitative significance).

A comparison of the limiting currents at a rotated disk electrode (RDE) for BP and 9,10-diphenylanthracene was made. The 9,10-diphenylanthracene oxidation is well established as a one-electron transfer.[17] The comparisons are seen in Figure 3 for two solvent systems, nitrobenzene and acetonitrile. Here i_L is the limiting current and $\omega = 2\pi N$, where N is the number of revolutions/second. It is clear from Figure 3 that the BP oxidation in nitrobenzene corresponds very closely to the one-electron oxidation of 9,10-diphenylanthracene except at the slowest rotation rates, where a slight degree of follow-up reactions is indicated for BP. In acetonitrile, BP (Figure 3, curve d) exhibits a considerably higher i_L than 9,10-diphenylanthracene (curve c) at ω slower than *ca.* 250 radians/sec. However, at higher rotation rates the follow-up reactions can be outrun and the BP i_L limits at about 400 radians/sec to the one-electron behavior. The "extra" current for BP is even more evident (Figure 3, curve e) when 1 *M* water is purposely added to the acetonitrile. Here, at the highest rotation rates used, the follow-up reactions cannot be completely outrun.

From the RDE data, the diffusion coefficients of 9,10-diphenylanthracene and BP in acetonitrile were calculated to be 2.12×10^{-5} and 2.18×10^{-5} cm²/sec, respectively. These are in excellent agreement with

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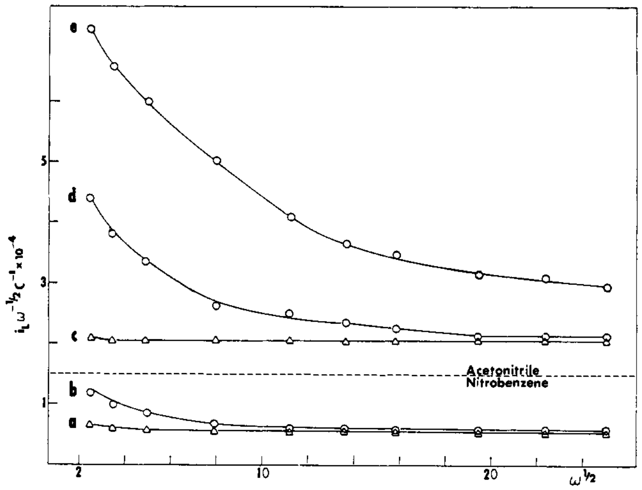

Figure 3. Rotated disk electrode comparisons of benzo[*a*]pyrene and 9,10-diphenylanthracene: curves a, c, 9,10-diphenylanthracene, curves b, d, e, benzo[*a*]pyrene; nitrobenzene solvent for bottom two curves; acetonitrile solvent for top three curves; curve e with 1 *M* water added.

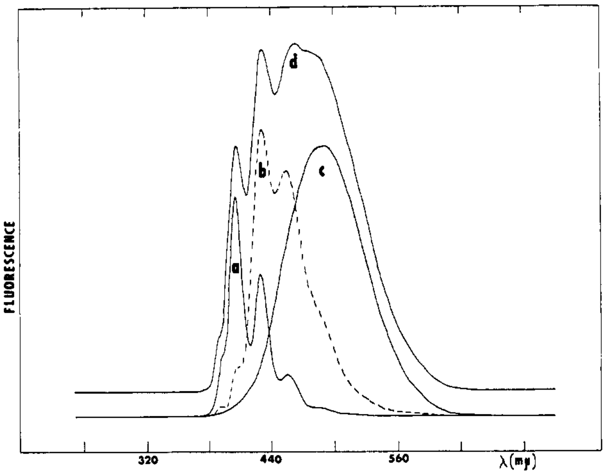

Figure 4. Fluorescence spectra in acetonitrile: (a) benzo[*a*]pyrene; (b) 6-hydroxybenzo[*a*]pyrene; (c) 6,6′-bibenzo[*a*]pyrenyl; (d) aliquot of constant potential electrolysis (+1.3 V) of benzo[*a*]pyrene in acetonitrile.

independent capillary diffusion measurements.[18] (The diffusion coefficients of BP and 9,10-diphenylanthracene vary in the different solvents. This accounts for the different current levels in acetonitrile and nitrobenzene shown in Figure 3.)

