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Kinetic and Mechanism of the Electrochemical Reduction of Fluoranthene in *N,N*-Dimethylformamide

Refat Abdel-Hamid

Department of Chemistry, Faculty of Science, Sohag, Egypt

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Synopsis. Detailed mechanism of electrochemical reduction of fluoranthene has been studied by cyclic voltammetric method in *N,N*-dimethylformamide solution using 0.1 mol dm^{-3} tetraethylammonium perchlorate as a supporting electrolyte. It was found that fluoranthene undergoes a reversible diffusion-controlled one electron-transfer wave followed by an irreversible one-electron one. The reaction in the presence of proton donor such as phenol was also studied. The results reveal that the kinetics of the reaction is first-order in anion radical, zero-order in fluoranthene and first-order with respect to phenol. The overall reaction is of the ECE$_h$ type. It is concluded that the mechanism of the electrochemical reduction of fluoranthene consists of (a) heterogeneous electron transfer to form an anion radical, (b) proton transfer reaction, (c) homogeneous electron transfer in which the neutral radical formed in (b) is reduced to the carbanion and finally (d) the rapid protonation of the carbanion.

Generally, the electrochemical reduction of aromatic hydrocarbons in aprotic solvents involves two one-electron successive steps yielding the anion radical and the dianion respectively.[1,2] Thus the typical cyclic voltammetry reduction pattern of aromatic hydrocarbons in aprotic solvents displays a one-electron reversible wave followed by a one-electron irreversible wave. In the presence of a proton donor such as phenol, a proton transfer reaction following the initial electron transfer step is common to the electrochemical reduction of these compounds. Although the electrochemical behaviour of aromatic hydrocarbons have been the subject of a large number of investigators,[3,4] very few studies have been done on the electrochemical reduction of fluoranthene. The only previous study includes fluoranthene as one of a series of investigated compounds,[5] detailed measurements were not reported.

The objective of the present study was detail electrochemical investigation of fluoranthene in *N,N*-dimethylformamide. Moreover, the study was extended to include the effect of proton-donor concentration on the reduction process. The kinetics and mechanism of the electrode process were proposed and discussed.

Experimental

A Princeton Applied Research Model 303 mercury-drop electrode system in (small) hanging-drop mode linked to a microprocessor-controlled polarograph with 16-bit DAC and three-channel Servoger 460 recorder was used for cyclic voltammetric measurements. The electrode area was 1.06 × 10^{-2} cm^2. The reference electrode was Ag/AgNO$_3$ (0.01 M) in 0.1 mol dm^{-3} tetraethylammonium perchlorate, TEAP, in *N,N*-dimethylformamide. The solutions were deoxygenated by passing pure nitrogen. The cell and referenced potentials were recorded simultaneously with current.

A. R. grade *N,N*-dimethylformamide was purified and dried using the method discribed previously[6] and stored over Linde type 4A Molecular Sieve under nitrogen atmosphere. Polarographic grade TEAP was dried under vacuum for at least 24 h and used as a supporting electrolyte. Fluoranthene (BDH) and phenol (BDH) were used.

Stock solutions of fluoranthene, 10^{-2} M, and phenol, 1.0 M, were prepared by dissolving the appropriate weights of each in appropriate volume of 0.1 M TEAP/DMF solution. Lower concentrations required were prepared by accurate dilution.

Results and Discussion

Cyclic voltammetric results of 5.0×10^{-4} M fluoranthene in a *N,N*-dimethylformamide solution containing 0.1 M TEAP for scan rates, v, of 14 to 308 mV s^{-1}, show two well-defined waves. A typical cyclic voltammogram is shown in Fig. 1 for fluoranthene. The peak current, i_p, of both waves varies systematically with varying scan rate. The ratio of the cathodic to the anodic currents, i_{pc}/i_{pa}, for the first wave amounts to 1.05 ± 0.05 through the scan rate range used (*c.f.* Table 1). It was found that the peak current for the first wave correlates with the square root of the scan rate, $v^{1/2}$, (correlation coefficient = 0.998). The slopes of the straight line graph obtained on plotting i_p against $v^{1/2}$ amounts to 2.51 ± 0.01 μA s$^{1/2}$ V$^{-1/2}$ for 0.5 mM fluoranthene from which the diffusion coefficient, D, of 3.09×10^{-6} cm^2 s^{-1} is evaluated.[7] Furthermore, it is found that the potential separation, $E_{pa}-E_{pc}$, amounts to 59.6 ± 2.3 mV (where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively) and the shape of the cyclic voltammetric wave as measured by its width $E_p-E_{p/2}$, is 56.00 ± 0.05 mV. These values are only slightly different than the theoritical values (59.1 and 56.5 mV at 25 °C for $n=1$ respectively[8]). This is probably due to a small uncompensated resistance. It is worthy to mention that the peak potential, E_p, receives no change on varying the scan rate. These facts reveal that the first wave is a reversible one electron transfer diffusion-controlled wave.

On the other hand, from the cyclic voltammograms covering the complete polarographic waves, one observes that for

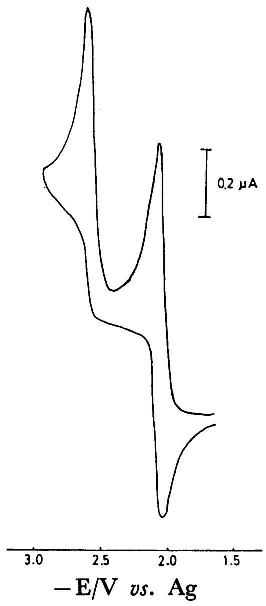

Fig. 1. Cyclic voltammogram of 5.0×10^{-4} M fluoranthene in TEAP/DMF solution at a sweep rate of 77 mV s^{-1} at HMDE.

