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Electrochemical characterization of hydrogen-bonding complexation between indoline and nitrogen containing bases

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ABSTRACT

The electrochemical behavior of indoline in non-aqueous media in the presence of nitrogen-containing bases was studied. Electrooxidation of indoline with strong bases displayed behavior consistent with the formation of a non-covalent hydrogen-bonding complex prior to the electrooxidation. This behavior was studied by cyclic voltammetry and ^{1}H NMR spectroscopy, and a 1:1 interaction between indoline and the base has been proposed. Electrochemistry experiments using a rotating ring disk electrode (RRDE) were performed to further understand the electrooxidation mechanism in the presence of bases. When the electrooxidation experiments were conducted using weak bases, different behavior was observed; in this case complexation of the electrogenerated radical cation with the base is proposed.

1. Introduction

Fuel cell devices can generate electrical power with high efficiency, at low cost, and without pollution, and therefore much research has been devoted to their development [1–7]. Historically, fuel cells utilize energy storage in the form of hydrogen gas. Liquid organic fuels, such as alcohols or hydrocarbons, have also been considered as energy carriers because they may be thermally dehydrogenated to produce the hydrogen gas optimally used in fuel cells. Such liquid fuel schemes have been expanded to include nitrogen heterocycles because their dehydrogenation has reduced enthalpy of reaction [8,9]. None of the thermal dehydrogenation schemes to produce hydrogen gas for fuel cells, however, has been shown to be energy efficient or cost effective.

An alternative approach uses liquid organic fuels that are *electrochemically* dehydrogenated directly in a PEM fuel cell to produce electrons and protons. The atomistic view of this process has the fuel undergoing a proton-coupled electron transfer (PCET) mechanism [10–12] whereby proton transfer and oxidation of the fuel could occur as either a concerted or a two-step process, forming a stable hydrogen-depleted product and electrons with sufficient electrochemical potential to produce power. In aprotic media such as a heterocyclic fuel, the PCET mechanism invokes an intermolecular hydrogen-bond that facilitates the proton transfer/deprotonation event [10,11]. The antecedent, then, to the rational design of electron transfer and oxidation processes in PEM liquid fuel cells is a more complete understanding of the influence of hydrogen bonding on proton transfer processes amongst representative heterocycles fuels and bases.

We selected an aromatic amine, indoline, as a model organic fuel to study the mechanism of the electrochemical dehydrogenation reaction. In this way we build upon previous work [13] on the electrochemical oxidation of indoline in the presence of added bases. These authors [13] sought to investigate the concentration and pK_a dependence of added bases to the oxidation of indoline, under the assumption that added base could facilitate the electrochemical dehydrogenation reaction of indoline to indole. The results obtained using cyclic voltammetry studies and ^{1}H NMR spectroscopy suggested that in the presence of added base an intermolecular hydrogen-bonding complex was formed between indoline and the base. Similar complexation, in addition to proton-coupled electron transfer, has been proposed for phenylenediamines and pyridines [14], as well as quinones and acidic proton donors [10,11,15–17]. Herein we report a more comprehensive study of indoline using a larger subset of bases with a wider range of pK_a values. We use cyclic voltammetry, ^{1}H NMR spectroscopy and rotating ring disk electrode (RRDE) methods to support the proposed hydrogen-bonding mechanism for the interaction of indoline with the bases.

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2. Experimental

2.1. Reagents and chemicals

Indoline, isoindoline, and most of the nitrogen-containing bases were purchased as reagent grade or better (Aldrich) and were used as received for the electrochemistry experiments. The bases 2,6-diisopropylpyridine and 2,4,6-triisopropylpyridine were synthesized as reported previously [18]. *N*-methylindoline was synthesized according to [19]. Tetrabutylammonium tetrafluoroborate ($TBABF_4$) was either recrystallized three times from ethanol and dried over P_2O_5 at 110 °C for 3 days, or purchased as electrochemical grade from Aldrich and used as received. Acetonitrile (MeCN) used in electrochemical experiments was dried by passing through a steel column containing alumina using a Pure Solv solvent purification system. All NMR solvents were from Cambridge Isotope Laboratories. Benzene-d_6 was dried over molecular sieves and acetonitrile-d_3 was distilled over calcium hydride. For the NMR experiments, 2,6-lutidine was distilled over $AlCl_3$ and 1,1,3,3-tetramethylguanidine was distilled over BaO. Solvents were stored in a glove box.

2.2. Electrochemistry

2.2.1. Cyclic voltammetry

Electrochemical measurements were performed using a CH Instruments Electrochemical Workstation model 750B or 660A. All cyclic voltammetry experiments used a glassy carbon disk working electrode (3 mm diameter), a non-aqueous silver/silver nitrate (10 mM $AgNO_3$ in 0.1 M $TBABF_4$ in MeCN) reference electrode and a platinum coil counter electrode. All experiments were conducted in a beaker-type cell with a 5 mL working volume under nitrogen atmosphere.