The RDE results show the initial oxidation of BP is a one-electron transfer as represented by reaction A in the general scheme of Figure 1. Because of the fast follow-up reactions, no attempt was made to use EPR for detection of the initial BP cation radical.

Benzo[*a*]pyrene Dimer. One of the expected reactions of the BP cation radical is dimerization. The formation of 6,6′-bibenzo[*a*]pyrenyl (BP-dimer) was established *via* fluorescence spectroscopy and separation techniques. Figure 4 shows the fluorescence spectra in acetonitrile of BP itself (curve a) and the authentic, chemically prepared BP-dimer (curve c). BP shows almost no fluorescence emission at about 480 mμ where the dimer fluoresces. To show BP-dimer was formed during constant potential electrolysis of BP, aliquots were taken and their fluorescence spectra recorded. Curve d in Figure 4 shows a typical spectrum from an acetonitrile electrolysis, where the presence of BP-dimer is clearly seen at 480 mμ. In acetonitrile, where the dimer solubility is low, the fluorescence spectra do not show a sharp peak. The dimer spectrum is better defined in propylene carbonate as solvent, but even in the acetonitrile case illustrated, BP-dimer formation is readily established.

Actually, in acetonitrile, much of the BP-dimer coats or films the platinum electrode during electrolysis. If, in a large scale electrolysis, the electrode was removed, washed, dried, and then "extracted" with hot benzene and the solution chromatographed on an alumina column, the BP-dimer could be shown to be a major component of the film by its fluorescence spectrum.

The further oxidation of BP-dimer was established in the following manner. The authentic dimer does not show a discrete oxidation peak up to +2.0 V in any of the solvents. However, all the background currents were higher in the presence of dimer than in its absence. Furthermore, in nitrobenzene where the dimer is most soluble, an ill-defined current hump at *ca.* +1.2 V was obtained. Actual proof of further oxidation of dimer was obtained by following the decay of the dimer fluorescence during controlled potential electrolysis at different potentials in propylene carbonate. In this way it was established that the fluorescence began to decay at about +0.9 V and decreased sharply to zero around +1.1 V. Separate electrolyses of authentic dimer and BP itself were examined in this manner.

This potential range for the BP-dimer oxidation is about the same as that of the parent BP. On the basis of simple HMO calculations for a planar structure one would predict BP-dimer to be about 400 mV more easily oxidized than BP. However, it is clear that the dimer structure would be seriously twisted, which is in accord with the observed oxidation potentials. (BP can be considered as a substituted anthracene and one finds the relative oxidation potentials of anthracene and bianthryl are very close, which is in accord with the present findings.)

A complete lack of absorption and fluorescence spectra following electrolysis of BP-dimer shows it is probably not oxidized to any simple hydroxy or quinoid type compounds. The appearance of a proton reduction wave after electrolysis suggests it undergoes further polymerization type reactions, but the actual products were not identified. Hence, reaction path B in Figure 1 actually contains some further oxidation steps of BP-dimer, but we do not have definitive evidence of the products.

Formation of 6-Hydroxybenzo[*a*]pyrene. The exhaustive electrolysis of BP in all solvents consumes between 5 and 6 e/mol. This high number of electrons cannot be explained by reaction paths A and B (Figure 1) alone. Even with further oxidation of BP-dimer, only 1–2 additional electrons, totaling 2–3 e/mol of BP, would be consumed. Clearly a major portion of BP cation radicals undergo another pathway and this was shown to be a nucleophilic attack by the water naturally present in all of the solvent systems.

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[18] J. Bacon and R. N. Adams, *Anal. Chem.*, in press.

