

Electroorganic Preparations

IV. Oxidation of Aromatic Hydrocarbons

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It is shown that aromatic hydrocarbons can be oxidized at a platinum electrode in acetonitrile containing sodium perchlorate. The half-wave potentials of the voltammetric curves are found to be directly related to the wave numbers of the p -bands in the ultraviolet absorption spectra of the hydrocarbons. The reaction product of the controlled potential oxidation of anthracene in acetonitrile containing pyridine and sodium perchlorate is shown to be 9,10-dihydroanthraquinylidipyridinium diperchlorate.

Electrolytic oxidation of aromatic hydrocarbons¹ yields mostly a mixture of hydroquinones, quinones, and acids, when the current density is used as the controlling factor. No controlled potential oxidations of aromatic hydrocarbons have been reported.

In the second part of this series² it was shown that some aromatic alcohols by controlled potential oxidation in acetonitrile containing sodium perchlorate and pyridine could be oxidized to the aldehydes and it was postulated that the first step of the oxidation in this inert medium was a loss of electrons from the aromatic system.

This investigation is concerned with the controlled potential oxidation of some aromatic hydrocarbons and their derivatives. The technique used to determine the optimal potential for the oxidation is the same as that used in Part II². The current-potential curve of the compound in acetonitrile is determined with a platinum microelectrode and the oxidation is performed at a potential about 0.15 V more positive than the half-wave potential of the compound in the medium used.

VOLTAMMETRIC INVESTIGATION

In Table I are compiled the results of the voltammetric investigation. In column 1 are given the compounds, in column 2 the wave numbers of the first p -band in their ultraviolet spectrum as defined by Clar³. The wave numbers were obtained from Clar³. Most of the spectra have been

Table 1. Half-wave potentials of the investigated compounds in unbuffered acetonitrile containing 0.5 M sodium perchlorate measured against the 0.1 N silver ion/silver electrode in acetonitrile.

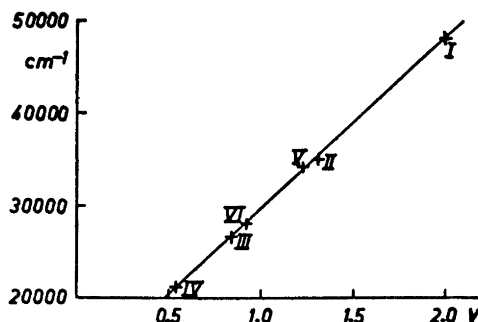
Compound	wave number cm^{-1}	$E_{1/2}$ V	shape
Benzene	48 100	2.00	deformed
Naphthalene	35 090	1.31	nearly normal
Anthracene	26 700	0.84	normal
Tetracene, 1. wave	21 230	0.54	normal
2. wave		1.20	normal
5,12-Dihydrotetracene		1.16	normal
Phenanthrene	34 190	1.23	nearly normal
1,2-Benzanthracene	27 860 *	0.92	normal
1,2,5,6-Dibenzanthracene, 1. wave	28 490 *	1.00	normal
2. wave		1.26	normal
Chrysene	31 350	1.13	normal
Pyrene, 1. wave	29 990	0.86	normal
2. wave		1.12	deformed
Benzo- <i>a</i> -pyrene	26 010	0.76	deformed
Biphenyl	40 000	1.48	deformed
Bianthryl, 1. wave		0.87	normal
2. wave		1.2	drawn out
Indene		1.23	normal
Fluorene	38 310	1.25	deformed
Fluoranthene	27 890	1.18	deformed
Toluene		1.93	deformed
Acenaphthene		1.11	deformed
Retene		1.18	normal
9,10-Dimethylanthracene		0.65	normal
Methylcholanthrene		0.69	normal
α -Nitronaphthalene		1.62	deformed
9-Nitroanthracene		1.25	normal
9-Anthrylpyridinium perchlorate		1.20	normal
9-Bromoanthracene, 1. wave		0.99	normal
2. wave		1.48	normal
9,10-Dibromoanthracene, 1. wave		1.15	normal
2. wave		1.47	normal
(9-Bromo-10-anthryl)pyridinium perchlorate		1.47	normal
Aniline		0.65	normal
Anisol		1.35	normal

