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Electrochemical reduction of 2-fluorenecarboxaldehyde: A mechanism with a grandparent–grandchild reaction

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Abstract

The electrochemical reduction of 2-fluorenecarboxaldehyde, **1**, has been investigated, principally in *N*,*N*-dimethylformamide. The initially formed anion radical undergoes an irreversible dimerization reaction with a rate constant of 2600 M^{-1} s^{-1}. The very basic dimer dianion is protonated by the starting material. This "grandparent–grandchild" reaction well accounts for the amount of conjugate base of **1** that is formed. The effect of adding various OH, NH and CH acids was investigated. The enhancement of the dimerization rate observed with the OH and NH acids is interpreted in terms of the formation of hydrogen-bonded complexes with the anion radical which in turn undergo more rapid dimerization reactions than does the uncomplexed anion radical.

Keywords: Aromatic aldehyde; Cyclic voltammetry; Dimerization; Proton donors; Hydrogen bonding

1. Introduction

The reduction of aromatic aldehydes has been a subject of investigation for many years [1–3]. In anhydrous aprotic media, the aldehyde is reduced to the anion radical (reaction (1)) which has a substantial lifetime. When a sufficiently active proton donor, HA, is present, the anion radical will be protonated, leading to an overall two-electron reduction (reactions (2)–(4)) because the protonated anion radical is normally more easily reduced than the starting material. An exception is benzaldehyde in the hydroxylic solvent ethanol where the α-hydroxybenzyl radical is more difficult to reduce than neutral benzaldehyde [4]

$$\mathrm{ArCHO} + e^- \rightleftharpoons \mathrm{ArCHO}^{-\cdot} \tag{1}$$

$$\mathrm{ArCHO}^{-\cdot} + \mathrm{HA} \rightleftharpoons \mathrm{ArCHOH}^{\cdot} + \mathrm{A}^- \tag{2}$$

$$\mathrm{ArCHOH}^{\cdot} + e^- \rightleftharpoons \mathrm{ArCHOH}^- \tag{3}$$

$$\mathrm{ArCHOH}^- + \mathrm{HA} \rightleftharpoons \mathrm{ArCH_2OH} + \mathrm{A}^- \tag{4}$$

The presence of weaker acids (or no intentionally added acid) usually leads to the formation of the dimer (pinacol) by reaction (5). Here, HA is not a sufficiently strong acid

$$\mathrm{ArCHO} + e^- \rightleftharpoons \mathrm{ArCHO}^{-\cdot} \tag{1}$$

$$2\mathrm{ArCHO}^{-\cdot} + 2\mathrm{HA} \rightarrow \mathrm{ArCH(OH)CH(OH)Ar} + 2\mathrm{A}^- \tag{5}$$

to protonate the anion radical so the protonation occurs later in the scheme. In such cases, the mechanism is less clear.

There has been a long and colorful history of the so-called "mother–daughter", "father–son" or "self-protonation" reactions [5]. The terminology, which in modern times should probably be converted to the more gender-neutral "parent–child" reaction, was first introduced by Elving [6] though such reactions had been

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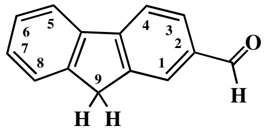
previously observed but not named [7,8]. Here, the product of the first electron-transfer reaction reacts by a proton transfer with the starting material eventually leading to product. For a reductive dimerization, for example, the overall reaction will be $4HY + 2e^- \rightleftharpoons (HYH)_2 + 2Y^-$. So, the overall reaction is a 1/2-electron reduction of acidic HY to form the dimer, $(HYH)_2$, and Y^-.

This is the normal "parent–child" reaction, where the product of the first electron-transfer exchanges a proton with the starting material. The mechanism proposed in the present work involves the dimerization of the initially formed anion radical to form a very basic dimer dianion which in turn reacts with the starting material. This may be regarded as a "grandparent–grandchild" reaction because the participants are separated by one generation [5b].