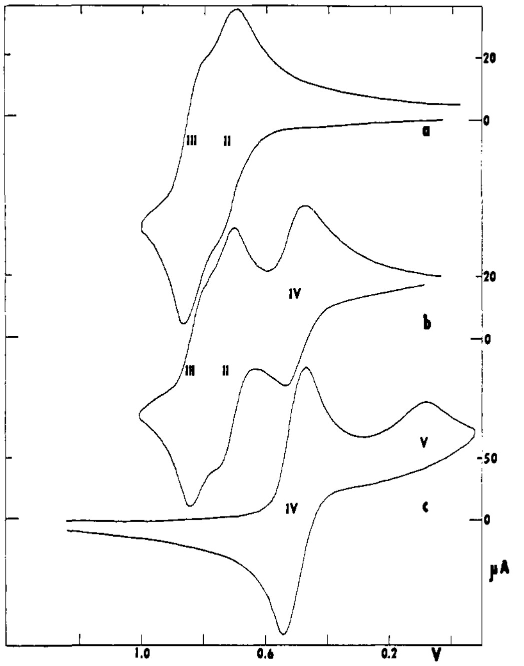


Figure 5. Cyclic voltammetry of 6-hydroxybenzo[*a*]pyrene in acetonitrile at various stages of electrolysis: (a) before electrolysis; (b) after approximately 2 electrons transferred; (c) complete electrolysis (4 electrons transferred). Controlled potential coulometry at +1.0 V, cyclic voltammetry sweep rate 4 V/min in all cases.

According to HMO calculations, the 6 position is by far the most reactive site in the BP cation radical. Nucleophilic interactions with water should produce 6-hydroxybenzo[*a*]pyrene (here abbreviated as 6-OH-BP). The 6-OH-BP should be easier to oxidize than parent BP. Thus further oxidation after the follow-up chemical interaction will contribute more current flow. This was already well illustrated in Figure 3, curve e, where the extra current due to 1 *M* water addition is evident and the follow-up reaction cannot be outrun even at 110 rev/sec at the RDE.

Chemically prepared 6-OH-BP has the CV shown in Figure 5, curve a, as merged peaks II and III. These match well the CV of the follow-up couple produced in the initial oxidation of BP (Figure 2a, peaks marked II and III) suggesting 6-OH-BP is formed. More definitive proof is afforded by the fluorescence spectra of Figure 4. Curve b is that for authentic 6-OH-BP. Curve d, for a controlled potential electrolysis of BP in acetonitrile, shows that, in addition to BP-dimer, 6-OH-BP is formed during the course of electrolysis (see later discussion of this fluorescence spectrum). Thus the sequence A through D of the general scheme in Figure 1 is established. The exact details of the hydroxylation sequence are not elaborated by the present experimental evidence, but step C is consistent with known hydroxylation reactions of hydrocarbons.

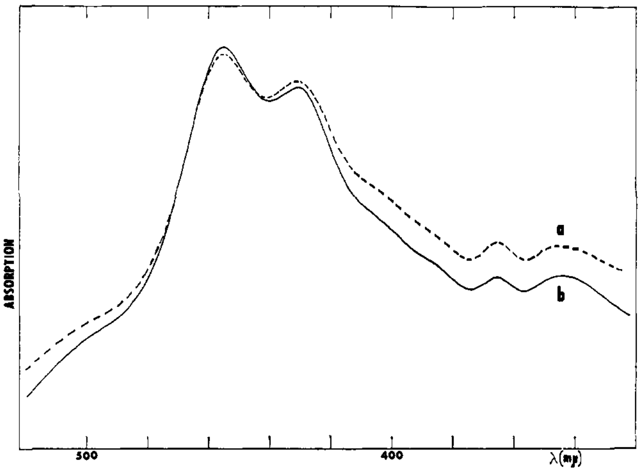


Figure 6. Absorption spectra in acetonitrile: (a) mixture of 1,6-, 3,6-, and 6,12-benzo[*a*]pyrene quinones prepared by classical oxidation; (b) mixture of same quinones prepared by constant potential electrolysis (+1.3 V) of benzo[*a*]pyrene.

