THE EXISTENCE OF A PARALLEL PATHWAY MECHANISM IN THE REDUCTION OF PYRIMIDINE ON MERCURY

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INTRODUCTION

The electrochemical reduction of the 3,4-N=C bond of pyrimidine implies two electron transfers and some protonation reactions [1-4]. In the range of pH 6-8, it gives rise only to a two-electron polarographic wave. The purpose of this communication is to characterize this wave by the impedance voltammetry , because this method is suitable to study multistep mechanisms [5]. By studying the potential dependence of electrochemical rate constants obtained in wider potential ranges with the impedance method, it was proved that many electrode reactions proceed by sequences of consecutive elementary reactions, some of them can be rate determining simultaneously [6,7]. In the case of pyrimidine reduction evidence will be presented that the mechanism includes parallel pathways.

RESULTS

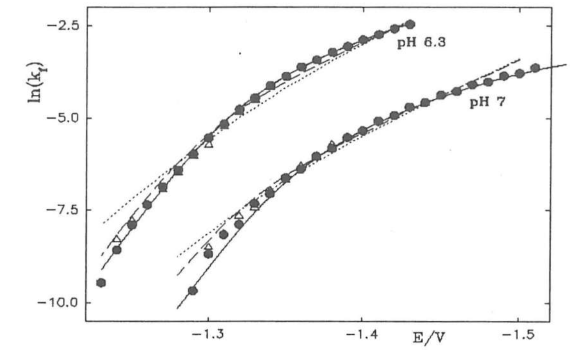

Fig. 1.– Experimental ln(k_f)–E data obtained: △ from polarography, • from the impedance voltametry. Theoretical curves for the sequential EC (·····), EE (– – –), and CEE(——) mechanism.

The forward rate constants, k_f, as a function of potential along the wave could be calculated from polarography in view of the irreversible character of the wave. From the ln(k_f)-E plots so obtained (Fig 1) an estimation of the charge transfer coefficient, α, between 0.55-0.65 could be deduced. The frequency dependence of the impedance data at every potential obeys a Randles circuit. From

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the real impedance components the charge transfer resistance, R_{ct}, can be calculated with good accuracy. The R_{ct}–E curves obtained at every pH can be appreciated in Fig 2.

Clear evidence that the mechanism is multistep can be inferred when calculating the theoretical R_{ct}–E curves for an irreversible simple process according to the equation, [5]:

$$R_{ct}=\frac{RT}{n^2F^2C_{ox}}\;\frac{1+\dfrac{a_0}{k_f}}{\alpha a_0} \qquad (1)$$

and using the values of k_f and α obtained from polarography, (Fig 3). The agreement with the experimental data is acceptable at the less negative potentials where the k_f and α values can be obtained directly from polarography. However, the data at the more negative potentials are higher and have a potential dependence different from those calculated with the k_f values extrapolated from polarography assuming a potential independent α value. This assumption may not be acceptable but, on the contrary, α may adopt lower values as the potential is becoming more negative.

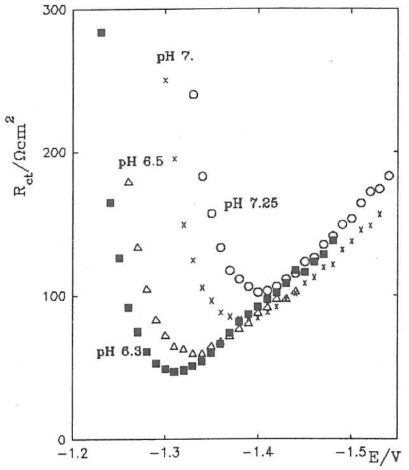


Fig. 2.– Experimental R_{ct} –E at the indicated pH values.

Effectively, the ln(k_f)–E plots obtained in a wider potential range by integration of eqn. (1) are curved, as can be seen in Fig. 1. The slopes of these plots suggest values for α around 0.5–0.6 at more positive potentials and around 0.2–0.13 at far negative potentials.

DISCUSSION

According to these results, there may be more than one rate determining step in the mechanism. If it is assumed, at first sight, that they are consecutive, a general sequential mechanism for two electron transfers can be formulated as CECEC and the corresponding equation for the forward rate constant can be written as:

$$\frac{1}{k_f}=\frac{1}{B_0}+\frac{\exp(\frac{1}{4}\phi)}{A_1}+\frac{\exp(\frac{3}{4}\phi)}{A_2}+\frac{\exp(\phi)}{B_2} \qquad (2)$$

assuming the stationary state for the intermediates and a value of α=0.5 for every individual electron transfer step [6,7].