* The spectrum measured in benzene solution.

measured in alcohol, but those marked with an asterisk were measured in benzene. The wave numbers used in Fig. 1 were, for comparative purposes, corrected to ethanol by the relationship: ν (ethanol) = ν (benzene) + 300 cm^{-1} , which is characteristic of *p*-bands. In column 3 are compiled the anodic half-wave potentials corrected for *iR*-drop in the solution measured against the 0.1 N silver ion/silver electrode, and in column 4 the shape of the voltammetric curve.

As the half-wave potentials of the compounds depend upon the surface of the microelectrode and the reaction products often alter the surface slightly

Fig. 1. The anodic half-wave potentials of some acenes and phenes plotted against the wave number of the first p -band in their ultraviolet absorption spectrum in alcohol. Benzene (I), naphthalene (II), anthracene (III), tetracene (IV), phenanthrene (V), 1,2-benzanthracene (VI).



the half-wave potentials are only reproducible within about 0.03 V although a standard procedure of wiping off the electrode before the measurement was used.

DISCUSSION

The cathodic half-wave potentials at the dropping mercury electrode of aromatic hydrocarbons ⁴⁻⁸ have been related to wave-mechanical calculations ^{5,8} and to absorption spectra ^{4,6,7}. It has been shown ⁶ that in a series of related hydrocarbons the half-wave potentials are proportional to the wave number of the first p -band as defined by Clar ³ in the ultraviolet absorption spectrum of the hydrocarbon following the equation $E_{\frac{1}{2}} = a + b\nu$, where a and b are constants and ν the wave number of the first p -band. When the wave numbers are replaced by the corresponding energies in electron volts, the slope ($\Delta E_{\nu} / \Delta E_{\frac{1}{2}}$) has been predicted ⁴ to be two.

As shown in Fig. 1 a similar relation is found between the wave number of the first p -band and the anodic half-wave potential at a platinum micro-electrode, $E_{\frac{1}{2}} = 0.543 \times 10^{-4}\nu - 0.61$, and it seems reasonable to expect that there in a series of related hydrocarbons would be a relation between the energy required to excite an electron corresponding to a defined band in the spectrum and the energy necessary to remove an electron completely from the aromatic system.

It was attempted to correlate the anodic half-wave potentials of a series of acenes with their *para*-localization energy as computed by Brown ⁹, but only a semi-quantitative accordance was found.

When the resonance system of a benzene ring in a polynuclear aromatic hydrocarbon loses two electrons the system acts as if the loss is restricted to a single benzene ring and the remaining separated resonance systems are apparently only affected to a minor degree. Thus tetracene yields a second wave at about the same potential as does 5,12-dihydrotetracene and both potentials are of the value which would be expected for a 2,3-dialkyl naphthalene.

The qualitative influence of a substituent on the half-wave potential can be predicted from its electron-attracting or electron-releasing properties as long as the steric circumstances permit the expected interaction between the substituent and the nucleus. An electron-releasing group as the methoxy

group or the amino group lowers the half-wave potential whereas an electron-attracting group as the nitro group or the quaternary ammonium group raises the half-wave potential in comparison with the unsubstituted hydrocarbon. A qualitative connection between the influence of a substituent on the half-wave potential and its σ -value as defined by Hammett was found, but no quantitative connection was detected.

