ASSESSING NON-AQUEOUS PROTON-COUPLED ELECTRON TRANSFER REACTIONS THROUGH ELECTROCHEMICAL METHODS

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ABSTRACT

Brian D. McCarthy: Assessing Non-Aqueous Proton-Coupled Electron Transfer Reactions Through Electrochemical Methods
(Under the direction of Jillian L. Dempsey)

The multi-decade proliferation of electrochemical hydrogen evolution catalysts has resulted in a relatively small handful of excellent catalysts. Thus, research has turned towards understanding catalytic mechanism in the hope of rationally guiding the next generation of catalysts. Specifically, recent focused effort has sought understanding of how homogeneous catalysts mediate the combination of two electrons from the electrode and two protons from solution-based sources. The individual proton and electron movements are frequently coupled such that the movement of one triggers the movement of the other, sometimes resulting in simultaneous transfer.

Intentional catalyst designs that favor stronger coupling have shown impressive catalytic rates. This realization has promoted increased scrutiny of proton-coupled electron transfer (PCET) reactivity. PCET reactions have both kinetic and thermodynamic components; this dissertation focuses on thermodynamic aspects of electrochemical PCET through the development of relationships between applied potential and non-aqueous acidity. Non-aqueous potential-pKa theory is demonstrated through the construction of two experimental diagrams. A third candidate example of a potential-pKa diagram is discussed in the context of the challenges and opportunities of gaining thermodynamic information from irreversible electrochemical data.

Two challenges were encountered during this research. First, direct reduction of acids by the electrode can obscure the desired PCET reactivity. Electrochemical analysis of over twenty acids in acetonitrile yielded a dataset of direct acid reduction potentials, information that was
used to guide later PCET studies. This work additionally summarized unique considerations associated with acid-base behavior in non-aqueous solvents. Second, metal complexes used for PCET and hydrogen evolution studies can degrade at the electrode. Successful identification of when decomposition/transformation occurs allows accurate interpretation of electrochemical data and provides a guide for selecting metal complexes likely to be more robust. This guidance, coupled with better understanding of PCET mechanism, will help enable economical and efficient catalysts for solar fuel production.
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TABLE OF CONTENTS

LIST OF TABLES .......................................................................................................................... xii

LIST OF FIGURES .......................................................................................................................... xiii

LIST OF ABBREVIATIONS AND SYMBOLS ................................................................................. xxviii

CHAPTER 1. Introduction ......................................................................................................................... 1

1.1 Need for Large Scale Fuel Synthesis ............................................................................. 1

1.2 Fuel Synthesis by Electrolysis ...................................................................................... 2

1.3 Proton-Coupled Electron Transfer Underpins H₂ Evolution ...................................... 4

1.4 Studying PCET by Cyclic Voltammetry ........................................................................ 7

1.4.1 Protonation Kinetics Can Shift Potential ............................................................. 8

1.4.2 Interpreting PCET within Catalysis ........................................................................ 9

1.4.3 Total catalysis gives rise to a second peak .......................................................... 10

1.5 Dissertation Overview ...................................................................................................... 12

CHAPTER 2. Electrochemical Reduction of Acids by Glassy Carbon .................................................. 13

2.1 Introduction .......................................................................................................................... 13

2.2 Results .................................................................................................................................. 15

2.2.1 Reference Electrode ................................................................................................. 15

2.2.2 Electrode Fouling ....................................................................................................... 16

2.2.3 Acid Reduction Measurements ................................................................................ 17

2.2.4 Reduction Potentials .................................................................................................. 19

2.2.5 Influence of Water ....................................................................................................... 22
A.5  

\( ^1 \)H NMR Spectra of Acids

---

APPENDIX B  

Preparation and Characterization of Compounds

B.1  

Literature Complexes and Ligands

B.2  

Novel Complexes

---

APPENDIX C  

Additional Data for Chapter 2

C.1  

Measurement of \( pK_a \)s by spectrophotometric titrations

C.2  

Cyclic voltammogram of silver nitrate

C.3  

Representative cyclic voltammograms of all acids studied at 100 and 1000 mV/s

C.4  

Cyclic voltammograms of all acids with and without 100 mM added water

C.5  

Reaction of trifluoromethanesulfonic acid with acetonitrile

---

APPENDIX D  

Bulk Electrolysis Methods

---

APPENDIX E  

Additional Details for Chapter 4

E.1  

Estimation of diffusion limited rate of reaction of 1\(^-\) and [Et\(_3\)NH][BF\(_4\)]

E.2  

Simulation details for \( E_{i}C_{i}E_{i} \) mechanism

---

APPENDIX F  

Additional Details for Chapter 5

F.1  

Cyclic voltammetry data for PCET reaction of MoCp\(_2\)(4-pedt) (1) and acids

F.2  

Modeling PCET of 1 with acids as stepwise ET-PT or PT-ET mechanisms

F.2.1  

Thermochemistry of an EC Reaction Mechanism

F.2.2  

Thermochemistry of a CE Reaction Mechanism

F.2.3  

Unifying EC and CE mechanisms

F.3  

Cyclic voltammetry data for PCET reaction of 2 and acids

F.4  

Cyclic voltammetry data for PCET reaction of 3 and acids

---

APPENDIX G  

Additional Details for Chapter 6

G.1  

Estimation of diffusion coefficients
LIST OF TABLES

Table 2.1. Average acid reduction potentials vs. Fc/Fc' in 0.1 M [Bu4N][PF6] CH3CN on GC at 25 mM and 100 mV/s..........................................................21

Table 2.2. pKₐ and homoconjugation values in CH₃CN for acids studied in this work and influence of 100 mM water on the reduction wave peak current.................................................................23

Table 3.1. Metal complexes known to electrochemically degrade in organic solvents under catalytic conditions to form electrode-adsorbed heterogeneous materials catalytically active for hydrogen evolution. ...........................................58

Table 6.1. Reaction equations for modeling stepwise PCET for complex 1 with 2-MePy/2-MePyH⁺ using DigiElch..........................................................102

Table E.1. Parameters used to simulate the data show in Chapter 4.................................................165

Table F.1. Summary of acids used for electrochemical PCET with 1 and observed E₁/₂. ..........................................................167

Table F.2. Summary of acids used for electrochemical PCET with 2 and average E₁/₂ for PCET..........................................................182

Table F.3. Summary of acids used for electrochemical PCET with 3 and average Eₚ,c or E₁/₂ for PCET..........................................................187

Table G.1. Measured peak-to-peak separation for 1 as a function of scan rate. ..........................................................193

Table G.2. Measured peak-to-peak separation for 1(H)⁺ as a function of scan rate. ..........................................................193
LIST OF FIGURES

Figure 1.1. Structure of the [Fe-Fe] active site (above) and structure of synthetic hydrogenase mimics (bottom).................................................................3

Figure 1.2. Square scheme representation of a homogeneous PCET reaction where species M receives one electron and one proton to form MH.................................................................4

Figure 1.3. Cartoon depictions of A) homogeneous termolecular CPET (case for two donors and one acceptor shown; more partners are possible) and B) electrochemical PCET ...........................................6

Figure 1.4. As applied potential changes throughout a variable-potential experiment, the PCET mechanism accessed may change as the driving force changes.................................................................7

Figure 1.5. Structure of Co(dmgBF\textsubscript{2})\textsubscript{2}(L)\textsubscript{2}.................................................................10

Figure 1.6. Proposed hydrogen evolution mechanism of Co(dmgBF\textsubscript{2})\textsubscript{2}(L)\textsubscript{2}, written here as 1...........................................................................................................10

Figure 1.7. Example of a total catalysis waveform for the electrochemical hydrogen evolution with 5 mM catalyst Co(dmgBF\textsubscript{2})\textsubscript{2}(CH\textsubscript{3}CN)\textsubscript{2} and 5 mM p-cyanoanilinium in acetonitrile at 100 mV/s with 0.25 M [Bu\textsubscript{4}N][PF\textsubscript{6}].................................11

Figure 2.1. Simulated cyclic voltammograms of an EC’ catalytic process in which direct substrate reduction (acid reduction) occurs at potentials a) far from catalysis, b) slightly overlapping with catalysis, c) strongly overlapping with catalysis, and d) nearly completely overlapping with catalysis.................................................13

Figure 2.2. Cyclic voltammograms of three acids in acetonitrile using a glassy carbon electrode showing the response of the electrode on subsequent scans.................................................................16

Figure 2.3. Cyclic voltammograms of 25 mM 4-cyanoanilinium (100 mM [Bu\textsubscript{4}N][PF\textsubscript{6}] acetonitrile solution) at 100 and 1000 mV/s showing the presence of a prewave on the forward sweep..................................................18

Figure 2.4. Cyclic voltammograms (100 mV/s) of 25 mM 4-chloroanilinium in a 100 mM [Bu\textsubscript{4}N][PF\textsubscript{6}] acetonitrile solution using two different glassy carbon working electrodes (w.e. 1 and w.e. 2).................................................................19

Figure 2.5. Cyclic voltammogram of 25 mM acetic acid at 100 mV/s in 100 mM [Bu\textsubscript{4}N][PF\textsubscript{6}] acetonitrile solution and the first derivative of the forward trace.................................................................20

Figure 2.6. Polarography of 1 mM perchloric acid on a dropping mercury electrode with added water in acetonitrile (A, B, C, E, F: 0, 0.01, 0.1, 1.0, 3.0, and 10 M added water).................................................................26
Figure 2.7. Cyclic voltammograms of 25 mM pyridinium chloride in 100 mM [Bu4N][PF6] acetonitrile solution at 100 mV/s showing reproducibility if only freshly polished working electrodes are used.................................30

Figure 2.8. Cyclic voltammograms of 100.5 mM acetic acid at 100, 500, 1000, 5000, and 9000 mV/s in 100 mM [Bu4N][PF6] acetonitrile solution.........................35

Figure 2.9. Plot of $E_{\text{inf}}$ values versus the respective $pK_a$ for each acid studied.....................36

Figure 2.10. Background subtracted cyclic voltammogram of 25 mM 4-cyanoanilinium at 100 mV/s, normalized to the current measured at $E_{\text{inf}}$. .................37

Figure 2.11. Acid potential windows in acetonitrile (25 mM acid, 100 mV/s) showing the range between an approximate thermodynamic potential $E_{\text{HA0}}$ (where proton reduction to hydrogen is thermodynamically possible) and the direct reduction potential $E_{\text{inf}}$.................................38

Figure 3.1. Simulated cyclic voltammograms of a catalyst without substrate undergoing electron transfer (black trace), catalyst with substrate undergoing simple redox catalysis (blue trace), and conversion of precatalyst to active catalyst in a prior PCET step (red trace). .................................................................45

Figure 3.2. Simulated chronoamperograms of a catalyst without substrate (black trace), catalyst with substrate undergoing simple redox catalysis (blue trace), and conversion of precatalyst to active catalyst in a prior PCET step (red trace). .................................................................47

Figure 3.3. Structures of targeted nickel complexes with either a methylene, amine, or sulfur atom at the bridgehead position of the phosphine ligand.................................49

Figure 3.4. Cyclic voltammogram of 0.4 mM 1 with ferrocene at 100 mV/s in 0.25 M [Bu4N][PF6] acetonitrile solution...............................................................50

Figure 3.5. Background subtracted cathodic peak currents for 1 plotted versus the square root of the scan rate...............................................................50

Figure 3.6. (A) Cyclic voltammograms of [Et3NH][BF4], 1, and 1 plus [Et3NH][BF4] at 100 mV/s in 0.25 M [Bu4N][PF6]. (B) Cyclic voltammograms using an electrode treated at -1.78 V for 60 s with 0.4 mM 1 and 10 mM [Et3NH][BF4], rinsed, and then scanned in a solution of 0.25 M [Bu4N][PF6] (black line) and in a solution of 10 mM [Et3NH][BF4] + 0.25 M [Bu4N][PF6] (pink) at 100 mV/s..................................................51

Figure 3.7. Scanning electron micrograph of a cross section of a glassy carbon plate electrolyzed with 0.3 mM 1 and 10 mM [Et3NH][BF4] for 30 minutes at -1.74 V vs. Fc+/Fc. ..................................................52

Figure 3.8 (A) XPS spectra of a bare glassy carbon plate and (B) a glassy carbon plate electrolyzed at -1.74 V for 30 minutes with 0.3 mM 1 and 10 mM [Et3NH][BF4]..................................................53
Figure 3.9. High resolution XPS spectra of the Ni 2p and S 2p regions for both 1 onto a gold plate and a glassy carbon electrode electrolyzed with 1 and [Et$_3$NH][BF$_4$]. .......................................................... 53

Figure 3.10. Structures of complexes 4 and 5. .......................................................... 54

Figure 3.11. Acid titrations of 0.5, 4, and 10 eq. of CF$_3$COOH into equimolar solutions of 4 and 5 (0.39 mM). The black traces are the respective acid- free voltammograms. .......................................................... 55

Figure 3.12. Structure of complex 6. ........................................................................... 56

Figure 3.13. Voltammograms of 0.4 mM 6, recorded at 100 mV/s in a 250 mM [Bu$_4$N][PF$_6$] CH$_3$CN solution. .......................................................... 57

Figure 4.1. Structure of 1. .......................................................................................... 59

Figure 4.2. Cyclic voltammograms of 0.7 mM 1 and 0.7 mM 1 plus one equivalent of [Et$_3$NH][BF$_4$]. .......................................................... 61

Figure 4.3. Scan rate dependence of cathodic peak current of prewave for a solution of 0.6 mM 1 and 0.5 eq. of [Et$_3$NH][BF$_4$] in acetonitrile. ................. 61

Figure 4.4. Square scheme depicting possible mechanisms for addition of two electrons and one proton to compound 1. ........................................................................... 62

Figure 4.5. UV-vis spectra of 0.4 mM 1 in CH$_3$CN with and without 50 mM [Et$_3$NH][BF$_4$]. .......................................................... 62

Figure 4.6. $^1$H NMR of 1.4 mM 1 without (bottom) and with 199 molar equivalents of [Et$_3$NH][BF$_4$] in CD$_3$CN. .......................................................... 62

Figure 4.7. (A) Simulated CVs for an E$_r$C$E_i$ reaction. (B) Prewave potential shift (relative to the cathodic peak of the original reversible wave) versus the rate of protonation. .......................................................... 64

Figure 4.8. $^1$H DOSY NMR spectrum of a 9 mM CD$_3$CN solution of [Et$_3$NH][BF$_4$]. .......................................................... 65

Figure 4.9. Cyclic voltammograms of equimolar solutions of 1 with sub-stoichiometric [Et$_3$NH][Cl] and either 0.24 M H$_2$O or D$_2$O. .......................................................... 66

Figure 4.10. Literature example of Ni-hydride mediated S-C bond cleavage. 63 .......................................................... 67

Figure 4.11. Proposed decomposition mechanisms of 1. .......................................................... 68

Figure 4.12. $^{31}$P ($^1$H) NMR spectrum of a solution of 1.8 mM 1, 50 mM [Et$_3$NH][BF$_4$], and 0.25 M [Bu$_4$N][PF$_6$] after electrolysis at -1.97 V using a 1 x 2 x 0.2 cm glassy carbon plate electrode (about 1 x 1 cm was actually immersed). .......................................................... 69

Figure 5.1. Structures of complexes 1 and 2. ........................................................................... 77
Figure 5.2. Cyclic voltammograms of 1 with and without added acid........................................77

Figure 5.3. Potential–pK_a diagram of 1. Plot of the observed oxidation potential of 0.2 mM 1 with 0.2 mM of various acids versus the pK_a of the acid used. .................................................................79

Figure 5.4. Possible resonance forms of 1. ..................................................................................79

Figure 5.5. Extinction coefficients of compound 1 in acetonitrile without acid (black) and with 5.2 equivalent of dimethylformamidium triflate (blue). .............................80

Figure 5.6. PCET square scheme for 1. ......................................................................................81

Figure 5.7. Nernstian dependence of the oxidation potential of 1 on the base/acid ratio. ........................................................................82

Figure 5.8. Generation of an experimental potential–pK_a diagram of compound 2 .................84

Figure 5.9. Nernstian dependence of reduction potential of 2 on base/acid ratio.....................85

Figure 5.10. Plot of the E_{1/2} value for a solution of 0.45 mM 2 versus the log of varying ratios of tosylate to p-toluenesulfonic acid. .........................................................86

Figure 5.11. Partial correction for homoconjugation for PCET of 2 with tosylate addition..............................87

Figure 5.12. Plot of the E_{1/2} value for a solution of 0.45 mM 2 versus the log of varying ratios of aniline to anilinium in solution. .........................................................88

Figure 5.13. Structure of compound 3. ......................................................................................89

Figure 5.14. Normalized linear sweep voltammograms of 0.3 mM 3 with 0.3 mM of various acids: phenol (pK_a = 29.14^{78}), acetic acid (pK_a = 23.51^{190}), 2,4,6-tribromophenol (pK_a = 20.35^{190}), triethylammonium (pK_a = 18.82^{75}), and benzylammonium (pK_a = 16.91^{75}). .........................89

Figure 5.15. Cyclic voltammogram of 0.3 mM 3 and 0.3 mM Et_3NH^+ at 10 V/s .........................89

Figure 5.16. Potential-pK_a plot of the observed potential of the PCET process of 3 with acids of varying pK_a(CH_3CN).................................................................90

Figure 5.17. Cyclic voltammogram of 0.3 mM 3 at 100 mV/s in 0.25 M [Bu_4N][PF_6]. ..............91

Figure 5.18. Cyclic voltammetry of 0.3 mM 3 with and without one molar equivalent of phenol at 100 mV/s in 0.25 M [Bu_4N][PF_6] solution.................................91

Figure 5.19. Extended potential-pK_a diagram of 3. .................................................................92

Figure 6.1. Structure of 1. .................................................................................................96
Figure 6.2. A) Background corrected cyclic voltammogram of 0.2 mM 1 at 20 mV/s in 0.25 M [Bu₄N][PF₆] CH₃CN solution. B) Background corrected cyclic voltammogram of 0.2 mM 1(H)⁺ (generated in situ from 0.2 mM 1 plus 2.5 mM dimethylformamidium) at 60 mV/s in 0.25 M [Bu₄N][PF₆] CH₃CN solution. ................................................................. 97

Figure 6.3. Working curve data for an EC mechanism where the C step occurs intramolecularly and a return redox event is still observed on the return scan. ...................................................................................... 98

Figure 6.4. Possible PCET mechanisms for 1. ........................................ 99

Figure 6.5. Literature example of oxidative CPET.................................. 100

Figure 6.6. Observed E₁/₂ as a function of scan rate for a solution of 0.4 mM 1 and 0.4 mM pyridinium (pKₐ = 12.53). .................................................. 100

Figure 6.7. A) CVs of 0.2 mM 1 with FeCp₂⁺ as an internal standard (not shown) as a function of relative buffer concentration (equimolar 2-MePy/2-MePyH⁺) at E₁/₂ at 0.1 V/s in 0.25 M [Bu₄N][PF₆] CH₃CN solution. B) Peak-to-peak separation as a function of buffer concentration relative to 1 at E₁/₂. ........................................ 101

Figure 6.8. Simulated cyclic voltammogram peak widths at 0.1 V/s as a function of 2-MePy/2-MePyH⁺ buffer concentration compared with experimental data. .......................................................... 103

Figure 6.9. Simulated cyclic voltammogram peak widths at 1 V/s as a function of buffer concentration compared with experimental data. .... 104

Figure 6.10. KIE study comparing the PCET peak width and E₁/₂ at 1 V/s of solutions containing 0.4 mM 1 and 0.4 mM 2-methylpyridinium (pKₐ = 13.32) and varying concentrations of either CH₃OH or CD₃OD. Data are the average of three separate experiments.......................................................... 105

Figure A.1. ¹H NMR spectrum of 4-bromoanilinium tetrafluoroborate in CD₃CN. ................ 113
Figure A.2. ¹H NMR spectrum of 4-chloroanilinium tetrafluoroborate in CD₃CN. .......... 114
Figure A.3. ¹H NMR spectrum of 4-nitroanilinium tetrafluoroborate in CD₃CN. .......... 114
Figure A.4. ¹H NMR spectrum of 4-tert-butylanilinium tetrafluoroborate in CD₃CN. .... 115
Figure A.5. ¹H NMR spectrum of anilinium tetrafluoroborate in CD₃CN. ................. 115
Figure A.6. ¹H NMR spectrum of dimethylformamidium triflate in CD₃CN............... 116
Figure A.7. ¹H NMR spectrum of N,N-dimethylanilinium tetrafluoroborate in CD₃CN. .. 116
Figure A.8. ¹H NMR spectrum of 4-methoxyanilinium tetrafluoroborate in CD₃CN........ 117
Figure A.9. ¹H NMR spectrum of 4-cyanoanilinium tetrafluoroborate in CD₃CN........... 117
Figure A.10. $^1$H NMR spectrum of triethylammonium tetrafluoroborate in CD$_3$CN. ........118
Figure A.11. $^1$H NMR of pyridinium tetrafluoroborate in CD$_3$CN. ........................................118
Figure A.12. $^1$H NMR of 2-methylpyridinium tetrafluoroborate in CD$_3$CN. ..........................119
Figure A.13. $^1$H NMR of 2,6-lutidinium tetrafluoroborate in CD$_3$CN. .................................119
Figure A.14. $^1$H NMR of 4-methoxypyridinium tetrafluoroborate in CD$_3$CN. ........................119
Figure A.15. $^1$H NMR of 2-aminopyridinium tetrafluoroborate in CD$_3$CN. ............................120
Figure A.16. $^1$H NMR of 2,4,6-trimethylpyridinium tetrafluoroborate in CD$_3$CN. ................120
Figure A.17. $^1$H NMR of 2-aminobenzimidazolium tetrafluoroborate in CD$_3$CN. ................120
Figure B.1. Structures of literature complexes and ligands. ......................................................121
Figure B.2. Structures of novel ligands and complexes prepared for this dissertation ..................122
Figure B.3. $^1$H NMR spectrum of PSP in CD$_3$CN (400 MHz). .............................................123
Figure B.4. $^{31}$P($^1$H) NMR spectrum of PSP in CD$_3$CN (400 MHz). .................................123
Figure B.5. $^1$H NMR of NiP$_2$(S$_2$-pyz) in d-DMSO (500 MHz). ..........................................124
Figure B.6. $^{31}$P($^1$H) NMR of NiP$_2$(S$_2$-pyz) in CD$_3$CN (400 MHz). ...............................125
Figure B.7. Cyclic voltammogram of 0.5 mM NiP$_2$(S$_2$-pyz) at 100 mV/s in acetonitrile with 0.25 M [Bu$_4$N][PF$_6$] .................................................................125
Figure B.8. Cyclic voltammogram of 0.5 mM NiP$_2$(S$_2$-pyz) at 100 mV/s in acetonitrile with 0.25 M [Bu$_4$N][PF$_6$] with and without 0.5 mM benzoic acid.........................125
Figure B.9. $^1$H NMR of NiP$_2$(4-pedt) in CD$_3$CN (400 MHz) .............................................127
Figure B.10. $^{31}$P($^1$H) NMR of NiP$_2$(4-pedt) in CD$_3$CN (400 MHz) ....................................127
Figure B.11. Cyclic voltammogram of 0.5 mM NiP2(4-pedt) at 100 mV/s in acetonitrile with 0.25 M [Bu$_4$N][PF$_6$] .................................................................128
Figure B.12. Cyclic voltammogram of 0.5 mM NiP$_2$(4-pedt) at 100 mV/s in acetonitrile with 0.25 M [Bu$_4$N][PF$_6$] with 0.5 mM 2,4,6-Br$_3$-PhOH or Et$_3$NH$^+$ ....................................................128
Figure B.13. Compound NiP$_2$S$_2$ with expected unique $^1$H peaks. .....................................129
Figure B.14. $^1$H NMR of NiP$_2$S$_2$ in CD$_3$CN (400 MHz) with proton assignments per Figure B.13. .................................................................130
Figure B.15. $^{31}$P($^1$H) NMR spectrum of NiP$_2$S$_2$ in CD$_3$CN (400 MHz) ........................130
Figure B.16. $^1$H-$^1$H gradient enhanced COSY NMR of NiP$_2$S$_2$ in CD$_3$CN (400 MHz). ........131

Figure B.17. Upfield region of $^1$H-$^1$H gradient enhanced COSY NMR of NiP$_2$S$_2$ in CD$_3$CN (400 MHz). ..................................................................................................................131

Figure B.18. $^1$H-$^{31}$P HMQC NMR spectrum (CD$_3$CN, 400 MHz) of NiP$_2$S$_2$. ..................132

Figure B.19. $^1$H NMR of (tman)(BF$_4$)$_2$ in CD$_3$CN (500 MHz). .........................................133

Figure B.20. $^1$H NMR of [Ni(tman)(4-pedt)](BF$_4$)$_2$ in CD$_3$CN (500 MHz). ..................134

Figure B.21. Cyclic voltammograms of 0.5 mM [Ni(tman)(4-pedt)](BF$_4$)$_2$
and (tman)(BF$_4$)$_2$ at 100 mV/s in acetonitrile with 0.25 M [Bu$_4$N][PF$_6$]. .................134

Figure C.1. Extinction coefficients of methyl orange and protonated methyl orange in acetonitrile. ..................................................................................................................................................................................................................135

Figure C.2. Extinction coefficients of 3-nitroaniline and 3-nitroanilinium in acetonitrile. .........................................................................................................................................................................................136

Figure C.3. UV-vis monitored titration of methyl orange with 4-tert-butylanilinium in acetonitrile. .................................................................................................................................................................................................................................................................136

Figure C.4. Plot of [protonated methyl orange]*[4-tert-butylanilinium]/[4-tert-butylanilinium]
versus [methyl orange]. ........................................................................................................................................................................................................................................................................137

Figure C.5. UV-vis monitored titration of 3-nitroaniline with 4-chloroanilinium. ...................138

Figure C.6. Plot of [3-nitroanilinium]*[4-chloroanilinium]/[4-chloroanilinium] versus [3-nitroaniline]. .................138

Figure C.7. Cyclic voltammogram of 0.05 mM silver nitrate in 100 mM [Bu$_4$N][PF$_6$] acetonitrile solution. ........................................................................................................................................................................................................................................139

Figure C.8. Cyclic voltammogram of 25 mM 4-bromoanilinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ........................................................................................................................................................................................................................................139

