Organic and Biological Chemistry

Controlled Potential Oxidation of Anthracene in Acetonitrile. II

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Abstract: Bianthrone is isolated from saturated solutions of anthracene in dry acetonitrile (less than 30 m*M* in water) which have been electrolyzed at controlled anode potential of +1.0 V (*vs.* Ag|0.1 *M* Ag^+). Coulometric data show that the electrode process(es) accounts for two of the three electrons lost per anthracene molecule. Evidence suggests an "ECEC" reaction sequence, *e.g.*, monovalent carbonium ion radical formed at the anode, hydrolysis, and further electrochemical oxidation with loss of proton(s) to give 9-anthranol which converts to the keto form and is (air) oxidized to bianthrone. When the electrolysis solution contains excess water or when the electrolysis is performed at anode potentials near +1.3 V, coulometric data, although erratic, show that three or more electrons per anthracene molecule are involved in the electrode processes; anthraquinone, the usual product of anthracene oxidations in aqueous media, is also obtained from the electrolysis solution.

Lund electrolyzed acetonitrile solutions which contained anthracene plus pyridine.[2] The half-wave potential ($E_{1/2}$) for the anthracene oxidation wave was less anodic (by 50–100 mV) in the presence of pyridine. Moreover, when these solutions were exhaustively electrolyzed at controlled anodic potential, coulometric data revealed that two electrons were lost per anthracene molecule; the electrolysis product isolated was the 9,10-dipyridinium perchlorate salt of anthracene. Lund concluded that the initial electrolysis step was the reversible two-electron oxidation of an anthracene molecule and that nucleophilic attack by pyridine on the divalent carbonium ion radical followed.

An earlier report from these laboratories described an attempt to extend Lund's approach to the electrolytic synthesis of other substituted hydrocarbons.[3] When anthracene was exhaustively electrolyzed at controlled anode potential in the presence of ethanol and under conditions otherwise identical with those used by Lund,[2] bianthrone (I) was the main electrolysis product. It was speculated that the initial electrode reaction was the loss of one π electron from anthracene, followed by coupling and further oxidation of the dimer. A reaction sequence of this kind had been suggested earlier by Lund.[2] Recent evidence lends further support to the validity of an initial one-electron anode reaction in the electrochemical oxidation of anthracene in acetonitrile, in nitrobenzene, and in methylene chloride.[4–6]

Peover and White concluded from rapid-scan cyclic voltammetric data that the electrochemical oxidation of anthracene in acetonitrile fits the so-called ECE scheme, *i.e.*, a (one-electron) electrochemical oxidation, followed by a chemical reaction, and then another (one-electron) electrochemical oxidation. The lifetime of the monovalent cation radical formed in the first anodic step was reported as a few milliseconds and the product of the follow-up irreversible chemical reaction is electroactive at the anode at potentials close to the $E_{1/2}$ of anthracene (*ca.* +0.9 V).[4] In this report additional data on the controlled potential oxidation of anthracene in acetonitrile are discussed in terms of the over-all reaction sequence which is more complex than ECE for an exhaustive electrolysis.

Experimental Section

Apparatus. Polarograph. A Sargent Model XV polarograph was used to record current–voltage curves. The electrodes were a silver wire (24 gauge) cathode coiled in a helix around a piece of 6-mm glass tubing into which a platinum wire was sealed. The exposed surface area of the platinum anode was *ca.* 0.1 cm^2; the anode was rotated at 600 rpm. The resistance of this cell was *ca.* 60 ohms; polarographic data were not corrected for the *iR* drop. All potentials are given *vs.* Ag|Ag^+ in 0.10 *M* silver perchlorate–0.5 *M* sodium perchlorate.

Potentiostat. The Kelly, Fisher, Jones controlled potential coulometric titrator previously described[3] was used for the exhaustive electrolysis experiments. The total electrolysis current passed in the exhaustive electrolyses was determined in two ways: by the gain in weight of the silver cathode[7] or by a graphic current–time integration method. A 9.70-ohm resistor was added in series with the electrolysis cell. The voltage drop across this resistor was recorded throughout the electrolysis on a Sargent Model SR (125 mV) strip-chart recorder (chart drive speed 0.10 in./min). Appropriate background corrections were made, and this coulometer was calibrated by generating known amounts of iodine from potassium iodide–potassium nitrate solutions. Replicate determinations of the total current by the two methods agreed to within 4%.