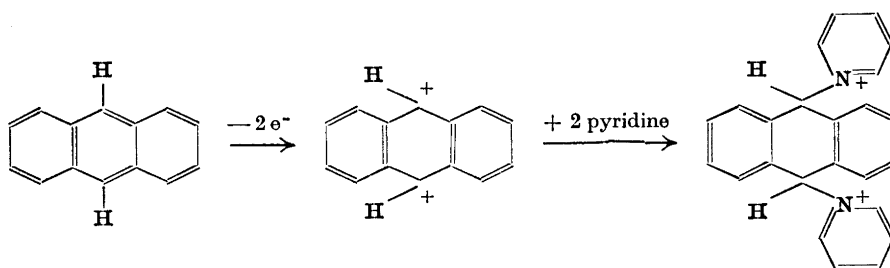
In an attempt to find the reason why some compounds yield deformed waves whereas other produce normal waves it is interesting to note the difference between indene and fluorene as indene yields a normal wave whereas fluorene produces a pronounced deformed wave. As will be shown in the preparative oxidation, anthracene yields in the presence of pyridine a product which is a derivative of dihydroanthracene. Assuming a similar reaction path in the oxidation of indene and fluorene the analogous oxidation product of indene would be a derivative of indane and would very likely be a stable compound, whereas a derivative of dihydrofluorene would be expected to be very unstable and to polymerize to a more or less defined product, in agreement with the fact that the reaction product covers the electrode with a black, insoluble layer which insulates the electrode from the solution.

The same considerations can be applied to other compounds giving deformed waves as benzene, diphenyl, fluoranthene and benzpyrene. In all cases the dihydro derivatives are unstable compounds. Naphthalene gives a slightly deformed wave and correspondingly dihydronaphthalene is only moderately stable.

The hydrocarbons which give a Diels-Alder adduct produce normal waves and there is a qualitative connection between the rate of formation of such adducts and the anodic half-wave potentials in such a way that the hydrocarbons having the lowest half-wave potential react most readily with maleic anhydride⁹. The presence of methyl substituents in the meso positions of anthracene lowers the half-wave potential and increases the rate of the addition of maleic anhydride whereas it decreases the percentage adduct in the equilibrium mixture of anthracene derivative and maleic anhydride¹⁰.

As may be expected, there is a qualitative connection between the anodic half-wave potentials of the acenes and the tendency to form photo oxides. The influence of substituents is mostly the same in both cases, meso methyl groups greatly facilitate the photochemical addition of oxygen and lowers the half-wave potential. 9,9'-Bianthryl, however, forms no photo oxide, whereas it is oxidized at the anode. The half-wave potential is not, however, as low as might be expected from the analogy between benzene-diphenyl and anthracene-9, 9'-bianthryl substantiating the assumption that the plane of one of the anthracene molecules forms an angle of nearly 90° with the plane of the other anthracene molecule in 9,9'-bianthryl¹¹.

The first step in the oxidation is probably a localization of two π -electrons either at the same carbon atom or at two carbon atoms due to the attraction of the positive electrode. In either case they are extracted from the aromatic resonance system leaving a divalent carbonium ion. In the case of anthracene the electron deficiency is localized most of the time in the 9 and 10 positions. In presence of an electron donor as pyridine the pyridine donates its unpaired electrons to the carbonium ion thus forming a pyridinium ion:



The compound thus formed contains only isolated benzene rings which further are somewhat deactivated by the presence of the pyridinium groups and the compound is therefore not further attacked anodically at the potential used for the oxidation of anthracene. If the oxidation had consisted of a dimerization to 9,9'-bianthryl a further oxidation of the reaction product would be expected.

The addition of anhydrous perchloric acid in acetonitrile does not change the anodic half-wave potentials of the hydrocarbons, whereas the presence of pyridine lowers the half-wave potentials from 0.05—0.1 V. This can be explained by assuming the electron transfer to be a reversible reaction. In the presence of pyridine the concentration of the carbonium ion would be very much lower than in the absence of an electron donor, and the measured half-wave potential is, therefore, lowered. As hydrogen ions are not involved in the oxidation the addition of hydrogen ions is of no effect.

In view of the fact that the anodic half-wave potentials of the aromatic carbinols mostly differ only about 0.1 V from the half-wave potentials of their parent compounds (α -naphthyl carbinol 1.25 V, naphthalene 1.31 V; anisyl alcohol 1.22 V, anisol 1.35 V; cinnamyl alcohol 1.36 V, methyl styrene 1.47 V) it seems likely to assume that the first step in this case also is a loss of two electrons from the resonance system as postulated in Part II².