Figure C.9. Cyclic voltammogram of 25 mM 4-bromoanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ........................................................................................................................................................................................................................................140

Figure C.10. Cyclic voltammogram of 25 mM 4-chloroanilinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ........................................................................................................................................................................................................................................140

Figure C.11. Cyclic voltammogram of 25 mM 4-chloroanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ........................................................................................................................................................................................................................................140

Figure C.12. Cyclic voltammogram of 25 mM 4-nitroanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ........................................................................................................................................................................................................................................141

Figure C.13. Cyclic voltammogram of 25 mM 4-nitroanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ........................................................................................................................................................................................................................................141
Figure C.14. Cyclic voltammogram of 25 mM 4-tert-butylanilinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................141

Figure C.15. Cyclic voltammogram of 25 mM 4-tert-butylanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................142

Figure C.16. Cyclic voltammogram of 25 mM acetic acid at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................142

Figure C.17. Cyclic voltammogram of 25 mM acetic acid at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................142

Figure C.18. Cyclic voltammogram of 25 mM anilinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................143

Figure C.19. Cyclic voltammogram of 25 mM anilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................143

Figure C.20. Cyclic voltammogram of 25 mM benzoic acid at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................143

Figure C.21. Cyclic voltammogram of 25 mM benzoic acid at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................144

Figure C.22. Cyclic voltammogram of 25 mM dimethylformamidium triflate at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................144

Figure C.23. Cyclic voltammogram of 25 mM dimethylformamidium triflate at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................144

Figure C.24. Cyclic voltammogram of 25 mM N,N-dimethylanilinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................145

Figure C.25. Cyclic voltammogram of 25 mM N,N-dimethylanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................145

Figure C.26. Cyclic voltammogram of 25 mM 4-methoxyanilinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................145

Figure C.27. Cyclic voltammogram of 25 mM 4-methoxyanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................146

Figure C.28. Cyclic voltammogram of 25 mM 4-cyanoanilinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................146

Figure C.29. Cyclic voltammogram of 25 mM 4-cyanoanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................146

Figure C.30. Cyclic voltammogram of 25 mM phenol at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. .................................................................147
Figure C.31. Cyclic voltammogram of 25 mM phenol at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 147

Figure C.32. Cyclic voltammogram of 25 mM pyridinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 147

Figure C.33. Cyclic voltammogram of 25 mM pyridinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 148

Figure C.34. Cyclic voltammogram of 25 mM salicylic acid at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 148

Figure C.35. Cyclic voltammogram of 25 mM salicylic acid at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 148

Figure C.36. Cyclic voltammogram of 25 mM p-toluenesulfonic acid monohydrate at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ......................... 149

Figure C.37. Cyclic voltammogram of 25 mM p-toluenesulfonic acid monohydrate at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ......................... 149

Figure C.38. Cyclic voltammogram of 25 mM trichloroacetic acid at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 149

Figure C.39. Cyclic voltammogram of 25 mM trichloroacetic acid at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 150

Figure C.40. Cyclic voltammogram of 25 mM triethylammonium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 150

Figure C.41. Cyclic voltammogram of 25 mM triethylammonium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 150

Figure C.42. Cyclic voltammogram of 25 mM trifluoromethanesulfonic acid at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 151

Figure C.43. Cyclic voltammogram of 25 mM trifluoromethanesulfonic acid at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 151

Figure C.44. Cyclic voltammogram of 25 mM trifluoroacetic acid at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 151

Figure C.45. Cyclic voltammogram of 25 mM trifluoroacetic acid at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 151

Figure C.46. Cyclic voltammogram of 25 mM 2-nitrophenol at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 152

Figure C.47. Cyclic voltammogram of 25 mM 2-nitrophenol at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile. ................................................................. 152
Figure C.48. Cyclic voltammogram of 25 mM water at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile. ................................................................. 153

Figure C.49. Cyclic voltammogram of 25 mM water at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile. ................................................................. 153

Figure C.50. Cyclic voltammogram of 2-nitrophenol at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 154

Figure C.51. Cyclic voltammogram of 4-bromoanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 154

Figure C.52. Cyclic voltammogram of 4-chloroanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 155

Figure C.53. Cyclic voltammogram of 4-cyanoanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 155

Figure C.54. Cyclic voltammogram of 4-methoxyanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 155

Figure C.55. Cyclic voltammogram of 4-nitroanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 156

Figure C.56. Cyclic voltammogram of 4-tert-butylanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 156

Figure C.57. Cyclic voltammogram of acetic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 156

Figure C.58. Cyclic voltammogram of anilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 157

Figure C.59. Cyclic voltammogram of benzoic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 157

Figure C.60. Cyclic voltammogram of dimethylformamidium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 157

Figure C.61. Cyclic voltammogram of N,N-dimethylanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution. ................................................................. 158
Figure C.62. Cyclic voltammogram of phenol at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution ........................................... 158

Figure C.63. Cyclic voltammogram of p-toluenesulfonic acid monohydrate at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution ........................................... 158

Figure C.64. Cyclic voltammogram of pyridinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution ........................................... 159

Figure C.65. Cyclic voltammogram of salicylic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution ........................................... 159

Figure C.66. Cyclic voltammogram of trichloroacetic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution ........................................... 159

Figure C.67. Cyclic voltammogram of triethylammonium chloride at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution ........................................... 160

Figure C.68. Cyclic voltammogram of trifluoroacetic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution ........................................... 160

Figure C.69. Cyclic voltammogram of trifluoromethanesulfonic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution ........................................... 160

Figure C.70. ¹H NMR spectra taken at 0.3 and 69 hours of 1.2 molar excess of acetonitrile reacted with trifluoromethanesulfonic acid for ca. three minutes followed by addition to CD₃CN such that the final concentration of trifluoromethanesulfonic acid equalled 125 mM ........................................... 161

Figure D.1. Photo of three-compartment bulk electrolysis cell used to produce hydrogen for detection by bulk electrolysis ........................................... 163

Figure E.1. Simulated CVs for the E_CiE mechanism using the parameters in Table E.1 (except E₁ was set as 0 V instead of -1.92 V) ........................................... 166

Figure F.1. Cyclic voltammogram of 0.2 mM 1, 0.2 mM dimethylformamidium triflate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s ........................................... 168

Figure F.2. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-cyanoanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s ........................................... 168

Figure F.3. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-trifluoromethylanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s ........................................... 169
Figure F.4. Cyclic voltammogram of 0.2 mM 1, 0.2 mM \( p \)-toluenesulfonic acid monohydrate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. .......................................................... 169

Figure F.5. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-(methylbenzoate)anilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 169

Figure F.6. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-trifluoromethoxyanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 170

Figure F.7. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-bromoanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 170

Figure F.8. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-chloroanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 170

Figure F.9. Cyclic voltammogram of 0.2 mM 1, 0.2 mM anilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 171

Figure F.10. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-tertbutylanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 171

Figure F.11. Cyclic voltammogram of 0.2 mM 1, 0.2 mM \( N,N \)-dimethylanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 172

Figure F.12. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-methylanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 172

Figure F.13. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-methoxyanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 172

Figure F.14. Cyclic voltammogram of 0.2 mM 1, 0.2 mM pyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 172

Figure F.15. Cyclic voltammogram of 0.2 mM 1, 0.2 mM trifluoroacetic acid, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 173

Figure F.16. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2-methylpyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu\(_4\)N][PF\(_6\)] CH\(_3\)CN solution at 100 mV/s. ............... 173
Figure F.17. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2,6-lutidinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................173

Figure F.18. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-methoxypyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................174

Figure F.19. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2-aminopyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................174

Figure F.20. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2,4,6-trimethylpyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................174

Figure F.21. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2-aminobenzimidazolium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................175

Figure F.22. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-trifluoromethyl-2,3,5,6-tetrafluorophenol, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................175

Figure F.23. Cyclic voltammogram of 0.2 mM 1, 0.2 mM pentabromophenol, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................175

Figure F.24. Cyclic voltammogram of 0.2 mM 1, 0.2 mM triethylammonium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................176

Figure F.25. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2,4,6-tribromophenol, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................176

Figure F.26. Cyclic voltammogram of 0.2 mM 1, 0.2 mM benzoic acid, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s. ........................................................................................................176

Figure F.27. EC mechanism for oxidation of 1 ........................................................................................................177

Figure F.28. The predicted relationship between $E_{1/2}$ and the $pK_a$ of HA for an EC reaction (+) reveals a linear region (---) with a slope of 59 mV/decade for $pK_a$ values greater than ca. 13. ................................................178

Figure F.29. CE mechanism for oxidation of 1 ........................................................................................................179

Figure F.30. The predicted relationship between $E_{1/2}$ and the $pK_a$ of HA for a CE reaction (−) reveals a linear region (---) with a slope of 59 mV/decade for $pK_a$ values less than ca. 14.25. ................................................180

Figure F.31. Overlay of the predicted relationship between $E_{1/2}$ and the $pK_a$ of HA for both the CE (+) and EC (−) mechanisms ........................................................................................................181
Figure F.32. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 4-CF₃-anilinium, at varying scan rates..................................................182

Figure F.33. Cyclic voltammograms of 0.45 mM 2 with one molar equivalent of p-toluenesulfonic acid, at varying scan rates.................................183

Figure F.34. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 4-bromoanilinium at various scan rates..........................183

Figure F.35. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 4-chloroanilinium at various scan rates.........................183

Figure F.36. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of anilinium at various scan rates........................................184

Figure F.37. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 4-tert-butylanilinium at various scan rates......................184

Figure F.38. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of trifluoroacetic acid at various scan rates........................184

Figure F.39. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 2,6-lutidinium at various scan rates..............................185

Figure F.40. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 2,4,6-trimethylpyridinium at various scan rates.............185

Figure F.41. Cyclic voltammograms of 0.5 mM 2 with one molar equivalent of 4-CF₃-2,3,5,6-F₄-PhOH at various scan rates.....................................185

Figure F.42. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of triethylammonium at various scan rates.......................186

Figure F.43. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of benzylammonium at 100 mV/s.........................................................187

Figure F.44. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of triethylammonium at 100 mV/s.........................................................188

Figure F.45. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of 2,4,6-tribromophenol at 100 mV/s....................................................188

Figure F.46. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of benzoic acid at 100 mV/s.................................................................188

Figure F.47. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of acetic acid at 100 mV/s.................................................................189

Figure F.48. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of 4-chlorophenol at 100 mV/s.........................................................189
Figure F.49. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of o-cresol at 100 mV/s ................................................................. 189

Figure F.50. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of 2,4,6-tri-tert-butylphenol at 100 mV/s ................................................................. 190

Figure F.51. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of phenol at 100 mV/s ................................................................................. 190

Figure G.1. Background subtracted cathodic peak currents for 0.4 mM 1 plotted versus the square root of the scan rate. ................................................................. 191

Figure G.2. Background subtracted cathodic peak currents for 0.4 mM 1(H)\(^{1+}\) (generated \textit{in situ} using excess dimethylformamidium triflate) plotted versus the square root of the scan rate ................................................................. 192

Figure G.3. \(^1\text{H}\) DOSY NMR spectrum of a CD\(_3\)CN solution of 2-methylpyridine. .............. 194
# LIST OF ABBREVIATIONS AND SYMBOLS

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CHAPTER 1. Introduction


1.1 Need for Large Scale Fuel Synthesis

Humanity is projected to require ever-larger amounts of energy – both to provide for the rising world population and to raise the standard of living for billions. While there are still large coal and natural gas reserves, the economically accessible oil reserves, on which modern transportation depends, are becoming depleted. Additionally, use of fossil fuels is resulting in increasingly large impending bills for humanity in the form of future climate change adaptation costs. Finally, Earth’s ecological resources are in grave danger from climate change and increasing population pressure.

Ironically, chemistry has both created and solved problems. Energy from chemical fuels improves standards of living, yet the emissions from their use contribute to climate change. Fertilizer synthesis enables the vast production of food, allowing for the feeding of large numbers of people, yet also allows for massive overpopulation and destruction of landscapes not normally suitable for farming. Chemistry has allowed more people to exist with higher qualities of life, yet it has also enabled the endangerment of current and future generations.

Chemistry has clearly made massive positive contributions to society. It is time to utilize that power to address the negative issues chemistry inadvertently helped create. Reduction of overpopulation can be achieved through lowering birth rates; one of the most effective ways of doing this is through improving education – hence upwards mobility – of young people, particularly girls. Birth rates are inversely related to standard of living; consequently, improving
standard of living for all should be a top priority. Increased access to clean water is necessary for productive, healthy lives, yet clean water resources are overused and dwindling.\textsuperscript{3,4} Shifting focus to water desalination could provide this needed fresh water and reduce destruction of remaining fresh water resources.

Accomplishing these large-scale goals will require tremendous amounts of energy. If this energy continues to come from fossil fuel consumption, the magnitude of the resulting climate change will be extremely destructive. Consequently, a paramount goal of chemistry today is the research of cleaner ways to utilize fossil fuels alongside the development of renewable ways to collect and store energy.

Vast effort has been devoted specifically to improving methods for collecting solar energy.\textsuperscript{5–7} A parallel, yet critical, effort is researching methods for storing that solar energy and assessing its economic viability.\textsuperscript{8} Efforts to store energy are also motivated by the realization that global transportation depends on easily transported chemical fuels. Two possible paths are being explored: 1) improving methods of storing electrical energy in batteries and supercapacitors\textsuperscript{9–12} and 2) finding improved ways to synthesize chemical fuels that can then drive motors or fuel cells.\textsuperscript{6,13,14}

1.2 Fuel Synthesis by Electrolysis

Fuel synthesis requires converting energy poor feedstocks into energy rich products using energy inputs. One convenient and scalable energy input is electricity, which would ideally be delivered from renewable energy sources. The process of converting energy poor feedstocks into chemical fuels is achieved via electrolysis – the transformation of molecules at an electrode surface into new species.

The ability of electrolysis to produce useful chemical fuels is well highlighted by the electrolysis of water into hydrogen and oxygen. In the simple form of this reaction, electrons are stripped from water molecules at one electrode, yielding oxygen, protons, and electrons. These
electrons and protons are recombined at the other electrode to form hydrogen. If the two electrodes are separated by a proton-permeable membrane, the hydrogen and oxygen can be collected separately and the hydrogen stored for future use. While there are outstanding challenges in storing hydrogen in an energy-dense fashion, significant progress has been achieved,\textsuperscript{15–17} buoying hopes that hydrogen can be a large scale clean fuel.

The electrolytic synthesis of hydrogen from water can be achieved quite simply by placing two electrodes into water with electrolyte and running current. Despite this simplicity, the predominant source of hydrogen is currently from natural gas, where steam reformation followed by the water gas shift reaction produces the desired hydrogen plus carbon dioxide, an undesirable byproduct. While many electrode materials can be used to electrolyze water, most do so with significant energy loses. Materials that can electrolytically synthesize water with great energy efficiency – such as platinum – are too expensive to consider for large-scale use.

In response, researchers have drawn inspiration from enzyme active sites, particularly hydrogenase derivatives. These active sites achieve high hydrogen evolution efficiency with minimal energy loss. Through careful studies of the [Fe-Fe] hydrogenase active site, it was found that a secondary coordination sphere proton shuttle – an amine – permitted protons to be delivered directly to the iron core that facilitated proton and electron combination (Figure 1.1).

![Figure 1.1](image.png)

\textbf{Figure 1.1.} Structure of the [Fe-Fe] active site (above) and structure of synthetic hydrogenase mimics (bottom). Red circles highlight possible proton shuttle location. Adapted by permission from Macmillan Publishers Ltd: \textit{Nature}, \textit{49}, 7456, copyright 2013.
This unique proton-shuttling feature of the hydrogenase active site was suspected years prior to verification; in that time numerous examples demonstrated that amine proton shuttles drastically improved hydrogen evolution rate and efficiency in molecular catalysts.18–21

1.3 Proton-Coupled Electron Transfer Underpins H₂ Evolution

Realization that hydrogen evolution efficiency and rate can be improved through intentional incorporation of proton relays has sharpened interest in how the movement of protons and electrons are coupled. Within the context of hydrogen evolution, the catalyst must orchestrate the union of two electrons and two protons. The elementary proton and electron transfer (PT and ET, respectively) steps in this reaction are frequently proton-coupled electron transfer (PCET) reactions wherein the movement of an electron induces movement of a proton or vice versa. PCET is traditionally viewed in terms of a square scheme (Figure 1.2) where concerted and stepwise routes are possible. Reactions that proceed via the stepwise routes necessarily proceed through high energy intermediates. Consequently, mechanistic study of PCET reactions involving transition metal complexes is an important step towards designing more efficient catalysts for hydrogen evolution reactions. Further, as PCET reactions are additionally relevant outside the subfield of fuel formation reactions, the quest to understand PCET in hydrogen evolution catalysts simultaneously contributes more broadly useful fundamental knowledge.

\[ M + H-A \leftrightarrow M^- + H-A \]

\[ MH^+ + A^- \leftrightarrow MH + A^- \]

**Figure 1.2.** Square scheme representation of a homogeneous PCET reaction where species M receives one electron and one proton to form MH. H-A represents an acid molecule, and ET, PT, and CPET indicate electron transfer, proton transfer, and concerted proton-electron transfer, respectively.
Our group has focused on understanding PCET processes in matters relevant to energy conversion and storage processes; specifically in the context of *homogeneous* electrochemical catalysts for the hydrogen evolution reaction (HER). As noted above, it has become increasingly clear that an understanding of electrochemical PCET processes are crucial for advancing HER and other catalytic processes. Studies of PCET reaction mechanisms to date have primarily involved organic substrates relevant to biological charge transport pathways, with only a few examples of transition metal-based systems.\(^{22–26}\) Further, while a rich literature exists for the study of homogeneous based PCET, where electron and proton transfers occur between discrete molecules (Figure 1.3A),\(^{23,26–30}\) there are fewer reports which detail individual electrochemical PCET steps (specifically where the electrode is a partner in the electron transfer reaction, Figure 1.3B).\(^{25,31–38}\) This is not due to a lack of methodology or theory – extensive information and experimental examples exist for the study of electrochemical mechanism.\(^{35,36,39–46}\) In addition, detailed theoretical analyses for mechanism-dependent electrochemical PCET rate expressions have been reported.\(^{47–49}\) However, only recently have these methods received more use in the study of PCET processes relevant to energy storage.\(^{35,37,38,41,45,50}\)

In the study of electrochemical mechanisms, elementary steps are generally divided into two categories: electrochemical (E) steps and chemical (C) steps. An E step involves the movement of an electron to/from the electrode whereas any other homogeneous chemical transformation corresponds to a C step. Additional subscripts may designate reversibility (subscript r) or irreversibility (subscript i) of individual steps, while the term (EC) indicates a concerted E and C step. This classic electrochemical nomenclature is readily paired with traditional homogeneous PCET terminology. For example, an electron transfer followed by a proton transfer, referred to as ET-PT in PCET literature, is designated more generally as an EC electrochemical mechanism. Meanwhile, the concerted-proton electron transfer – CPET – pathway would be designated (EC).
Proton transfer generally occurs between discrete molecular proton donors and proton acceptors; however, electron transfer may occur between solution species or, as considered more frequently, to and from the electrode directly. As electron transfer occurs between solution and an electrode, two interesting, and, as of yet, incompletely explored influences on the PCET mechanism arise.

First, the kinetic barrier of the CPET pathway is impacted. In purely homogeneous systems, PCET may involve three discrete molecules which must encounter one another in a ternary reaction for a CPET process (Figure 1.3A). While the formation of high-energy, charged intermediates are circumvented, this termolecular reaction can give rise to a high kinetic barrier. As such, stepwise ET-PT or PT-ET mechanisms are often favored kinetically. Conversely, for electrochemical PCET, the reaction between the PCET substrate and the proton donor/acceptor occurs at an essentially infinite electrode surface (Figure 1.3B). As such, the kinetic barriers for an electrochemical CPET process will be different than the termolecular homogeneous example.

Figure 1.3. Cartoon depictions of A) homogeneous termolecular CPET (case for two donors and one acceptor shown; more partners are possible) and B) electrochemical PCET. Reprinted with permission from ACS Catalysis 2016, 6, 3644. Copyright (2016) American Chemical Society.
Second, the electron transfer driving force changes during a potential-sweep electrochemical experiment. It has been demonstrated that via careful selection of chemical oxidants, the PCET oxidation of a tungsten-hydride bond can be induced to undergo a CPET mechanism. In an electrochemical experiment such as cyclic voltammetry, the driving force for electron transfer changes as a function of time. This suggests that the PCET mechanism may change during a single experiment as the potential is swept (Figure 1.4). It has already been demonstrated that mechanisms for hydrogen evolution can in some cases switch from ECEC to EECE as the applied potential is scanned cathodically. This strongly suggests that a change of potential may promote a change in the mechanism of an individual PCET event.

**Figure 1.4.** As applied potential changes throughout a variable-potential experiment, the PCET mechanism accessed may change as the driving force changes. Reprinted with permission from *ACS Catalysis* 2016, 6, 3644. Copyright (2016) American Chemical Society.

### 1.4 Studying PCET by Cyclic Voltammetry

As detailed above, catalysis involves elementary steps whose kinetics may be investigated by a variety of spectroscopic and electrochemical methods. A key question for driving the design of more energy-efficient catalysts is whether the elementary steps may be controlled through rational design of catalysts or experimental conditions. Towards this, recent efforts have focused on furthering cyclic voltammetry techniques for the study of PCET systems.
PCET can be triggered by electron transfer at an electrode surface. In the absence of proton transfer, reversible electron transfer for the reduction \( P + e^- \Rightarrow Q \) occurs at the electrode as governed by the Nernst equation:

\[
E = E^{0'} - \frac{RT}{nF} \ln \left( \frac{C_P}{C_Q} \right)
\]

where \( C_P \) and \( C_Q \) are the concentrations of P and Q at the electrode surface, respectively, and \( E^{0'} \) is the formal reduction potential. The concentrations of P and Q at the electrode surface vary with the applied potential accordingly.

If proton transfer is now permitted, the observed current flow vs. applied potential will vary as a function of the reversibility of proton transfer, protonation kinetics, and thermodynamics. Should proton transfer be irreversible the resulting cyclic voltammogram may show a loss of the reversible electron transfer. The potential at which electron transfer occurs in this case can heavily depend on the proton source concentration and protonation kinetics; this is discussed in more detail below and in Chapter 4.

**1.4.1 Protonation Kinetics Can Shift Potential**

When proton transfer follows electron transfer, the rate of proton transfer influences the potential of the PCET wave in a cyclic voltammogram. For Nernstian electron transfer followed by protonation, protonation of the small amount of reduced complex present at potentials positive of the reduction potentials induces rapid repopulation at the electrode of reduced complex. Further protonation results in more reduction and a peak appears in the cyclic voltammogram at potentials positive of the reduction potential in the absence of acid. Faster pronation rates and higher acid concentrations cause can cause larger equilibria distortion and peaks that are shifted further positive.

The peak location potential as a function of acid concentration ([BH\(^+\)]) and protonation rate \( k_1 \) can be described as:

\[
E_{\text{peak}} = E_{l/0}^0 - \frac{RT}{F} (0.78) + \frac{RT}{2F} \ln \left( \frac{k_1 \cdot [BH^+] \cdot RT}{Fv} \right)
\]
where $E_{i}^{0}$ is the potential of electron transfer in the absence of BH$, R$ is the gas constant, $F$ is the Faraday constant, $T$ temperature, and $v$ is the scan rate. Support for this type of EC mechanism is gained if the difference in peak potential depends linearly on the log([BH$^+$]) with a slope of ca. 30 mV/decade. This type of analysis can be carried out for hydrogen evolution catalysis when catalytic turnover can be shut off,$^{38}$ and for systems that do not undergo catalysis. As the rate of the chemical step directly corresponds to the peak shift magnitude, this type of potential shift is often referred to as a kinetic shift.

1.4.2 Interpreting PCET within Catalysis

For molecules designed to be hydrogen evolution catalysis, addition of a proton source can give greatly enhanced current flow and loss of reversibility. The resulting wave shape then depends on the kinetics and thermodynamics of the individual catalytic steps.$^{46,55}$ Care must be taken in interpreting hydrogen evolution PCET by cyclic voltammetry however, as both direct electrode reduction of the proton source and catalyst decomposition can result in new redox features. These cases are discussed in Chapters 2 and 3, respectively.

Kinetic information of protonation steps can be gleaned from catalytic cyclic voltammograms. A clear example of this was the analysis of the hydrogen evolution mechanism of a cobaloxime derivative (Figure 1.5) in acetonitrile with various organic acids acting as proton sources.$^{56}$ Utilization of foot-of-the-wave analysis (FOWA), a technique that analyzes just the current response at the beginning of the catalytic wave,$^{42,46,57}$ allowed the kinetics of the first protonation step following reduction to be determined.$^{56}$ Analysis of the catalytic plateau current gave the protonation kinetics of the second protonation step. In most cases, plateau analysis gives the rate limiting step, as was the case for this cobaloxime. Finally, an acid-independent rate constant was determined from the maximum current attained. This holistic analysis suggested the mechanism shown in Figure 1.6.
10

**Figure 1.5.** Structure of Co(dmgBF₂)₂(L)₂.

**Figure 1.6.** Proposed hydrogen evolution mechanism of Co(dmgBF₂)₂(L)₂, written here as 1. Rate constants were determined by FOWA ($k_1$), plateau current analysis ($k_2$), and interpretation of the maximum attainable current ($k_3$). Reprinted with permission from *ACS Catalysis* 2016, 6, 3326. Copyright (2016) American Chemical Society.

