# VOLTAMMETRIC STUDIES ON THE REDUCTION OF SOME METHYL ANTHRACENE DERIVATIVES

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The electrochemical reduction mechanism of 2-methyl-, 9-methyl and 9,10-dimethyl anthracene has been investigated by cyclic and differential pulse voltammetric methods in N,N-dimethyl-formamide solutions containing tetraethylammonium perchlorate as a supporting electrolyte. It was found that these compounds are reduced electrochemically via an ECE mechanism consisting of a reversible one-electron transfer to form a radical anion , followed by a proton transfer reaction and by a second one-electron transfer.

It has been shown that the electrochemical reduction of aromatic hydrocarbons in aprotic solvents proceeds via the ECE mechanism[1]. In the literature, the greatest attention has been devoted the electrochemical reduction of anthracene[1-5] and 9,10-diphenylanthacene[1,3]. In contrast, scanty literature data have been found concerning the electroreduction of ethyl anthracene derivatives.

Here are reported the results of cyclic and differential pulse voltammetric study of the compounds, 2-methyl-, 9-methyl-, and 9,10-dimethyl-anthracene. The mechanism of the electrode process was proposed and discussed.

## EXPERIMENTAL

### Instrumentation

Voltammetric analyses were carried out with an EG & G model 303 mercury-drop electrode system in (small) hanging-drop and dropping modes linked to a microprocessor-controlled polaragraph with 16-bit DAC and three-channel Servoger 460 recorder. $Ag/AgNO_3$ (0.1 M) in 0.1 M tetraethylammonium perchlorate (TEAP) in N,N-dimethylformamide (DMF) was used as reference electrode. The electrode area was $1.06 \times 10^{-2}$ $cm^2$. Medium used was DMF containing 0.1 M TEAP at 25°C. The solutions were deoxygenated by passing extra pure nitrogen. The cell and reference potential were recorded simultaneuously with current.

The standard wave form of differential pulse voltammetry was the same as previously described by Bartle et al[6]. The parameters of the differential pulse wave form are, pulse height, -80 mV; pulse width, 84 ms; ramp rate, -14 mV/s ; drop time, 250 ms. The computation of theoretical pulse voltammograms was done making use of the equation derived by Rufkin and Evans[7]. Since the basis of this treatment is fast-electron transfer of a given number of electrons, adherence to this model was tested by comparison of computed and experimental peak widths at halfheight. Computations of theoretical pulse voltammograms was performed on an Apple IIe computer using a PASCAL computer programme.

### Reagents

N,N-dimethylformamide (A.R. grade BDH) was purified and dried according to the method described previously[8] and stored over Linde type 4A molecular sieves under nitrogen atmosphere. Tetraethylammonium perchlorate (polarographic grade) used as a supporting electrolyte, was dried under vacuum for at least 24 hrs. 2-methylanthracene, 9-methylanthracene and 9,10 dimethylanthracene (BDH) were used.

A stock solution of tetraethylammonium perchlorate (0.1 M) in DMF was prepared by dissolving the appropriate weight in appropriate volume. Solutions of the aromatic hydrocarbons (10.0 mM) were prepared from a fresh electrolyte solution on the day of measurements. The DMF solutions are not stable for long periods due to the decomposition of the solvent

## RESULTS AND DISCUSSION

The anthracene methyl derivatives investigated yield a well defined cyclic and differential pulse voltammograms. A typical curve is illustrated in Figure.1. The cyclic voltammograms (Fig.1) exhibit reversible couple followed by an electrochemically irreversible reduction. The same feature is found for all the subject compounds. The magnitude of the second cathodic wave is approximately equal to that of the first wave , which suggests that an equal number of electrons is involved in each of the two reduction processes.

The first wave for all the subject compounds is essentially reversible wave as seem by the ratio

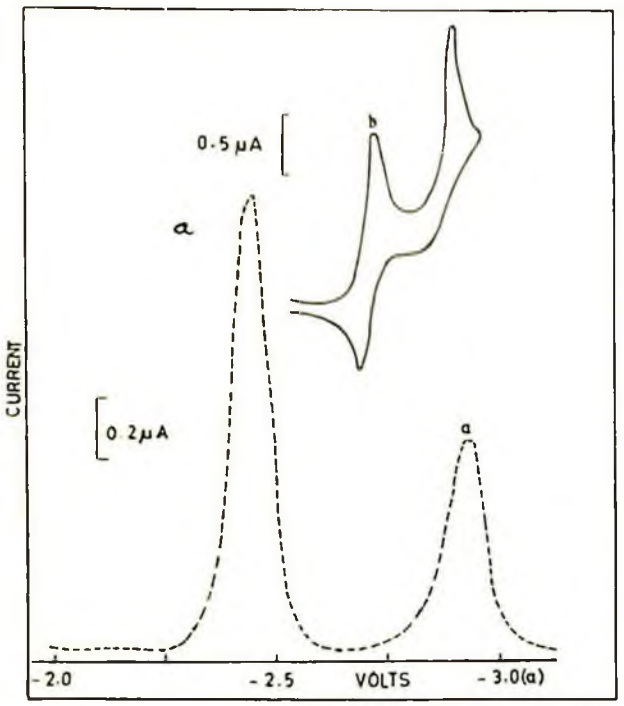



Fig. 1 Voltammograms of 0.61 mM 2-methyl anthracene a)Cyclic Voltammogram b)d.p.p

of cathodic and anodic heights[9] for scan rates from 14 - 308 mV/ sec (see Table 1). This ratio is within 5% of unity and neither cathodic nor anodic peak shifts at these scan rates, indicating the insignificance of preceeding or following coupled chemical reactions. Least square fits of peak currents vs square root of the scan rate yield a linear graph with a correlation coefficients around 0.996 which confirm the well behaved nature of the frst wave and the lack of kinetic complications[9]. The diffusion coefficients for the compounds under investigation are evaluated[10] from the slopes of the linear graph of $i_p - \sqrt{\nu}$. The results obtained are collected in Table 1.