The CV of 6-OH-BP (Figure 5a) suggests it undergoes a further two-stage oxidation as indicated in the general scheme by steps E and F. The product of step E is the 6-oxobenzo[*a*]pyrene radical. If 6-OH-BP is electrolyzed in the cavity of the EPR spectrometer, a well-defined EPR spectrum is readily obtained. With its many small, coalesced proton splittings, it has not been possible to completely resolve this spectrum, but there seems little doubt that it is the aforementioned radical species. The second one-electron oxidation, step F, produces the 6-oxobenzo[*a*]pyrene cation (*not a cation radical*). Three of its resonance forms are shown in the general scheme. Further nucleophilic attack of water (hydroxylation) in step G leads to the isomeric dihydroxybenzo[*a*]pyrenes. Since each of the hydroxylated compounds is more easily oxidized than its predecessor, the dihydroxy-BP's will be further oxidized in step H to the corresponding isomeric benzo[*a*]pyrene quinones (BP-quinones). Unequivocal evidence for the formation of these BP-quinones is presented next.

BP-Quinones. After exhaustive controlled potential electrolysis of BP in acetonitrile at +1.3 V, the solution was evaporated to a small volume under vacuum at room temperature and the tetraethylammonium perchlorate precipitated by benzene addition and filtered off. Further evaporation to dryness under vacuum yielded reddish crystals. These were separated on partially deactivated alumina (activity grade III) using benzene. Three fractions were isolated and identified by absorption spectra and melting points as the 1,6-, 3,6-, and 6,12-BP-quinones.[16]

The absorption spectra of the mixture of BP-quinones formed during the electrolysis was compared with that from a chemical oxidation.[15] The latter is known to produce the BP-quinones with a reported isomer ratio of 46.7% 1,6-, 33.3% 3,6-, and 20% of the 6,12-BP-quinone.[16] The absorption spectra of the solutions following electrolytic or chemical oxidation are shown in Figure 6 as curves a and b, respectively. From their similarity it can be concluded that both processes yield very similar ratios of isomeric quinones. The HMO calculations for 6-oxobenzo[*a*]pyrene cations show the three most reactive positions (in order of decreasing reactivity) are 1, 3, and 12. Hence the predicted positions of hydroxylation (step G) agree well with the ratio of BP-quinones obtained in the electrolysis.

Although the isolation and chemical identification of the quinones is ample proof of the overall pathway of steps E through H, it additionally can be shown that the BP-quinones increase in concentration during the controlled potential coulometry of both BP and 6-OH-BP. The quinones are just barely seen, if at all, in the time interval of an initial cyclic polarogram (before controlled potential coulometry). This is somewhat reasonable since they are formed in a secondary follow-up chemical reaction. (Ignoring BP-dimer formation for the moment, step C is the first chemical follow-up process and step G the second.) Additional evidence will be presented later which shows that step G is considerably slower than C.

Thus, in Figure 2a, a single cyclic polarogram of BP before controlled potential electrolysis, shows only a very slight indication of the quinone system as redox couple IV. However, as seen in Figure 2b, after an electrolysis time corresponding to 3 e/mol of BP, there is a large increase in the quinone concentration (peak IV). In addition, the protons released in the overall oxidation can be seen as peak V. After exhaustive electrolysis (5.2 e/mol of BP), Figure 2c shows a further increase in BP-quinones and protons (note current scale for relative peak height increases). Comparable growth of BP-quinone concentrations are evidenced when 6-OH-BP is coulometrically oxidized. Figure 5a shows the cyclic polarograms before electrolysis and curves b and c are after 2 and 4 e/mol, respectively. The increase in peak height of redox couple IV is unmistakeable. Thus, the overall sequence of steps E through H is substantiated by the CV of BP and 6-OH-BP as well as the chemical identification of products.