### 1.4.3 Total catalysis gives rise to a second peak

To avoid the complexity in interpreting protonation kinetics for hydrogen evolution catalysts, one possibility is reducing the proton concentration to that of the catalyst. In this fashion it may be expected that each catalyst molecule with react stoichiometrically with a proton and so giving information on just that first proton transfer. In the case of the cobaloxime derivative (**Figure 1.5**) discussed above, under electrochemical catalytic conditions with an appropriately small amount of proton source, total catalysis actually occurs instead of stoichiometric proton transfer.$^{56,58}$

Total catalysis occurs when the kinetics of catalysis are fast enough such that prior to the primary redox wave the small amount of reduced catalyst (as governed by the Nernst equation)
consumes all of the available substrate to produce product and regenerated oxidized catalyst. Consequently, the normal redox wave of the catalyst is observed after the catalytic peak (Figure 1.7). Extracting accurate kinetic information from the catalytic peak position in this case is possible, but is significantly restricted to a small parameter range; therefore, more versatile methods like foot-of-the-wave analysis are generally preferred.\textsuperscript{38,56} Assignment of a feature as total catalysis can be checked via observation of the suspected catalytic peak location as a function of acid concentration, catalyst concentration, and scan rate.\textsuperscript{56}

This PCET behavior results from fast catalysis and/or low acid concentrations. Probing the kinetics and thermodynamics of discrete PCET steps can require working with acid concentrations of the same concentration as the complex. For complexes that are catalytic, the possibility of total catalysis means that new peaks observed may be misinterpreted as a discrete PCET event involving all of the complex at the electrode surface, rather than the small fraction expected in total catalysis.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure17.png}
\caption{Example of a total catalysis waveform for the electrochemical hydrogen evolution with 5 mM catalyst Co(dmgBF\textsubscript{2})\textsubscript{2}(CH\textsubscript{3}CN)\textsubscript{2} and 5 mM \textit{p}-cyanoanilinium in acetonitrile at 100 mV/s with 0.25 M [Bu\textsubscript{4}N][PF\textsubscript{6}]. All of the acid is consumed near the reaction layer, resulting in the appearance of initial catalytic current followed by the Co\textsuperscript{III} redox wave. Reprinted with permission from \textit{ACS Catalysis} 2016, 6, 3644. Copyright (2016) American Chemical Society.}
\end{figure}
1.5 Dissertation Overview

As highlighted above, successfully investigating PCET mechanisms using cyclic voltammetry requires consideration of a broad range of possibilities. There are a few useful checks prior to rigorous analysis. It should be assessed if there is any contribution from direct electrode reduction of the proton source (Chapter 2) and if the complex undergoing suspected PCET decomposes (Chapter 3 and part of Chapter 6). The possibility of catalytic turnover and total catalysis responses can also be evaluated.\textsuperscript{46,56,58}

Following these checks, discrete PCET steps can be investigated. Examples presented in this chapter highlight how proton transfer kinetics can be probed using cyclic voltammetry. The bulk of the research described here focuses on how the thermodynamics of PCET influence electrochemical responses. Chapter 4 describes our initial investigation of a nickel complex that undergoes reductive PCET in a concerted process prior to decomposition. Motivated by this result, focus turned towards investigating systems where reversible PCET is observed. The influence of thermodynamics on reversible PCET cyclic voltammetric responses is assessed in Chapter 5 and experimental examples presented. While this thermodynamic analysis explained the observed potential shifts, analysis of the PCET mechanism of a molybdenum complex required further investigation as presented in Chapter 6.
CHAPTER 2. Electrochemical Reduction of Acids by Glassy Carbon


2.1 Introduction

Homogeneous hydrogen evolution catalysts are often evaluated electrochemically in acetonitrile, where an electrode supplies electrons and a Brønsted acid provides protons:

\[
\text{catalyst} + 2e^- + 2\text{HA} \rightarrow \text{catalyst} + 2\text{A}^- + \text{H}_2 \quad (1)
\]

A possibly serious complication in these studies is direct acid reduction by the electrode at potentials that overlap with molecular catalysis (Figure 2.1).

\[
2\text{HA} + 2e^- \rightarrow \text{H}_2 + 2\text{A}^- \quad (2)
\]

Figure 2.1. Simulated cyclic voltammograms of an EC’ catalytic process in which direct substrate reduction (acid reduction) occurs at potentials a) far from catalysis, b) slightly overlapping with catalysis, c) strongly overlapping with catalysis, and d) nearly completely overlapping with catalysis. Solid gray line indicates that only acid is present while the dotted blue line indicates that catalyst and acid are present. Simulated using DigiElch electrochemical simulation software (Gamry Instruments); \( \alpha = 0.5 \), \( k_s = 10,000 \text{ cm/s} \), \( k_{\text{catalysis}} = 10,000 \text{ M}^{-1} \text{ s}^{-1} \), \([\text{catalyst}] = 0.01 \text{ M} \), \([\text{substrate}]_0 = 5 \text{ M} \).
It has been noted that the catalytic currents observed for some catalysts may have contributions arising from direct substrate reduction.\textsuperscript{59} As accurate extraction of kinetic data from catalytic cyclic voltammograms relies on the observed current;\textsuperscript{40} competing direct reduction complicates kinetic analysis. Direct reduction of substrate can also yield cyclic voltammograms (CVs) that mimic prototypical catalytic responses,\textsuperscript{44} especially that of catalysis exhibiting substrate depletion,\textsuperscript{55} making it unclear whether the catalyst is responsible for the current enhancement. As many hydrogen evolution catalysts operate at fairly cathodic potentials, the possibility of direct acid reduction by both relatively strong and relatively weak acids becomes an even greater concern.

These issues are minimized when acid-only controls are run. Surprisingly, acid-only cyclic voltammograms are not always reported with catalytic data. The widespread use of glassy carbon working electrodes for non-aqueous hydrogen evolving catalysts may provide one reason. Glassy carbon is often cited as non-catalytic,\textsuperscript{60–62} incorrectly implying that the direct reduction of protons to form hydrogen occurs at such negative potentials as to be inconsequential. While glassy carbon indeed reduces acids at more negative potentials than platinum,\textsuperscript{63} reduction processes can still occur. Moreover, when stronger acids are employed, reduction is expected to occur at relatively positive potentials.\textsuperscript{59} While aqueous proton reduction has been extensively studied on many electrode materials, especially platinum,\textsuperscript{64,65} and remains the subject of active research,\textsuperscript{65} little data is available on the reduction of acids in acetonitrile by glassy carbon. One report described the use of different electrodes to achieve wider potential windows for acids in acetonitrile, but only data for acetic acid was shown.\textsuperscript{63}

Water, whether intentionally added or present as contamination, is a further complication. Dramatic increases in catalytic current have been reported for some catalysts in acetonitrile with added water.\textsuperscript{66,67} For these cases water has been suggested to act as a proton relay capable of more easily reaching the metal centers of sterically crowded molecular
catalysts. Water has been noted to shift the reduction potential of perchloric acid on mercury
cathodically by hundreds of millivolts, having stabilized the acidic species against reduction.\textsuperscript{68} It
is unclear whether the reduction potentials of weaker acids could be affected as well, potentially
resulting in overlapping direct reduction in the potential regime of a catalyst.

Motivated by our interest in molecular electrocatalysts for hydrogen evolution, we were
interested in better understanding the potential window limits of glassy carbon. Accordingly, the
goal of this work is to establish useful approximate working ranges for common acids in
acetonitrile for the specific purpose of catalytic hydrogen evolution. Reduction potentials of 20
acids in acetonitrile on glassy carbon are reported along with details on the influence of water.

\section*{2.2 Results}

\subsection*{2.2.1 Reference Electrode}

Two non-aqueous reference electrodes were tested: 1) a reference electrode in which a silver wire was immersed in an acetonitrile solution containing 100 mM \textbf{[Bu}_4\textbf{N][PF}_6\textbf{]} and 10 mM \textbf{AgNO}_3; and 2) a pseudo-reference in which a silver wire was immersed in an acetonitrile
solution containing 100 mM \textbf{[Bu}_4\textbf{N][PF}_6\textbf{]}. In both cases the silver wire and electrolyte solution
were contained in a glass tube fitted with a porous Vycor glass frit. Ferrocene was added at the
end of each measurement set as an absolute reference. Reference electrode 1 was observed to
occasionally contaminate the bulk solution with silver ions, as suggested by an oxidation at
approximately \(-0.24\) V vs. \(\text{Fc/Fc}^+\). By comparison to pure silver nitrate, the contamination
proved to be the stripping of reduced silver off the glassy carbon electrode (Appendix C). This
contamination of the bulk solution with silver ions was observed to result in variable reduction
potentials for some acids. Silver is likely a better catalyst for hydrogen evolution than glassy
carbon; as such, any silver contamination may shift the acid reduction potential more positive.

A Ag/AgCl pseudoreference immersed in an acetonitrile electrolyte solution in a glass
tube equipped with a porous Vycor frit was not used because silver chloride is somewhat
soluble in acetonitrile (especially if solution chloride anions are present),\textsuperscript{69} and we wished to
avoid the possibility of solution contamination by silver ions. Consequently, pseudo-reference electrode 2 was chosen for acid reduction measurements. Over a thirty minute period the pseudo-reference electrode was observed to drift 15 ± 14 mV by monitoring the $E_{1/2}$ position of the ferrocene/ferrocenium couple (0.8 to 1.8 mM ferrocene) in a 100 mM [Bu$_4$N][PF$_6$] acetonitrile solution. While extensive studies were not done, the solute may influence drift rate.

### 2.2.2 Electrode Fouling

Significant variability between sequential CVs was observed if the glassy carbon working electrodes were not polished prior to each scan. Pyridinium chloride was the clearest example (Figure 2.2a). Upon subsequent scans the current density greatly decreased. It was difficult to observe the ferrocene/ferrocenium wave after these scans. Visual examination of the glassy carbon electrode post measurement revealed that the surface was coated in a mirror-like yellow film. Figure 2.2b/c show the positive and negative shifts of the reduction current for subsequent scans of trifluoroacetic and acetic acid, respectively. Such variability was minimized for most acids when only fresh electrode surfaces were used (see below for exceptions).

**Figure 2.2.** Cyclic voltammograms of three acids in acetonitrile using a glassy carbon electrode showing the response of the electrode on subsequent scans. Scan rate = 100 mV/s, 100 mM [Bu$_4$N][PF$_6$].
2.2.3 Acid Reduction Measurements

To avoid electrode fouling, freshly polished and electrochemically pretreated glassy carbon electrodes were used for each CV. In a typical experiment, a number of glassy carbon electrodes were polished in alumina/water slurries, ultrasonicated, and rinsed with acetone before being brought into a nitrogen filled glovebox. Prior to adding acid, each glassy carbon electrode was electrochemically pretreated (by cyclically scanning between approximately 0.7 and –2.8 V at 100 mV/s three times in 100 mM \([\text{Bu}_4\text{N}]\).[PF_6] solution), and a background scan recorded in the 100 mM \([\text{Bu}_4\text{N}]\).[PF_6] acetonitrile solution.

It was checked if the glassy carbon electrode surface changed over time after pretreatment. After pretreatment, a background scan was taken and the electrode was rinsed in acetonitrile. It was then left under nitrogen for two hours before the acquisition of a second background scan. Little difference was observed between the two scans.

Twenty acids over an approximately 26 pK_a unit range plus water were selected for measurement. The reduction wave of each acid at 25 mM was independently measured three times at 100 mV/s. An additional scan at 1000 mV/s was taken of each acid at 25 mM. Representative CVs of each acid at 25 mM for both 100 and 1000 mV/s scan rates are recorded in Appendix C. Comparison of the 100 and 1000 mV/s scans revealed that the current response usually did not peak in the 1000 mV/s scan as compared to the clear maximums observed at the 100 mV/s scan rate. While detailed electrochemical measurements of these acids were not the goal of this work, below are general observations.

For two acids – benzoic acid and 4-nitroanilinium – the return sweep cathodically crossed the forward sweep. For benzoic acid this curve crossing was more pronounced at higher concentrations and less distinct at faster scan rates. 4-nitroanilinium also displayed curve crossing; however, at higher scan rates the crossing did not appear to decrease.

Anilinium, benzoic acid, 4-methoxyanilinium, and 4-cyanoanilinium reproducibly showed cathodic current peaks preceding the main reduction. Figure 2.3 shows the current response of
4-cyanoanilinium at 100 and 1000 mV/s – at 1000 mV/s the prewave increased proportionally more relative to the main reduction. Upon repeating the 100 mV/s scan, without polishing, the prewave vanished. No prewave is seen in a literature example for a solution of 10 mM 4-cyanoanilinium,

suggesting the presence of prewaves may depend on small variations of the glassy carbon electrode surface. However, a concentration dependence study of 4-cyanoanilinium revealed a lack of a prewave at 5 and 10 mM but an appearance of the prewave at 25 mM.

![Cyclic voltammograms of 25 mM 4-cyanoanilinium (100 mM [Bu₄N][PF₆] acetonitrile solution) at 100 and 1000 mV/s showing the presence of a prewave on the forward sweep.](image)

**Figure 2.3.** Cyclic voltammograms of 25 mM 4-cyanoanilinium (100 mM [Bu₄N][PF₆] acetonitrile solution) at 100 and 1000 mV/s showing the presence of a prewave on the forward sweep.

For every acid, measurements at 100 mV/s and 25 mM were made with two separate glassy carbon electrodes and compared. In most cases the only noticeable difference was variation in peak currents, however, seven of the acids containing aromatic groups – 4-bromoanilinium, 4-chloroanilinium, 4-tertbutylanilinium, anilinium, N,N-dimethylanilinium, 4-methoxyanilinium, and p-toluenesulfonic acid monohydrate – showed substantially dissimilar CVs taken immediately after one another using only freshly prepared glassy carbon electrodes. **Figure 2.4** shows one representative example for 4-chloroanilinium where the wave shape and wave position changed dramatically. To check whether or not this acid was particularly sensitive to changing electrode surfaces, both electrodes were removed, repolished and re-pretreated.
Following acquisitions of two new scans in the same solution, also shown in Figure 2.4, revealed that while neither scan resembled the prior scans in location or peak current, both traced each other very closely. Repeating this measurement yielded highly variable wave shapes and positions but did not confirm that the final scans taken after a later time overlaid as shown in Figure 2.4. 

$^1$H NMR analysis of aliquots of the 4-chloroanilinium solution prior to any measurements and after measurements revealed no differences in the bulk solution — the only observed peaks were of 4-chloroanilinium, $[\text{Bu}_4\text{N}][\text{PF}_6]$, and acetonitrile.

Figure 2.4. Cyclic voltammograms (100 mV/s) of 25 mM 4-chloroanilinium in a 100 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ acetonitrile solution using two different glassy carbon working electrodes (w.e. 1 and w.e. 2). Scan number indicates the total number of scans taken total.

2.2.4 Reduction Potentials

As shown in Figure 2.5, reduction values were calculated by taking the derivative of the forward scan for each acid at 25 mM and identifying the maximum of this derivative as the irreversible reduction potential inflection point, $E_{\text{inf}}$. 
Figure 2.5. Cyclic voltammogram of 25 mM acetic acid at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile solution and the first derivative of the forward trace. The dashed vertical line denotes the inflection point potential.

Table 2.1 summarizes the inflection reduction potential $E_{\text{inf.}}$ for each acid studied as the average of three independent scans measured at 100 mV/s. Values of $E_{\text{inf.}}$ for the various acids spanned most of the cathodic solvent window, ranging from $-0.65$ to $-2.60$ V vs. Fc/Fc$. While the standard deviation was typically on the order of tens of millivolts, 4-chloroanilinium, dimethylformamidium, and p-toluenesulfonic acid showed greater than 100 mV standard deviation. Dimethylformamidium was particularly inconsistent – measurements taken within a few hours with identical solvent and materials sources yielded values differing by over 600 mV. At room temperature, $^1$H NMR dimethylformamidium was not observed to react with deuterated acetonitrile. Table 2.1 also details which acids were found to be variable (e.g., yield irreproducible CVs scan to scan; see Figure 2.4 and associated discussion above), show curve crossing on the return scan, or to have a distinct prewave.
Table 2.1. Average acid reduction potentials vs. Fc/Fc⁺ in 0.1 M [Bu₄N][PF₆] CH₃CN on GC at 25 mM and 100 mV/s. CVs were ohmic drop corrected prior to \(E_{\text{inf.}}\) determination.

<table>
<thead>
<tr>
<th>acid</th>
<th>(E_{\text{inf.}}) (V)(^a)</th>
<th>notes(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>not obs.</td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>-2.60 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>acetic</td>
<td>-2.36 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>triethylammonium</td>
<td>-2.29 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>benzoic</td>
<td>-2.25 ± 0.02</td>
<td>c.c.; pw.</td>
</tr>
<tr>
<td>4-cyanoanilinium</td>
<td>-2.06 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>dimethylformamidium</td>
<td>-2.00 ± 0.34</td>
<td></td>
</tr>
<tr>
<td>4-methoxyanilinium</td>
<td>-1.95 ± 0.08</td>
<td>pw.; var.</td>
</tr>
<tr>
<td>salicylic</td>
<td>-1.94 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>N,N-dimethylanilinium</td>
<td>-1.90 ± 0.06</td>
<td>var.</td>
</tr>
<tr>
<td>4-chloroanilinium</td>
<td>-1.86 ± 0.11</td>
<td>var.</td>
</tr>
<tr>
<td>anilinium</td>
<td>-1.83 ± 0.07</td>
<td>pw.; var.</td>
</tr>
<tr>
<td>4-bromoanilinium</td>
<td>-1.83 ± 0.06</td>
<td>var.</td>
</tr>
<tr>
<td>4-tert-butylanilinium</td>
<td>-1.83 ± 0.05</td>
<td>var.</td>
</tr>
<tr>
<td>trifluoroacetic</td>
<td>-1.81 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>pyridinium</td>
<td>-1.77 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>p-toluenesulfonic</td>
<td>-1.76 ± 0.15</td>
<td>var.</td>
</tr>
<tr>
<td>trichloroacetic</td>
<td>-1.56 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>-1.24 ± 0.02</td>
<td>c.c.</td>
</tr>
<tr>
<td>trifluoromethanesulfonic</td>
<td>-1.06 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>4-nitroanilinium</td>
<td>-0.65 ± 0.02</td>
<td>c.c.</td>
</tr>
</tbody>
</table>

\(a\)Provided value given as the average of three independent measurements, except for dimethylformamidium, for which eight measurements are averaged. Error given as ± one standard deviation. A minimum standard deviation of 0.02 V is given based on the observed drift of the pseudoreference in a half hour period. \(^b\)Acids displaying curve crossing on the return scan are denoted c.c., pw. designates acids showing cathodic prewaves, and var. indicates acids which showed significantly different CVs in the same solution with two different glassy carbon electrodes.

Since the surface chemistry, and hence electrochemical response, of glassy carbon is complex,\(^7\) it was checked whether electrodes from an another supplier could yield different \(E_{\text{inf.}}\) values. Consequently, in addition to the \(E_{\text{inf.}}\) value reported in Table 2.1 for benzoic acid found using CHI electrodes (3 mm diameter), benzoic acid was analyzed additionally with electrodes from two other suppliers (eDAQ, 1 mm diameter GC electrode and BASI, 3 mm diameter GC...
electrode) using identical procedures. The eDAQ electrodes yielded an $E_{\text{inf.}}$ of $-2.27 \pm 0.02$ V and the BASi electrode gave an $E_{\text{inf.}}$ of $-2.27 \pm 0.02$ V, which is similar to the $-2.25 \pm 0.02$ V value determined using the CHI electrodes. This suggests that small variations between different glassy carbon electrodes can result in slightly different values, however, the values reported here should still serve as useful approximate values.

2.2.5 Influence of Water

CVs were recorded at 100 mV/s for each acid without added water and with 100 mM added water (Appendix C). The solvent system used to dry the acetonitrile in this study was reported by the manufacturer (Pure Process Technology) to reduce water content to 1-5 ppm, equivalent to 0.001 – 0.005 mM. Independent measurement was not sought but every effort was taken to minimize potential contact with residual water by rigorous drying of glassware and by doing all experiments in a nitrogen filled glovebox. Table 2.2 reports the $pK_a$ values and homoconjugation constants (where available) of each acid and qualitative notes on the influence of water on the peak current. For all acids, the $E_{\text{inf.}}$ values with 100 mM water present fell within the values for $E_{\text{inf.}} \pm 1 \sigma$ without added water. Six acids showed an increase in current density upon addition of water (Table 2.2). While small difference in electrode surface area could lead to a false current increase or decrease with water, independent measurement of the surface areas of the electrode surface areas of our electrodes using chronoamperometry of ferrocene solutions and the Cottrell equation allowed conversion of the CVs to current density specific to the particular electrode used for that scan. This permitted quantitative comparison of the current density with and without added water.
Table 2.2. pK$_a$ and homoconjugation values in CH$_3$CN for acids studied in this work and influence of 100 mM water on the reduction wave peak current. Data on perchloric acid, hydronium, acetonitrile, and water are included for reference.

<table>
<thead>
<tr>
<th>acid</th>
<th>pK$_a$ in CH$_3$CN</th>
<th>ref.</th>
<th>log($K_f$) (species)$^b$</th>
<th>current increase with water?$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>perchloric</td>
<td>1.57</td>
<td>72</td>
<td>-</td>
<td>n/a</td>
</tr>
<tr>
<td>hydronium</td>
<td>2.2</td>
<td>73</td>
<td>3.9 (B$_2$H$^+$), 4.7 (B$_3$H$^+$), 5.3 (B$_4$H$^+$)</td>
<td>n/a</td>
</tr>
<tr>
<td>trifluoromethanesulfonic$^d$</td>
<td>2.6</td>
<td>72</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td>dimethylformamidium</td>
<td>6.1</td>
<td>74</td>
<td>-</td>
<td>~</td>
</tr>
<tr>
<td>4-nitroanilinium</td>
<td>6.22</td>
<td>75</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td>4-cyanoanilinium</td>
<td>7</td>
<td>76</td>
<td>$\leq$ 0.6 (estimated)$^e$</td>
<td>no</td>
</tr>
<tr>
<td>p-toluenesulfonic$^f$</td>
<td>8.6</td>
<td>77</td>
<td>3.0 (HA$_2^-$)</td>
<td>no</td>
</tr>
<tr>
<td>4-bromoanilinium</td>
<td>9.43</td>
<td>75</td>
<td>-</td>
<td>~</td>
</tr>
<tr>
<td>4-chloroanilinium</td>
<td>9.7</td>
<td>a</td>
<td>-</td>
<td>~</td>
</tr>
<tr>
<td>anilinium</td>
<td>10.62</td>
<td>75</td>
<td>0.6 (B$_2$H$^+$)</td>
<td>~</td>
</tr>
<tr>
<td>trichloroacetic</td>
<td>10.75</td>
<td>72</td>
<td>2.5 (HA$_2^-$)</td>
<td>no</td>
</tr>
<tr>
<td>4-tert-butylanilinium</td>
<td>11.1</td>
<td>a</td>
<td>-</td>
<td>~</td>
</tr>
<tr>
<td>N,N-dimethylanilinium</td>
<td>11.43</td>
<td>75</td>
<td>-</td>
<td>~</td>
</tr>
<tr>
<td>4-methoxyanilinium</td>
<td>11.86</td>
<td>75</td>
<td>-</td>
<td>~</td>
</tr>
<tr>
<td>pyridinium</td>
<td>12.53</td>
<td>75</td>
<td>0.8 (B$_2$H$^+$)</td>
<td>no</td>
</tr>
<tr>
<td>trifluoroacetic</td>
<td>12.65</td>
<td>72</td>
<td>3.9 (HA$_2^-$)</td>
<td>yes</td>
</tr>
<tr>
<td>salicylic$^g$</td>
<td>16.7</td>
<td>72</td>
<td>3.3 (HA$_2^-$)</td>
<td>yes</td>
</tr>
<tr>
<td>triethylammonium</td>
<td>18.82</td>
<td>75</td>
<td>~ 0 (B$_2$H$^+$)</td>
<td>yes</td>
</tr>
<tr>
<td>benzoic</td>
<td>21.51</td>
<td>77</td>
<td>3.6 (HA$_2^-$)</td>
<td>no</td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>22.85</td>
<td>77</td>
<td>2.0 – 2.2 (HA$_2^-$)$^h$</td>
<td>no</td>
</tr>
<tr>
<td>acetic</td>
<td>23.51</td>
<td>77</td>
<td>3.9 (HA$_2^-$)</td>
<td>yes</td>
</tr>
<tr>
<td>phenol</td>
<td>29.14</td>
<td>78</td>
<td>4.2 (HA$_2^-$), 5.7 (H$_2$A$_2^-$)</td>
<td>yes</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>$\geq$ 32.2</td>
<td>79</td>
<td>-</td>
<td>n/a</td>
</tr>
<tr>
<td>water</td>
<td>38-41$^i$</td>
<td>80</td>
<td>-</td>
<td>n/a</td>
</tr>
</tbody>
</table>

$^a$For pK$_a$ values determined in this work an “a” is given. All other pK$_a$ values taken from the references indicated. $^b$K$_f$ is the homoconjugation formation constant. The species formed is shown in parentheses; data taken from reference 72, where the most recent values were used. Reference 77 lists alternative homoconjugation for acetic acid (4.5) and benzoic acid (3.9); however, it was not clear how these values were obtained. Species with neutral conjugate bases are designated B, while species with anionic conjugate bases are denoted A. All K$_f$ values were rounded to one decimal place. Hyphens indicate that no data were found. $^c$For the acids which showed irreproducible CVs a ~ is shown instead. $^d$The pK$_a$ of trifluoromethanesulfonic acid was measured as 2.6 (ref 72) and recently estimated as 0.7 (ref 81). We note that the direct reaction of acetonitrile with trifluoromethanesulfonic acid (see Electrode and Solvent Fouling section and reference 82) render these pK$_a$ values suspect. $^e$The homoconjugation constant of 4-cyanoanilinium was estimated as being less than that of anilinium in ref 83. $^f$We utilized the monohydrate form; it is unclear what form this acid was in for the listed pK$_a$. $^g$Salicylic acid is also reported to form a (2HA) complex with a pK$_a$ of 13.6.72 $^h$See reference 77 for compilation of homoconjugation values of 2-nitrophenol. $^i$Estimated values from reference 80.
2.3 Discussion

2.3.1 Acetonitrile as Solvent

Acetonitrile acid-base chemistry and the role of acetonitrile as an electrochemistry solvent has been intensely studied.\(^{84,85}\) Solutes can behave very differently in acetonitrile relative to water: acetonitrile has an smaller dielectric constant of 36 relative to water (\(\varepsilon = 78\)), a stronger dipole moment of 4.0 D (water = 1.9 D),\(^{86}\) and is aprotic. While there is considerable evidence that pure acetonitrile self-associates, discussion continues about whether this association occurs through a parallel or antiparallel structure.\(^{87-89}\)

![Diagram of acetonitrile parallel and antiparallel structures]

A strong linear dipole moment favors parallel alignment, while pi-orbital interactions favor the antiparallel structure. These proposed self-association structures yield insight into how acetonitrile solvates charged species. The specific solvation of cations in acetonitrile occurs at the nitrogen lone pair; alternatively, anion solvation has been suggested as a Lewis acid type interaction through the partial positive charge present on the nitrile carbon.\(^{90}\)

![Diagram of cation and anion solvation]

Cylindrical symmetry\(^ {90}\) and the availability of an electron lone pair renders acetonitrile more effective at cation solvation, albeit weakly for some cations. Specific solvation of metal cations may occur more strongly. Conversely, decreased anion solvation ability is the result of steric
hindrance, only weak interaction with the partial positive charge, lack of cylindrical symmetry and consequential restriction of rotation, and electrostatic repulsion by the nitrile pi-orbitals. An alternative anion solvation pathway may be proposed based on a suggestion for neutral Brønsted acid-base interactions with acetonitrile’s methyl protons.

\[
\begin{array}{c}
\text{Y}^- \\
\text{H} \quad \text{C} \quad \text{C} \quad \text{N}^+ \\
\text{H}^+
\end{array}
\]

Neither anion solvation pathway is evidently very stabilizing, evidenced by the very weak acidic properties (autoprotolysis constant of at least 32.279) and the poor anion solvation abilities of acetonitrile. These weak basic (except in the case of specific metal solvation) and very weak acidic properties of acetonitrile result in a solvent that strongly differentiates acids and bases, as formation of neither CH₃CN⁺ nor CH₂CN⁻ is favorable. Indeed, attempts to form CH₂CN⁻ with lithium or sodium resulted in solvent polymerization.91 As a consequence of the poor anion solvation ability and strongly differentiating nature of acetonitrile, acids are weaker in acetonitrile compared to water. Significant progress has been made in measuring the pKₐ values of neutral and cationic acids in acetonitrile, and recent work has expanded the pKₐ scale to 28 units.75,77

Perchloric acid⁶⁸,⁹²,⁹³ and trifluoromethanesulfonic acid⁹⁴ are experimentally reported strong acids in acetonitrile, forming CH₃CN⁺ – the strongest possible acidic species in acetonitrile. However, this original picture was imperfect. Dissociation has since been acknowledged as incomplete for perchloric acid⁶³,⁸³ and by analogy trifluoromethanesulfonic acid must also dissociate incompletely as it is slightly weaker than perchloric acid in acetonitrile. Furthermore, stable formation of protonated acetonitrile does not appear to occur in the case of trifluoromethanesulfonic acid, which forms a variety of degradation products in acetonitrile (see discussion below).⁸²,⁹⁵ Actually, any stable protonated acetonitrile species likely exists not as CH₃CN⁺ – the early idealized picture – but as the disolvate, (CH₃CN)₂H⁺.⁹⁵
Water strongly influences the electrochemistry of strong acids in acetonitrile. Addition of water to acetonitrile solutions of perchloric acid shifts the reduction potential of perchloric acid more negative (Figure 2.6), indicating that a) water preferentially solvates CH$_3$CNH$^+$ (or a higher solvate like (CH$_3$CN)$_2$H$^+$), rendering it more energetically stable and so more difficult to reduce, and b) that CH$_3$CNH$^+$ protonates water to form H$_3$O$^+$, which has a larger pK$_a$ than CH$_3$CNH$^+$ and is thus thermodynamically more difficult to reduce (see below). While the pK$_a$ of H$_3$O$^+$ in acetonitrile is approximately 2.2, H$_3$O$^+$ readily forms di-, tri-, and tetrahydrate clusters in acetonitrile (see formation constants in Table 2.2), each of which are expected to have larger pK$_a$s than hydronium and thus be thermodynamically more difficult to reduce. The pK$_a$ of neutral water in acetonitrile has been estimated between 38-41; however, it has been noted that such values that exceed the autoprotolysis constant of acetonitrile may be meaningless. For weaker acids, water can have the opposite effect, stabilizing the dissociation products and so increasing acid strength.