The solution to be electrolyzed (*ca.* 30 ml) was contained in one compartment of an H cell fitted with ground-glass joints. The working electrode was a platinum foil anode with approximately 6 cm^2 (projected) surface area. The functions of the auxiliary (or counter) and reference electrodes were combined in a silver

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Table I. Electrolysis of "Dry" Solutions at Anode Potential +1.0 V (*vs.* Ag|Ag$^+$)

Run	Anthracene concn, m*M*	Mole ratio,[a] ROH:anthracene	Total current[b] Ag	Total current[b] Chart	H_2O in anolyte at Start, m*M*	H_2O in anolyte at Finish, m*M*
13	10	45.0 a	2.12	...	27	46
20	40	11.2 a	2.14	...	40	45
21	10	45.0 a	1.90	...	18	22
30	10	45.0 a	2.04	2.07	16	23
31	10	45.0 a	2.07	2.05	15.5	16
33	10	45.0 a	2.08	2.10	19	20
22	10	o	1.99	...	26	30
23	1	o	2.00	2.00	24	24
26	10	45.0 b	2.01	2.03	15	20
28	10	45.0 c	2.05	2.13	14	21

[a] a, ethanol; b, 2-methylpropanol-1; c, 1-butanol; o, no alcohol added. [b] Expressed as Faradays/mole of anthracene.

wire cathode (250 mm of 16 gauge, coiled into a helix of *ca.* 20-mm diameter); this electrode occupied a compartment in the H cell separate from the working (anthracene) solution. Migration of the products of the electrolysis into this compartment was minimized by keeping the height of the catholyte slightly greater than that of the anolyte and by the fine-porosity fritted-glass disk in the connecting arm of the H cell. For some runs a methyl cellulose plug was added to the connecting arm to reduce further the migration of the solution between the compartments.[8] The catholyte was acetonitrile, 0.1 *M* in silver perchlorate and 0.5 *M* in sodium perchlorate. The resistance of this cell was *ca.* 650 ohms when the methyl cellulose plug was used and *ca.* 500 ohms when the plug was not used.

Spectrometers. Ultraviolet–visible absorption spectra were recorded on a Beckman Model DK-2 spectrophotometer. Infrared spectra were obtained on a Baird-Atomic Model KM-1 spectrophotometer (sodium chloride optics).

Gas Chromatograph. Research Specialities Model 600 and Perkin-Elmer Model 800 with flame ionization detectors and a 3% SE-30 on Gas Chrom Z (100–120 mesh) column (0.1 × 72 in.) operated at 230° or at 310° was used. At the lower temperature 9-anthrone and anthracene could be detected. At 310° bianthrone and anthraquinone could be detected.

Reagents and Solutions. Anthracene (Matheson Coleman and Bell) was recrystallized from absolute ethanol (mp 216–217°). Anthraquinone (Eastman), 9-anthrone (Eastman), and bianthrone (K & K Bianthronyl, No. 2295) were used as obtained. Chemically pure sodium perchlorate (Amend Drug and Chemical Co.) was dried in a vacuum oven at 145° for 24 hr to remove water. Karl Fischer analysis of the dried salt[9] showed less than 0.05% water. The dried product was stored over phosphorus pentoxide in a vacuum desiccator. Reagent grade silver nitrate (Matheson Coleman and Bell) was air dried at 130° for 2 hr and then fused at 230–240° for 30–45 min; Karl Fischer analysis showed less than 0.2% water.

Acetonitrile (Eastman, Practical Grade) was purified by distillation from phosphorus pentoxide (*ca.* 10 g/l. of acetonitrile); Karl Fischer analysis showed less than 1 m*M* water in the distilled solvent. More thorough purification of the solvent[10] appeared to have no effect on our results. A 0.20 *N* silver perchlorate solution was prepared carefully using Lund's method.[2] The solution was made 0.5 *N* in sodium perchlorate and used both for the voltammetric and coulometric studies; analysis showed water content 11–30 m*M*.