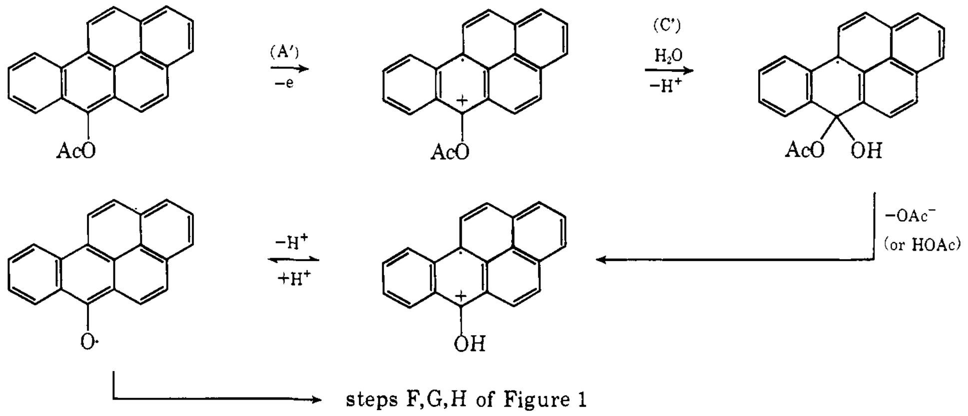
Relative Rates of Chemical Follow-Up Reactions. The first hydroxylation reaction (step C) is fairly rapid since redox couples III and IV appear in the initial cyclic polarogram of BP oxidation as seen in Figure 2a. The second follow-up reaction (step G) is considerably slower, since its oxidation products, the BP-quinone(s) only appear slightly or not at all. This is more evident in the initial cyclic polarogram of 6-OH-BP (Figure 5a) where no quinone couple is seen.

More explicit proof of the relative slowness of step G is contained in the following argument. It is clear from the CV of Figures 2 and 5 that the dihydroxy-BP's are easier to oxidize than 6-OH-BP, which, in turn, is easier to oxidize than the parent BP. Thus, as soon as 6-OH-BP is formed, it should rapidly undergo electro-oxidation in steps E and F. Now, if step G is rapid, the 6-oxobenzo[*a*]pyrene cation (6-O-BP$^+$), which is the final product of steps E and F, should rapidly hydroxylate to the dihydroxy-BP and be further oxidized at the electrode surface to BP-quinone. Thus, the concentration of 6-OH-BP should at all times be very low. It should be impossible to obtain a strong fluorescence spectrum indicating its presence in an aliquot of a controlled potential electrolysis of BP. However, if step G is slow, the oxidation of dihydroxy-BP will be predominantly in the bulk of the solution. As dihydroxy-BP is formed it can be *chemically* oxidized by electro-generated 6-O-BP$^+$ as

$$BP(OH)_2 + 6\text{-O-BP}^+ \longrightarrow BPQ + 6\text{-OH-BP} + H^+$$

Thus, an appreciable "regenerated" concentration of 6-OH-BP can be expected if an aliquot of the controlled potential electrolysis solution of BP is taken for the fluorescence spectrum. On the other hand, if one attempts *in situ* electrolysis of BP directly in the cuvette of a fluorescence spectrometer, any 6-OH-BP would be immediately oxidized at the electrode surface and no 6-OH-BP fluorescence should be obtained. This is exactly what happens experimentally. (The above discussion in no way affects the overall consumption of electrons—it is analogous to the ECC "nuance" of general ECE reactions in electrochemistry.)

Quantitative Product Yields. The controlled potential coulometry of BP cannot be followed in detail because of the two product pathways, one leading to dimer and the other to quinones. The nonintegral value of 5.2 e/mol BP in exhaustive electrolysis does not allow an estimate of the relative amounts of dimer *vs.* quinones formed due to the indeterminate further oxidation of dimer. Dimerization should be absent with the compound 6-acetoxybenzo[*a*]pyrene (6-Ac-BP) and its CV and coulometry were studied in acetonitrile. The CV is almost identical with that of BP itself, with an initial oxidation at *ca.* +1.2 V, and follow-up couples corresponding to 6-OH-BP and BP-quinones. The formation of 6-OH-BP and then its disappearance during controlled potential coulometry can be followed by fluorescence spectra of aliquots of the solution. As expected, no evidence of dimer formations was found. The complete oxidation required almost exactly 4 e/mol of 6-Ac-BP, leading exclusively to BP-quinones. This is consistent with the scheme shown.