![Figure 2.6](Image)

**Figure 2.6.** Polarography of 1 mM perchloric acid on a dropping mercury electrode with added water in acetonitrile (A, B, C, E, F: 0, 0.01, 0.1, 1.0, 3.0, and 10 M added water). Adapted with permission from Coetzee, J. F., Kolthoff, I. M. *J. Am. Chem. Soc.* 1957, 79, 6110-6115. Copyright (1957) American Chemical Society.

### 2.3.2 Homocoujugation

Due to the weak cation and even weaker anion solvating ability of acetonitrile, dissociated species can gain additional stability by forming homocoujugated complexes with the parent compound. In the prototypical example, acid HA dissociates in solvent S to form
solvated H⁺ (by solvent or HA) and A⁻, followed by association of A⁻ with HA to form the hydrogen-bonded homoconjugation complex [A⋯HA]⁻.

\[
\text{HA} + S \rightleftharpoons \text{H}^+ + \text{A}^- \quad \text{or} \quad 2\text{HA} \rightleftharpoons \text{H}_2\text{A}^+ + \text{A}^- \quad (3)
\]

\[
\text{A}^- + \text{HA} \rightleftharpoons [\text{A⋯HA}]^- \quad (4)
\]

Homoconjugation can consequently increase the apparent acidity of the parent acid by displacing the equilibrium towards deprotonation at the expense of reducing the overall concentration of free HA.

As homoconjugation can complicate electrochemical studies of hydrogen evolving catalysts and result in multiple catalytic cyclic voltammetric waves, it is desirable to know at which concentrations homoconjugation is less influential. It is not feasible to generally comment at which concentrations homoconjugation becomes less appreciable for all acids, but a value of 0.001 N (0.001 M effective acidic proton concentration) was proposed. A parameter \( \kappa \) was recently suggested to provide a more specific estimate for the extent of homoconjugation:

\[
\kappa = K_f C_0 \quad (5)
\]

where \( C_0 \) is the total acid concentration and \( K_f \) is the formation constant of the homoconjugation complex:

\[
K_f = \frac{[[\text{A⋯HA}]^-]}{[\text{A}^-][\text{HA}]} \quad (6)
\]

For \( \kappa \gg 1 \), the acid completely homoconjugates; for \( \kappa \ll 1 \), the acid does not appreciably homoconjugate. For example, an acid with \( \log(K_f) = 2.0 \) (\( K_f = 100 \)) has a \( \kappa \) equal to 10 when [acid]\_total = 0.1 M. As most catalytic studies use acid concentrations between 0.01 and 1 M, homoconjugation is almost certainly always occurring in measurements that utilize homoconjugating acids.

Homoconjugation is expected to influence acid electroreduction. If the acid is reduced to hydrogen, an equivalent of the conjugate base is formed and the concentration of conjugate base will rapidly increase near the electrode surface, engaging in homoconjugation reactions.
with the parent acid if favorable and so perturbing the $K_f$ equilibrium. These homoconjugates ([A ... HA$^-$]) may have reduction potentials different than the parent acid; along those lines of logic homoconjugation has been suggested to produce multiple catalytic reduction waves for hydrogen evolving catalysts. Artero and co-workers have suggested that complications arising from homoconjugation can be successfully accounted for theoretically on an acid-by-acid basis.

Preferably, acids should be chosen with small, or preferably nonexistent, homoconjugation properties. For example, 2-nitrophenol has very weak (or nonexistent) homoconjugation tendencies because the ortho-positioned nitro group stabilizes the neutral, undissociated phenol proton by intramolecular hydrogen bonding preferentially over hydrogen bonding with dissociated 2-nitrophenoxide. However, as detailed below, 2-nitrophenol is unsuitable for hydrogen evolution catalysis because of its very positive reduction potential. Cationic acids, which form neutral conjugate bases, may also be expected to form homoconjugated complexes more weakly, as cationic and especially neutral species are generally more easily solvated by acetonitrile than anionic species. Table 2.2 displays the $\log(K_f)$ values of three cationic acids – anilinium, pyridinium, and triethylammonium. The $\log(K_f)$ values are all less than one, such that $\kappa = 10$ is only obtainable with 1–10 M acid.

If acids that homoconjugate must be used, the complications arising from homoconjugation can be reduced by using 1:1 mixtures of acid and the conjugate base. Under the condition of pseudo-first order catalysis (no meaningful change in substrate concentration near the electrode) the amount of A$^-$ produced by deprotonation of HA will drive the equilibrium of equation 3 to the right, increasing the contribution of homoconjugation over the timescale of the experiment. By using 1:1 mixtures of acid and conjugate base, the amount of A$^-$ produced during catalysis will not meaningful change the concentration of A$^-$ already present. Hence, the extent of homoconjugation will be approximately the same throughout the measurement, rather than increasing in importance in the case where no conjugate base is initially present.
If acids that do not homoconjugate appreciably must be used, then using 50/50 mixtures of acid/conjugate base to reduce changes on the experimental timescale and/or using the theoretical methods developed by Artero et al. to correctly account for homoconjugation should be used. 83

2.3.3 Electrode and Solvent Fouling

While it is established that glassy carbon (GC) electrodes readily adsorb solvent impurities and become easily fouled by analytes, 71,99 this fact is rarely discussed in the non-aqueous electrochemical hydrogen evolution community. Figure 2.2 graphically demonstrates that even using an electrode only twice without polishing yielded inconsistent CVs. Most dramatic was the case of pyridinium, which appeared to form an insulating film after one reductive scan. This has precedent: reduction of quaternary pyridiniums in water resulted in film deposition on glassy carbon 100 and quaternary pyridiniums were also reported to adsorb readily onto platinum electrodes, forming an insulating layer. 101 Additionally, preliminary studies in our group, using a variety of homogeneous catalysts for hydrogen evolution, have yielded irreproducible CVs when the same working electrode was used for multiple scans without polishing, strongly suggesting that the electrode surface can be noticeably altered scan to scan. Surface modification can even involve deposition of heterogeneous particles which can independently evolve hydrogen. 102 As shown in Figure 2.7, using only freshly prepared electrode surfaces resulted in reproducible scans. Accordingly, reiterated here, glassy carbon working electrodes – whether used for acid reduction or catalytic studies – should be polished between every scan. Even with only freshly polished electrodes the possibility exists that fouling occurring during a single scan will influence the recorded voltammogram.
Apart from electrode fouling, the bulk solvent composition itself can change. While little information is available on the interactions of common acids with acetonitrile, trifluoromethanesulfonic acid reacts with acetonitrile, forming a multitude of products.\textsuperscript{82} At higher ratios of trifluoromethanesulfonic acid to acetonitrile (14:1 and 2:1), over ten species were formed. At lower ratios (1:200), only acetamide was seen. It should be noted that for the 1:200 experiment the mixture of acetonitrile and trifluoromethanesulfonic acid was boiled in CD\textsubscript{2}Cl\textsubscript{2} prior to spectral acquisition. We independently confirmed that trifluoromethanesulfonic acid reacts with acetonitrile at room temperature by \textsuperscript{1}H NMR (Appendix C).

These unknown degradation products could interact with a catalyst in unanticipated ways – including degrading the catalyst. It is crucial that acids be checked for possible direct interactions with the solvent and catalyst prior to reduction. Of the acids studied here, only trifluoromethanesulfonic acid is known to interact with acetonitrile and it is anticipated that the weaker acids, incapable of protonating acetonitrile, will be relatively unreactive.

### 2.3.4 Acid Reduction

Four possible categories for acid (HA) reduction at an electrode in solvent S have been proposed;\textsuperscript{60} note that acid reduction does not necessarily stipulate the formation of H\textsubscript{2}:
I \quad HA + S \rightleftharpoons H^+ S + A^-
\quad H^+ S + e^- \rightleftharpoons 1/2 H_2 + S

II \quad HA + e^- \rightleftharpoons 1/2 H_2 + A^-

*for certain metal electrodes:*
\quad HA + e^- \rightleftharpoons H_{ads} + A^- \rightarrow 1/2 H_2

III \quad HA + e^- \rightleftharpoons HA^{**}

IV \quad HA \cdots R + e^- \rightleftharpoons [HA + R]^{**}

Category I acids are strong acids which dissociate to form solvated protons and conjugate base prior to the reduction of solvated protons to form hydrogen. Of the acids studied here, only trifluoromethanesulfonic acid approaches pure Category I in strength and as noted above reacts directly with acetonitrile. Category II acids are not strong enough to be dissociated, so hydrogen evolution occurs via direct acid reduction. In the case of a platinum electrode, the hydrogen evolution process occurs through downstream processes of electrode-adsorbed hydrogen atoms – e.g., interaction of a surface bound hydrogen atom with a solution proton and an additional electron. Variations of this process, such as coupling of 2 H_{ads}, occur for other metal electrodes.

It is unclear how Category II processes would occur on glassy carbon, but possible hydrogen atom adsorption or a bimolecular process involving two acid molecules may be envisioned. Glassy carbon possesses surface oxygen-containing sites, including carboxylic acid and alcohol functionalities that may serve as surface “docking sites” for protons prior to final reduction to hydrogen.

Category III acids have a sufficiently low lying LUMO such that direct hydrogen evolution (i.e., via a Category II route) is preceded at more positive potentials by the formation of a radical species. Finally, Category IV describes the scenario where reduction results in release of an atom or group from the host acid. This category is a unique subset of Category III acids in which
reduction is concomitant with fragmentation of the acid. Alternatively, acid radicals can undergo further chemistry with the parent acid through self-protonation reactions$^{103-105}$

$$\text{HA}^{-} + \text{HA} \rightleftharpoons \text{H}_2\text{A}^{+} + \text{A}^{-}$$

The four proposed acid reduction pathways were based on experiments done in organic solvents with platinum working electrodes. Reduction of acids in acetonitrile with glassy carbon working electrodes is distinctive in that glassy carbon is often cited as a “non-catalytic” surface for hydrogen evolution.$^{60,61,65}$ With hydrogen evolution requiring more driving force on glassy carbon, alternative reduction pathways necessitating less driving force, such as those forming radicals, may out-compete hydrogen evolution. As product distribution measurements were not undertaken here, it is unclear whether the acids in this study are reduced to evolve hydrogen (Category II) or radical anions (Categories III and IV).

Acids used for catalytic hydrogen evolution studies are usually assumed to only donate protons to the catalyst. While it may be more likely that the reduced catalyst accepts protons from the acid to form hydrogen, solution electron transfer from the catalyst to the acid – forming radical acid species – should also be possible. The resulting cyclic voltammograms would likely be very similar to that for catalytic hydrogen evolution, and could easily be misinterpreted as catalytic hydrogen evolution. Further analysis that confirms hydrogen as the dominant or sole product (e.g., by gas chromatography) is therefore necessary. As most literature catalysts are reported along with gas chromatography measurements of produced hydrogen, it seems that this alternative pathway of catalytic solution electron transfer to reduce the acid is either very uncommon or underreported.

Insight into the reduction pathways of some acids studied here may be gleaned. A significant subset of the aromatic acids yielded highly variable CVs in the same solution using different, freshly prepared electrodes. In the case of 4-chloroanilinium, a secondary experiment was performed to evaluate possible differences between different electrodes. The solution was initially scanned with two different electrodes, both of which were removed, repolished, re-
pretreated in blank electrolyte, and then used to measure CVs in the original 4-chloroanilinium solution. While the first two scans did not match (Figure 2.4), the second set was very similar, suggesting that the bulk solution composition had changed since the first measurement. A change in the bulk composition is not consistent with any one CV experiment, however, as only a small amount of acid near the electrode surface is reduced.

If reduction were occurring by a radical pathway, however, the first measurement could initiate bulk solution radical chemistry. The second measurement would have probed the solution as it began changing, and by the time the two electrodes had been repolished and re-pretreated, this chemistry had yielded a new bulk composition. However, this time course analysis of 4-chloroanilinium was not reproducible – while the wave shapes, positions, and peak currents were clearly different from scan to scan, there was no consistent trend when comparing separate experiments. $^1$H NMR analysis of dried samples of the solution before and after electrochemistry revealed no differences, suggesting that bulk solution radical chemistry did not occur.

While no bulk solution radical chemistry was observed, reduction to form radicals near the electrode – where chemistry on the timescale of a single cyclic voltammogram could result in variable near-electrode solution compositions scan-to-scan – could still explain the irreproducible nature of some of the acids. The possibility that aromatic compounds can be reduced to radicals followed by further reduction and/or decomposition is the subject of textbook explanations of various electrochemical mechanisms.\(^{106}\) It was not within the scope of this work to further experimentally investigate the possible formation of radicals, although we note that reduction to radical species is the likely pathway of some of the reported acids.

### 2.3.5 Reduction Potentials

The reduction potentials of 20 acids at 25 mM and 100 mV/s in 0.1 M [Bu$_4$N][PF$_6$] acetonitrile solutions are reported in Table 2.1 (additional cyclic voltammograms at 1000 mV/s are included in Appendix C). No reduction was observed for water. For no acid was the
reduction observed to be reversible, unlike the reversible or quasi-reversible nature of acid reduction seen on platinum electrodes. It should be noted that the reported values may show a small dependence on electrolyte identity; fortunately most acetonitrile electrochemistry is carried out with 0.1 M [Bu₄N][PF₆].

Due to the lack of reversibility, no thermodynamically precise reduction values could be assigned. However, it was still desirable to report reduction potential for the acids studied for comparative purposes. Reduction values were obtained by finding the maximum of the derivative of the forward scan – the inflection point, $E_{\text{inf}}$. A similar method was proposed as a way to estimate the mid-wave potential for catalytic CVs, although it should be noted that the theory used in that work is not translatable to the strictly irreversible processes seen here. Alternative methods were considered, including a) taking the potential at maximum peak current, b) the potential at half peak current, and c) defining a threshold current density as the ‘onset’ potential. Peaks were not always observed, especially at higher scan rates where depletion of the acid did not occur quickly enough to result in a peak in the potential window studied. The loss of peak shape at higher scan rates is clearly illustrated for acetic acid which was measured up to 9000 mV/s (Figure 2.8). Methods a and b were consequently not chosen, and method c, setting a threshold current density, is inherently arbitrary. The $E_{\text{inf}}$ method was chosen here for practicality. It should also be noted that while taking the derivative of a reversible cyclic voltammogram is equivalent to a differential pulse voltammogram of the same system, this is not the case for an irreversible process. For an irreversible process equilibrium is not maintained during the forward/backward potential steps of differential pulse voltammetry, resulting in a different current response.
Using $pK_a$ values either taken from the literature or determined in the present study, $E_{\text{inf.}}$ values for each acid were plotted against the appropriate $pK_a$ (Figure 2.9). Figure 2.9 also includes a gray region which indicates where it is thermodynamically impossible to reduce an acid to hydrogen and its conjugate base. This boundary of this zone was calculated using equation 7:

$$E_{\text{HA}}^0 = E_{H^+/H_2}^0 - (2.303RT/F) \cdot pK_a(\text{HA})$$  \hspace{1cm} (7)

Where $-0.028 \text{ V (vs. Fc/Fc^+)}$ was used as the value of $E_{H^+/H_2}^0$. See reference 83 for a recent discussion of $E_{H^+/H_2}^0$ values.

A linear trend is observed between $E_{\text{inf.}}$ values for each acid and the respective $pK_a$ (Figure 2.9), with weaker acids having more negative $E_{\text{inf.}}$ values. This is consistent with linear trends seen in DMSO$^{61,108}$ and with gas phase measurements,$^{109}$ supporting the thermodynamic suggestion that weaker acids require more driving force to yield hydrogen (see discussion above). 4-nitroanilinium lies relatively close to the thermodynamic boundary as compared to the main group of acids, and 2-nitrophenol occurs within the zone where hydrogen evolution should be thermodynamically prohibited. Deviation from the linearity of reduction potential versus $pK_a$
has been observed for nitro- and cyano-substituted methylantracenes, derivatives in which the possibility of resonance interactions between the nitro/cyano group and the aromatic system were cited as possible explanation. Similar resonance interactions likely apply here, possibly encouraging direct reduction to radical species which would have different thermodynamic requirements. Alternative reduction pathways involving formation of radical species are suggested to account for the deviation from linearity of some of the anilinium compounds (see discussion above).

![Figure 2.9](image)

**Figure 2.9.** Plot of $E_{\text{int.}}$ values versus the respective $pK_a$ for each acid studied. The gray region is an estimation of the zone in which the applied potential is thermodynamically insufficient to reduce acids to hydrogen ($2\text{HA} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{A}^-$). See text for details.

The potential at which it is thermodynamically possible to reduce an acidic proton with known $pK_a$ was estimated using equation 7 with $-0.028 \text{ V}$ as the value for $E_{H^+/H_2}^{0}$. The usefulness of equation 7 has been questioned as it does not account for multiple phenomena, including homoconjugation, which significantly affects most acids in acetonitrile at the concentrations usually employed. Consequently, the thermodynamic region depicted in Figure 2.9 is oversimplified, as these values should be acid and concentration dependent. The thermodynamics of acid reduction to hydrogen continues to be discussed and further comment here is not the intended goal of this work.
The $E_{\text{inf.}}$ values in Table 2.1 do not accurately convey the amount of background current passed at potentials prior to $E_{\text{inf.}}$, especially for acids which exhibited prewaves (Figure 2.3, see Table 2.1). Prewaves can be explained by adsorption of the reduced product where the adsorption free energy reduces the energy – and so applied potential – needed for reduction. To more accurately capture the presence of background current like prewaves, an alternative method of presenting the background current passed between the minimum thermodynamic potential $E_{H_A}^0$ and $E_{\text{inf.}}$ is shown in Figure 2.10. Here, the current has been background subtracted and normalized relative to the current passed at $E_{\text{inf.}}$. A color gradient was subsequently mapped onto the normalized current versus potential values.

**Figure 2.10.** Background subtracted cyclic voltammogram of 25 mM 4-cyanoanilinium at 100 mV/s, normalized to the current measured at $E_{\text{inf.}}$. The color scale was mapped onto the normalized current values, where white indicates no current being passed above the background current and dark blue indicates the level of current passed at the inflection point.

The color scale in Figure 2.10 of 4-cyanoanilinium reflects what the $E_{\text{inf.}}$ value does not: the presence of a prewave prior to the main reduction event. Using this method, a mapped gradient color scale was generated for each acid studied (Figure 2.11) and acids were categorized into three categories: a) eight recommended acids that showed reproducible
backgrounds, b) eight acids with erratic backgrounds, and c) four acids we suggest as unsuitable for electrochemical hydrogen evolution studies in acetonitrile.

Figure 2.11. Acid potential windows in acetonitrile (25 mM acid, 100 mV/s) showing the range between an approximate thermodynamic potential $E_{HA}^0$ (where proton reduction to hydrogen is thermodynamically possible) and the direct reduction potential $E_{inf}$. The color scale was constructed by choosing a representative CV with an $E_{inf}$ close to the average $E_{inf}$ value and normalizing between 0 (background current without acid, white) and 1 (current at $E_{inf}$, dark blue). Data more positive than the thermodynamic reduction potential $E_{HA}^0$ (based on equation 7) was then removed. Prewaves and significant current prior to $E_{inf}$ are visible for some acids. Unsuitable acids: 1) The $E_{inf}$ value of 2-nitrophenol was more positive than the $E_{HA}^0$ for 2-nitrophenol, 2) pyridinium upon reduction was observed to passivate the electrode, which may occur accidently during catalysis without strictly avoiding any direct reduction, 3) 4-nitroanilinium has a very limited potential range and so was judged unsuitable, 4) trifluoromethanesulfonic acid can react directly with acetonitrile; see main text.

Figure 2.11 captures the presence of prewaves or other significant non-background current being passed prior to the $E_{inf}$ value, and so highlights the fact that certain acids (e.g., p-toluencesulfonic acid) pass some current above background over most of the potential range while other acids (e.g., pyridinium) pass relatively little current prior to the main reduction wave. It is hoped that Figure 2.11 can be used to rapidly choose candidate acids such that a) the acid
can be thermodynamically reduced to hydrogen at the relevant redox potential of a given catalyst and b) that direct electrode acid reduction is avoided.

### 2.3.6 Influence of Water

Cyclic voltammograms were recorded for each acid with and without 100 mM added water. For six acids – acetic acid, p-toluenesulfonic acid monohydrate, triethylammonium, trifluoroacetic acid, phenol, and trifluoromethanesulfonic acid – the peak current density increased (see Appendix C). Five of these acids have anionic conjugate bases, and so it would be expected that upon reduction each equivalent of conjugate base would homoconjugate with the parent acid, limiting the amount available for reduction. Water could stabilize these anionic conjugate bases (heteroconjugation), freeing additional acid for reduction and resulting in enhanced peak current. Why then did triethylammonium, which forms a neutral conjugate base and homoconjugates comparatively weakly (Table 2.2), show a current increase? A possible explanation is the chloride counteranion. Reduction results in release of chloride:

\[
[BH^+][Cl^-] + e^- \rightleftharpoons [BH] + Cl^- \quad (8)
\]

In the absence of water, chloride released after reduction may obtain stability by homoconjugating with the parent acid, again decreasing the amount of parent acid available for reduction. Water is expected to preferentially solvate chloride and consequently free additional acid for reduction, resulting in increased current. It is possible that less or no current increase would be seen for a triethylammonium species with a softer counteranion and indeed a sample of triethylammonium tetrafluoroborate showed no current increase upon addition of 100 mM water.

However, these explanations are insufficient. Specifically, why did the current dramatically increase for acetic and trifluoroacetic acid but not trichloroacetic acid? The stabilizing influence of water is clearly more subtle and warrants further investigation.

The key question originally posed was to determine whether water shifted the reduction potential as is observed for perchloric acid. For weak acids it has been noted that water can
stabilize the dissociated products and so increase the apparent acidity. As stronger acids are thermodynamically easier to reduce, it was hypothesized that the addition of water might result in a positive shift in reduction potential and so potentially interfere with catalysis.

While slight shifts in reduction potential were observed upon addition of 100 mM water for some acids, in no case did the $E_{\text{inf.}}$ values for added water fall outside $E_{\text{inf.}} \pm 1 \sigma$ when no water was present. While more significant potential shifts were observed for some acids, these same acids exhibited variability scan to scan (see Table 2.1), hence, we could not trust that the potential had shifted. Unlike perchloric acid, all of the acids studied except trifluoromethanesulfonic acid are weak acids, and so proton transfer to water to form hydronium is not expected to occur to any great extent. The current enhancement reported for some electrocatalysts upon water addition has largely been attributed to water’s ability to act as a proton relay capable of more readily accessing the sterically crowded metal sites as compared to the parent acid. Since the addition of water did not appear to significantly shift $E_{\text{inf.}}$ for any acid studied, the current enhancements seen for some literature catalysts when water is added are unlikely due to shifts in the direct acid reduction potential. An alternative explanation is that the increased acidity of acids in acetonitrile with water present results in faster catalytic rates as a result of the increased driving force for deprotonation; however, our data indicates any change in $pK_a$ with 100 mM added water does not strongly influence the reduction potential at GC. While larger concentrations of water were not studied, at some ratio of acetonitrile/water the acid $pK_a$ values will change enough to effect a clear change in the reduction potential. This critical ratio is expected to be unique for each acid and further study would be welcome.

