Reduction Mechanism of Selected Aromatic Hydrocarbons in DMF

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The electrochemical reduction of pyrene, coronene, flouranthene and picene in 0.1 M TEAP/DMF solutions were studied by cyclic voltammetry and convolution potential sweep voltammetry at 25°C. The results generally confirmed the previously proposed mechanism for the reduction of aromatic hydrocarbons. Results indicate that these compounds undergo reduction by ECE mechanism to the final product. The first step is a reversible one-electron transfer to yield an anion radical. This is protonated and reduced to the carbanion irreversibly and finally protonated rapidly to the end product.

The electroreduction of aromatic hydrocarbons in aprotic solvents has been the subject of a large number of studies[1-3]. Although the results of the previous studies on pyrene[4-7], Coronene[5-8], fluoranthene[5-7] and picene[7] fit very well with the assumed mechanisms and the known chemistry of these compounds, few studies have been made using some of the more recent electrochemical techniques.

EXPERIMENTAL

The experiments were performed at 25°C in dimethylformamide (DMF) containing 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte. The working electrode was a HMDE with surface area of 1.06×10^{-2} cm^2. The reference electrode was an $Ag/AgNO_3$(0.01 M) in 0.1 M TEAP in DMF.

The cell and voltammetric apparatus were the same as previously described[9]. Convolution and correction (ohmic drop and sphericity) procedures were the same as described by Saveant et al[10]. The solutions were deoxygenated by passing pure nitrogen. The cell and reference potentials were recorded simultaneously with current.

Pyrene, coronene, fluoranthene and picene (A.R. grade BDH) were used. Dimethylformamide (A.R. grade BDH) was purified and dried using the method described previously[11] and stored over Linde type 4A molecular sieves under nitrogen atmosphere. Polarographic grade TEAP (Fluka) was dried under vacuum for at least 24 hrs and used as a supporting electrolyte.

Stock solutions of depolarizer, 10^{-2} M, were prepared by direct weighing and dissolving in known volume of 0.1 M TEAP/DMF solution. Low concentrations required were prepared by accurate dilution.

Calculations were made using a FORTRAN program and performed on an AMDAHL V7 Computer.

RESULTS AND DISCUSSION

Cyclic Voltammetry:

The cyclic voltammograms of the various aromatic hydrocarbons listed in Table 1 were recorded in DMF solutions containing 0.1 M TEAP at 25°C. The cyclic voltammograms of these compounds are all characterized by two cathodic steps showing well-defined current maxima but no anodic wave for the second one on the reverse scan for scan rates of 14-308 mV/sec. A typical cyclic voltammogram is shown in Fig.1 for pyrene. A closer inspection of the cyclic voltammograms reveals that the first step is electrochemically reversible while the second one is irreversible as shown below.

Peak currents vs sweep rate:

The cathodic peak currents, i_p, in the cyclic voltammogram of the two waves for all investigated compounds are proportional to $\sqrt{\gamma}$ showing diffusion as the rate-limiting step[12]. From the slopes the diffusion coefficient, D, for the subject compounds are evaluated[13]. The results obtained are recorded in Table 1.

Peak potential vs sweep rate (γ)

One of the principle tests for electrochemical reversibility rests on the magnitude of the slope in the plot of E_p versus $\log\gamma$[12,14]. Slopes in the range 0 and 30 mv per decade are indicative of reversible electron transfer and provide informations about the order of the secondary chemical reactions. The values greater than 30 mv per decade are expected for totally irreversible waves on the basis of equation (1)[12].