PREPARATIVE OXIDATION

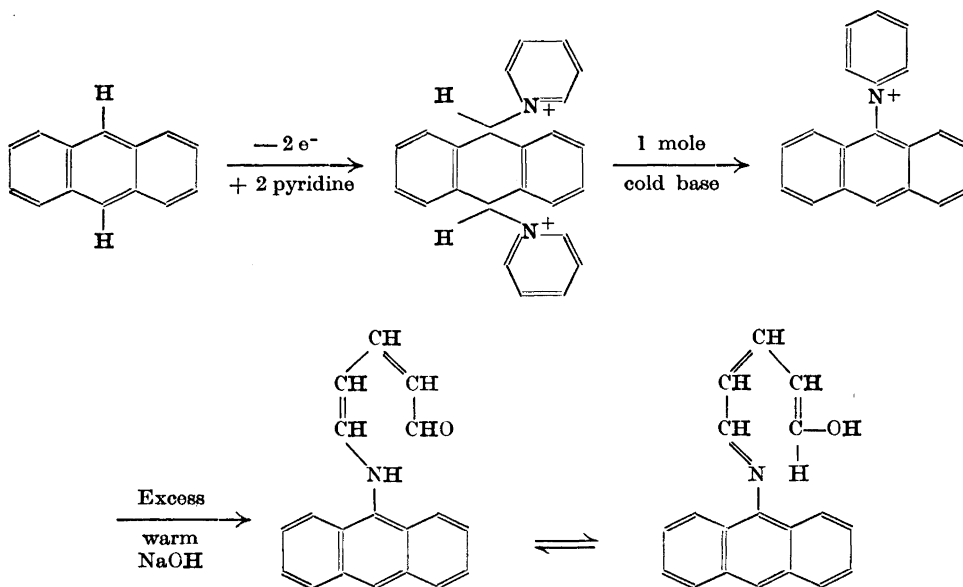
The controlled potential oxidations were performed in anhydrous acetonitrile or acetone containing sodium perchlorate and pyridine. It was found that the oxidation of anthracene at an anode potential of + 0.95 V vs the 0.1 N silver ion/silver electrode yielded a watersoluble ionic compound which was identified as 9,10-dihydroanthranilyldipyridinium diperchlorate by analysis of the diperchlorate, the diiodide and the dipicrate, m.p. 169.5°—171° (168.5°—170°, Barnett and Cook¹²) and by its infrared and ultraviolet spectrum. The ultraviolet spectrum showed only a very slight absorption at wave lengths above 280 $m\mu$ indicating that the compound did not contain the anthracene resonance system.

The 9,10-dihydroanthranilyldipyridinium diperchlorate was also formed by addition of sodium perchlorate to an aqueous solution of the dibromide prepared according to Barnett and Cook¹², and the compounds were found to be identical.

As 9,10-dihydroanthracene is not planar three isomers (two *cis* and one *trans* isomer) of the 9,10-dihydroanthranlyldipyridinium diperchlorate are theoretically possible, but only one has been isolated. The configuration of the isolated isomer is not known.

As described for the dibromide¹² the diperchlorate yielded on addition of a little less than 1 equiv. cold base or contact with an ion exchange resin IRC-50 9-anthrylpyridinium perchlorate. This conversion could be detected simply on heating the diperchlorate with water and it also proceeded to a certain degree during the electrolytic oxidation in the presence of the excess of pyridine giving the reaction mixture a yellow colour.

Barnett and Cook¹² treated 9,10-dihydroanthranlyldipyridinium dibromide with excess of warm sodium hydroxide and isolated in a yield of 3.5 % a chocolate-brown compound to which they suggested the formula $C_{14}H_9-NH-CH=CH-CH=CH-CH=O$. The 9,10-dihydroanthranlyldipyridinium diperchlorate was treated with excess of warm sodium hydroxide and there was isolated in a yield of 55 % a chocolate-brown compound with an analysis close to that found by Barnett and Cook. The infrared spectrum of the compound (in chloroform solution) showed a band at 1648 cm^{-1} . As 2,4-hexadienal¹³ shows a band (in chloroform solution) at 1642 cm^{-1} the infrared spectrum of the compound supports the proposed formula containing a dienal. The band did not, however, possess the intensity to be expected of a dienal, but this can be explained by a strong enolisation. By enolisation the unsaturation of the side chain comes into conjugation with the anthracene resonance system. A high degree of enolisation is also suggested by the strong dark-red colour of the solution in chloroform, as a solution of the pure dienal would be expected to give a faint, yellow solution.