2.4 Conclusion

The electroreduction of 20 acids plus water on glassy carbon in acetonitrile was investigated. Figure 2.11 presents the approximate potential windows in which acids may be used for catalytic hydrogen evolution while a) avoiding direct reduction and b) allowing for the thermodynamic possibility of reduction to hydrogen. Figure 2.11 additionally includes our
recommendations for which acids to use, which acids give problematic backgrounds, and which acids are generally unsuitable for hydrogen evolution catalysis in acetonitrile. We reiterate that accurately determining the thermodynamic potential is more complex$^{83,98,110}$ than what was considered here.

Although the proper acid selection should minimize interference, backgrounds of respective acid reduction at the correct concentration and scan rate should always be provided alongside catalytic cyclic voltammograms. This work is not intended to replace independent acid-only measurements; especially as only one concentration and scan rate were thoroughly investigated for each acid here. While alternative electrodes were not tested, it has been noted that mercury coated gold electrodes can shift direct acid reduction potentials more negative, providing a larger working potential window.$^{63}$ The importance of polishing the working electrode before every measurement, while perhaps assumed by most researchers, is also underscored. The addition of 100 mM water was not found to clearly shift the reduction potential at GC of any acid studied, although current enhancement was observed for some acids when water was added.
CHAPTER 3. Identifying Electrochemical Transformation of Precatalyst to Active Catalyst

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3.1 Introduction

Over the last two decades researchers have become increasingly aware that homogeneous catalysts are actually precatalysts, in some cases for heterogeneous active species.\(^{112-115}\) Several reported “catalysts,” including a few notable examples, have been discovered to in fact be pre-catalysts.\(^{102,116-120}\) The possibility of heterogeneous catalysis is a concern because significant resources may be dedicated to pursuing a promising line of related complexes under the assumption that the active species is homogeneous and molecular in nature. For homogeneous catalysis, carefully tuning the ligand scaffold may yield large improvements in catalytic activity. However, for a homogeneous pre-catalyst that transforms into a heterogeneous catalyst, tuning the ligand set to improve activity without knowing it is a pre-catalyst is not a rational route. Mechanistic studies are also frequently used to assess why a molecular species is a good (or bad) catalyst; if the molecular species is in fact a pre-catalyst, assessment of the catalytic mechanism will lead to erroneous conclusions.

Significant work since the 1990’s has led to the proposal of a diverse set of tests to assess if catalysis occurs from an in situ generated heterogeneous species.\(^{112,113,115,121,122}\) These tests can be summarized generally as:

1) Kinetic analysis: Is there an induction period between the start of catalytic conditions and product formation that may signal conversion of pre-catalyst to active catalyst?
2) In situ stability study: Is the catalyst stable under the operating conditions? Do new species form that may be the active catalyst?

3) Post-mortem analysis: After a catalytic run, can the original catalyst be isolated and reused? Did other side products form that might be the true active catalyst?

4) Poisoning experiments: Does catalysis continue after the addition of chemical poisons known to shut down catalysis from heterogeneous species?

These experiments were primarily developed for characterizing homogeneous catalysis under thermal or photolytic conditions. Many catalysts, however, are electrochemical catalysis, especially those designed to catalyze the synthesis of chemical fuels like hydrogen. Only recently has attention been directed towards identification of methods to detect electrochemical catalysts that transform under electrolysis conditions.

3.2 Detecting Electrochemical Decomposition/Transformation

While a putative electrochemical catalyst may be stable under purely reducing or oxidizing conditions, the addition of substrate – such as a proton source – may induce catalyst transformation to a new molecular species or even catalyst decomposition. The reducing conditions at an electrode surface in particularly can result in ligand loss and formation of a heterogeneous metal-containing deposit on an electrode surface. With the addition of electrons to a metal complex, the need for additional electrons from the ligand decreases, potentially increasing ligand lability or even prompting ligand loss. While in solution nucleation of heterogeneous particles may need heterogeneous impurities, the presence of an electrode surface during electrochemical measurements offers a template for heterogeneous particle growth.

It is not straightforward to detect complex decomposition during an electrochemical experiment. The techniques listed above for thermal or photolytic catalysis have an advantage in that potentially a large amount of species is undergoing decomposition, enough that
techniques such as spectroscopy are useful for characterization in situ. During a cyclic voltammetry experiment, however, only the tiny amount of material at the electrode surface may be decomposing. While spectroscopy can be performed on the thin reaction layer at an electrode surface, this requires special setups not usually available.

Rather, a set of techniques has developed to allow for the identification of catalyst decomposition. These methods can begin with qualitative assessment of a catalytic cyclic voltammogram followed by various electrochemical probes and analytical techniques.

3.2.1 Prewave

Homogeneous electrochemical catalysis is typically triggered by a redox wave in the absence of substrate. For simple redox catalysis, reversible reduction of catalyst P by one electron to species Q in the absence of a substrate A yields a reversible cyclic voltammogram (black trace, Figure 3.1). Upon the addition of substrate A, species Q can transfer an electron to substrate A to regenerate the original oxidized catalyst P plus product B (blue trace, Figure 3.1). If there is a limited amount of substrate A, then the cyclic voltammogram will show a peak followed by a diffusional tail as substrate is depleted.

When the original molecular species is a precatalyst, however, the cyclic voltammogram may change. Frequently, in the case of proton reduction catalysis, initial reduction of the precatalyst is followed by protonation. In some cases, this protonation event does not lead immediately to catalysis. Instead, the combined protonation/reduction results in transformation of the precatalyst into the active catalyst. This new active catalyst likely possesses a redox potential at a different potential than the original precatalyst; when this potential is more negative than the precatalyst, actual catalysis does not begin until later in the scan. Consequently, a diagnostic CV arises where a prewave is followed by a catalytic wave at more negative potentials (red trace, Figure 3.1).
The amount of current passed at the prewave relative to the precatalyst redox wave without substrate is sometimes linearly related to the number of electrons passed during the transformation. For the case of proton reduction catalysts, titration of acid to a solution of the suspected precatalyst can also give an idea of the number of protons transferred per precatalyst molecule – the number of acid equivalents required to reach the maximum attainable prewave current gives an estimate of the number of protons involved.\textsuperscript{102,123} In the case of a cobalt clathrochelate complex, the number of electrons and protons passed as deduced from the prewave neatly corresponded to hydrogenation and hydrogenolysis of all of the C=N and B-O bonds, respectively.\textsuperscript{102}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.png}
\caption{Simulated cyclic voltammograms of a catalyst without substrate undergoing electron transfer (black trace), catalyst with substrate undergoing simple redox catalysis (blue trace), and conversion of precatalyst to active catalyst in a prior PCET step (red trace). Chemical and electron transfer steps shown in figure are color-coded to correspond to their simulated CV. Electron transfers were set at 1 cm s\textsuperscript{-1} with $\alpha = 0.5$, chemical steps as $1 \times 10^6$ M\textsuperscript{-1} s\textsuperscript{-1}, concentration of species P and substrate A as 1 and 5 mM, respectively, scan rate as 1 V/s, diffusion coefficients of all species as $1 \times 10^{-5}$ cm\textsuperscript{2} s\textsuperscript{-1}, and the $E_{1/2}$ of the X/Y couple is 0.1 V negative of the P/Q couple. The red asterisk (*) denotes the prewave associated with irreversible transformation of the precatalyst into the active catalyst. Simulated using DigiElch 7.}
\end{figure}
3.2.2 Potential-Initiated Desorption of Adsorbed Species

It is not unusual to see new oxidative (for reductive catalysis) or reductive (for oxidative catalysis) events on the return trace of a catalytic cyclic voltammogram. These new features can provide useful information on the buildup of catalytic intermediates, such as oxidation of metal hydride intermediates in hydrogen evolution catalysis. \(^{38}\) Whether these redox features are reversible or irreversible, the symmetry of the redox wave provides quick information on the phase of the species. Symmetric events are usually associated with surface-adsorbed species while asymmetric waves generally mean the species is homogeneous. If possible, scan rate analysis of the background subtracted peak current of these waves can provide a second test for the phase identity: the peak current will depend linearly on \(\sqrt{\text{scan rate}}\) for homogeneous species while for electrode-adsorbed species the peak current varies linearly with scan rate. \(^{39}\)

3.2.3 Induction Periods

Catalyst decomposition or transformation can also be detected using controlled potential methods. If the applied electrode potential is stepped from a voltage where no redox events occur to a potential past the observed catalytic wave, significantly more current will pass in the presence of substrate (blue trace, Figure 3.2) compared to a solution of just the catalyst (black trace, Figure 3.2). If, however, the initial molecular species transforms under catalytic conditions to form the true active catalyst, an induction period may be observed (red trace, Figure 3.2).

This induction period may correspond to an initial slow formation of active catalyst or even the buildup of a heterogeneous active catalyst on the electrode surface as more precatalyst diffuses to the electrode surface. \(^{124}\) Figure 3.2 shows a chronoamperogram experiment, but induction periods may also be observed in plots of product generation vs. time.
**Figure 3.2.** Simulated chronoamperograms of a catalyst without substrate (black trace), catalyst with substrate undergoing simple redox catalysis (blue trace), and conversion of precatalyst to active catalyst in a prior PCET step (red trace). Chemical and electron transfer steps shown in figure are color-coded to correspond to their simulated chronoamperogram. Electron transfers were set as 1 cm s\(^{-1}\) with \(\alpha = 0.5\), catalytic steps with a rate constant of 100 M\(^{-1}\) s\(^{-1}\), species P concentration as 1 mM, substrate A concentration as 500 mM, diffusion coefficients of all species as \(1 \times 10^{-5}\) cm\(^2\) s\(^{-1}\), rate of \(Q + A \rightarrow X\) as 1 M\(^{-1}\) s\(^{-1}\), the potential step as 0.3 V negative relative to the \(E_{1/2}\) of the P/Q couple, and the X/Y couple as 0.1 V positive relative to the P/Q couple. Simulated using DigiElch 7.

### 3.2.4 Rinse Tests

The most common test for *in situ* formation of a heterogeneous active catalyst is the rinse test.\(^{25,102,114,122–129}\) Two primary variants exist. In the first, a linear sweep voltammogram is taken with a clean electrode in a solution of catalyst and substrate – the scan is started prior to any redox features and is stopped after scanning through the suspected catalytic peaks. This electrode is rinsed with neat solvent and then used to perform an identical linear sweep voltammogram in a solution containing only substrate. If current beyond background is observed, then this is strong evidence that at least a portion of the catalytic response is due to an electrode adsorbed active catalyst.

The second primary version of the rinse test involves performing a bulk electrolysis under catalytic conditions – usually using a large surface area electrode, such as a glassy
carbon plate. After the catalytic run, the electrode is rinsed with neat solvent and used to perform another bulk electrolysis using a solution of only substrate. Quantification of the amount of current passed, relative to background, as well as product formed (e.g., through headspace analysis for volatile products), allows evaluation if the active catalyst is in fact a surface-adsorbed species.

Important caveats to the rinse test have been raised. Recently, it was realized that the rinse test performed for a hydrogen-evolving cobalt macrocycle\textsuperscript{130} failed to detect that the active species was indeed an electrode adsorbed product.\textsuperscript{124} The rinse test failed because the precatalyst decomposition product – the true active catalyst – was only weakly adsorbed to the electrode surface. Additionally, this heterogeneous active catalyst was unstable when rinsed with deionized water – a pH range and potential range outside of its zone of stability (formation occurred in a pH $\approx 2.2$ phosphate buffer under applied potential). Consequently, a negative rinse test result does not immediately rule out the possibility that the true catalyst is a heterogeneous material. For the cobalt macrocycle, confirmation that the active catalyst was heterogeneous came from two forms: evidence of an induction period and using surface analysis techniques.

### 3.2.5 Electrode Surface Analysis

Heterogeneous deposits on electrode surfaces can be directly probed using a variety of analytic methods. Microscopy methods (e.g., SEM and TEM) permit visual detection of surface-adsorbed particles or films and spectroscopy methods (e.g., XPS, EDX, and Auger) allow elemental analysis of electrode surfaces. For the case of the cobalt macrocycle discussed above which eluded the rinse test, rapid drying of an electrode post electrolysis without rinsing reduced loss of the weakly adsorbed active catalyst. Subsequent analysis by SEM and EDX confirmed the presence of cobalt-containing nanoparticles.\textsuperscript{124}
3.3 Case Studies

Three case studies of molecular species transforming into heterogeneous species active for hydrogen evolution will be discussed; these illustrate the techniques discussed above for identification of transformation from precatalyst to active catalyst.

3.3.1 Case 1: NiP₂S₂ Complex

Inspired by the proton active sites of enzymes – particularly the [Fe-Fe] hydrogenase – we targeted a series of nickel complexes with varying substituents on the backbone of the bidentate phosphine ligand (Figure 3.3). It had been shown that amine groups located near the metal atom can drastically improve the hydrogen evolution rate of a series of nickel catalysts.¹⁸⁻²¹ Given the proposal that sulfur atoms in the active site of the nitrogenase enzyme may play a role in the synthesis of ammonia from nitrogen,¹³¹ we sought to compare a catalyst series where the second coordination sphere contained either a methylene space, N-methylamine, or a sulfur atom. Irregularities in the preliminary cyclic voltammetry analysis resulted in focused effort on the methylene bridgehead complex. This investigation revealed that 1 decomposes under reducing and protic conditions to form a heterogeneous electrode-adsorbed species active for hydrogen generation. Compound 2 was found to exhibit similar electrochemical responses; consequently, series comparison of compounds 1-3 was not carried out as intended.

Figure 3.3. Structures of targeted nickel complexes with either a methylene, amine, or sulfur atom at the bridgehead position of the phosphine ligand.

3.3.1.1 Characterization of 1

Compound 1 was prepared in 15% yield via a related approach to a previously reported derivative of 1 with a methyl amine group at the bridgehead of the phosphine (Appendix B).¹³²
One- and two-dimensional NMR confirmed the structure of 1 shown in Figure 3.3. A reversible, one-electron wave assigned to the Ni^{II/III} couple is observed via cyclic voltammetry (CV) with an $E_{1/2}$ of $-1.92$ V as well as an irreversible oxidation attributed to the Ni^{III/II} couple with $E_{p,a} = -0.34$ V (Figure 3.4). The redox properties of 1 are very similar to the previously reported methyl amine derivative.  

![Cyclic voltammogram of 0.4 mM 1 with ferrocene at 100 mV/s in 0.25 M [Bu$_4$N][PF$_6$] acetonitrile solution. The Ni$^{II/III}$ couple has an $E_{1/2}$ of -1.92 V and the irreversible Ni$^{III/II}$ couple has an $E_{p,a}$ of -0.34 V.](image1)

Scan rate studies of the Ni$^{II/III}$ couple reveal that 1 is under diffusion control when the peak cathodic current is plotted versus the square root of the scan rate (Figure 3.5), as expected for a homogeneous species, with a diffusion coefficient of $1 \times 10^{-5}$ cm$^2$ s$^{-1}$ found using the Randles-Sevcik equation. The Nicholson method was used to estimate a value of 0.1 cm s$^{-1}$ for the heterogeneous electron transfer rate constant ($k^0$) of the Ni$^{II/III}$ couple.  

![Background subtracted cathodic peak currents for 1 plotted versus the square root of the scan rate.](image2)
3.3.1.2 Electrochemistry of 1 in the presence of acid

Addition of 10 mM [Et₃NH][BF₄] (pKₐ = 18.82 in CH₃CN) to a solution of 1 results in loss of the reversible Ni^{II}/I wave and the appearance of two irreversible waves, both positive of the direct electrode reduction of [Et₃NH][BF₄] as shown in Figure 3.6A. The large current of the second wave suggests proton reduction catalysis. The onset of the first wave occurs hundreds of millivolts positive of the Ni^{II}/I reduction. As discussed above, prewaves preceding apparent catalytic waves have been observed previously for nickel and cobalt complexes and in these cases assigned to either ligand hydrogenation or decomposition of the initial molecular species into a heterogeneous, electrode adsorbed material. ¹⁰²,¹²⁰,¹³⁴,¹³⁵ 1 was also found to transform into an electrode-bound active species via a rinse test: in a solution of 1 and 10 mM [Et₃NH][BF₄], an electrode was scanned through the prewave and second wave, rinsed with acetonitrile and transferred to a solution of only 10 mM [Et₃NH][BF₄]. In this acid-only solution, the catalytic response was maintained (Figure 3.6B). Dipping an electrode in a solution of 1 and 10 mM [Et₃NH][BF₄] without applied bias did not produce the same result.

![Figure 3.6](image_url)

**Figure 3.6.** (A) Cyclic voltammograms of [Et₃NH][BF₄], 1, and 1 plus [Et₃NH][BF₄] at 100 mV/s in 0.25 M [Bu₄N][PF₆]. (B) Cyclic voltammograms using an electrode treated at -1.78 V for 60 s with 0.4 mM 1 and 10 mM [Et₃NH][BF₄], rinsed, and then scanned in a solution of 0.25 M [Bu₄N][PF₆] (black line) and in a solution of 10 mM [Et₃NH][BF₄] + 0.25 M [Bu₄N][PF₆] (pink) at 100 mV/s.
3.3.1.3 **Characterization of treated electrodes**

X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to characterize the electrode surface after treatment with 1 and [Et$_3$NH][BF$_4$]. SEM of glassy carbon plate electrodes electrolyzed in solutions of 1 and [Et$_3$NH][BF$_4$] revealed the presence of a smooth film with no evidence for discrete particles (**Figure 3.7**), contrasting similar studies where nanoparticle deposition was observed.\textsuperscript{102,120,135,136}

![Figure 3.7. Scanning electron micrograph of a cross section of a glassy carbon plate electrolyzed with 0.3 mM 1 and 10 mM [Et$_3$NH][BF$_4$] for 30 minutes at $-1.74$ V vs. Fc$^+/Fc$.](image)

XPS analysis of a bare glassy carbon plate revealed the presence of only carbon and oxygen (**Figure 3.8A**), as expected for glassy carbon which normally has surface oxygen moieties.\textsuperscript{99} Plates electrolyzed with 1 and [Et$_3$NH][BF$_4$], however, were found to have additional elements (**Figure 3.8B**) including Ni, F, S, and P. For comparison, XPS spectra were obtained for dropcast samples of 1. The relative atomic ratios of Ni:S:P in the dropcast spectrum of 1 were 1:1.8:2, as expected for a species with two sulfur and two phosphorus atoms per nickel atom. In contrast, the relative atomic ratios of Ni:S:P in the electrolyzed sample were 1:1.23:0.34, indicating that the deposited material has substantially different atomic stoichiometry than 1.
Figure 3.8 (A) XPS spectra of a bare glassy carbon plate and (B) a glassy carbon plate electrolyzed at −1.74 V for 30 minutes with 0.3 mM 1 and 10 mM [Et₃NH][BF₄]. The presence of sodium is due to an unknown impurity which was also observed as a minor component in the dropcast 1 data.

While the XPS binding energy positions for the Ni 2p and S 2p peaks in the high resolution spectra of electrodes post electrolysis of 1 (Figure 3.9) did not permit unambiguous assignment of the species, nickel metal – with a binding energy of 852.6 eV\textsuperscript{137} – can be ruled out, at least within the XPS sampling depth (~10 nm). The Ni 2p peak at 853.9 eV may possibly represent the presence of nickel sulfide; NiS was recently suggested to be the electro-decomposition product of [Ni(bdt)₂][Bu₄N] under protic and reducing conditions.\textsuperscript{134}

Figure 3.9. High resolution XPS spectra of the Ni 2p and S 2p regions for both 1 onto a gold plate and a glassy carbon electrode electrolyzed with 1 and [Et₃NH][BF₄].
To assess the hydrogen evolution ability of the deposited material, a glassy carbon plate was held at $-1.7 \text{ V}$ for 10 minutes in a solution of 0.4 mM $1$ and 10 mM $[\text{Et}_3\text{NH}]\text{[BF}_4\text{]}$. After rinsing the electrode, the plate was held at $-1.7 \text{ V}$ vs. $\text{Fc/Fc}^+$ in a bulk electrolysis cell containing 25 mM $[\text{Et}_3\text{NH}]\text{[BF}_4\text{]}$ for 15 minutes. Sampling of the headspace by gas chromatography confirmed the production of hydrogen with a Faradaic efficiency of approximately 100% (see Appendix D for full details).

This example demonstrates that observation of a suspicious prewave in the catalytic cyclic voltammograms led to successful identification of the true catalyst as a heterogeneous decomposition product of the original nickel complex. Surface techniques confirmed the presence of an amorphous film on the electrode surface after electrolyzing $1$ with acid present. Elemental analysis via XPS in particular showed that the heterogeneous material is not identical in elemental composition to the original homogeneous complex, ruling out simple deposition.

3.3.2 Case 2: Initial Ligand Transformation

Similar to case 1 above, analysis of a nickel complex with two tridentate ligands revealed a prewave during attempted hydrogen evolution catalysis (complex $4$, Figure 3.10) followed on the anodic return scan of a suspected stripping wave.$^{123}$ Similar rinse tests and surface analysis (TEM and XPS) confirmed that the initial homogeneous compound $4$ decomposes under protic and reducing conditions to form electrode-adsorbed nanoparticles. These nanoparticles are then responsible for hydrogen evolution.

Figure 3.10. Structures of complexes $4$ and $5$. 
Intriguingly, if the conformer of 4 without C=N bonds is prepared (complex 5, Figure 3.10), no prewave is observed in the cyclic voltammograms under catalytic conditions. While no prewave was observed (Figure 3.11), the presence of an anodic stripping event is seen. This stripping event was suspected to correspond to the oxidation of elemental nickel deposited on the electrode. Indeed, analysis of an electrode after exposure to catalytic conditions using a rinse test and surface analysis methods showed that 5 also decomposes to form an electrode-adsorbed species.

![Graph]

**Figure 3.11.** Acid titrations of 0.5, 4, and 10 eq. of CF₃COOH into equimolar solutions of 4 and 5 (0.39 mM). The black traces are the respective acid-free voltammograms. Voltammograms recorded at 100 mV/s in 0.1 M [Bu₄N][PF₆]CH₃CN solutions. Adapted with permission from Martin, D. J., McCarthy, B. D., Donley, C. L., Dempsey, J. L. Chem. Commun. 2015, 51, 5290-5293. Published by The Royal Society of Chemistry.

Via comparison with compound 5, the prewave seen for complex 4 was assigned as the hydrogenation of the C=N of one of 4’s ligands. This was the first clear evidence that a prewave event can be directly related to the decomposition of a vulnerable ligand moiety. This provides empirical support to prior suggestions that C=N bonds could be hydrogenated during electrochemical proton reduction.¹⁰²,¹³⁵

### 3.3.3 Case 3: Catalyst Decomposition Without Substrate

In the prior two examples of compounds 1 and 4, catalyst decomposition was promoted by the addition of substrate. However, reduction or oxidation events in the absence of substrate can still result in catalyst transformation or even formation of heterogeneous materials. In some cases, electrochemical reduction or oxidation is simply not reversible, with the complex
geometry and/or ligand environment changing substantially. This new potentially catalytically active species will likely have a different redox potential for subsequent electron transfer steps during catalysis.

However, initial reduction or oxidation can result directly in complex decomposition. Compound 6 (Figure 3.12), the iron(II) analogue of compound 4, undergoes an initial reversible electron transfer followed by an irreversible electron transfer. The following anodic return sweep reveals the presence of a stripping wave – the simple change of iron to nickel results in compound decomposition and electrode deposition for the iron species. A rinse test failed to show the presence of a surface-adsorbed film; however, cyclic voltammetry of a solution of a simple iron(II) salt gave a redox feature analogous to a stripping wave at a similar potential as that of 6. This lent support to the hypothesis that 6 transforms under reducing conditions to form neutral iron on the electrode surface.

Figure 3.12. Structure of complex 6.

3.4 Vulnerable Structural Moieties

As the number of reports of molecular species which decompose grows (examples in Table 3.1) grows, empirical comparison has permitted identification of some key structural motifs that are susceptible to decomposition. Cobalt and nickel compounds containing C=N and N-O bonds were reported by a number of groups\textsuperscript{102,120,136,138,139} to decompose in acidic and reducing conditions to Co and Ni containing nanoparticles respectively. Firm experimental evidence that C=N bonds can predispose a complex to decomposition was provided by our group via direct comparison of two complexes either with or without C=N bonds.\textsuperscript{123}
Figure 3.13. Voltammograms of 0.4 mM 6, recorded at 100 mV/s in a 250 mM [Bu₄N][PF₆] CH₃CN solution. The solid black voltammogram was recorded with a switching potential of past the second reduction; the dashed blue voltammogram was recorded with a switching potential prior to the second reduction. Adapted from Polyhedron, Vol 114, Martin, D. J., McCarthy, B. M., Piro, N. A., Dempsey, J. L., Synthesis and electrochemical characterization of a tridentate Schiff-base ligated Fe(II) complex, Pages 200-204, Copyright (2015), with permission from Elsevier.

The presence of Ni-S bonds also appear to render compounds lacking C=N or N-O bonds susceptible to decompositions, as discussed by Roberts¹³⁴ and our group.²⁵ In these cases, it appears that cleavage of adjacent S-C bonds – with concomitant ligand destruction – is favored by Ni-S sulfur bonds.²⁵,¹³⁴ Finally, we recently demonstrated with an Fe complex that protic conditions are not required for electrocatalytic decomposition.¹²⁹

3.5 Conclusions

The race for improved homogeneous electrochemical catalysts, particularly in the context of fuel synthesis, has resulted in increased awareness that these catalysts may actually be precatalysts. Similar to the dedicated efforts from the late 1990’s that resulted in a toolset of methods for detecting catalyst transformation/decomposition,¹¹²,¹²¹ methods suited for electrochemical catalysis have also become defined. These range from qualitative analysis of cyclic voltammograms to more rigorous surface analysis checks. As the number of electrochemical catalysts continues skyrocketing, it is crucial that special scrutiny be paid to the true catalyst active state.
Table 3.1. Metal complexes known to electrochemically degrade in organic solvents under catalytic conditions to form electrode-adsorbed heterogeneous materials active for hydrogen evolution.