Table 1. Cyclic voltammetric data for 5 mM fluoranthene in N,N-dimethylformamide containing 0.1 M tetraethylammonium pherchlorate solutions at 25 °C

Sweep. rate mV s^{-1}	First wave		Second wave	
	$E_p - E_{p/2}$ mV	i_{pc}/i_{pa}	i_{pc} uA	$-E_p$ mV
14	58	1.00	0.50	2612
20	58	0.98	0.46	2620
39	64	1.07	0.76	2626
77	60	1.05	1.05	2633
154	62	1.08	1.39	2640
308	62	1.12	1.90	2658

the second electrode process the anodic counterpart of the cathodic peak is lacking. This behaviour suggests that the second electron transfer is electrochemically unidirectional *i.e.* totally irreversible or is coupled to an irreversible chemical follow-up reaction. Moreover, the cathodic peak current is proportional to the square root of the scan rate (correlation coefficient=0.999) which is consistent with diffusion as the rate-limiting step.

In order to establish that the charge-transfer reaction in the cathodic reduction of fluoranthene is intrinsically slow *i.e.* the electrochemical process is totally irreversible, one can apply relation (1) between the peak potential, E_p, and the peak current, i_p, in a totally irreversible wave.[8)]

$$E_p = \frac{(\ln 10)RT}{Bn_bF}\log i_p + \text{constant}. \qquad (1)$$

The value of the transfer coefficient, B, obtained assuming that $n_b=1$ (0.38) bears out the total irreversibility of the second wave.

All the above results reveal that fluoranthene, F, undergoes a reversible one electron transfer, $E_p=2.088\pm0.003$ V, to form anion radical, $F^{\overline{\cdot}}$, followed by an irreversible second wave at higher negative potentials. The anion radicals are reasonably stable during the time of the experiments.

On the addition of proton donor, phenol, the first wave does not increase in peak current or change in the peak potential, while for the second one a change in both the peak current and the peak potential is observed.

The dependence of the peak potential, E_p on the voltage scan rate, v, during the voltammetric reduction of fluoranthene for the second wave is given by the following equation,[9)]

$$dE_p/d\log v = [\ln 10/(b+1)]RT/F, \qquad (2)$$

where b is the reaction order in B, the primary product of electron transfer reaction (3),

$$A + e \rightleftharpoons B, \qquad (3)$$

the other notations are conventional. The $dE_p/d\log v$ value of fluoranthene in TEAP/DMF solutions in the presence of 50.0 mM phenol as a proton donor is measured using the linear least-square fit method of E_p *versus* $\log v$. The theoretical value of $b=1$ corresponding to the protonation reaction (4) with phenol in excess is 29.6 at 25 °C.

$$F^{\overline{\cdot}} + \text{PhOH} \longrightarrow F\cdot\text{-H} + \text{PhO}^- \qquad (4)$$

It was found that value of $dE_p/d\log v$ closes to the theoretical value (30.7±3.1 mV/decade). Accordingly, one can conclude that, the reaction is first-order with respect to the primary product of the electron transfer reaction.

The dependence of E_p on the concentration of fluoranthene, C_A, is tested using equation 5, where a and i are the reaction order in A, substrate, and the products formed whice further participate in the process.[9)]

$$dE_p/d\log C_A = [(a+b+i-1)/(b+1)]\ln 10(RT/F). \qquad (5)$$

For the reaction (3), $a=0$, $b=1$, $i=0$, and $dE_p/d\log C_A$ is also zero. The data obtained for different concentrations of fluoranthene ($5.0\times10^{-4}-2.0\times10^{-4}$ M), reveal that both a and i are zero and $dE_p/d\log C_A$ is zero as well.

It was found that E_p of the second wave depends on the concentration of the proton donor. This dependence is given by equation 6, where x is the reaction order in X(phenol) for the protonation reaction (4).

$$dE_p/d\log C_x = [(X\ln 10)/(b+1)]RT/F. \qquad (6)$$

It is expected that x equals 1 and $dE_p/d\log C_x$ equals 29.6 mV/decade at 25 °C. The experimental value obtained for $dE_p/d\log C_x$ amounts to 28.4±4.3 mV/decade scan rate of 154 mV s^{-1}. This indicates that the apparent reaction order in phenol closes unity.

The rate law for the electrochemical reduction of fluoranthene on the basis of the above facts can be written as follows:

$$\text{Rate} = K_{odsd}[F^{\overline{\cdot}}][\text{PhOH}]. \qquad (7)$$

The rate in equation (7) is equivalent to the following rate.[10)]

$$\text{Rate} = K_{obsd}[F^{\overline{\cdot}}]^2[\text{PhOH}]/[F]. \qquad (8)$$

The results obtained are consistent with the ECE$_h$ mechanism proposed previously for the voltammetric reduction of aromatic hydrocarbons.[10)] Accordingly, the electrochemical reduction reaction of fluoranthene in DMF proceeds *via* the following steps. (a) A heterogeneous reversible one electron transfer step (9) followed by (b) protonation reaction of $F^{\overline{\cdot}}$ radical anion by phenol (10), then followed by a homogeneous electron transfer (11) and finally rapid protonation of the resulting carbanion (12). The electroreduction scheme can be represented as

$$F + e \rightleftharpoons F^{\overline{\cdot}} \qquad (9)$$

$$F^{\overline{\cdot}} + \text{PhOH} \dashrightarrow F\cdot\text{-H} + \text{PhO}^- \qquad (10)$$

$$F\cdot\text{-H} + F^{\overline{\cdot}} \rightleftharpoons F\text{-H}^- + F \qquad (11)$$

$$F\text{-H}^- + \text{PhOH} \dashrightarrow F\text{-H}_2 + \text{PhO}^- \qquad (12)$$

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