The oxidation of 9,10-dibromoanthracene in the presence of pyridine followed the same reaction path as the oxidation of anthracene, but only (9-bromo-10-anthryl)pyridinium perchlorate was isolated probably due to instability of the analogous product 9,10-dibromo-9,10-dihydroanthranlyldipyridinium diperchlorate. In this connection it is interesting to note that the half-wave potential of the second wave of 9-bromoanthracene (1.48 V) and that of 9,10-dibromoanthracene (1.47 V) is close to the half-wave potential of (9-bromo-10-anthryl)pyridinium perchlorate (1.47 V).

EXPERIMENTAL

The apparatus used for the voltammetric investigation and the preparative oxidations was the same as described in Part I⁴, II², and III¹⁵.

The acetonitrile, sodium perchlorate and silver perchlorate were purified in the same manner as described in Part II². The acetone was Riedel-de-Haën analytical grade.

The following compounds were prepared according to the given references: anthracene¹⁶, 9,9'-bianthryl¹⁷, 9-nitroanthracene¹⁸, 9-bromoanthracene¹⁹, 9,10-dibromoanthracene²⁰, and 9,10-dimethylantracene²¹.

The other compounds investigated were commercially available or were obtained from Dr. L. F. Fieser, Dr. Hakon Lund or Mr. F. Lund. The author wishes to acknowledge with thanks the receipt of these hydrocarbon samples.

Oxidation of anthracene. In 150 ml of a deaerated solution of 15 g anhydrous sodium perchlorate and 4 ml pyridine in acetonitrile was suspended 1.00 g of anthracene, and the anthracene was oxidized at an anode potential of +0.90—+0.95 V vs the 0.1 N silver ion/silver electrode. The anolyte was stirred with a magnetic stirrer and purified nitrogen was bubbled through the solution during the oxidation. As the oxidation proceeded the anthracene gradually dissolved. The amount of electricity required for the oxidation corresponded to a two-electron oxidation. After completion of the reaction the acetonitrile was evaporated *in vacuo* at temperatures not exceeding 30°. To the dry residue were added 40 ml of water, the precipitate was filtered off and washed with small portions of cold water. After drying the precipitate was dissolved in acetonitrile and precipitated with dry ether. One further recrystallization from acetonitrile/ether yielded a white compound (1.35 g). The compound turns yellow at about 170° and decomposes at about 215°. (Found: C 53.71; H 3.70; N 5.17; Cl 13.30. Calc. for C₂₄H₂₀O₈N₂Cl₂: C 53.72; H 3.76; N 5.24; Cl 13.41.) The compound had an absorption maximum at 251 mμ and showed only a very faint absorption at wave lengths above 280 mμ. Its infrared spectrum contained no carbonyl absorption. The compound was readily soluble in acetonitrile and acetone, soluble in 50 % aqueous alcohol, but less soluble in absolute alcohol and water and insoluble in benzene and ether. The compound formed a picrate, m. p. 169.5—171°. (Found: C 54.47; H 2.94; N 14.03. Calc. for C₃₈H₂₄O₁₁N₈: C 54.55; H 3.05; N 14.14). By adding an excess of sodium iodide in acetone to a solution of the compound in acetone an iodide was obtained, m. p. 143° (decomp.). (Found: C 49.17; H 3.27; N 4.80; I 43.19. Calc. for C₂₄H₂₀N₂I₂: C 48.86; H 3.41; N 4.75; I 42.98). The compound was identified as 9,10-dihydroanthranlyldipyridinium diperchlorate.