<table>
<thead>
<tr>
<th>molecule</th>
<th>vulnerable features</th>
<th>acid</th>
<th>decomposition product</th>
<th>ref. (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]: R = Ph, X = F</td>
<td>C=N and N-O bonds</td>
<td>HClO₄</td>
<td>Co and O containing nanoparticles</td>
<td>102, 135 (2012, 2013)</td>
</tr>
<tr>
<td>[2]: R = Ph, X = Ph</td>
<td>C=N and N-O bonds</td>
<td>CF₃COOH / Et₃NH⁺ / CH₃COOH</td>
<td>Co and O containing nanocubes</td>
<td>139 (2013)</td>
</tr>
<tr>
<td>Ni-S bonds</td>
<td></td>
<td>Et₃NH⁺</td>
<td>Ni/S or Ni/S/Se containing particles</td>
<td>140 (2014)</td>
</tr>
<tr>
<td>C=N bonds</td>
<td></td>
<td>HClO₄</td>
<td>Co and O containing nanoparticles</td>
<td>120 (2014)</td>
</tr>
<tr>
<td>C=N and N-O bonds</td>
<td></td>
<td>HClO₄</td>
<td>Ni containing nanoparticles</td>
<td>136 (2014)</td>
</tr>
<tr>
<td>Ni-S bonds</td>
<td></td>
<td>4-Br-anilinium</td>
<td>Ni/S containing film</td>
<td>134 (2014)</td>
</tr>
<tr>
<td>Ni-S bonds</td>
<td></td>
<td>CF₃COOH</td>
<td>Fe/Ni/S containing film</td>
<td>141 (2015)</td>
</tr>
<tr>
<td>C=N bonds, Ni-S bonds</td>
<td></td>
<td>CF₃COOH</td>
<td>Ni/S containing amorphous film with nanoparticles</td>
<td>123 (2015)</td>
</tr>
<tr>
<td>Ni-S bonds</td>
<td></td>
<td>Et₃NH⁺</td>
<td>Ni/S containing amorphous film</td>
<td>25 (2015)</td>
</tr>
<tr>
<td>Fe-S bonds, C=N bonds</td>
<td></td>
<td>n/a</td>
<td>not reported</td>
<td>129 (2016)</td>
</tr>
</tbody>
</table>
CHAPTER 4. Concerted Proton-Coupled Electron Transfer for a Nickel Complex

Adapted with permission from McCarthy, B. D., Donley, C. L., Dempsey, J. L. Chem. Sci. 2015, 6, 2827-2834. Published by The Royal Society of Chemistry.

4.1 Introduction

As detailed in Chapter 3, the number of homogeneous species that are actually precatalysts for heterogeneous catalysts is growing. Common structural motifs that render a molecular more susceptible to decomposition are becoming apparent. Understanding the mechanism by which a catalyst degrades can help inform strategies to protect against degradation in future systems. Consequently, mechanistic details of the initial electrochemically initiated steps leading to decomposition of 1 (Figure 4.1) were probed. Specifically, we sought to examine the PCET process that initiates structural modification of 1. How many protons and electrons are initially transferred to the molecular species? Do the electron transfer (ET) and proton transfer (PT) steps occur sequentially or through a concerted process?  

![Figure 4.1. Structure of 1.](Image)

While some mechanistic insight to PCET processes in molecular hydrogen-evolving electrocatalysts have been provided through both theoretical\textsuperscript{29-31,37,38} and electrochemical\textsuperscript{27,28,39} studies, examining PCET for 1 is complicated by the fact that these steps are part of a degradation mechanism which ultimately produces an ill-defined heterogeneous material. To minimize complications, PCET reactivity was examined at stoichiometric and sub-stoichiometric
acid-catalyst ratios (up to one equivalent of acid), allowing us to determine how PCET modification proceeds when only one equivalent of protons is present. Even under these limiting conditions, caution was necessary when interpreting results: the larger diffusion coefficient of \([\text{Et}_3\text{NH}^+]\) relative to 1 (see below) means that even for solutions prepared with 1:1 ratios of 1:1\([\text{Et}_3\text{NH}^+]\) more than one equivalent of \([\text{Et}_3\text{NH}^+]\) per molecule of 1 can arrive at the electrode on the CV time scale.

To approximate a 1:1 ratio of 1:1\([\text{Et}_3\text{NH}^+]\), a solution of \([\text{Et}_3\text{NH}^+]\) was titrated into a solution of 1 and the reversible \(\text{Ni}^{[\text{II}]}\) wave of 1 monitored by CV until reversibility was lost. Assuming that acid at the electrode preferentially reacts irreversibly with unreacted 1, complete loss of the reversible wave of 1 should indicate an approximate 1:1 ratio of 1:1\([\text{Et}_3\text{NH}^+]\).

With one equivalent of \([\text{Et}_3\text{NH}]\text{[BF}_4\text{]}\) the resulting irreversible prewave (Figure 4.2) corresponds to the transfer of about two electrons, as determined via current integration. As might be expected for a system undergoing degradation, it was difficult to reliably measure exactly two electrons each time this experiment was repeated; however, the number of electrons passed was consistently found to be between 1.5 and 2. A scan rate study of this new irreversible wave found that the peak current varied linearly with the square root of the scan rate (Figure 4.3), as expected for a freely diffusing species, indicating that the 2-electron/1-proton electrochemistry occurs in solution and not on the electrode surface.\(^{39}\) We suggest that this proton/electron reactivity forms a hydride species, a putative intermediate in many catalytic cycles for the Ni-mediated formation of \(\text{H}_2\).\(^{21,147,148}\)

Notably, the peak of this irreversible prewave appears ca. 0.28 V positive of the cathodic peak position of the reversible wave of 1 observed in the absence of \([\text{Et}_3\text{NH}]\text{[BF}_4\text{]}\). In order to explain this large positive shift for the two-electron irreversible wave with one equivalent of acid present, we recognized that the coupled one proton and two electron transfers that give rise to this prewave can occur through stepwise (sequential) mechanisms or involve concerted proton-electron transfer (CPET). Specifically, we considered a stepwise PT-ET-ET mechanism (an
electrochemical CEE mechanism), a stepwise ET-PT-ET mechanism (an electrochemical ECE mechanism), and a CPET-ET process (here denoted (EC)\textsubscript{concerted}) (Figure 4.4).

**Figure 4.2.** Cyclic voltammograms of 0.7 mM 1 and 0.7 mM 1 plus one equivalent of [Et\textsubscript{3}NH][BF\textsubscript{4}]. Recorded at 100 mV/s in 0.1 M [Bu\textsubscript{4}N][PF\textsubscript{6}] acetonitrile solution.

**Figure 4.3.** Scan rate dependence of cathodic peak current of prewave for a solution of 0.6 mM 1 and 0.5 eq. of [Et\textsubscript{3}NH][BF\textsubscript{4}] in acetonitrile.

A CEE mechanism beginning with the protonated intermediate 1H\textsuperscript{+} would be expected to be more easily reduced than 1 by virtue of the positive charge and so account for the 0.28 V potential shift. A variation of this mechanism is transient formation of a hydrogen-bonded complex. Intramolecular hydrogen bonding has been used to explain the positive peak shifts of the electrochemistry of organic molecules\textsuperscript{36} and inorganic compounds (e.g., the “hangman effect”).\textsuperscript{144} Neither UV-vis or \textsuperscript{1}H NMR found any evidence of interaction between 1 and over 100 molar equivalents of [Et\textsubscript{3}NH][BF\textsubscript{4}] (Figure 4.5 and Figure 4.6, respectively). This lack of
evidence does not rule out transient interactions producing an undetectable population of \( 1\text{H}^+ \) or hydrogen-bonded \( 1 \), but no evidence supporting a CEE mechanism was found.

**Figure 4.4.** Square scheme depicting possible mechanisms for addition of two electrons and one proton to compound \( 1 \). Relevant constants indicated.

**Figure 4.5.** UV-vis spectra of 0.4 mM \( 1 \) in CH\(_3\)CN with and without 50 mM \([\text{Et}_3\text{NH}]\text{[BF}_4\text{]}\). Addition of \([\text{Et}_3\text{NH}]\text{[BF}_4\text{]}\) to a solution of only 0.25 M \([\text{Bu}_4\text{N}]\text{[PF}_6\text{]}\) was found to shift the baseline upwards, so the 50 mM spectrum above was background subtracted with a spectrum of only 50 mM \([\text{Et}_3\text{NH}]\text{[BF}_4\text{]}\).

**Figure 4.6.** \(^1\text{H} \text{NMR of 1.4 mM 1 without (bottom) and with 199 molar equivalents of [Et}_3\text{NH}]\text{[BF}_4\text{]} in CD}_3\text{CN. Solvent impurities are denoted. No peak shift of any of 1's peaks was observed.**
An EC-type pathway could also explain the positive shift of the reduction wave in the presence of protons.\textsuperscript{28,29} For a $E_rC_i$ mechanism (reversible electron transfer followed by irreversible chemical reaction)

$$E_r: P + e^- \rightleftharpoons Q$$
$$C_i: Q + A \xrightarrow{k} QA$$

the magnitude of the rate constant $k$ can have a dramatic effect on the CV peak position and shape. In the absence of reactant A, electron transfer, if reversible and Nernstian, results in predictable relative concentrations of P and Q at the electrode surface based on the reduction potential.\textsuperscript{106,149} Even at potentials sufficiently positive of the formal reduction potential, small concentrations of the reduced species Q will still exist, as predicted by the Nernst equation. If Q reacts with substrate A to irreversibly form species QA, more Q will be produced near the electrode to maintain equilibrium. For large rate constants this results in a shift of the peak to potentials more positive than the formal reduction potential, as shown by simulation in Figure 4.7 for an $E_rC_iE_i$ process. The peak shift magnitude is dependent on both the heterogeneous electron transfer rate constant $k^0$ (cm s\textsuperscript{-1}) for the P/Q couple and the second order forward rate constant $k$ (M\textsuperscript{-1} s\textsuperscript{-1}).

For the simpler $E_rC_i$ mechanism the new peak position $E_p$ is given by\textsuperscript{40,144}

$$E_p = E_0' - 0.78 \frac{RT}{F} + \frac{RT}{2F} \ln \left( \frac{RTk_{obs}}{F \nu} \right)$$

where $k$ is the rate of the chemical step (e.g., protonation, $k_{obs} = k[A]$). As the mechanism here involves a second electron transfer, digital simulations were performed to model the peak shift. Prior to simulation, several constants were estimated experimentally. As described in Chapter 3, $k^0$ for 1 was estimated by the Nicholson method to be 0.1 cm s\textsuperscript{-1}. The rate constant $k$ is unknown; however, the upper limit for $k$ is expected to be the diffusion limited rate $k_{\text{diff}}$, which is the maximum rate two reactants can diffuse to one another in solution. The value $k_{\text{diff}}$ was estimated using the Debye-Smoluchowski relation,\textsuperscript{150} $k_{\text{diff}} = 4\pi N_A (D_1 + D_2) \beta$. 

63
where $D_1$ and $D_2$ are the diffusion coefficients of the two reacting species (here $1$ and $\text{Et}_3\text{NH}^+$) and $\beta$ is the effective reaction radius, taken as the sum of the radii for $1$ and $\text{Et}_3\text{NH}^+$ and estimated to be 8.5 Å. As both reactants $1^-$ and $\text{Et}_3\text{NH}^+$ are charged, $\beta$ was further modified to reflect electrostatic interactions (see Appendix E). The diffusion coefficient of $1$ (assumed to be equal to that of $1^-$) was found electrochemically to be $1 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ (see Chapter 3).

Figure 4.7. (A) Simulated CVs for an $E_2C\text{E}_1$ reaction. (B) Prewave potential shift (relative to the cathodic peak of the original reversible wave) versus the rate of protonation. The horizontal green line indicates the experimentally observed peak shift while the vertical blue line indicates the estimated diffusion limited rate for $1$ and $[\text{Et}_3\text{NH}][\text{BF}_4]$, see text for details. Simulated with DigiElch: $\alpha = 0.5$ for (A) and 0.3, 0.5, or 0.7 as indicated for (B); $k_0 = 0.1 \text{ cm s}^{-1}$ for both E steps; $[P] = [A] = 0.005 \text{ M}$; surface area of electrode = 0.071 cm$^2$; $\alpha = 0.5$ used for $E$ of second electron transfer where $E_2$ was 0.5 V more positive than the $E$ for the first step (see Appendix E).

The diffusion coefficient of $[\text{Et}_3\text{NH}][\text{BF}_4]$ was estimated using $^1\text{H}$ DOSY NMR on a 500 MHz Bruker spectrometer. The pulse width was calibrated by varying the pulse width until null peaks were observed for both triethylammonium peaks, with the calibrated $90^\circ$ pulse found to be 8.55 μs. $T_1$ and $T_2$ relaxation times for both triethylammonium peaks were estimated using inversion recovery experiments. These relaxation times were utilized to check that the $^1\text{H}$ DOSY
experiment was run with sufficient delay times to allow for proton relaxation. The proton peak for
CHD₂CN was found to relax very slowly; in order to decrease the measurement time the
relaxation delays used were only long enough for the triethylammonium peak; hence the value
found for CHD₂CN is not accurate. The DOSY data were processed in MestReNova version
8.1.0-11315 using the built-in Bayesian DOSY Transform method. From this data (Figure 4.8),
the diffusion coefficient of Et₃NH⁺ in acetonitrile was found to be 2.2 x 10⁻⁵ cm² s⁻¹.

![Figure 4.8.](image)

Using these experimentally determined diffusion coefficients of 1 and Et₃NH⁺, the
maximum diffusion limited rate was estimated as 4.5 x 10¹⁰ M⁻¹ s⁻¹. Figure 4.7B plots the
prewave peak shift versus the forward rate constant. Around 10⁹ M⁻¹ s⁻¹ the peak shift actually
becomes more negative, as predicted theoretically for an ECE mechanism. The peak shift
experimentally observed is in excess of the simulated peak shifts for an ECE mechanism
(Figure 4.7B). Even allowing the transfer coefficient α to vary away from the assumed value of
0.5 to 0.3 and 0.7 (0.3 to 0.7 is the general range of observed α values) does not reproduce
the large observed peak shift.

With an ECE mechanism found theoretically implausible by digital simulations and with
no evidence of a CEE mechanism, a concerted (EC)concertedE mechanism was considered. For
concerted pathways not involving heavy atom bond cleavage\textsuperscript{151} electrochemical kinetic isotope effects have been used as a diagnostic for CPET.\textsuperscript{34,152–156} Therefore, cyclic voltammograms were obtained of 1 in the presence of sub-stoichiometric amounts of [Et\textsubscript{3}NH][Cl] (to permit observation of the position of 1’s reversible wave) and either 0.24 M H\textsubscript{2}O or 0.24 M D\textsubscript{2}O. These solutions were allowed to equilibrate for ca. 5 minutes after addition of H\textsubscript{2}O/D\textsubscript{2}O. The chloride salt rather than the BF\textsubscript{4}\textsuperscript{-} salt of Et\textsubscript{3}NH\textsuperscript{+} was utilized to avoid the possibility of BF\textsubscript{4}\textsuperscript{-} hydrolysis.\textsuperscript{157} A clear kinetic isotope effect is observed with a difference in prewave peak positions of ca. 20 mV (\textbf{Figure 4.9}). This is consistent with a concerted pathway where simultaneous transfer of a proton with the electron reduces the magnitude of the applied potential necessary for reduction by decreasing buildup of negative charge on 1 in the transition state. This data consequently supports a CPET to 1 followed by a second reduction as the initial mechanism of degradation.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure4.9.png}
\caption{Cyclic voltammograms of equimolar solutions of 1 with sub-stoichiometric [Et\textsubscript{3}NH][Cl] and either 0.24 M H\textsubscript{2}O or D\textsubscript{2}O.}
\end{figure}

\textbf{4.2 Proposed Decomposition Mechanism}

The decomposition of hydrogen-evolving catalysts into surface-adsorbed catalytically active species has only recently received dedicated attention. A summary of complexes reported to electrochemically decompose into electrode adsorbed materials active for hydrogen evolution in acetonitrile was presented in Chapter 3. Although at present the dataset is small, clear structural similarities have emerged that may bias a complex towards decomposition.
Specifically, complexes with C=N or N-O bonds, which are reported to be susceptible to hydrogenation and hydrogenolysis, respectively, make up the majority of the reports.

Multiple literature examples in Chapter 3 show cases of molecules that decompose while lacking C=N or N-O bonds. This work adds another example of a complex lacking C=N or N-O bonds that degrades. Notably, several of these complexes have Ni-S bonds, indicating that Ni-S bonds may render a complex susceptible to degradation under reducing and protic conditions. CV data featuring catalytic prewaves exists for other Ni-S species proposed to be molecular electrocatalysts, suggesting that these compounds also decompose, possibly into heterogeneous species also active for hydrogen evolution.

The formation of Ni/S containing material upon degradation of 1 suggests degradation of the organosulfur ligands. While no literature was found explicitly for electrochemical C-S cleavage by nickel, numerous examples of Ni-catalyzed desulfurization of C-S bonds have been reported. Ni compounds have been found to insert into C-S bonds, occasionally releasing the alkyl group if a hydride equivalent is available, including the example presented in Figure 4.10.

![Figure 4.10](image)

Figure 4.10. Literature example of Ni-hydride mediated S-C bond cleavage.

While nickel hydrides are not necessary for desulfurization, they are implicated in some cases of Ni-mediated C-S cleavage. In the case of compound 1, it is plausible that initial formation of a nickel hydride then initiates C-S cleavage in the 1,3-propanedithiolate ligand. Figure 4.11 presents two possible pathways by which 1-propanethiol or propane fragments would be released. Formation of short-lived Ni=S bonds, followed by dimerization, has been proposed for Ni desulfurization.
One caveat is that C-S insertion by nickel does not always proceed to a single product. C-S bond cleavage of dibenzothiophene by a nickel compound was found by $^{31}$P NMR to slowly form a variety of Ni containing products.\textsuperscript{61} We attempted to probe the degradation of 1. Attempts to isolate the nickel hydride 1-H via reaction of 1 with NaBH$_4$ and LiEt$_3$BH were unsuccessful (no reactivity was seen with either hydride source). Several experiments were done to try identifying decomposition fragments directly from bulk electrolysis experiments. A solution of 1.8 mM 1 and 50 mM [Et$_3$NH][BF$_4$] was electrolyzed at $-1.97$ V using a 1 x 2 x 0.2 cm glassy carbon plate (about 1 x 1 cm was immersed) in an air-tight cell for 15 minutes. No detectable byproducts (such as propane) were observed upon sampling of the headspace by GC. $^{31}$P{$^1$H} NMR of the solution revealed unreacted 1, free phosphine ligand, and four unidentified peaks (Figure 4.12). The appearance of free phosphine helps explain the decrease in phosphorus content of 1 upon degradation, as observed by XPS (Chapter 3), and suggests the loss of free phosphine during decomposition. Two of the unidentified peaks were located near that of 1, suggesting a similar structure; however, the other two were located further downfield. This
multitude of P-containing species is in line with literature precedent for S-C bond cleavage resulting in a multitude of Ni species.\textsuperscript{61}

\textbf{Figure 4.12}. $^{31}$P\{$^1$H\} NMR spectrum of a solution of 1.8 mM 1, 50 mM [Et$_3$NH][BF$_4$], and 0.25 M [Bu$_4$N][PF$_6$] after electrolysis at -1.97 V using a 1 x 2 x 0.2 cm glassy carbon plate electrode (about 1 x 1 cm was actually immersed). Free dppp phosphine ligand is observed (-16 ppm), as well as unreacted 1 at 12.97 ppm. Use of CH$_3$CN instead of CD$_3$CN explains why both the free 1 peak (12.40 ppm in CD$_3$CN) and the free dppp ligand (-16.65 in CD$_3$CN) show up approximately 0.65 ppm further downfield than expected.

In an attempt to isolate any volatile fragments (such as 1-propanethiol), the electrolysis solution was vacuum distilled at room temperature into a Schlenk flask immersed in liquid nitrogen. No P-containing species were detected in the distillate by $^{31}$P\{$^1$H\} NMR. GC/MS of the distillate found only triethylamine. The lack of fragments detected does not rule out their presence, only that if present their concentration was below detection limits.

While cleavage of the C-S bond/s seems likely based on literature precedent and Ni/S film formation, no conclusive evidence was found experimentally, although the 1:1.23 Ni:S ratio in the final deposited film suggests at least some sulfur is lost to solution. Insertion of a Ni(0) species, formed at the electrode, into the P-C bond was also considered.\textsuperscript{17,64} Given that any Ni(0) or Ni(I) species are likely immediately protonated at the electrode, and that numerous
reports of stable electrocatalysts with phosphine-based ligands exist,\textsuperscript{21,147} this alternate pathway to decomposition seems unlikely.

### 4.3 Conclusions

The mechanism of decomposition of 1 was investigated to determine what occurs prior to the observed formation of an electrode adsorbed film containing Ni and S. Importantly, the initial degradation mechanism of 1 appears to involve a CPET step rather than stepwise electron and proton transfers. Additionally, comparison of the structure of 1 with that of other molecules reported to electrochemically degrade suggests the vulnerability of species containing Ni-S bonds. This vulnerability may stem from Ni-mediated S-C bond cleavage followed by further decomposition. More generally, this work underscores the vulnerability of molecular electrocatalysts to degradation.

This work outlines an approach to electrochemically studying CPET using metal complexes. Further questions remain, foremost being: (1) what are the products of proton and electron addition? and (2) can PCET be tuned between stepwise and concerted pathways? Compound 1 is not ideal for answering these questions due to the meager synthetic yield, poor solubility, mismatched diffusion coefficient relative to the acid source, and ultimate loss of homogeneity. Resolution of these concerns motivates exploration of similar electrochemistry using a related family of metal compounds, as described in the final two chapters of this dissertation.
CHAPTER 5. Decoding Proton-Coupled Electron Transfers with Potential-pKₐ Diagrams

5.1 Introduction

Proton-coupled electron transfer (PCET) processes are widespread in biology and chemical catalysis. PCET reactions are also fundamental to the conversion of energy-poor feedstocks into energy-rich fuels. This is epitomized by the complex multi-proton and multi-electron processes required to reduce carbon dioxide or transform water into hydrogen and oxygen. Given the sheer breadth of areas for which PCET plays an important role, intense research worldwide has focused on improving our fundamental understanding of PCET.

One useful tool in this effort is plots of reduction potential vs. solution free energy. This free energy may be pH for an aqueous PCET system. In the case of pH, these potential-pH plots are generally termed Pourbaix diagrams, although Pourbaix diagrams with free energy axes other than pH also exist. These diagrams provide a rich array of information about the redox-active species within the potential–pH range studied. The relationship between potential and pH for PCET can be understood with a Nernst equation. For the reaction of \( m \) protons and \( n \) electrons with a redox species \( M \):

\[
M + mH_{\text{solv}}^{+} + ne^{-} \rightleftharpoons MH_{m}^{-}(n-m)
\]

the relationship between applied potential \( (E) \) and the relative concentrations of the product and the reactants is:

\[
E = E^{0r} - 2.303 \frac{RT}{nF} \log \left( \frac{[MH_{m}^{-}(n-m)]}{[M][H_{\text{solv}}^{+}][m]} \right)
\]
where \( R \) is the gas constant, \( T \) temperature, and \( F \) the Faraday constant. The formal potential, \( E^0' \), includes the activity coefficients of the species involved (usually assumed to be pH-independent) and the reaction's net change in standard chemical potential.\(^{156}\) A more complete Nernst equation also includes a term containing the species’ diffusion coefficients; this term is usually approximated as zero.\(^{171}\)

The observed reduction potential is usually reported as the half-wave potential, \( E_{1/2} \); this is conveniently measured via cyclic voltammetry (CV). At \( E_{1/2} \) the concentration of \( \text{MH}_m^{-(n-m)} \) and \( \text{M} \) are equivalent, leaving only the effective solvated proton concentration (activity):

\[
E_{1/2} = E^0' - 2.303 \frac{RT}{nF} \log \left( \frac{1}{[\text{H}_{\text{solv}}^+]^m} \right)
\]

At room temperature the familiar pH-dependent Pourbaix expression results:\(^{156}\)

\[
E_{1/2} = E^0' - 0.059 \frac{m}{n} \text{pH}
\]

For pH-dependent redox events, the slope of \( E_{1/2} \) vs. pH informs the stoichiometry of protons and electrons. For example, slopes of 29, 59, and 118 mV/pH unit suggest \( 2e^-/1H^+ \), \( 1e^-/1H^+ \), and \( 1e^-/2H^+ \) processes, respectively. The intersections of pH-dependent and -independent regions provide \( pK_a \) values of the species involved and the potentials of pH-independent regions are the reduction potentials for pure electron transfers.\(^{172,173}\)

This wealth of information provided by potential–pH diagrams makes them quite useful; however, PCET is not purely an aqueous phenomenon. Active sites in enzymes may be non-aqueous in character due to hydrophobic amino acid residues and/or exclusion of water molecules.\(^{174}\) Moreover, an extensive number of studies involving PCET reactions – spanning catalysis,\(^{175}\) biomimetic model complexes,\(^{176}\) and materials chemistry\(^{177,178}\) – are performed in non-aqueous solvents. As such, analogous diagrams for interpreting PCET thermochemistry in non-aqueous systems would be highly desirable.

Directly applying the specific Pourbaix theory described above to non-aqueous solvents is problematic. The Nernstian Pourbaix relationship is a thermodynamic relationship where the
independent variable is the solution free energy as manifested by the hydrogen ion activity, $a_{H^+}$. The hydrogen ion activity represents the effective solvated proton concentration (with $a_{H^+} \sim [H^+]$ frequently assumed). Herein is the key problem – what is the physical meaning of a solvated proton in a non-aqueous, aprotic solvent? For example, acetonitrile decomposes when treated with very strong acids rather than forming a stable protonated complex. Accordingly, PCET in dry non-aqueous solvents is generally viewed to occur through direct interaction of the proton donor with proton acceptor.