The ln(k_f)–E curves for pyrimidine reduction have been analyzed according to eqn. (2). It can be seen from Fig. 1 that the mechanism EC has to be discarded, the fit to the EE mechanism is acceptable but the CEE mechanism is to be preferred because it reproduces better the rather low slope at the more negative potentials. The corresponding coefficients B_0, A_1 and A_2 can be calculated at every pH from the fitting of the experimental k_f–E or R_{ct}–E data to the equations for the CEE mechanism.

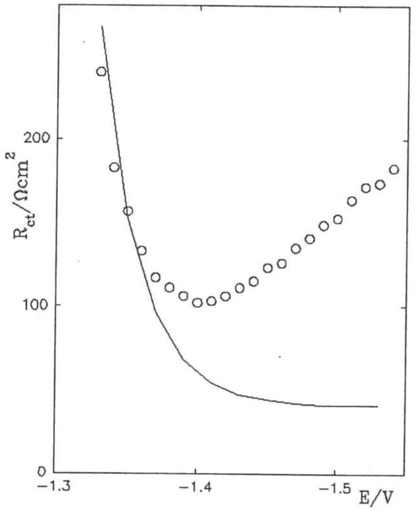


Fig. 3.– Experimental R_{ct} –E curve at pH 7 (o) and calculated for the irreversible case with data obtained or extrapolated from polarographic k_f values (—)

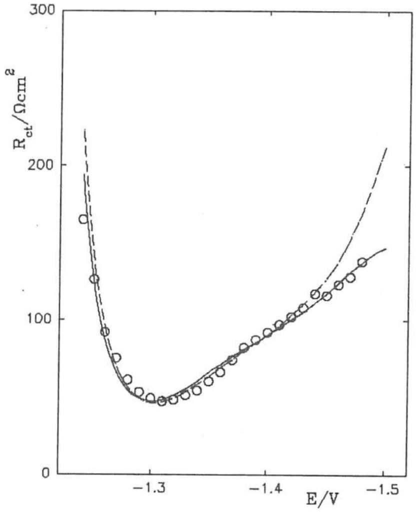


Fig. 4.– Experimental Rct –E curve at pH 6.3 (o) and calculated for the sequential CEE mechansim (- - -) or the branched CEE mechanism (—)

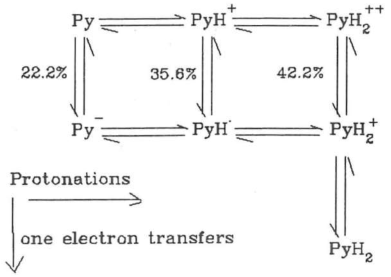
However, the theoretical R_{ct}–E curves do not follow exactly the experimental points at the more negative potentials (Fig. 4). The R_{ct} function is more sensitive to the mechanism because it contains k_f and α simultaneously. The experimental behaviour suggests that at more negative potentials the coefficient α does not tend to zero so swift as expected for a sequential CEE mechanism. This is an indication of the existence of a parallel pathway in which the chemical step is competing with an electron transfer.

Another evidence in favour of a branched mechanism is the pH dependence of the coefficients B_0, A_1 and A_2. Although log B_0 and log A_1 follow a linear dependence with pH with slopes of-1.1 and −2.1, respectively, which could be understood in the scope of the sequential CEE mechanism, the pH dependence of A_2 is better described in terms of a second degree polynomium of a_{H^+}. This implies the involvement of three species with different degrees of protonation in the first electron transfer.

Consideration of the so called "scheme of squares" enables us to deduce a different equation for the potential dependence of the rate constant under the assumptions that only one of the previous protonations and the two electron transfers steps are rate determining:

$$\frac{1}{k_f} = \frac{\exp(\frac{1}{2}\phi) + C\exp(\frac{1}{4}\phi)}{A_1\exp(\frac{1}{4}\phi) + D} + \frac{\exp(\frac{3}{4}\phi)}{A_2} \qquad (3)$$

The four coefficients A_1, A_2, C and D can be obtained from the fitting of eq. (3) to the experimental $\ln(k_f)$–E or R_{ct}–E plots. The theoretical $\ln(k_f)$–E curves for the branched CEE mechanism cannot be distinguished in Fig. 1 from the sequential CEE mechanisms. However, the more involved R_{ct}–E data do fit better to the branched mechanism, especially at the more negative potentials (Fig. 4). Moreover, this mechanism provides expressions for the coefficients A_1 and A_2 which are second degree polynomia of a_{H^+}, and that are able to explain the experimental behaviour. The most probable reaction pathway can be sketched as:



where the percentages of participation in the parallel first electron transfer routes at pH 7 has been indicated.

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