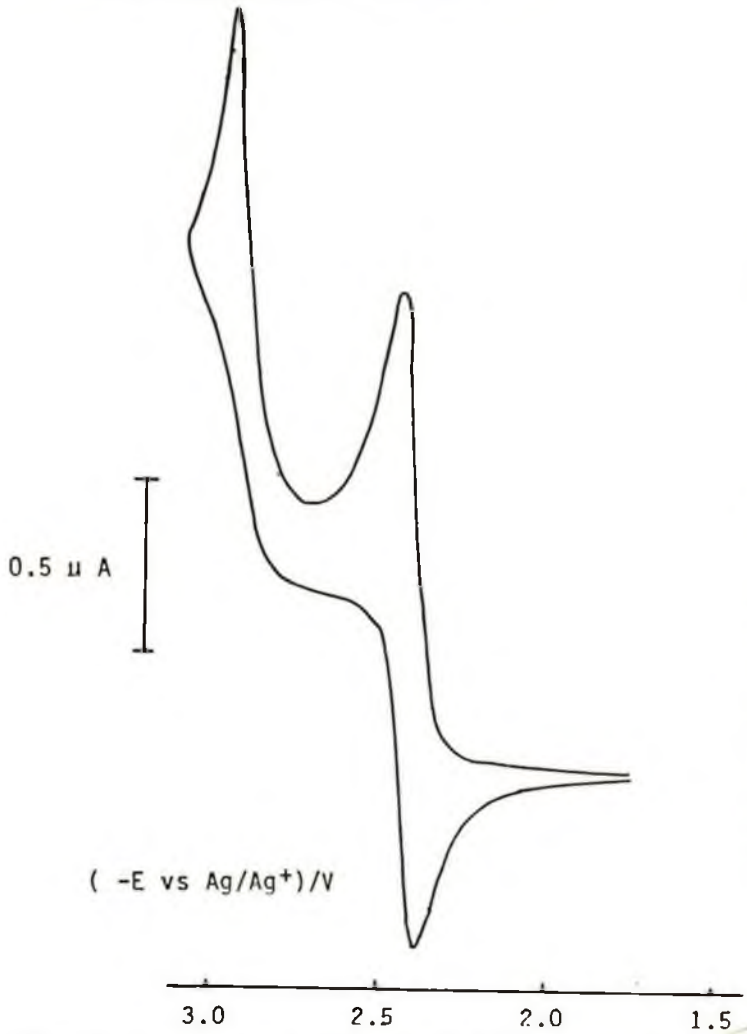


Fig. 1 Cyclic voltammogram of 0.5M pyrene in TEAP/DMF solution at sweep rate of 77 mV/sec at 25°C.

$$E_p = \frac{2.301\ RT}{2n_a\ F} \log \sqrt{\nu} + \text{const} \qquad (1)$$

The observed slopes for the first wave in all cases is very small indicating that the first wave is a reversible electron-transfer process . With every aromatic hydrocarbons studied, the observed slopes for the second wave are significantly larger than expected for a reversible process (Table 1), thereby showing the irreversible nature of the second wave.

WIDTH AND POTENTIAL SEPARATION OF THE WAVES:

The observed width of the cyclic voltammetric wave, $E_p - E_{p/2}$, are of about 58 mv for the first wave with all of the compounds studied while varying between 70 to 85 mv for the second one (Table 1). Moreover, the potential separations (ΔE_p), $E_p^a - E_p^c$, are approximatly 58 mV (where E_p^a and E_p^c are the anodic and cathodic peak potentials respectively) for the first wave for all the subject substrates. These results confirm the reversible one-electron transfer nature of the first wave while absence of the anodic counterpart for the cathodic second wave confirm its irreversibility.