This difference is manifested in the aqueous and non-aqueous definitions of $pK_a$. In water, the $pK_a$ for an acid HA in solvent S is related to the solvated hydrogen ion activity by:

$$pK_a = -\log(K_a) = -\log\left(\frac{a(A^-)a(HS^+)}{a(HA)}\right)$$

Conversely, non-aqueous $pK_a$ values are defined with respect to the $pK_a$ of reference compounds rather than using a questionable solvated proton activity:

$$pK_a(HA) = pK_a(ref) + \Delta pK_a$$

The driving force for proton transfer in non-aqueous solvents is determined by comparing the relative $pK_a$ values of the species involved. This is different from in water where the driving force is related to the $pK_a$ of the acceptor or donor and the solution pH. While proton transfer in water can also occur directly from an acid donor and acceptor in a general acid reaction, the concept of the solvent medium donating/accepting protons is unique to water and similar protic solvents.

As the thermodynamics of proton transfer in non-aqueous solvents are dictated by $pK_a$ differences, rather than pH, the free energy axis for a non-aqueous Pourbaix diagram should also depend on $pK_a$. This work explores the thermochemical parameters through which potential–$pK_a$ diagrams can be constructed.

Via construction of two experimental potential–$pK_a$ diagrams, it will also be demonstrated that useful thermochemical information of transiently stable species can be obtained. We reveal
that non-aqueous potential–pK\textsubscript{a} theory depends on the acid pK\textsubscript{a} as well as a Nernstian term for the relative concentrations of acid and conjugate base. This theory contextualizes the handful of prior experimental examples where observed $E_{1/2}$ values have been related to acid pK\textsubscript{a} or concentrations of acid and conjugate base in non-aqueous solvents.\textsuperscript{180–184} Non-aqueous potential–pK\textsubscript{a} diagrams are expected to become a useful tool in the study of non-aqueous PCET as they provide essentially the same rich information as aqueous Pourbaix diagrams.

5.2 Results and Discussion

5.2.1 Non-aqueous potential–pK\textsubscript{a} theory

Equations (1a) and (1b) describes a general PCET reaction of substrate M involving $n$ electrons and $m$ protons, with the proton supplied by solvated hydrogen ions (1a) or a molecular acid HA (1b):

\[
\begin{align*}
\text{M} + m\text{H}^+ + ne^- & \rightleftharpoons \text{MH}^{-(n-m)}_m \quad (1a) \\
\text{M} + m\text{HA} + ne^- & \rightleftharpoons \text{MH}^{-(n-m)}_m + mA^- \quad (1b)
\end{align*}
\]

In aqueous solutions, proton donation may occur by either equation (1a) or (1b).\textsuperscript{167,185} Equation (1b) is operative in aprotic, non-aqueous solvents and can be described as three half reactions (equations (2) – (4)), each with an associated free energy term:

\[
\begin{align*}
\text{M} + ne^- & \rightleftharpoons \text{M}^{-n} \quad \Delta G^0_1 \quad (2) \\
m\text{HA} & \rightleftharpoons m\text{H}^+ + mA^- \quad \Delta G^0_2 \quad (3) \\
\text{M}^{-n} + m\text{H}^+ & \rightleftharpoons \text{MH}^{-(n-m)}_m \quad \Delta G^0_3 \quad (4)
\end{align*}
\]

The overall free energy, $\Delta G^0_{\text{net}}$, of the equation (1b) PCET reaction is:

\[
\Delta G^0_{\text{net}} = \Delta G^0_1 + \Delta G^0_2 + \Delta G^0_3 \quad (5)
\]

Equation (2) refers to the reduction potential of species M in the absence of acid while equation (4) reflects the PCET product pK\textsubscript{a}. These two terms are constant for a specific species
M. However, $\Delta G^0_2$ depends on acid identity. The free energy of dissociation is linked to the $pK_a$ of a given acid in the solvent used multiplied by the number of acid molecules $m$ involved in the PCET reaction:

$$\Delta G^0_2 = m \cdot 2.303RTpK_a(HA) \quad (6)$$

The overall PCET free energy $\Delta G^0_{net}$ can be related to the formal potential by:

$$E^{0'} = -\frac{\Delta G^0_{net}}{nF} \quad (7)$$

where $n$ is the number of electrons transferred and $F$ is the Faraday constant. Equations (5)-(7) can be combined to yield the expected dependence of the formal potential of the electrochemical PCET on the $pK_a$ of added acid:

$$E^{0'} = -\frac{\Delta G^0_1}{nF} - \frac{\Delta G^0_3}{nF} - 2.303 \frac{mRT}{nF} pK_a(HA) \quad (8)$$

Equation (8) can be conceptually described by acknowledging that $\Delta G^0_1$ is the formal reduction potential of $M^{0/-n}$ and that $\Delta G^0_3$ reflects the PCET product $pK_a$. Consequently, equation (8) can be rewritten as:

$$E^{0'} = E^{0'}(M^{0/-n}) + 2.303 \frac{mRT}{nF} pK_a(MH^m_{m-(n-m)}) - 2.303 \frac{mRT}{nF} pK_a(HA) \quad (9)$$

The first two terms remain constant when only acid identity is changed. At 298 K, equation (9) predicts that the potential for a PCET process depends on the added acid $pK_a$ via equation (10):

$$E^{0'} = E^{0'}(M^{0/-n}) + 0.059 \frac{m}{n} \left[ pK_a(MH^m_{m-(n-m)}) - pK_a(HA) \right] \quad (10)$$

The reaction is thermodynamically favorable for acid $pK_a$ values smaller than the PCET product $pK_a$, with equation (10) predicting that the observed potential will shift positive by an amount dependent on the acid $pK_a$. The plot of $E^{0'}$ vs. $pK_a$ of the added acid is expected to yield a $pK_a$-dependent region with a slope of $0.059 \cdot m/n \cdot pK_a(HA)$; consequently, the slope magnitude reflects the ratio of the number of protons ($m$) and electrons ($n$) involved. This is
analogous to the physical meaning of the slope magnitude in pH-dependent regions of aqueous Pourbaix diagrams.\textsuperscript{171,173}

### 5.2.2 Consideration of Nernstian Equilibria

Equation (8) describes how the formal potential varies with the \( pK_a \) of the added acid; however, the potential response is also expected to vary with the concentration of acid and conjugate base for a Nernstian PCET process. For the PCET reaction in equation (1b), a Nernstian term can be added to equation (8) to give:

\[
E^{0r} = \left[ -\frac{\Delta G_1^0 + \Delta G_3^0}{nF} - 2.303 \frac{mRT}{nF} pK_a(\text{HA}) \right] - 2.303 \frac{RT}{nF} \log \left[ \frac{[\text{MH}_{m-(n-m)}][\text{A}^-]^m}{[\text{M}][\text{HA}]^m} \right] \tag{11}
\]

where the first bracketed term is the formal potential of the PCET process, equation (8).

At the half-wave potential \( (E_{1/2}) \), the concentrations of \( \text{MH}_{m-(n-m)} \) and \( \text{M} \) are equivalent and the last term in equation (11) simplifies to yield equation (12):

\[
E_{1/2} = -\frac{\Delta G_1^0}{nF} - \frac{\Delta G_3^0}{nF} - 2.303 \frac{mRT}{nF} pK_a(\text{HA}) - 2.303 \frac{RT}{nF} \log \left[ \frac{[\text{A}^-]}{[\text{HA}]} \right] \tag{12}
\]

Equation (12) predicts that \( E_{1/2} \) will have an \( m/n \) dependence on \( \log([\text{A}^-]/[\text{HA}]) \). For 1:1 acid:base “buffered” solutions where the concentrations of acid and base are much greater than the concentration of the redox active molecule, this Nernstian-specific term approaches zero.

### 5.3 Experimental Application of Theory

There are a few examples of potential-\( pK_a \) relationships for molecular species that undergo PCET,\textsuperscript{146,180–183} however, in none of these cases is the PCET clearly occurring reversibly. Verifying the predictions of potential-\( pK_a \) theory would ideally utilize system(s) featuring stable PCET products and electrochemically reversible PCET. Independent measurement of reduction potentials and \( pK_a \)s could then check the accuracy of the predicted values from the experimental potential-\( pK_a \) plot.

Two experimental potential-\( pK_a \) diagrams were created for two inorganic complexes (Figure 5.1): \( \text{MoCp}_2(S_2C_2(H)-4\text{-pyridin-yl}) \) (1) and \( [\text{Ni(bdt)}_2(\text{Bu}_4\text{N}) \) (2). Both possess redox non-
innocent dithiolate ligands. Compound 1 additionally features a pendant pyridine as a possible protonation site. These two complexes exhibit reversible PCET; discussion of extending potential-pK\textsubscript{a} theory to a system with overall irreversible behavior follows.

![Structures of complexes 1 and 2.](image)

**Figure 5.1.** Structures of complexes 1 and 2.

### 5.3.1 Construction of Potential–pK\textsubscript{a} Diagram for Compound 1

In acetonitrile, 1 is reversibly oxidized at −0.20 V vs. Fc\textsuperscript{+}/0 as shown by its cyclic voltammogram (CV) in **Figure 5.1**. Addition of one mole equivalent (relative to 1) of a sufficiently strong acid like protonated dimethylformamide (pK\textsubscript{a}(CH\textsubscript{3}CN) = 6.1\textsuperscript{72}) results in complete protonation of 1, forming [1(H)]\textsuperscript{1+}. Protonation shifts the redox wave positive by over 200 mV (Figure 5.1) and is assigned as the [1(H)]\textsuperscript{2+/1+} oxidation. Addition of a weaker acid such as 2-methylpyridinium (pK\textsubscript{a}(CH\textsubscript{3}CN) = 13.32\textsuperscript{75}) resulted in the appearance of a broadened yet reversible oxidation event at potentials between that of 1 and [1(H)]\textsuperscript{1+} (Figure 5.2).

![Cyclic voltammograms of 1 with and without added acid.](image)

**Figure 5.2.** Cyclic voltammograms of 1 with and without added acid. CVs of 0.2 mM 1 in CH\textsubscript{3}CN at 100 mV/s with 0.25 M [Bu\textsubscript{4}N][PF\textsubscript{6}] with no acid (black), 0.2 mM of dimethylformamidium (pK\textsubscript{a} = 6.1\textsuperscript{72}, red), or 0.2 mM 2-methylpyridinium (pK\textsubscript{a} = 13.32\textsuperscript{75}, blue).
The oxidation potential of 1 in the presence of one equivalent of acid was measured with 27 discrete acids spanning a pK_a range of over 15 units (Appendix F). From this data, a potential–pK_a diagram was constructed (Figure 5.3). An overall S-shape is observed consisting of two pK_a-independent regions and one pK_a-dependent region. The curvature resulting in the S-shape is discussed below. With the most acidic proton sources, 1 is protonated regardless of oxidation state and the observed potential corresponds to the [1(H)]^{2+/1+} couple. For the weakest acids employed, 1 is not appreciably protonated prior to oxidation. For acids with pK_a values between these two regions, pK_a-dependent potentials are observed. The middle portion of this region shows a clear linear correlation between E and pK_a. Interference of the curved regions prevented satisfactory linear fitting, so a trend line with a 59 mV/decade slope anchored at the intersection of a pK_a of 15.2 and potential of -0.20 V was used. This anchor was chosen based on the known pK_a of 1 as 15.2.\(^{186}\)

The potential–pK_a diagram of 1 has significant predictive power. The potential of the [1]^1+ and [1(H)]^{2+/1+} couples can be directly ascertained as -0.20 and 0.01 V, respectively. The intersection of the sloped PCET region with the two pK_a independent regions allowed the pK_a of [1]^1+ to be predicted 11.7. While [1]^1+ is electrochemically stable, efforts to chemically isolate [1]^1+ have been unsuccessful,\(^{186}\) so precluding direct measurement of the pK_a of [1]^1+. Hence, the ability to use 1’s potential–pK_a diagram to estimate the pK_a of [1]^1+ as 11.7 is particularly valuable. The pK_a of [1]^1+ can be also confirmed as 11.7 with Hess’s law using the pK_a of 1 and the oxidation potentials of 1 and [1(H)]^{1+}.\(^{186}\)
Figure 5.3. Potential–pKₐ diagram of 1. Plot of the observed oxidation potential of 0.2 mM 1 with 0.2 mM of various acids versus the pKₐ of the acid used. The solid horizontal line near 0 V is a linear fit for acids of pKₐ ≤ 9.7, the horizontal line near -0.2 V is the oxidation potential of 1 in the absence of acid, and the diagonal line is a trend line with a slope of 59 mV/decade anchored at a pKₐ of 15.2 and -0.2 V (see main text). Dashed vertical lines were drawn from the intersection of the trend line with the horizontal lines.

The observed coupling of the oxidation potential of 1 with the pKₐ of the acid utilized can be rationalized by either invoking electron delocalization between the molybdenum dithiolene core and the pendant pyridine (Figure 5.4) or a through space effect. UV-vis revealed that the complex color changes significantly once protonated (Figure 5.5), lending support to delocalization as the cause of the coupling between pKₐ and potential.

Figure 5.4. Possible resonance forms of 1. Mo oxidation can be invoked in further resonance forms.

Assignment of protonation at the pyridine moiety – as opposed to a sulfur atom or Mo – is supported by the absence of change in the oxidation potential upon addition of similar-strength acids to the analogous pendant phenyl version of 1. Furthermore, the pKₐ of 1 (15.2 ± 0.1) is within the typical range for pyridiniums.
Figure 5.5. Extinction coefficients of compound 1 in acetonitrile without acid (black) and with 5.2 equivalent of dimethylformamidium triflate (blue).

The PCET process underpinning the potential–pK_a diagram of 1 can be interpreted with a thermochemical square scheme (Figure 5.6). Per Hess’s law, the net free energy change of the [1(H)]^{1+} to [1]^{1+} reaction should be identical regardless of mechanism.\(^{23}\) Gratifyingly, the square scheme yields the same net free energy of ca. –67 kJ/mol for both the stepwise EC (electron transfer followed by proton transfer) and CE (proton transfer followed by electron transfer) mechanisms. This consistency further supports the accuracy of the thermochemical values obtained from potential–pK_a diagrams.

Prior to oxidation, the strength of the acid used will determine the protonation equilibrium of 1. For sufficiently weak acids, 1 is not protonated and is oxidized at –0.20 V – the same potential as without added acid. Conversely, for very strong acids, 1 is protonated regardless of oxidation state. It is for acids of strength between these two extremes that proton transfer and electron transfer are coupled.
For acids of intermediate strength, \( \mathbf{1} \) will be protonated to some extent prior to oxidation, and so a population of \([\mathbf{1}(\mathbf{H})]^1+\) exists in solution. However, the oxidized species \([\mathbf{1}(\mathbf{H})]^2+\) is more acidic than \([\mathbf{1}(\mathbf{H})]^1+\), thus the acid/base equilibrium is expected to favor \([\mathbf{1}]^1+\) in this intermediate pK\(_a\) range.\(^{186}\)

Two stepwise mechanisms may be considered – EC or CE (E = electron transfer and C = chemical step). In the EC pathway, \([\mathbf{1}(\mathbf{H})]^1+\) is oxidized followed by deprotonation by conjugate base (A\(^-\)). For the CE pathway, a rapid thermal equilibrium between \(\mathbf{1}\) and \([\mathbf{1}(\mathbf{H})]^1+\) allows oxidation to occur through the more thermodynamically accessible \([\mathbf{1}]^{1+\text{eq}}\) pathway. For both the EC and CE mechanisms, the oxidation potential depends on the protonation equilibrium values.\(^{40}\) Satisfyingly, the expected location of the oxidation event varies with a 59 mV/decade dependence on the actual equilibrium constant, which is defined by the difference in the pK\(_a\) values of \([\mathbf{1}(\mathbf{H})]^1+\) or \([\mathbf{1}(\mathbf{H})]^2+\) and HA. This is consistent with the thermodynamic analysis presented earlier. Additionally, curvature in the oxidation potential position is observed for acids with pK\(_a\) values near that of the redox active species – consistent with the potential–pK\(_a\) diagram of \(\mathbf{1}\) (full description given in Appendix F).\(^{187}\)

As both the EC and CE pathway result in the expected 59 mV/decade dependence on acid pK\(_a\), it is expected that the concerted proton electron transfer pathway will have the same relationship. Rigorous analysis of \(\mathbf{1}\)'s PCET mechanism is the subject of current research.
In addition to the relationship predicted and established between \( E_{1/2} \) and acid pK\(_a\), equation (12) also indicates \( E_{1/2} \) will vary with the concentrations of acid and conjugate base. Measurement of the \( E_{1/2} \) of 1 as a function of the base/acid ratio for 2-methylpyridine/2-methylpyridinium resulted in a slope of 62 mV/decade (Figure 5.7), consistent with the expected slope of 59 mV/decade from equation (12) for a one proton, one electron Nernstian PCET process. In this case, acid identity is not altered and the observed shift in oxidation potential is purely the result of the Nernstian term in equation (12).

\[ \text{Figure 5.7. Nernstian dependence of the oxidation potential of 1 on the base/acid ratio. A) Cyclic voltammograms of the oxidation of 1 as a function of the ratio of 2-methylpyridine to 2-methylpyridinium. The initial concentration of 2-methylpyridinium and 1 (45 mM and 0.4 mM, respectively) were constant throughout the experiment. B) Plot of the recorded oxidation potentials versus the log of the ratio of 2-methylpyridine to 2-methylpyridinium for this experiment.} \]

5.3.2 Construction of Potential–pK\(_a\) Diagram for Compound 2

To provide a second potential–pK\(_a\) diagram example, the electrochemical PCET of compound 2 was analyzed in a similar fashion to 1. In the absence of acid, 2 is reversibly reduced by one electron at \(-0.92 \text{ V vs. Fc}^{\ast}\) (Figure 5.8A). In the presence of one equivalent of
various acids a quasi-reversible reduction wave is observed for acids of $pK_a$(CH$_3$CN) lower than ca. 12 (cyclic voltammograms for 2 with all acids provided in Appendix F). **Figure 5.8A** demonstrates this for the addition of anilinium ($pK_a = 10.62$) to 2: at 1,500 mV/s the $[2]^{1+/0}$ oxidation of 2 is reversible even with added anilinium, showing that a **reductive PCET process occurs reversibly near the $2^{0/1^-}$ couple.**

For acids of lower $pK_a$, faster scan rates were required to observe the return PCET oxidation; this suggests that the initial PCET product formed by adding electrons and protons to 2 is not stable. Indeed, a previous report found that 2 decomposed at the electrode surface in the presence of excess acid.$^{134}$ This stability appears to be related to acid strength: for stronger acids, the product is less stable and consequently higher scan rates are required to obtain reversible PCET at the electrode surface. For acids of $pK_a$ greater than about 12, reversibility was maintained even at lower scan rates, although in a few instances partial loss of the return oxidation was observed.

Plotting the $E_{1/2}$ values found for the new waves versus the $pK_a$ of the added acid (**Figure 5.8B**) shows two distinct regions. A $pK_a$-dependent region has an $E_{1/2}$–$pK_a$ relationship of 63 mV/$pK_a$ unit, close the predicted 59 mV/$pK_a$ unit slope of Eq. (8) for a process involving an equal number of protons and electrons (the current magnitude does not double, ruling out a two proton, two electron process). This linear region curves into a $pK_a$-independent region located at the potential of the reversible reduction of $[2]^{0/1^-}$. The intersection of the extrapolated $pK_a$-dependent PCET region with the $pK_a$–independent region yields the $pK_a$ of $[2(H)]$ as 11.8. As clean isolation of $[2(H)]$ has not yet been possible in our hands, this $pK_a$ estimate from the potential–$pK_a$ diagram demonstrates the utility of these diagrams to provide thermochemical information of transiently stable species.
Figure 5.8. Generation of an experimental potential–pK_a diagram of compound 2. A) Cyclic voltammograms of 0.5 mM 2 in CH_3CN with and without 0.5 mM anilinium. Maintenance of oxidative feature on the reverse scan confirms reversibility of PCET at this scan rate. B) Potential–pK_a diagram plotting the observed reversible potential of the PCET process with acids of varying pK_a (CH_3CN). Each data point is the average of several scans at different scan rates. The sloped line is a linear fit to data points of pK_a < 11.5; this line was extrapolated to smaller pK_a values (gray line) and higher pK_a values. Horizontal dashed black line is the E_1/2 potential of the reversible [2]^0\textsuperscript{-} reduction in the absence of acid and the dashed vertical line is positioned at the intersection of pK_a dependent and independent lines.

Next, as for 1, the relationship between E_1/2 and acid and conjugate base concentration was examined. A solution of 2 with one equivalent of 4-Cl-anilinium was titrated with 4-Cl-aniline, resulting in a negative potential shift of the PCET wave (Figure 5.9A). Plotting the observed E_1/2 potential versus the inverse log of the calculated ratio of [4-Cl-aniline]/[4-Cl-
anilinium] at $E_{1/2}$ yielded a linear relationship with a slope of 61 mV/decade (Figure 5.9B). This is consistent with the 59 mV/decade slope predicted by equation (12) for a one proton, one electron Nernstian PCET process.

![Figure 5.9.](image)

**Figure 5.9.** Nernstian dependence of reduction potential of 2 on base/acid ratio. A) Cyclic voltammograms of a solution of 0.45 mM 2 with 0.45 mM 4-Cl-anilinium titrated with increasing amounts of 4-Cl-aniline. Taken at 200 mV/s in 0.25 M [Bu$_4$N][PF$_6$]. B) Plot of the $E_{1/2}$ value for seven titrations of 4-Cl-aniline versus the calculated log of the ratio of the concentrations of 4-Cl-aniline to 4-Cl-anilinium at $E_{1/2}$.

The 4-Cl-anilinium/4-Cl-aniline data of Figure 5.9 represents an idealized case where individual molecules of acid and conjugate base interact weakly. Many acids aggregate in non-aqueous solvents where solvation is poor (e.g., dimers of carboxylic acids). Additionally, acid (HA) may interact with its conjugate base (A$^-$), a process termed homoconjugation (discussed more thoroughly in Chapter 2):$^{97,179,188,189}$

$$A^- + HA \rightleftharpoons A^- \cdots HA$$

Homoconjugation can have a profound influence – the concentration of non-associated acid is reduced, the acidity of HA may be increased through stabilization of newly generated
conjugate base with unreacted parent acid, and the homoconjugated species has a different 
$pK_a$.\textsuperscript{179}

Substituted anilinium acids generally homoconjugate weakly (the homoconjugation 
formation constant for anilinium is about 4);\textsuperscript{72} consequently, the 4-Cl-anilinium/4-Cl-aniline data 
in the main text were not expected to show significant deviations from the predicted slope. 
When the same titration is performed with $p$-toluenesulfonic acid, which possesses a large 
homeconjugation constant of about 1000,\textsuperscript{72} the plot of $E_{1/2}$ potential plotted versus the inverse 
log of the tosylate concentration is non-linear (Figure 5.10).

**Figure 5.10.** Plot of the $E_{1/2}$ value for a solution of 0.45 mM 2 versus the log of varying ratios of 
tosylate to $p$-toluenesulfonic acid. Percentage values (in red) next to each data point indicate 
the percentage of $p$-toluenesulfonic acid homoconjugated in the bulk solution.

The overall non-linearity of the titration data matches the expected equilibrium of $p$-
toluenesulfonic acid with its homoconjugated form. This data can be partially corrected (Figure 
5.11) by calculating how much non-homoconjugated acid is initially present based on the 
homoconjugation formation constant and initial concentrations, followed by estimation of the 
concentrations of tosic acid and tosylate at the $E_{1/2}$ value. The homoconjugation formation 
constant of $p$-toluenesulfonic acid is known to be approximately 1000,\textsuperscript{72} and so calculations 
were performed to estimate the amount of $p$-toluenesulfonic acid existing as free acid, the
amount present as the homoconjugated product, and the amount of conjugate base remaining. Using this analysis, the amount of free acid present at the electrode prior to the experiment beginning may be approximated. Figure 5.11 compares the raw data with the data corrected for homoconjugation.

As Figure 5.11 shows, homoconjugation could not be completely corrected. Multiple factors render this challenging. First, as soon as PCET begins occurring at the electrode surface the relative concentrations of acid, conjugate base, and homoconjugated acid/base pair begin to change rapidly. Second, the homoconjugated acid (of unknown \( pK_a \)) may still participate in PCET electrochemistry. Consequently, studies with this sort of analysis should, if possible, strive to utilize acid/base pairs that homoconjugate weakly and to utilize dilute solutions.

A second example of a non-Nernstian response was seen for titration of aniline to a 1:1 mixture of 2 and anilinium; a slope of 46 mV/decade was observed (Figure 5.12). Compared to \( p \)-toluenesulfonic acid, anilinium and aniline associate much more weakly in acetonitrile. A more plausible explanation is that as the aniline concentration increases, the \( E_{1/2} \) shifts close to

---

**Figure 5.11.** Partial correction for homoconjugation for PCET of 2 with tosylate addition. Blue points are the plot of the \( E_{1/2} \) value for each CV titration of tosylate (\( \text{TsO}^- \)) versus the calculated log of the ratio of the concentrations of tosylate to \( p \)-toluenesulfonic acid at \( E_{1/2} \) *assuming no homoconjugation*. Red points show the data corrected for homoconjugation per the main text.
the original redox couple of 2 in the absence of acid (\(E_{1/2}(2^{0/1-})\)) – only 10 equivalents of added base are required to shift the observed \(E_{1/2}\) to within 20 mV of \(E_{1/2}(2^{0/1-})\). As detailed for 1, and also seen in the potential-pK\(_a\) diagram of 2, curvature is observed between the linear PCET region and the pK\(_a\)-independent region. For anilinium, addition of aniline shifts the redox potential into the curved region. 4-chloroanilinium exhibits Nernstian behavior because it both homoconjugates weakly and because the PCET redox wave without added base is over 100 mV positive of \(E_{1/2}(2^{0/1-})\).

![Graph](image)

**Figure 5.12.** Plot of the \(E_{1/2}\) value for a solution of 0.45 mM 2 versus the log of varying ratios of aniline to anilinium in solution.

### 5.3.3 Using Irreversible Voltammograms Data for Potential-pK\(_a\) Diagrams

Potential-pK\(_a\) theory predicts that non-stoichiometric PCET should result in potential-pK\(_a\) slopes of \(m/n \cdot 59\) mV/decade, with \(m\) and \(n\) equaling the number of protons and electrons, respectively. The NiP\(_2\)S\(_2\) complex (compound 3, **Figure 5.13**) described in Chapters 4 and 5 was found to exhibit one proton, two electron PCET and so may show non-stoichiometric PCET slopes in a its potential-pK\(_a\) diagram.