Procedures. Solutions were deaerated before electrolysis by bubbling for 30 min with high-purity nitrogen (McGraw-Edison Co., West Orange, N. J.) which had been passed through two drying tubes tightly packed with anhydrous magnesium perchlorate, a scrubbing tower containing concentrated sulfuric acid, and another filled with freshly distilled, dry acetonitrile. A nitrogen atmosphere was maintained over the electrolysis solution throughout the run. The maximum increase in water content of the solution was *ca.* 10 m*M* in 24 hr. If bubbling with nitrogen continued during the electrolysis the water content increased by about 200 m*M* after 24 hr. Some solutions were preelectrolyzed at *ca.* +1.6 V for *ca.* 30 min prior to addition of the anthracene and the alcohol with no apparent effect on the results of the electrolysis.

After completion of the electrolysis (when the current had decreased to residual current levels) the anolyte was transferred to a (100 ml) one-necked flask and the solvents were removed by evaporation (in a vacuum) on a Roto-Vap at less than 40°.[11] The residue A was extracted with two 30-ml portions of carbon tetrachloride; these were combined and the solvent evaporated as before giving residue B which contained the bulk of the electrolysis products. Additional product could be obtained by a second extraction of residue A with two 30-ml portions of absolute ethanol and recovering solutes as before. Product identifications were based on melting points and ultraviolet–visible and infrared spectra.

Results

The $E_{1/2}$ for the oxidation wave of anthracene under the present conditions was +0.88 V.[3] The alcohols used are not oxidized at potentials less anodic than +1.2 V. The supporting electrolyte was discharged at potentials more anodic than *ca.* +1.7 V.

Bianthrone was the major product isolated after exhaustive electrolysis, at controlled anode potential of +1.0 V, of acetonitrile solutions of anthracene (1.0–40 m*M*) when the water content did not exceed *ca.* 50 m*M* throughout the electrolysis.[12] Moreover, coulometric data (11 runs) showed an average of 2.05 ± 0.06 electrons lost per anthracene molecule. Identical results were obtained when no nucleophile was present in the electrolysis solution as well as in the presence of ethanol, 1-butanol, 2-butanol, 2-methylpropanol-1, or 3-methylbutanol-1. The same results were obtained for ethanol-to-anthracene mole ratios from 0 to 45 (Table I). Analysis by gas–liquid partition chromatography of samples taken from the electrolysis solution near the end of several runs showed the presence of large amounts of 9-anthrone; there was no indication that bianthrone was present in large quantities.

Anthraquinone (as well as bianthrone) was isolated from solutions which had been electrolyzed at *ca.* +1.4 V and also from solutions containing relatively large amounts of water, *i.e.*, more than *ca.* 70 m*M*. Large amounts of anthraquinone were obtained when the water content of the electrolysis solution was increased. In all cases more than two electrons (usually between three and four) per anthracene molecule were lost in the electrode reaction(s); there were wide varia-

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(11) Attempts to separate the products by silica column chromatography were not successful; anthracene is oxidized to anthraquinone (R. M. Roberts, C. Barter, and H. Stone, *J. Phys. Chem.*, **63**, 2077 (1959)), and it is suspected that anthrone and bianthrone may also be oxidized.

(12) Initially these solutions were supersaturated in anthracene; the excess dissolved as the electrolysis progressed.

Table II. Electrolysis at Anode Potentials above +1.0 V (*vs.* Ag|Ag$^+$) and Electrolysis of "Wet" Solutions

Run	Anthracene concn, m*M*	Mole ratio EtOH:anthracene	Anode potential, V	—Total current^a— Ag	Chart	H_2O in anolyte at Start, m*M*	Finish, m*M*	Products^b
24	10	0	+1.4	3.05	3.26	17	28	9
25	10	270	+1.4	4.13	4.39	18	18	>9
27	10	45	+1.4	3.20	3.43	15	37	. . .
32	10	0	+1.4	3.55	3.72	18	28	4
19	1.0	450	+1.0	3.31	. . .	40	69	. . .
29	10	0	+1.0	4.46	4.65	450 (added)		1
18	10	0	+1.0	2.73	. . .	37	256	. . .

