ELECTROREDUCTION OF 3-BROMOPYRENE IN DMF. A NEW ORGANIC ELECTROCHEMICAL OSCILLATOR

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The reduction of 3-bromopyrene in DMF at a mercury electrode for scan rates lower than 0.1 V s^{-1} is accompanied by a slow adsorption of an intermediate, resulting in a catalytic behaviour. The current oscillations take place in a region of the negative faradaic impedance.
Key words: Electroreduction; 3-Bromopyrene; Current oscillations.

The irreversible reduction of halogen substituted aromatic compounds (AX) in aprotic media involves in general[1–8] the reversible formation of an anion radical
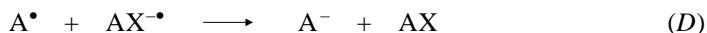
$$AX \; + \; e \; \rightleftarrows \; AX^{-\bullet} \; , \tag{A}$$
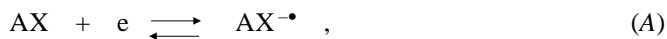
followed by cleavage of the carbon–halogen bond

$$AX^{-\bullet} \; \longrightarrow \; A^{\bullet} \; + \; X^{-} \; . \tag{B}$$
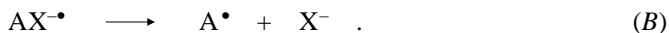
A further reduction of the resulting neutral aryl radical proceeds either at the electrode, by the ECE mechanism

$$A^{\bullet} \; + \; e \; \rightleftarrows \; A^{-} \tag{C}$$

or in the solution

$$A^{\bullet} \; + \; AX^{-\bullet} \; \longrightarrow \; A^{-} \; + \; AX \tag{D}$$

by the DISP1 mechanism, if the forward reaction (*B*) is the rate determining step. The final step is the protonation of the anion A^{-} yielding the hydrocarbon. Moreover, it was

shown[2] that the abstraction of H-atom from the solvent like DMSO by some neutral aryl radicals is a concurrent reaction to steps (*C*) and (*D*).

For the electroreduction of 3-bromopyrene in DMF the ECE mechanism can be expected on the basis of the behaviour found for other bromoarenes[2–5,7]. However, a more complicated reduction process leading to oscillations of current has been observed by us at lower scan rates.

Spontaneous current or potential oscillations in heterogeneous systems have been widely investigated in recent years[9]. Advantages of those studies are straightforward control of the parameters (e.g. a potential or a series resistance) which shifts the system to a state of instability, and a relatively short timescale of oscillations[10]. Different kinds of electrochemical oscillators have been reported, including catalytic oxidation of organic molecules at noble metals like platinum[11,12] and the electrocatalytic reduction of inorganic ions at mercury, e.g. indium in the presence of thiocyanate[13–15]. A new type of an organic oscillator is reported here.

EXPERIMENTAL

Bromination of pyrene in CCl_4 and crystallization from ethanol was used to synthesize[16] and purify 3-bromopyrene; 0.1 M tetrabutylammonium perchlorate (Fluka) was applied as a supporting electrolyte, *N*,*N*-dimethylformamide (DMF, Lab Scan) was dried over sodium hydride and purified using copper sulfate; each step was followed by distillation under reduced pressure.

A three-electrode cell consisting of a static mercury dropping electrode (SMDE, Laboratorni pristroje, Prague), a Pt counter electrode and an Ag/Ag^+ reference electrode in acetonitrile were used. All potentials reported here were recalculated to SCE. Cyclic voltammetric curves and amperometric measurements were performed with a PAR 273A potentiostat controlled by a computer. A polarograph PA4 and a recorder XY, model 4106 (Laboratorni pristroje, Prague) were also used to study the current oscillations and an oscilloscope HO79 (Hameg, Frankfurt) to observe the potential oscillations. Argon gas was bubbled through the solution before each experiment. Measurements were performed at 22 °C. The temperature effects were investigated in the range between 1.5 and 40 °C, using a thermostat U2C (MLW, Germany).