2.2.1.1. General procedure for cyclic voltammetry experiments. A solution of indoline at a concentration of 10 mM was prepared in dry acetonitrile containing 0.1 M $TBABF_4$. A measured amount (5 mL) of this solution was transferred to the beaker-type electrochemical cell and the solution was deoxygenated by bubbling N_2 into solution for 2 min. The electrodes were inserted into the cell and the cyclic voltammetry was performed. The working electrode was polished using 0.05 μm alumina paste after each CV experiment. The nitrogen-containing bases were added neat to the solution in measured aliquots and the solution was stirred to ensure complete mixing before the next CV was performed.

2.2.2. Rotating ring disk electrode experiments

The rotating ring disk electrode (RRDE) experiments were conducted using a 5.6 mm diameter glassy carbon disk working electrode with a 1.67 mm wide platinum ring separated by PTFE insulation. A PAR636A electrode rotator controlled the rotational speed of the electrode. The ring potential was controlled by a PARSTAT 2263 potentiostat while a VersaSTAT4 controlled the disk. The experiments were performed in a three-electrode Luggin capillary electrochemical cell. A coiled Pt wire was used for the counter electrode and all measurements were referenced to a saturated calomel reference electrode (SCE). The scan rates were 25 mV/s at a rotation speed of 800 rpm, unless otherwise stated.

2.2.2.1. General procedure for rotating ring disk electrode experiments. A 1 mM solution of indoline was prepared in dry acetonitrile containing 0.1 M $TBABF_4$. A 0.5 mM solution of the nitrogen-containing bases was added in measured aliquots to the indoline solution. The working electrode was polished using 0.3 and 0.03 μm alumina paste before each RRDE measurement. The onset oxidation potentials were determined from the intersection of the two tangents drawn at the rising current and background charging current of the linear scan voltammogram.

2.3. NMR experiments

^1H NMR characterizations were conducted using a Bruker 400 MHz instrument where chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane using the residual solvent peak as a secondary reference standard. Samples using anhydrous reagents were prepared under a nitrogen atmosphere.

2.3.1. General procedure for NMR titration experiments

Solutions containing 50–80 mM indoline were prepared in the appropriate deuterated solvent, and 500 μL was subsequently transferred to a screw cap NMR tube. A 2 mM solution of the nitrogen-containing base was prepared in a vial in the same deuterated solvent and fitted with a septum. Aliquot amounts of the base solution were added via syringe through the rubber septa. The ^1H NMR spectrum was recorded after each addition and the chemical shift of the N–H proton on indoline was noted. Alternatively, separate NMR samples were prepared for different indoline:base ratios, and in these cases the NMR samples were prepared in a glove box with capped sample tubes so as to prevent solvent evaporation.

3. Results and discussion

3.1. Electrochemistry of indoline in the presence of strong bases

The voltammetric behavior of the indoline oxidation in acetonitrile (MeCN) is shown in Fig. 1a. The cyclic voltammogram (CV) of indoline exhibits an irreversible one-electron oxidation peak (E_{ox}) at 0.375 V with a current density of about 4 mA/cm^2 at a scan rate of 100 mV/s (Fig. 1a, trace A). The irreversibility of this oxidation peak is likely due to the indoline radical cation forming dimers and polymers, consistent with reports from the structurally similar aniline [20]. Upon addition of a “strong” base, which for the purpose of the present work is defined as a base whose pK_a of its protonated form is higher than the pK_a of protonated indoline, there is an increase in the oxidation current density as well as a shift in the oxidation onset to lower potentials. These onset oxidation potentials (E_{onset}) were defined from the intersection of the two tangents drawn at the rising current and background charging current of the CVs [21–23]. Fig. 1a (trace B) shows the CV of indoline in the presence of four molar equivalents of 2,6-lutidine (pK_a = 6.6). The increase in the oxidation current of indoline in the presence of this strong base suggests a mechanism involving a chemical step, which is the formation of a hydrogen bonding complex, followed by an electrochemical step, and then a chemical reaction which could include the loss of a proton or additional indoline reactions, including the formation of dimers or other coupling products [27–29]. The increase in current density, then, may be due to the facilitation of the chemical reaction step by the addition of the exogenous base [13]. The increase in current density is accompanied by a cathodic shift of the oxidation potentials, as has been reported previously in the electrochemical oxidation of phenolic compounds in the presence of added bases [30].

A selection of other strong bases, covering a range of pK_a values between 5 and 14, were investigated to determine the effect of pK_a on the electrochemical behavior of the indoline-base mixtures. (None of these bases exhibited oxidation current in the indoline oxidation window). Fig. 1b summarizes the bases selected and plots the observed shift in the E_{onset} of indoline upon the addition