2-Fluorenecarboxaldehyde (**1**), is an aromatic aldehyde that also possesses acidic character by virtue of the protons in the 9-position (pK_a of fluorene in DMSO is 22.6 [9]). In a recent study of the reduction of 9,9′-spirobi-(9*H*-fluorene)-2-carboxyaldehyde [10], 2-fluorenecarboxyaldehyde was used as a model to interpret the electrochemistry of the spiro compound. It was observed that some sort of a "parent–child" reaction was occurring but the complete description of the mechanism was deferred.



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2. Experimental

2.1. Chemicals and reagents

Anhydrous *N*,*N*-dimethylformamide (DMF, Aldrich, 99.8+%, <0.005% H_2O), anhydrous dimethyl sulfoxide (DMSO, Aldrich 99.9+%, <0.005% H_2O) and anhydrous acetonitrile (ACN, Aldrich 99.8%, <0.001% H_2O) were used as received and transferred via syringe under nitrogen. The electrolyte was tetrabutylammonium perchlorate (Bu_4NClO_4, Fluka, electrochemical grade) that had been vacuum dried at 70 °C overnight. 2-Fluorenecarboxaldehyde (Aldrich, 99+%), 2,2,2-trifluoroethanol (Aldrich, 99.5%), methanol (HPLC solvent Aldrich, water 0.01%), cyclohexanone oxime (Aldrich, 99%), 3-aminopyridine (Aldrich, 99%), fluorene (Aldrich, 99%), 2-pyrrolidinone (Aldrich, 99%), methyl ethyl ketone (Mallinckrodt, 0.01% water), and sodium *tert*-butoxide (Aldrich, 97%) were used as received. Nitrogen or argon, presaturated with solvent, was used as purge gas.

2.2. Electrochemical cells, electrodes and instrumentation

All electrochemical experiments were performed using an EG&G Princeton Applied Research Potentiostat/Galvanostat, model 283, using a standard three-electrode cell. The working electrode was either a glassy carbon disk (0.3-mm diameter; Bioanalytical Systems) or an EG&G HMDE (hanging mercury drop electrode), model 303A, with an area of 0.0145 cm^2. A fresh mercury drop was used for each scan. In some experiments a glassy carbon disk electrode (0.0814 cm^2) was used. A platinum coil counter electrode was used along with a silver reference electrode (SRE) comprising a silver wire immersed in 0.10 M Bu_4NPF_6/0.01 M silver nitrate/acetonitrile and separated from the sample solution by a porous Vycor™ frit. For DMF solvent, the ferrocene/ferrocenium, Fc^+/Fc, potential was measured close in time to the studies of **1** and was found to be +44 mV vs. the SRE. This calibration was not done for DMSO and ACN so results for these two solvents are reported vs. the SRE. The experiments were conducted at 298 K. The solution resistance was partially compensated via IR compensation through positive feedback. Digital simulations were conducted using DigiSim from Bioanalytical Systems, version 3.03, which was used to account for the remaining solution resistance.

Controlled-potential coulometry was carried out in a 15-mL electrolysis cell. A platinum gauze electrode (ca. 4 cm^2) was used as the working electrode. The working and counter electrode compartments were separated by two sheets of tracing paper held in place between the two halves of a clamped O-ring joint. The working electrode potential was maintained about 300 mV negative of the reduction peak. Coulometry was carried out at room temperature.

3. Results and discussion

3.1. Qualitative studies

Fig. 1 contains a series of voltammograms that illustrate the qualitative behavior of the electrochemical reduction of **1**. The initial negative-going sweep in curve A reveals a partially reversible cathodic peak (Ic) at about −2.2 V accompanied by an associated anodic peak (Ia) on the return scan. There is also an irreversible anodic peak, IIIa, at about −0.8 V. Peak Ia increases relative to Ic as the scan rate is increased and this is accompanied by a decrease in the height of IIIa. The Ic/Ia pair is assigned to the neutral/anion radical couple, reaction (6), while IIIa is due to the irreversible oxidation of the anion formed by deprotonation of **1** (reaction (7)). For comparison, the parent fluorenide shows an anodic peak on platinum at −1.069 V vs. Fc^+/Fc in DMSO [11]