[a] Expressed as Faradays/mole of anthracene. [b] Moles of bianthrone/mole of anthraquinone. Mass spectra (kindly provided by Dr. John T. Walsh) on samples of products from several of these runs at +1.4 V showed low-intensity peaks at (*m*/*e*) 210 and 222. These results might indicate formation of very small amounts of the 9,10-dihydroxy and 9-ethoxy derivatives of anthracene.

tions among these coulometric data. The identity and the amounts of added nucleophile appeared to have no effect on the general results of these electrolyses (Table II), although ethanol is oxidized at +1.4 V.

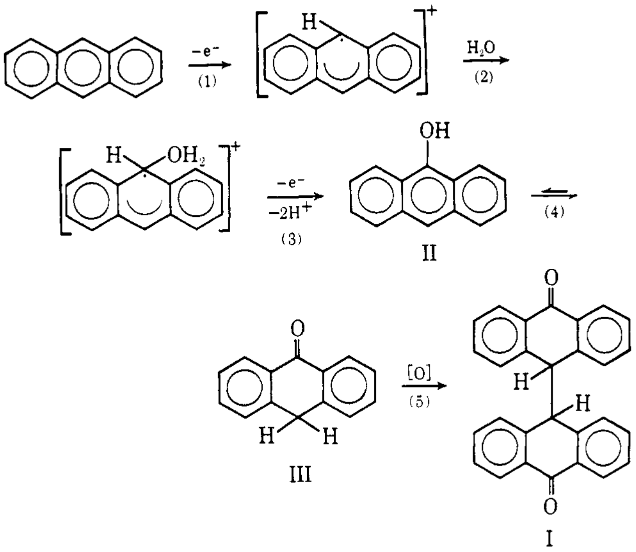
Discussion

Oxidation of anthracene to bianthrone involves loss of three electrons from each anthracene molecule. However, the coulometric data reveal that only two electrons are lost electrochemically when anthracene is oxidized at +1.0 V in "dry" acetonitrile. Several reaction pathways which involve two electrons in electrochemical oxidation(s) plus a one-electron oxidation in a purely chemical reaction and which are otherwise consistent with these results can be written. Although the actual pathway cannot be determined unequivocally from these results, several factors emerge which are of interest and importance to the ultimate elucidation of the over-all mechanism for the electrochemical oxidation of anthracene in acetonitrile; some of these considerations may also be useful for interpreting results of exhaustive electrolysis of other aromatic hydrocarbons in this and in other solvents.

The initial step is an electrolytic oxidation of anthracene; this may be a one- or a two-electron process. As noted above recent studies using rapid-scan cyclic voltammetry and electron spin resonance indicate that the initial step in the electrochemical oxidation of anthracene in acetonitrile appears to be a one-electron reaction.[4-6]

The (first) follow-up chemical reaction is likely one of the following: (1) dimerization of carbonium ion radicals formed at the anode, (2) coupling of a carbonium ion radical and an (unoxidized) anthracene molecule, or (3) reaction of the carbonium ion radical with the solvent or with water (even the most anhydrous solutions were at least 16 m*M* in water). Because no nitrogen-containing aromatic product was detected, reactions of the carbonium ion radicals with acetonitrile are not considered further.[13,14]

Hydrolysis of carbonium ion radicals is probably an important reaction in these systems regardless of whether hydrolysis preceeds or follows dimerization.[15] If hydrolysis occurs before dimerization and is followed by further oxidation and loss of two protons, 9-anthranol (II) would be produced. This compound would not persist in the electrolyte because in polar solvents the keto–enol equilibrium, which is rapidly established, greatly favors the other isomer, 9-anthrone (III).[16,17] Conversion of 9-anthrone to bianthrone (I) is easily effected by mild oxidizing agents.[18-20]



In the solvent-supporting electrolyte system used in this work, 9-anthrone did not show an anodic (polarographic) wave. Attempts to electrolyze these solutions at an anode potential of +1.0 V were unsuccessful: currents at residual levels only were observed. Moreover, only 9-anthrone was detected in the electrolysis solution by glpc; however, bianthrone was also found when this electrolysis solution was carried through the usual procedure for isolating the electrolysis products.