RESULTS AND DISCUSSION

Reduction at Higher Scan Rates

At higher scan rates ($v > 0.1$ V s^{-1}) at room temperature the electroreduction of 3-bromopyrene in DMF at a mercury electrode occurs via the ECE mechanism, i.e. its behaviour is similar to that described for other bromoarenes[2–5,7]. The irreversible, two-electron reduction of the C–Br bond followed by the reversible, one-electron redox reactions of pyrene and its radical anion, are observed in cyclic voltammograms. The current of the first peak is proportional to $v^{1/2}$ and the peak potential E_p depends on v. The value of coefficient $\partial E_p/\partial \log v = -29$ mV per decade of the scan rate after IR

correction, is in agreement with the theory of both ECE and DISP1 mechanisms. To distinguish between them, the analysis of the parameter p is necessary[1,6].
In the Eq. (*1*)

$$p = k_d c^0 / k_2^{3/2} \, (Fv/RT)^{1/2} \qquad (1)$$

k_2 and k_d are rate constants of the cleavage step (*B*) and the solution electron transfer (*D*), respectively, and c^0 is the bulk concentration of the reactant. The value of p approaching zero indicates the predomination of the ECE pathway[1,6], whereas the DISP1 mechanism prevails when $p > 10^3$. The disproportionation step (*D*) is not far from the diffusion-controlled limit[1,5] giving $k_d \approx 10^8$ mol^{-1} s^{-1} and $c^0 = 0.5$ mmol l^{-1}. The cleavage rate constant k_2 is much higher than 5 000 s^{-1} because even at $v = 250$ V s^{-1} no anodic peak and no significant decrease of the cathodic peak current are observed in voltammograms. Using the above values, the upper limit of the competition parameter can be calculated from Eq. (*1*); the value $p = 14$ indicates the ECE mechanism.

Adsorption/Desorption Phenomena

An unusual behaviour of the first process was found at the room temperature for scan rates lower than 0.1 V s^{-1}, as shown in Fig. 1. The peak current of the main peak Ia is much higher than expected for a diffusion-controlled process and it increases with decrease of the scan rate, reaching the value which corresponds to a three-electron reduction at $v = 0.015$ V s^{-1}. The height of this peak is strongly temperature-dependent, giving $\partial I_p/\partial T = 0.18$ μA K^{-1}, whereas for the diffusion current corresponding to the reversible reduction of pyrene (peak II) $\partial I_p/\partial T = 0.008$ μA K^{-1}. These results indicate
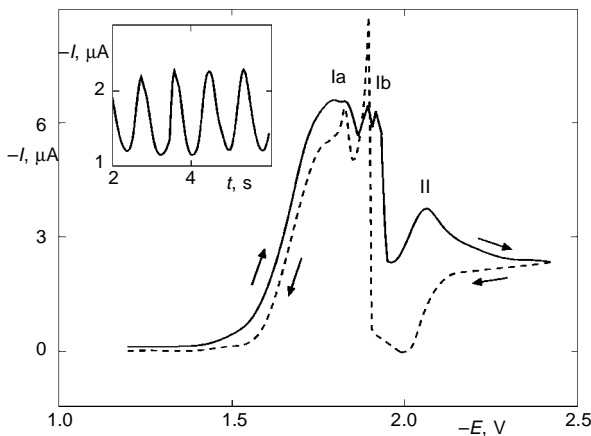

FIG. 1
Cyclic voltammogram of 0.5 mM 3-bromopyrene in DMF with 0.1 M TBAP at 22 °C, scan rate 0.03 V s^{-1}. Cathodic peaks correspond to the catalytic process of bromopyrene (Ia), reduction of adsorbed species (Ib) and the reversible reduction of pyrene (II). Insert: typical oscillatory time series for the current recorded at the potential $E = -1.94$ V

the catalytic nature of the reduction process Ia. However, the value $\partial E_p/\partial \log v = -31$ mV per decade of the scan rate corresponds to the ECE or DISP1 mechanism.