Analogous to the preparation of 9-anthrylpyridinium bromide¹² the 9-anthrylpyridinium perchlorate was obtained by adding a little less than one equivalent of sodium hydroxide to a 50 % aqueous alcoholic solution of the diperchlorate and evaporating part of the solvent after the reaction was completed. M. p. 269—272°. (Found: C 64.28; H 4.14; N 3.90; Cl 10.03. Calc. for C₁₅H₁₄O₄NCl: C 64.13; H 3.97; N 3.94; Cl 9.97). On addition of excess of sodium iodide in acetone to a solution of the compound in acetone the iodide was obtained, m. p. 260—64°. (Found: C 59.67; H 3.83; N 3.44; I 33.25. Calc. for C₁₅H₁₄NI: C 59.55; H 3.68; N 3.65; I 33.12). The 9-anthrylpyridinium perchlorate had maxima (in alcohol) at 389, 369, and 352 mμ.

Treatment of 9,10-dihydroanthranlyldipyridinium diperchlorate with excess of sodium hydroxide. To 1.0 g of the diperchlorate were added 50 ml 1 N sodium hydroxide and 50 ml chloroform. The mixture was refluxed for 1 h and cooled. The dark-purple chloroform layer was separated from the aqueous layer, to which were added 25 ml 1 N sodium

hydroxide and 50 ml chloroform. The mixture was again refluxed for 1 h, cooled and the layers were separated. The pooled chloroform layers were washed with water and most of the chloroform evaporated *in vacuo*. On addition of ether a chocolate-brown compound was obtained, 290 mg (55 %). (Found: C 80.85; H 5.30; N 4.88. Calc. for $C_{17}H_{13}ON$, $\frac{1}{2}H_2O$: C 80.83; H 5.71; N 4.96). The infrared spectrum of the compound showed a relatively weak carbonyl band at 1648 cm^{-1} (in chloroform solution).

Oxidation of 9,10-dibromoanthracene. A suspension of 2.0 g 9,10-dibromoanthracene in 150 ml of a solution of 15 g sodium perchlorate and 4 ml pyridine in acetone was oxidized at an anode potential of +1.2 V vs the 0.1 N silver ion/silver electrode in acetone. The oxidation was not run to completion, but was stopped after a consumption of electricity of 910 coulomb (80 % of the theoretical amount). The current was rather low as it was governed by the rate of dissolving the 9,10-dibromoanthracene. The undissolved, unreacted dibromoanthracene was filtered off, part of the solvent was evaporated *in vacuo* and the residue diluted with water. The precipitate was filtered off, dried and extracted in a Soxhlet extractor with carbon tetrachloride, which dissolved unreacted dibromoanthracene. The residue, 1.3 g, was dissolved in hot acetone. On addition of carbon tetrachloride a precipitate, 0.95 g, was obtained. M. p. $270-272^\circ$. (Found: C 52.18; H 3.05; N 3.24; Br 18.75; Cl 8.51. Calc. for $C_{19}H_{13}O_4NBrCl$: C 52.50; H 3.02; N 3.22; Br 18.38; Cl 8.16). The compound formed a picrate, m. p. $237-240^\circ$. (Found: C 52.90; H 2.53; N 9.93; Br 14.18. Calc. for $C_{23}H_{15}O_7N_4Br$: C 53.35; H 2.68; N 9.94; Br 14.17). The compound showed maxima (in 50 % aqueous ethanol) at 399, 378 and 359 μ . The compound was identified as (9-bromo-10-anthryl)pyridinium perchlorate.

Oxidation of naphthalene. 1.0 g of naphthalene was dissolved in 150 ml of a solution of 15 g sodium perchlorate and 4 ml pyridine in acetonitrile. The naphthalene was oxidized at an anode potential of +1.4 V vs the 0.1 N silver ion/silver electrode. The current decreased rapidly from 0.2 A to about 5 mA. No visible layer covered the electrode, but after the electrode had been wiped off the current again started at about 0.2 A. The current decreased, however, rapidly to a negligible value. The amount of electricity consumed was less than 5 % of the theoretical amount and no oxidation products could be isolated from the reaction mixture.

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