On the basis of these and previously reported results as well as the above considerations, a reasonable sequence of reactions for the "electrochemical" oxidation of anthracene to bianthrone in acetonitrile containing small amounts of water (our "dry" conditions) at a controlled anode potential of +1.0 V is: (1) E (reaction 1); (2) C, hydrolysis (reaction 2); (3) EC or CE, oxidation–deprotonation (reaction 3); (4) C, dimerization, *i.e.*, chemical oxidation (reaction 5).

It is of interest to note that if a second hydrolysis step occurred before dimerization of 9-anthrone, the

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product, 9,10-dihydroxyanthracene, would be very readily oxidized to anthraquinone.[21–23] Thus, it seems that this alternative is not an important one in the reaction sequence occurring in the drier electrolysis solutions. It may, however, account for the fact that anthraquinone was obtained in appreciable amounts from electrolysis solutions which contained greater amounts of water even when the electrolysis was performed at an anode potential of +1.0 V. Apparently when the water content of the electrolysis solution is increased, the rate of the second hydrolysis reaction may be enchanced sufficiently to compete effectively with the dimerization step. A somewhat similar situation has been described by Mann and O'Donnell.[15] Anthraquinone is the principal product of the oxidation of anthracene in water solution, either by chemical or by electrochemical means.[24]

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Molecular Asymmetry. VIII.
trans-Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene[1]

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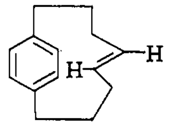
Abstract: *trans*-Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene (**1**) has been synthesized by reduction of *trans*-bicyclo-[8.2.2]tetradeca-5,10,12,13-tetraene-4,7-dione (**2**) with an excess of lithium aluminum hydride and aluminum chloride in a 1:3 ratio. Platinum complexes of the olefin **1** containing optically active α-methylbenzylamine were prepared. Fractional crystallization to constant rotation of the complex containing (*R*)-(+)-α-methylbenzylamine afforded (−)-*trans*-dichloro(*trans*-bicyclo[8.2.2.]tetradeca-5,10,12,13-tetraene)(α-methylbenzylamine)platinum(II) (**4a**), $[\alpha]^{25}$D −35.1°. Fractional crystallization of the enantiomeric complex containing (*S*)-(−)-α-methylbenzylamine gave complex **4b**, $[\alpha]^{25}$D +37.7°. Decomposition of partially resolved complex **4a** with aqueous sodium cyanide at room temperature afforded optically inactive olefin **1**. This observation suggests that the molecule is undergoing spontaneous racemization at this temperature.

The optical instability of *trans*-cyclononene and *trans*-cyclodecene[3] led to a consideration of suitably substituted *trans*-cyclic olefins which would possess molecular dissymmetry and which would be capable of existence as stable optically active enantiomers.[4] *trans*-Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene (**1**) seemed a logical choice. With only eight carbon atoms bridging the *para* positions of the benzene ring, the molecule is highly strained, and rotation of the *trans*-olefinic bond with respect to the rest of the ring would be expected to be severely hindered. The olefin **1** was obtained by reduction of *trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene-4,7-dione (**2**) with an excess of lithium aluminum hydride and aluminum chloride in a 1:3 ratio.[5–7] The *trans*-enedione **2** results from oxidative cleavage of the furan ring of 15-oxatricyclo-[8.2.2.1^{4,7}]pentadeca-4,6,10,12,13-pentaene (**3**), the product of cross-dimerization of *p*-xylylene and 2,5-dihydro-2,5-dimethylenefuran.[8,9]



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[2] (a) Deceased, June 4, 1966; (b) National Institutes of Health Predoctoral Fellow, 1963–1966; to whom inquiries may be addressed at Hoffmann-La Roche, Inc., Nutley, N. J. 07110.

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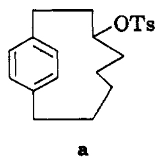
[9] The olefin **1** has been described as the product of solvolysis of bicyclo[8.2.2]tetradeca-10,12,13-trien-4-ol *p*-toluenesulfonate (a) in acetic acid.[8b]



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