Moreover, an additional post-peak Ib observed at more negative potentials (Fig. 1) can be divided into smaller peaks due to the current oscillations, as it will be discussed later. The temperature dependence of its height is much less pronounced, $\partial I_p/\partial T = 0.024$ μA K^{-1}, in contrast to the catalytic peak Ia. The characteristics of the peak Ib suggest a strong but relatively slow adsorption of the reactant or an intermediate. At more negative potentials the cathodic current rapidly decreases due to the desorption process, until the reduction of pyrene occurs (peak II). This current decrease occurs at a potential independent of scan rate indicating that the desorption is fast. On the reverse scan a sharp spike is found at potentials when the adsorption starts (Fig. 1) followed by high cathodic current, similar to that observed during the forward scan. It supports the auto-catalytic nature of the process Ia, in which the adsorbed species participate. At lower temperatures, when the adsorption is stronger, a position of the spike shifts to more positive potentials with an increase of the scan rate. The height of the spike decreases at the same time (Fig. 2). That behaviour supports the view of the slow adsorption process in the time scale used. The dependence of both reduction peaks Ia and Ib on the scan rate is more evident at lower temperatures due to stronger adsorption and the absence of current oscillations. A typical example for the temperature of 1.5 °C is shown in Fig. 3. The cathodic peak Ia appears at scan rates higher than 0.03 V s^{-1}, when there is not enough time for the adsorption process.

If the adsorbed species is the parent 3-bromopyrene, the peak Ib should have a similar catalytic nature as the peak Ia, and should be well developed at the lowest scan rate, but this is not the case (Fig. 3). Thus, the adsorption of an intermediate radical (AX$^{-\bullet}$ or A$^{\bullet}$) can be postulated. Moreover, it is highly probable that the above adsorption facilitates the disproportionation reaction (D) at the interface. Thus, the regeneration of the parent reactant in step (D) can explain the catalytic nature of the peak Ia. According
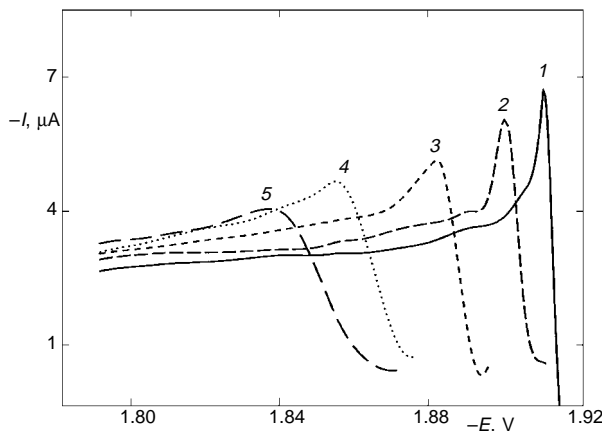

Fig. 2

Current spikes in the reverse part of cyclic voltammograms of 3-bromopyrene recorded at 1.5 °C. Scan rates (1) 15, (2) 18, (3) 30, (4) 50, (5) 100 mV s^{-1}

to the theoretical kinetic-zone diagrams[1,17,18] a shift from the ECE to the DISP1 mechanism is observed for low values of the rate constant k_2 and high values of k_d and c^0. The last condition is fulfilled because for the reaction at the interface the adsorption of a reactant has the same effect as an increase of its concentration for a solution process. On the other hand, it can be postulated that for the adsorbed radical anion $AX^{-\bullet}$ the value of the cleavage rate constant k_2 is much smaller than that for the ECE process at $v > 0.1$ V s^{-1}. Moreover, the rapid desorption observed at negative potentials is fully understood for the negative radical ion. However, the suggested mechanism needs further confirmation.

It can be added here that the unusual reduction of 9-bromoanthracene and 9,10-dibromoanthracene in DMF has been reported in the literature[19], but the experimental support of the proposed explanation has been unsuccessful. On the other hand, a similar behaviour has been also observed in the reduction of olefin–mercury(II) compounds[20] and has been ascribed to the formation of rapidly adsorbed radical intermediates.