TRANSFER COEFFICIENT FROM VARIOUS PROPERTIES OF THE SECOND CYCLIC VOLTAMMETRIC WAVE:

When the wave is irreversible, the slope is given by 2.301 RT/2αnF(equation 1).The transfer coefficient α obtained in this manner are listed in Table 2. The transfer coefficients are consistent

TABLE 1

CYCLIC VOLTAMMETRIC DATA FOR THE AROMATIC HYDROCARBONS IN 0.1 M TEAP/DMF SOLUTIONS AT 25°C

Compound	$D \times 10^6$ cm^2/sec	$K(E_p) \times 10^3$ cm /sec	First Wave $-E_p$ V	ΔE_p mV	$E_p - E_{p/2}$ mV	Second wave $-E_p$ V	$E_p - E_{p/2}$ mV	S
Pyrene	5.31	7.17	2.380	60	58	2.940	70	41.0
Coronene	4.17	6.12	2.400	57	57	2.915	75	44.1
Fluoranthene	3.09	5.18	2.120	59	60	2.630	85	45.2
Picene	4.42	6.04	2.580	58	58	2.858	75	51.0

E_p measured at ν = 77 mV/sec; S = slope of equation 1 ; Standard deviations are D ± 2% ; $k(E_p)$ ± 2% ; S ± 3%.

TABLE 2

TRANSFER COEFFICIENTS FOR THE SECOND CV WAVE DETERMINED BY SEVERALINDEPENDENT METHODS.

Compounds	Transfer oefficients $E_p - \log\nu$	$(E_p - E_{p/2})$	$E_p - \log i_p$	av
Pyrene	0.72	0.68	0.66	0.68 ± 0.03
Coronene	0.67	0.63	0.59	0.63 ± 0.03
Fluoranthene	0.65	0.56	0.62	0.61 ± 0.04
Picene	0.58	0.63	0.52	0.58 ± 0.04

with those obtained from other properties related to irreversible CV waves.

The width of the wave in an irreversible system has been shown by Nicholson and Shain [12] to depend only on the transfer coefficent according to the following equation.

$$E_p - E_{p/2} = 1.857\ (RT/\alpha n_a F) \quad ...2$$

The transfer coefficients calucalated from this equation by using the tabulated values for the widths of the wave in Table 1 are listed in Table 2. Least squares fits of peak potential, E_p, and the peak current, i_p, according to equation (3) yield straight lines (correlation coefficients of 0.996) for all studied compounds. The transfer coefficients obtained from the slopes are compiled in Table 2.

$$E_p = 2.301\ RT/(\alpha n_a F) \log i_p + \text{Constant} \quad ....3$$

For each aromatic hydrocarbon, the values of the transfer coefficients obtained by these three methods agree to within the experimental error. The constancy of these values provides additional support for the conclusion that the second CV wave is irreversible.

The CV results presented here thus far indicate that the compounds under investigation undergo stepwise reduction; the first step is a reversible one-electron transfer to form an anion radical. The overall reaction can be described as an ECE reaction until a compound reduces to the final product.

For a totally irreversible process, the electron transfer rate constant at the cyclic voltammetric peak potential $k(E_p)$ in units of cm/ sec can be calculated using the data in Table 1&2 and the following equation:[16]

$$k(E_p) = 2.18\ [D\alpha nF\nu/(RT)]^{\frac{1}{2}} \quad ...4$$

Where D is the diffusion coefficient (in cm^2 per sec), α is the transfer coefficient for the electrode process, n is the number of electrons transferred in the rate-limiting step and ν is the scan rate (V/sec). The values obtained at the CV peak potentials of the various aromatic hydrocarbons studied are tabulated in Table 1. This reveals that $k(E_p)$ is insensitive to the change of aromatic hydrocarbon.

CONVOLUTION POTENTIAL SWEEP VOLTAMMETRY:

Linear sweep and cyclic voltametry have the disadvantage that the potential dependent rate law must be selected before the calculations are carried out. It has been demonstrated recently [10,17] that convolution of the current with the integrals of the type

$$I = \frac{1}{\pi^{\frac{1}{2}}} \int_0^t \frac{i(V)}{(t - V)^{\frac{1}{2}}}\, dV \quad ...5$$

directly from the experimental current - voltage curves (i - E) and data processing in terms of both current and convoluted current (I) allow this disadvantage to be overcome. It is no longer necessary, under these conditions, to state the charge transfer rate law a priori. This is instead obtained as a result of the treatment of data.