TABLE 1

VOLTAMMETRIC DATA OF THE FIRST WAVE FOR THE METHYL ANTHRACENE DERIVATIVES IN 0.1 M TEAP/DMF AT 25°C

| Derivative | $\frac{i\ pa}{i}$ | $D \times 10^6$ $cm^2/s$ | $E_s$ mV | $E_p - E_{p/2}$ mV | $W_{1/2}$ mV | $-E_p$ mV |
|---|---|---|---|---|---|---|
| 2-Methyl | 0.96±0.02 | 2.93 | 57.6 | 58.6 | 95.2 | 2498+1 |
| 9-Methyl | 0.95±0.03 | 3.14 | 55.2 | 54.1 | 92.0 | 2450+3 |
| 9,10-dimeth | 0.96±0.02 | 3.62 | 55.0 | 54.8 | 93.2 | 2462+1 |

Peak seperation for the first wave ($\Delta E_p$), within the scan rates of investigation for all the subject compounds are within 4 mV of ideality (59.1 mV) [9] for a reversible one-electron reduction (c.f Table 1). Furthermore, wave shape parameter, $E_p - E_{p/2}$, lies close to its normal value (56.5 mV) for a reversible reaction. Moreover, reversibility is tested by a comparison of the computed theoritical and experimental differential pulse voltammetric peak widths at half-maximum height, $W_{1/2}$. It is found here that $W_{1/2}$'s of all the anthracenes (Table 1) are close to the theoritical value for a reversible one-electron reaction. All of the above are consistent with a reversible one-electron reduction process at the scan rates indicated.

The second reduction step of the three studied anthracenes exhibits no anodic wave on the reverse scan. Such a behaviour suggests that the second wave is electrochemically unidirectional i.e.irreversible. The plot of $E_p$ against the scan rate ($\log \nu$) yields straight lines with slopes between 43.1 and 34.0 mV per decade (Table 2). Such values are larger than excepted for a reversible process (slope 30 mV per decade) [9]. In addition, the widths of the CV wave is not reversible. Finally, the comparison of the experimental with the computed theoritical diffrerential pulse voltammetric peak widths at half height, $W_{1/2}$, reveals that, for all the subject aunthracenes, $W_{1/2}$ is much higher

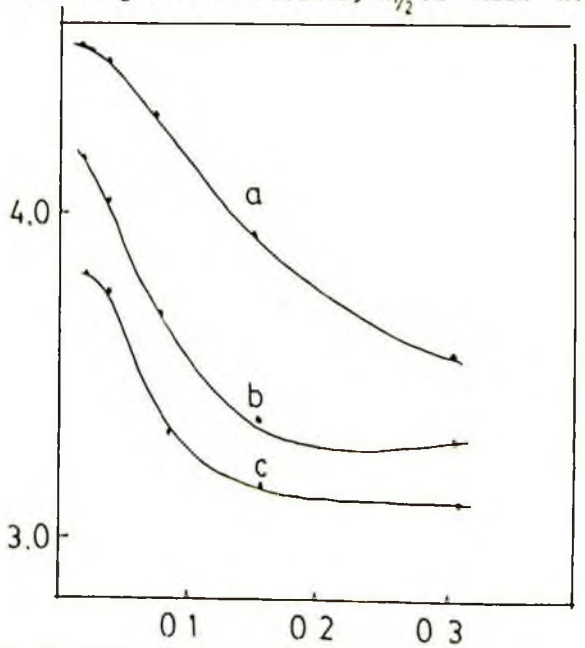



Fig. 2 Current parameter vs scan rate
a) 2-methyl b) 9-methyl
c) 9,10-dimethyl - anthracene

than 96 mV (c.f. Table 2). This provides additional support for the conclusion that the second wave is irreversible.

Figure 2 shows the plots obtained of the current parameter $i_p/\nu^{1/2}$ for the second CV wave as a function of scan rate for the three compounds studied. The plots indicate that it is not

TABLE 2

VOLTAMMETRIC DATA OF THE SECOND CV WAVE FOR THE ANTHRACENES IN 0.1 M TEAP/DMF MEASURED AT = 77 mV/s AT 25°C.

| Derivative | $-E_p$ mV | Slope mV | $E_p - E_{p/2}$ mV | $W_{1/2}$ mV |
|---|---|---|---|---|
| 2-Methyl | 2980±3 | 43.1±0.2 | 68±2 | 105 ± 2 |
| 9-Methyl | 2960±2 | 43.9±0.1 | 66±3 | 102 ± 3 |
| 9,10-Dimethyl | 2944±4 | 34.2±0.3 | 67±4 | 104 ± 2 |

constant and decreases with increasing scan rate. Thus, one can conclude that this reaction is considered as an ECE reaction [11].

All the above facts indicate that the above three methyl derivatives of anthracene undergo two reduction steps. The first wave is a reversible difusion-controlled one-electron transfer step to yield radical anion. The radical anion is then protonated to a neutral radical which is reduced to the final prduct. The overall reaction is thus an ECE type.

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