Ph. D. THESES

Examination of the electrochemical oxidation of halogeno-anilines in acetonitrile solvent

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I. Introduction

The electrochemical oxidation of para-substituted anilines has been examined by Bacon and Adams in weakly acidic aqueous media. The given stoichiometric equation of the dimerization reaction in case of anionic leaving group is the following:

\[
2 \text{H}_2\text{N} - \begin{array}{c} \text{X} \\ \end{array} \rightarrow \begin{array}{c} \text{X} \\ \end{array} - \text{N} - \begin{array}{c} \text{NH} \\ \end{array} + 3\text{H}^+ + \text{X}^- + 2\text{e}^{-}
\]

Later Amatore et al. have studied the detailed mechanism of the radical stabilization in the initial step of the dimerization in unbuffered aprotic solvent, N,N-dimethyl-formamide. The type of dimerization and its kinetic and thermodynamic parameters have been determined by fast and conventional CV methods. The results showed, that in the case of p-anisidine the mechanism of the dimerization is of radical-substrate type, but in the case of p-chloro- and p-bromo-anilines it is of radical-radical type. These measurements were carried out on gold working electrode. Farsang et al. have isolated the products of macroelectrolysis with controlled potential coulometry (CPC) in unbuffered acetonitrile solution. These isolated products were identified with MS measurements.

The aim of our investigations was to confirm in acetonitrile solution the validity and details of the head to tail coupling mechanism in aqueous solution described first by Bacon and Adams.
II. Experimentals

The $n_{\text{app}}$ value of the electrodimerization in voltammetric time scale can be determined as described by Amatore et al. with a reference substance of known $n_{\text{app}}$. (Ferrocene was used in our case) by two independent pair of voltammetric methods (LSV and CA; RDE and CA). At these measurements at the given substance concentration and the pair of methods used the results were evaluated at the same characteristic time ($T_c$). These measurements were carried out at platinum microelectrode ($d=10 \, \mu \text{m}$), and gold rotating disk electrode ($d=3 \, \text{mm}$). The applied methods were LSV and chronoamperometry (CA) or chronocoulometry (CC).

CPC macroelectrolysis followed by an offline HPLC-UV system was used for separation and for determination of the total electron consumption of the electrolysis.

The $pK_a$ values of halogeno-anilines were calculated from potentiometric titrations with a self-made parameter-estimating program. Glass electrodes were calibrated with picric-acid / n-tetrabutyl-ammonium-picrate buffers at four concentration ratios offered by Chantooni and Kolthoff. The halogeno-aniline samples were titrated with perchloricacid titrant in acetonitrile. The titrant was diluted from anhydrous acetic acid solution of 1 M perchloric acid and was used immediately.

For fast CV measurements, the potentiostat was built in the workshop of the Chemistry Department of the Ecole Normale de Superieure in Paris and was a generous gift from Professor Amatore.

For digital simulation of experimental curves BAS Digisim 2.1™ software was used.
III. New results

1. The apparent number of electron consumption for all mentioned halogeno-anilines were determined with combination of different electrochemical methods. The theoretical value could only be achieved in the case of trihalogeno-anilines. The calculated $n_{\text{app}}$ values for all substances examined are collected in Table 1.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>4-halogeno-anilines</th>
<th>2,4-dihalogeno-anilines</th>
<th>2,4,6-trihalogeno-anilines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Pt}_{\text{UME}}$</td>
<td>$\text{Au}_{\text{RDE}}$</td>
<td>$\text{Pt}_{\text{UME}}$</td>
</tr>
<tr>
<td>Cl</td>
<td>0.95</td>
<td>1.04</td>
<td>1.27</td>
</tr>
<tr>
<td>Br</td>
<td>1.07</td>
<td>1.05</td>
<td>1.29</td>
</tr>
<tr>
<td>I</td>
<td>1.20</td>
<td>1.04</td>
<td></td>
</tr>
</tbody>
</table>

2. The mechanism of the electro-oxidation of iodide in acetonitrile solution was proved by digital simulation and $n_{\text{app}}$ measurements.

3. Macroelectrolysis followed by HPLC analytical determinations of decreasing concentration of the starting trichloro-substrate gave the expected $n_{\text{app}} = 1.5$ when the degree of oxidation was lower than about 15–20% based on the starting quantity of the substrate.

4. The acid-base properties of these compounds were established, and the role of the eliminated halogenide-ions on the voltammetric response function was presented. Further on it was demonstrated how the increasing electron-withdrawing effect of the different halogen species increases the main irreversible voltammetric peak potentials and decreases the basicity of the primary amino group of the aromatic ring. These measurements showed that the trichloro and tribromo-anilines are not basic at all. Measured pKa values are collected in Table 2.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>4-halogeno-anilines</th>
<th>2,4-dihalogeno-anilines</th>
<th>2,4,6-trihalogeno-anilines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>9,2</td>
<td>8,5</td>
<td>-</td>
</tr>
<tr>
<td>Br</td>
<td>10,3</td>
<td>8,8</td>
<td>-</td>
</tr>
<tr>
<td>I</td>
<td>10,8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5. The existence of an instabil radical was proved by fast scanning cyclic voltammetry carried out at a microelectrode.

6. The transfer coefficients were be determined from the slope of the EP ox vs. log v curve at higher rates of polarization. (EPox is the peak potential of the forward CV peak, and v is the rate of polarization.) These values are $\alpha_{ox} = 0.52$, and $\alpha_{ox} = 0.47$ for trichloroaniline, and tribromoaniline. Eq. (3) can be used for the estimation of the formal redox potential Eo0 values of the tri-halogenoanilines.

7. The formal redox potentials were measured and calculated. Eo0 = 1.155 V vs. ref. for trichloroaniline, and Eo0 1.165 V vs. ref. for the tribromoaniline.

8. The rate constant of the radical-radical electrodimerization was determined by the ratio of the backward and forward peak currents at different scan rates. $k_{app} = 2.0 \times 10^7$ M$^{-1}$s$^{-1}$ for 2,4,6-trichloroaniline, $k_{app} = 2.5 \times 10^7$ M$^{-1}$s$^{-1}$ for 2,4,6-tribromoaniline.

9. The dependence of the anodic peak potential on the concentrations of the two substrates and the rate of polarization was studied. The anodic peak potentials depend on the polarization rates applied. A mean slope of 20 mV/decades was found but the concentration of the substrate does not affect the shift of the peak potential values. These two characteristic features of the function studied correspond only to a single mechanism of the possible dimerization mechanisms suggested by Nadjo and Savéeant and this is the e-p-RRC-p mechanism.

10. The mechanism was confirmed with digital simulation. A good correlation was found between the experimental and calculated CV curves based on this mechanism and the calculated kinetik parametes.
VI. Publications

**Journals:**

Pusztai Sz., Dankházi T., Farsang Gy.
A halogénezés szerepe halogén-anilinek elektrooxidációjában, acetonitril oldószerben

Pusztai, Sz., Dankházi, T., Farsang, G.
The electrooxidation of halogeno-anilines at microelectrodes in acetonitrile solution

Sz. Pusztai, J. Pánczél, T. Dankházi, G. Farsang
The electrodimerization mechanism of 2,4,6-trichloro- and tribromoanilines in unbuffered acetonitrile

**Conferences:**

Pusztai, Sz., Dankházi, T., Farsang, Gy.: The role of halogen substituents in the electrodimerization of halogeno-anilines

G. Farsang, T. Dankházi, P. Simon, M. Kádár, Sz. Pusztai: The voltammetric oxidation of halogenoanilines in acetonitrile solvent