The initial one-electron oxidation of 6-Ac-BP followed by hydroxylation (steps marked A′ and C′) are perfectly analogous to steps A and C of Figure 1 for BP itself. In this case, however, the hydroxylated intermediate, rather than losing a proton, loses an acetate ion and it is thus two electrons less "rich" than in the case with BP as initial substrate. Hence, the intermediate does not undergo the oxidation steps D and E, but arrives at the 6-oxobenzo[*a*]pyrene radical stage "directly." (Either acetate ion or acetic acid may be lost, but the details of the acid–base relationships are only speculative.)

In either event, the 6-oxobenzo[*a*]pyrene radical now follows the previous BP pathway F, G, and H, consuming 3 more e/mol of 6-Ac-BP and forms exclusively quinones. The total electron consumption should be 4 e/mol of 6-Ac-BP, as found experimentally. The observed fluorescence spectrum of 6-OH-BP (which is actually never formed in steps A′, C′, etc.) is again explicable in terms of the slowness of reaction G. After exhaustive electrooxidation of 6-Ac-BP, if the potential is reversed, and an exhaustive reduction carried out, 2 e/mol are required. This is perfectly consistent with quantitative reduction of quinones formed in step H.

Knowing that 6-Ac-BP yields exclusively BP-quinones, a comparison can be made of the relative quantities of quinones formed in the exhaustive controlled potential electrolyses of equivalent amounts of BP and 6-Ac-BP. Such a comparison for the peak heights of the quinones obtained from BP and 6-Ac-BP showed *ca.* 82% BP is converted to BP-quinones. Incidentally, the exhaustive electrolysis of 6-OH-BP consumes 4 e/mol, yielding all quinones. This result is again consistent with the general scheme.

Comments on CV of BP-Quinones. Anyone familiar with the general redox properties of quinones in nonaqueous media will presumably question the CV in Figures 2 and 5, where the quinones are seen as a quasi-reversible two-electron process (peaks IV) at the relatively positive potential of *ca.* +0.5 V. Authentic BP-quinones reduce in two reversible, one-electron peaks *ca.* −0.5 and −0.9 V in acetonitrile, which is common for quinones. However, in the presence of excess protons, these peaks are completely obliterated and shifted to the single peak at +0.5 V. Since 6 protons/mol of BP are released, the quinone single peak behavior is seen in the CV of BP. The CV of authentic BP-quinones can be made to match that of Figures 2 and 5 by addition of the correct amount of protons. (All three quinone isomers are reduced at about the same potential and are essentially indistinguishable in the absence or presence of protons and the term BP-quinone(s) is used here collectively.) The details of these protonation interactions and their effect on the CV of the BP-quinones are not of major importance to the present results and will be reported elsewhere soon.[19]

One minor point in the scheme remains obscure. This concerns the ill-defined peak VI (Figure 2, curve a), which follows the initial oxidation of BP. This peak is eliminated by addition of water. It most likely corresponds to the formation of BP dication. Alternatively, it could represent oxidation of the product from solvent interaction with the BP cation radical. We are unable to distinguish between these possibilities. Either interpretation would only change the general scheme in steps C and D. In keeping with this, controlled potential electrolysis at potentials more or less anodic than peak VI give the same intermediates, the same final products, and the same number of total electrons transferred.

The results presented herein represent, we believe, the most extensive study to date of the anodic oxidation of an aromatic hydrocarbon. Individual steps of the proposed scheme are authenticated by independent spectroscopic and chemical identifications of products and are consistent with the short term cyclic voltammetry and larger scale electrolyses. This reaction scheme should provide a framework for evaluation of other hydrocarbon electrooxidations. (Analogous results are already indicated for the electrooxidation of perylene and benz[*a*]anthracene.)

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[19] Lj. Jeftić and G. Manning, manuscript in preparation.