Current Oscillations

The current oscillations in the potential range of the adsorption–desorption processes are the most interesting feature in Fig. 1. Spontaneous current oscillations lasting more than 20 min were observed in amperometric experiments. In the potential range corresponding to the desorption process oscillations with a constant amplitude and period were observed, as shown in diagram inserted in Fig. 1. A typical period was 0.87 ± 0.01 s at the temperature of 22 °C. The conditions at which oscillations occur are similar to those established[13–15,21] for the In(III)/SCN$^-$ oscillator. Due to the desorption of a catalyst a negative faradaic impedance with absolute value smaller than the ohmic cell resistance appeared. The latter one is of the order of 1 kΩ, for the DMF solution, although part of the ohmic drop is compensated. No external series resistance is necess-

Fig. 3
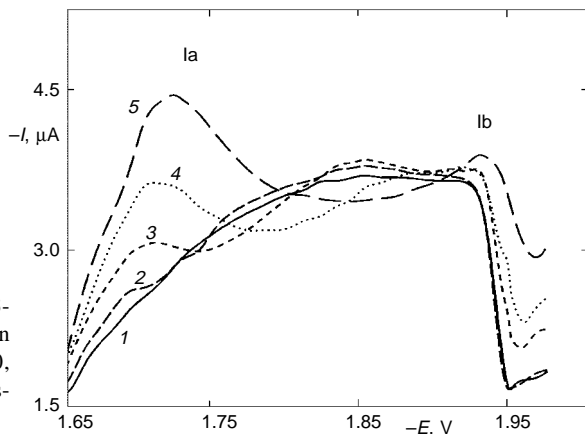
Cathodic peaks for the reduction of 3-bromopyrene in DMF at 1.5 °C. Scan rates (*1*) 15, (*2*) 18, (*3*) 30, (*4*) 50, (*5*) 100 mV s^{-1}. For Ia and Ib see discussion in text

ary for the appearance of oscillations in the system under investigation. In the recent theory for electrochemical instabilities of this kind[21] current oscillations under potentiostatic control are conditioned by out-of-phase potential oscillations in two parts of the circuit (the working electrode and an internal cell resistance)[22]. That requirement is just fulfilled in the system under investigation with a relatively high internal cell resistance. Simultaneous out-of-phase potential oscillations at the working and the counter electrodes during the current oscillations, with the same period for all three phenomena, were observed as shown in Fig. 4. That result fully supports proposed theory[21]. However, in contrast to In(III)/SCN⁻ oscillator the catalyst is formed spontaneously during the overall process.

In the potential range where monoperiodic oscillations exist, their amplitude increases with negative potential shift. In logarithmic coordinates an amplitude of oscillations was found to be linear function of potential (expressed with respect to the estimated bifurcation potential) with the correlation coefficient of 0.972 and the slope of 0.49. This result is in agreement with the theoretical prediction for an ordinary (supercritical) Hopf bifurcation[23,24], which is a smooth transition of a system from a stationary state to a stable time-periodic behaviour (periodic orbit). It can be noted that similar behaviour was found[13] for the In(III)/SCN⁻ oscillator.

At more positive potentials triperiodic oscillations were found with two shorter amplitudes (S) followed by a longer one (L) in the series SSLSSL... The more complex periodic and chaotic oscillations (observed e.g. for the In(III)/SCN⁻ system[13]) were not found, but there is a wide range of potentials where aperiodic oscillations exist. Their features depend strongly on the internal cell resistance and their reproducibility is low.

In conclusion, taking into account that the ECE mechanism is very common in organic electrochemistry in aprotic solvents of a higher resistance, it is probable that similar oscillations can appear in a number of systems with a slow adsorption of intermediates acting as catalysts.
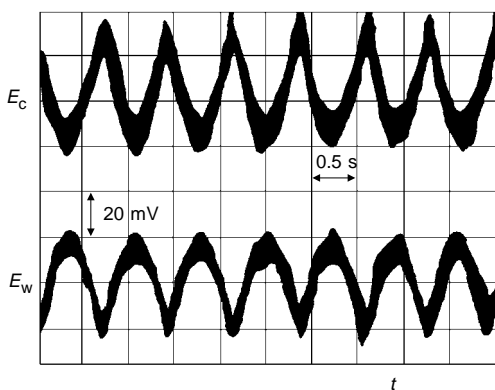

FIG. 4

Simultaneous potential oscillations at the working electrode E_w and the counter electrode E_c during the potentiostatic experiment at $E = -1.94$ V

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