Figure 2 shows the original current - potential curve, (i - E), and the convoluted current - potential curve, (I - E), for 5.0×10^{-4} M fluoranthene in 0.1 M TEAP/DMF solution as a representative example. The same feature is also observed for all the aromatic hydrocarbons under investigation. The I(E) curves obtained are analysed according to the pure diffusion (DO) and to

TABLE 3

LOGARITHIMIC ANALYSIS RESULTS ACCORDING TO THE PURE DIFFUSION (DO) AND TO THE PURE KINETICS (KP) FOR THE i - E AND I - E CURVES OF THE AROMATIC HYDROCARBONS AT 25°C.

Compounds	First Wave			Second Wave	
	SDO mV	-E° V	SKP mV	SDO mV	SKP mV
Pyrene	61.0 ± 1.0	2.413±0.005	95.9	108.9	61.5±1.1
Coronene	56.9 ± 2.1	2.420±0.003	136.8	97.9	60.9±0.8
Fluoranthene	57.5 ± 0.9	2.074±0.004	74.0	144.0	61.0±2.0
Picene	58.3 ± 1.1	2.592±0.003	110.2	138.0	61.1±2.3

SDO = slope of equation 6 ; SKP = slope of equation 7

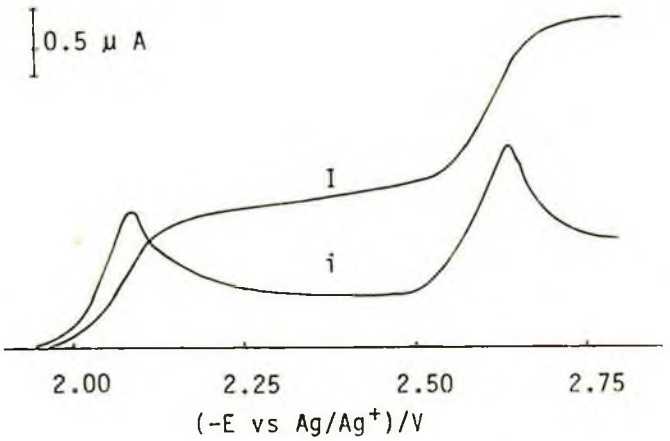


Fig. 2 Current, i; convoluted current, I, versus electrode potential for 0.5mM fluoranthene in 0.1M TEAP/DMF solution at 25°C.

the pure kinetic (KP) logarithmic relationships making use equations 6 and 7 respectively[10] and the slopes of the I(E) curves are determined

$$E = E^\circ + (RT/nF) \ln [I_l - I]/I \quad ...6$$

$$E = E^\circ + (RT/2nF) \ln k + (RT/nF) \ln [(I_l - I)/I] \quad .7$$

where I_l is the limiting convoluted current, I is the convoluted current at E and the remaining symbols have their usual significance. The results for the two waves for scan rates of 14-308 mV/sec of the subject compounds are collected in Table 3.

The logarithmic plots are found to be satisfactorily linear for all the scan rates between 14-308 mV/sec for all studied aromatic hydrocarbons.

The slopes of the DO and the KP analysis for the first and the second cathodic waves respectively are close to the theoretical value of the RT/nF (59.1/n mV at 25°C for decimal logarithms per decade). This indicates that the number of electrons transferred in the rate limiting step is one for both waves of all subject compounds.

Neither the KP nor the DO slopes for the first and the second cathodic waves, for all compounds studied are the right slopes (Table 3).

From the results obtained one can conclude that all of the aromatic hydrocarbons under investigation undergo two step reduction. The first step is a reversible one-electron transfer to yield an anion radical. The second step corresponds to a one-electron transfer process and satisfies the ECE mechanism[10]. These facts are consistent with the results obtained in cyclic voltammetric study.

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