Accordingly, the PCET of 3 was studied over a range of acid strengths (all cyclic voltammograms in Appendix F). Stronger acids resulted in more positive \(E_{p,c}\) (**Figure 5.14**). For acids of pK\(_a\) greater than about 24, some return oxidation is observed at 100 mV/s and the \(E_{1/2}\)
of this partially reversible wave lies on top of the normal reduction potential of 3. The lack of total reversibility indicates that reduced 3 is unstable on the electrochemical timescale in the presence of acid even for weaker acids; this is in agreement with previous findings of the ultimate decomposition of 3.\textsuperscript{25} Reversibility in the stronger acid region was probed with Et\textsubscript{3}NH\textsuperscript{+} ($pK_a$ 18.82\textsuperscript{75}) by increasing the scan rate; no reversibility was seen up to 10 V/s (Figure 5.15).

![Figure 5.13. Structure of compound 3.](image)

![Figure 5.14. Normalized linear sweep voltammograms of 0.3 mM 3 with 0.3 mM of various acids: phenol ($pK_a$ = 29.14\textsuperscript{78}), acetic acid ($pK_a$ = 23.51\textsuperscript{190}), 2,4,6-tribromophenol ($pK_a$ = 20.35\textsuperscript{190}), triethylammonium ($pK_a$ = 18.82\textsuperscript{75}), and benzylammonium ($pK_a$ = 16.91\textsuperscript{75}).](image)

![Figure 5.15. Cyclic voltammogram of 0.3 mM 3 and 0.3 mM Et\textsubscript{3}NH\textsuperscript{+} at 10 V/s. No reversibility of PCET wave is seen.](image)
As no reversibility was observed, the potential-pKa diagram was constructed by plotting the cathodic peak potential (E\textsubscript{p,c}) the pK\textsubscript{a} of the acid used for CVs showing no reversibility (Figure 5.16). Two regions are observed – a pK\textsubscript{a}-dependent region with a slope of 40 mV/dec and a pK\textsubscript{a}-independent region straddling the $3^{0/1-}$ reduction potential without acid. The experimental slope of 40 mV/pK\textsubscript{a} unit is about 10 mV greater than the predicted 29.5 mV/dec slope predicted for the one proton, two electron PCET previously found for 3.$^{25}$

![Potential-pKa diagram](image)

**Figure 5.16.** Potential-pK\textsubscript{a} plot of the observed potential of the PCET process of 3 with acids of varying pK\textsubscript{a}(CH\textsubscript{3}CN). Data were recorded for 0.3 mM solutions of 3 with one equivalent of the respective acid at 100 mV/s in 0.25 M [Bu\textsubscript{4}N][PF\textsubscript{6}] CH\textsubscript{3}CN solution. Each data point is the average of the peak cathodic current from three separate scans. Solid red line is a linear fit to red data points; this was extrapolated to intersect the horizontal dash black line which is the $3^{0/1-}$ reduction potential (E\textsubscript{1/2} = -1.92 V).

The potential-pK\textsubscript{a} diagram of 3 suggests that another PCET region should exist representing the one electron, one proton transformation from $3^{1-}$ to $3H^{1-}$. This 59 mV/dec line could then terminate at the intersection of the $3^{1/2-}$ potential and the pK\textsubscript{a} of 3\textsuperscript{2-}. The $3^{1/2-}$ potential in the absence of acid is an electrochemically irreversible reduction with an E\textsubscript{p,c} of -2.523 V vs. Fc\textsuperscript{+/0} (Figure 5.17). This reduction is irreversible even at faster scan rates (up to 5 V/s).
Figure 5.17. Cyclic voltammogram of 0.3 mM 3 at 100 mV/s in 0.25 M [Bu₄N][PF₆].

Despite the irreversible nature of the $3^{1/-2}$ couple, it was attempted to measure additional points in the potential-$pK_a$ diagram of 3 by triggering PCET from the $3^{1/-2}$ couple. Figure 5.18 shows the electrochemistry of 3 with phenol to more negative potentials, the weakest acid accessed in this study ($pK_a = 29.14^{78}$). Two new reductions are observed with peak potentials of ca. 2.24 V and -2.46 V vs. Fc$^{+/0}$.

Figure 5.18. Cyclic voltammetry of 0.3 mM 3 with and without one molar equivalent of phenol at 100 mV/s in 0.25 M [Bu₄N][PF₆] solution.
These new, ill-defined reductions suggest that any reduced $3^+$ may be in equilibrium with the protonated form $3^+(H)$, leading to further electron transfer from the electrode and ultimate decomposition. This is supported by the overall irreversible character of PCET with $3$ (as detailed in Chapters 3 and 4).

Similar ill-defined new reduction peaks were observed using the other three of the weakest acids used in constructing the potential-pK\textsubscript{a} diagram of $3$: 4-chlorophenol, o-cresol, and 2,4,6-tri-tert-butylphenol. In each case, very similar CVs were obtained as that for phenol. At faster scan rates, the minor reduction peak ($E_{p,c}$ about -2.24 V for phenol) disappears, suggesting it to be a minor side process. When the potentials for both reductions are plotted in an extended potential-pK\textsubscript{a} diagram of $3$ (Figure 5.19) it is clear that neither represent a thermodynamically-driven PCET process.

![Figure 5.19](image.png)

**Figure 5.19.** Extended potential-pK\textsubscript{a} diagram of $3$. Pink circles represent the two irreversible peak potentials obtained with weaker acids. Dashed horizontal line between $3^{1+}$ and $3^{2+}$ is the peak cathodic potential observed in the absence of acid.

Satisfactorily accessing a second sloped region for $3$ may hinge on utilizing very weak acids of pK\textsubscript{a} > 30, however, this would be near or above the maximum expected for acetonitrile which itself has an estimated autoprotolysis constant of about ≥ 32.2.⁷⁹
Interpreting the potential-pKₐ dependence for a system with apparently irreversible PCET requires careful consideration. As irreversible voltammograms can be dominated by kinetic factors, thermodynamic information may be unobtainable and so the slope obtained in the diagram of 3 might not reflect the stoichiometry in protons and electrons.

An elegant example of extracting thermodynamic information from irreversible voltammograms is that of aqueous phenol oxidation as studied by Costentin and co-workers. Two factors made extracting thermodynamic information complex: 1) phenol self-inhibition at higher concentrations and 2) a rate-determining dimerization of phenol upon oxidation. The former was mitigated through judicious use of low phenol concentration and appropriate scan rate. The latter was addressed by assuming that the electron and proton transfers prior to dimerization were fast and reversible; in turn the irreversible peak potential could be described as a combination of the expected Pourbaix dependence and the dimerization rate:

$$E_p = E_{ap}^0 + 0.903RT/F - (RT\ln(10)/3F)\log(4RTk_{dimerization}C^0/3Fv)$$

where $E_{ap}^0$ is the pH-dependent potential, $R$ is the gas constant, $T$ the temperature, $F$ the Faraday constant, $k_{dimerization}$ the dimerization rate, and $C^0$ the initial concentration of phenol. Once the $k_{dimerization}$ is known, the experimentally observed peak potentials ($E_p$ values) can be used to calculate the pH-dependent $E_{ap}^0$ values and so produce a Pourbaix plot.

One assumption in this analysis was that the proton and electron transfer steps prior to dimerization were stepwise and reversible. PCET for 3, however, likely proceeds through an initial concerted PCET due to the lack of match between digital simulation of the stepwise modeling and observation of a H/D KIE, as detailed in Chapter 4. Consequently, new expressions would be needed to correct the predicted thermodynamic shift. If, however, the initial concerted PCET is not reversible, then interpreting the potential-pKₐ slope found for 3 does not translate easily to thermodynamic information.
The potential-$pK_a$ slope observed for 3 in the non-reversible case would likely depend on a combination of the thermodynamics of the specific acid plus a kinetic component. This kinetic component is the CPET heterogeneous electron transfer constant $k_{s(CPET)}$ (simultaneous reaction of acid with 3 at the electrode), which in turn may depend on acid $pK_a$ through a linear free energy relationship (LFER). Such a LFER in combination with a thermodynamic shift could explain the non-ideal potential-$pK_a$ slope seen for 3.

5.4 Conclusions

For eighty years, Pourbaix theory has proven to be of great practical and fundamental utility. The potential–$pK_a$ diagrams reported and validated in this work permit similar analyses of electrochemical PCET in non-aqueous aprotic solvents. Remarkably, essentially the same information available from an aqueous Pourbaix diagram is provided by non-aqueous potential–$pK_a$ diagrams, including:

1) Number of discrete species

2) Thermodynamically stable species at a specific applied potential and with an acid of a given $pK_a$

3) $pK_a$ values

4) Reduction potentials of pure electron transfer processes

5) Stoichiometry in protons and electrons for each PCET event

In the application of this theory, we emphasize that potential–$pK_a$ diagrams cannot be constructed without the availability of a self-consistent acid $pK_a$ scale for the specific solvent employed. Fortunately, a large body of $pK_a$ values is available as a result of work done in the late 1900’s72 as well as more recent and rigorous work.75,77,191

Our efforts to create experimental potential-$pKa$ plots have demonstrated the utility of the theory presented here. This work has also underscored specific considerations. Factors such as homoconjugation and dimerization can change the overall free energy of a PCET event. Irreversible electrochemical PCET can be used to generate meaningful potential-$pK_a$ diagrams if
the electron and proton transfers are fast and reversible. There is a current lack of theory to allow for the correction of irreversible PCET voltammograms in the case of concerted PCET. This is an opportunity for future research.

The familiarity of Pourbaix diagrams combined with the relative simplicity of the potential–$pK_a$ theory should facilitate utilization of potential–$pK_a$ diagrams. Given the widespread and myriad use of aqueous Pourbaix diagrams, and the ubiquity of PCET reactions in non-aqueous solvents, it is anticipated that non-aqueous potential–$pK_a$ diagrams will also find diverse applications.
CHAPTER 6. Investigating the PCET Mechanism for a Mo Complex

6.1 Introduction

Deciphering the mechanisms of proton-coupled electron transfer (PCET) reactions remains a current challenge in chemistry. Efforts to address this challenge are frequently motivated by the belief that desirable catalytically driven reactions can be rationally improved if the underlying mechanisms are understood. As large-scale fuel production from renewable energy sources almost certainly requires PCET reactions (as detailed in Chapter 1), there is additional strong motivation to understand what governs the mechanisms of PCET.

The thermodynamically controlled PCET discussed in Chapter 5 for the complex MoCp₂(4-pedt) (Figure 6.1) left interesting unanswered questions about the specific PCET mechanisms at work. As the PCET was reversible, it is also possible that different mechanisms may occur on the forward and reverse portions of the cyclic voltammogram – in other words, the initial oxidative PCET may proceed through a different mechanism than the return reductive PCET. The mechanism may also change across the potential-pKₐ diagram of 1. Herein, we investigate the possible PCET mechanisms of 1.

![Figure 6.1](image)

Figure 6.1. Structure of 1.

6.2 Possible PCET Mechanisms

It was found during this study that the oxidized forms of 1 (both unprotonated and protonated forms) slowly decompose on the electrochemical timescale. Previous work found
that 1 could not be chemically isolated, however, it was not known what the rate of decomposition of oxidized 1 was. Cyclic voltammetry at relatively slow scan rates was used to probe decomposition of $1^{1+}$ and $1(H)^{2+}$ (Figure 6.2).

Examination of the CVs at these slower scan rates reveals that the magnitude of the return reduction event is less than the magnitude of the forward oxidation – some of the oxidized species is lost. The decomposition rate can be obtained by the method of Nicholson and Shain using the ratio of the forward and return peak currents and a simulated working curve (Figure 6.3) to determine the rate of decomposition. The working curve (originally simulated by Nicholson and Shain$^{54}$) is the result of simulated CVs for various decomposition rates in an intramolecular EC mechanism where an irreversible chemical step follows a reversible electron transfer. The ratio of the forward peak current to the return peak current was found empirically to depend on the decomposition rate and the time passed during a CV experiment between the $E_{1/2}$ of the redox couple and the switching potential; consequently, the simulated working curve allows quick estimation of the decomposition rate.

Figure 6.2. A) Background corrected cyclic voltammogram of 0.2 mM 1 at 20 mV/s in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution. B) Background corrected cyclic voltammogram of 0.2 mM $1(H)^{1+}$ (generated in situ from 0.2 mM 1 plus 2.5 mM dimethylformamide) at 60 mV/s in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.
As accurately defining a baseline to account for diffusion is challenging, an alternative method of defining the ratio of the forward oxidative current to the return reductive current was used. In this method, the peak forward current \( (i_{p,f})_0 \), switching potential current \( (i_{sp})_0 \), and peak reverse current \( (i_{p,r})_0 \) is used to calculate the ratio of \( \frac{(i_{p,r})}{(i_{p,f})} \) using a semiempirical relationship (see Figure 6.2 for a visual definition):

\[
\frac{i_{p,r}}{i_{p,f}} = \frac{(i_{p,r})_0}{(i_{p,f})_0} + \frac{0.485(i_{sp})_0}{(i_{p,f})_0} + 0.086
\]

The intersection of this ratio with the working curve in Figure 6.3 gives the value of \( \log(k_f \tau) \), where \( \tau \) is the time in seconds passed between the \( E_{1/2} \) of the redox process and the switching potential. With this, the decomposition rate can be calculated. Using the data shown in Figure 6.2, decomposition rates were estimated for \([1]^+\) as 0.05 and \([1(H)]^2+\) as 0.04 s\(^{-1}\), respectively.

![Figure 6.3](image)

**Figure 6.3.** Working curve data for an EC mechanism where the C step occurs intramolecularly and a return redox event is still observed on the return scan. As the working curve data was not generated at each possible value of \( \log(k_f \tau) \), the blue dashed line was drawn (0.05 unit steps on the x-axis) at the experimental current ratio and the intersection with the extrapolated working curve used to estimate the \( \log(k_f \tau) \) value. Working curve data from ref. 54, see main text for details on its creation.

With these decomposition rates, a more complete mechanistic scheme can be drawn for 1 (Figure 6.4). The reduction potentials and \( pK_a \) values were determined in Chapter 5. For acids
of pKₐ between that of 1 and [1]¹⁺, PCET is expected to occur. The feasibility of stepwise vs. concerted pathways will be addressed sequentially.

![Possible PCET mechanisms for 1.](image)

**Figure 6.4.** Possible PCET mechanisms for 1.

### 6.3 Scan Rate and Buffer Concentration Effects

New experimental datasets of 1 with acid were collected prior to modeling the stepwise pathway. Mechanistic studies of electrochemically-triggered PCET have occasionally used scan rate to test the mechanism.³¹ One key parameter of an electrochemical CPET mechanism is the heterogeneous electron transfer constant $k_s$(CPET). The influence of this constant can be probed by raising the scan rate which can result in the CPET associated electron transfer becoming more rate limiting and give a corresponding increase in peak-to-peak separation (Figure 6.5).¹⁵⁵ To test the PCET response of 1 with scan rate, a solution of equimolar 1 and pyridinium (pKₐ = 12.53) was analyzed over a range of scan rates (Figure 6.6).

With increasing scan rate, the midpoint position of the observed wave shifted to more positive potentials, finally reaching the potential of the [1(H)]²⁺/¹⁺ couple in the absence of proton transfer at 40 V/s. At these concentrations of 1 and acid, increasing scan rate appears to shift the mechanism from PCET to pure ET; there is not enough time available for PT to occur. As both the stepwise and concerted pathways require interaction of the proton acceptor, this does not rule out either pathway. Increase in peak-to-peak separation was observable for the
aminophenol literature example (Figure 6.5) because PT occurred intramolecularly – this is not the case for 1.

Figure 6.5. Literature example of oxidative CPET. At faster scan rates, the peak-to-peak separation increases, indicative of rate limitation by \( k_{\text{CPET}} \). Red lines indicate simulated CPET mechanism using DigiElch. Adapted with permission from Costentin et al. J. Am. Chem. Soc. 2006, 128, 4552-4553. Copyright (2006) American Chemical Society.

Figure 6.6. Observed \( E_{1/2} \) as a function of scan rate for a solution of 0.4 mM 1 and 0.4 mM pyridinium (\( pK_a = 12.53^{75} \)).

In the original construction of 1’s potential-\( pK_a \) diagram, the peak-to-peak separation \( (\Delta E_p) \) was greater than the 59 mV/decade expected for a Nernstian process for acids with \( pK_a \) values between that of 1 and 1\. Greater than Nernstian \( \Delta E_p \) is expected for both stepwise and concerted pathways at low buffer concentrations; consequently, the specific values of \( \Delta E_p \) is expected to be diagnostic of the operating mechanism. CVs were obtained for a solution of 1
with varying buffer concentrations of 2-MePy/2-MePyH$^+$ (Figure 6.7A). At a $\text{pK}_a$ of 13.32, 2-MePyH$^+$ is approximately midway between the strength of 1 and 1$^+$. With increasing buffer concentration, the PCET wave of 1 plus buffered 2-MePy/2-MePyH$^+$ lost broadness and ultimately reached a nearly Nernstian peak width of ca. 60 mV/decade at about a ratio of buffer to 1 of 30 (Figure 6.7B).

**Figure 6.7.** A) CVs of 0.2 mM 1 with FeCp$_2$ as an internal standard (not shown) as a function of relative buffer concentration (equimolar 2-MePy/2-MePyH$^+$) at $E_{1/2}$ at 0.1 V/s in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution. B) Peak-to-peak separation as a function of buffer concentration relative to 1 at $E_{1/2}$.

### 6.4 Modeling Stepwise Mechanism

A stepwise PCET pathway for 1 where was modeled using *DigiElch* using a combination of all possible EC and CE pathways for forward oxidation and return reduction (*Table 6.1*). As it has been shown theoretically that either stepwise pathway can account for the thermodynamic peak shifts, focus was directed towards matching the experimental wave shapes and the peak widths as a function of buffer concentration in particular. For the *DigiElch* models, the thermochemical data obtained previously (Chapter 6) was used along with new measurements of the diffusion coefficients and heterogeneous electron transfer rate constants of 1 and [1(H)]$^{1+}$. The Randles-Sevck equation was used to estimate diffusion coefficients of 1 and [1(H)]$^{1+}$ as $1.2 \times 10^{-5}$ cm$^2$ s$^{-1}$, respectively (Appendix G). The Nicholson method was used to
estimate the heterogeneous electron transfer rate constants of 1 and \([\text{1(H)}]^{1+}\) as 0.4 ± 0.1 and 0.6 ± 0.2 cm s\(^{-1}\), respectively (Appendix G).

### Table 6.1. Reaction equations for modeling stepwise PCET for complex 1 with 2-MePy/2-MePyH\(^+\) using DigiElch.

<table>
<thead>
<tr>
<th>electrode reactions</th>
<th>parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1^{1+} \rightleftharpoons 1)</td>
<td>(E^{0'} = -0.2, V; \alpha = 0.5; k_s = 0.4, \text{cm s}^{-1})</td>
</tr>
<tr>
<td>(1(\text{H})^{2+} \rightleftharpoons 1(\text{H})^{1+})</td>
<td>(E^{0''} = +0.01, V; \alpha = 0.5; k_s = 0.6, \text{cm s}^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>solution reactions</th>
<th>parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 + \text{HB}^{1+} \rightleftharpoons 1(\text{H})^{1+} + \text{B})</td>
<td>(K_{eq}(1) = \frac{k_{f1}}{k_{b1}} = 76; k_{f1} \text{ and } k_{b1} \text{ varied per text (M}^{-1}, \text{s}^{-1}))</td>
</tr>
<tr>
<td>(1^{1+} + \text{HB}^{1+} \rightleftharpoons 1(\text{H})^{2+} + \text{B})</td>
<td>(K_{eq}(2) = \frac{k_{f2}}{k_{b2}} = 0.02; k_{f2} \text{ and } k_{b2} \text{ varied per text (M}^{-1}, \text{s}^{-1}))</td>
</tr>
<tr>
<td>(1 \rightarrow \text{decomposition})</td>
<td>(k_{d1} = 0.05, \text{s}^{-1})</td>
</tr>
<tr>
<td>(1^{1+} \rightarrow \text{decomposition})</td>
<td>(k_{d1} = 0.04, \text{s}^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>species</th>
<th>diffusion coefficient (x10(^{-5}) cm(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 and 1(^{1+})</td>
<td>1.2</td>
</tr>
<tr>
<td>1(\text{H})(^{1+}) and 1(\text{H})(^{2+})</td>
<td>1.5</td>
</tr>
<tr>
<td>2-MePy and 2-MePyH(^+)</td>
<td>3.3</td>
</tr>
</tbody>
</table>

While modeling the 2-MePy buffer data, it was found that the diffusion coefficient of the acid/base pair influenced the observed peak widths (\(\Delta E_p\)). \(^1\text{H}\) NMR diffusion-ordered spectroscopy (DOSY) was used to estimate the diffusion coefficient of 2-MePy as 3.3 \(\times\) 10\(^{-6}\) cm\(^2\) s\(^{-1}\) (Appendix G); in modeling it was assumed that 2-MePyH\(^+\) had the same coefficient.

Using these parameters, decomposition rates, and equilibrium constants calculated for solutions of 1 and 2-MePy/2-MePyH\(^+\), DigiElch was used to simulate the buffer-dependence CVs of Figure 6.7 using the equations shown in Table 6.1. During initial simulations, it was found that the magnitude of the decomposition rate \(k_{d1}\) (decomposition of 1\(^{1+}\)) significantly affected the observed peak widths (Figure 6.8A). The rate of \(k_{d2}\) (decomposition of 1(\text{H})\(^{2+}\)) did not influence the peak width over the range studied (Figure 6.8B); this is rationalized by considering that with a buffered solution of 2-MePy/2-MePyH\(^+\), 1(\text{H})\(^{2+}\) will be quickly
deprotonated and so limit the amount of time decomposition can occur. While the decomposition rates $k_{d1}$ and $k_{d2}$ were estimated experimentally (see above), the possible error of these measurements is not known.

![Graph](image)

**Figure 6.8.** Simulated cyclic voltammogram peak widths at 0.1 V/s as a function of 2-MePy/2-MePyH$^+$ buffer concentration compared with experimental data. A) $k_{d1}$ fixed as 0.04 s$^{-1}$, $k_{d1}$ varied as shown. B) $k_{d1}$ fixed as 0.05 s$^{-1}$, $k_{d2}$ varied as shown. Parameters: all PT rates $1 \times 10^{10}$ or greater, using thermodynamic information from 1’s square scheme for the case of 2-MePy, $k_s(1) = 0.4$ cm s$^{-1}$, $k_s(1(H^+)) = 0.6$ cm s$^{-1}$, $[1]_0 = 0.2$ mM, 0.0079 cm$^2$ electrode, and $\alpha = 0.5$ for all electron transfers. Simulated using DigiElch 7.

To address this, CVs were obtained of 1 with buffered solutions of 2-MePy/2-MePyH$^+$ at 1 V/s to minimize the amount of time that 1$^+$ could decompose. As the rate constants for proton transfers are not known, a range of values was simulated. The slower rate constant of both protonation equilibriums ($k_{b1}$ and $k_{b2}$ per Table 6.1) were matched and the faster rate constant calculated accordingly per the equilibrium constant. For simulated minimal PT rates above or
equal to $1 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$, the simulated peak widths were approximately equal to that of the 1 V/s experimental peak widths (Figure 6.9). As the estimated diffusion limited rates for interaction of 1 and $1^\text{eq}$ with acid or base are ca. $3 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ (calculated in the same method outlined in Appendix E), it is plausible that 1 undergoes stepwise PCET.

Figure 6.9. Simulated cyclic voltammogram peak widths at 1 V/s as a function of buffer concentration compared with experimental data. The slow PT transfer steps in both protonation equilibrium were set as shown and the appropriate equilibrium constant used to calculate the other rate. Parameters: used thermodynamic information from 1's square scheme for the case of 2-MePy, $k_s(1) = 0.4 \text{ cm s}^{-1}$, $k_s(1(\text{H})^+) = 0.6 \text{ cm s}^{-1}$, $[1]_0 = 0.2 \text{ mM}$, 0.0079 cm$^2$ electrode, $k_{d1} = 0.05 \text{ s}^{-1}$, $k_{d2} = 0.04 \text{ s}^{-1}$, and $\alpha = 0.5$ for all electron transfers. Simulated using DigiElch 7.

6.5 Probing for CPET

While the stepwise simulations matched the experimental data, it is possible that CPET still occurs. Evidence for or against specific examples of electrochemical PCET being has varied.\textsuperscript{25,34,37,152–156,193–196} Chapter 4 of this thesis details one such example where a combination of DigiElch modeling and kinetic isotope effect (KIE) studies suggested that CPET occurred. Only recently has the commercial software DigiElch implemented the ability to model CPET reactions involving the electrode, a redox-active species, and an external acid/base (as opposed to intramolecular CPET triggered by a redox event\textsuperscript{31,34}). To our knowledge, there is only one literature example where this feature was utilized;\textsuperscript{37} in this case the heterogeneous electron transfer parameter $k_{\text{CPET}}$ was manually varied until the simulated CV matched the
experimental wave. While a good fit was achieved this way, the absence of a KIE and the good match of the stepwise DigELch simulations with experiment ruled out CPET.\textsuperscript{37}

The presence or absence of a H/D KIE is often taken as supporting evidence of CPET.\textsuperscript{34,152–156} This is rationalized by considering that the heterogeneous electron transfer parameter for CPET should depend on the acid source used and hence whether H or D is transferred. For some examples of quasi-reversible CPET, switching from H to D is manifested by an increase in the peak-to-peak separation of the redox wave,\textsuperscript{34,152} although the magnitudes of these increases were not reported. If an H/D KIE is observed, the KIE magnitude may be estimated by determining values of the kinetic parameter $k_{s(CPET)}$ for both the H and D and taking the ratio of $k_{s(H)}/k_{s(D)}$.\textsuperscript{31,33}

The H/D KIE of 1 with 2-MePyH$^+$ was assessed by titrating a solution of 0.4 mM 1 and 0.4 mM 2-MePyH$^+$ with either CH$_3$OH or CD$_3$OD at 1 V/s, per literature precedent for electrochemical KIE studies in acetonitrile.\textsuperscript{31,36} Shown in Figure 6.10, neither the peak width of the PCET wave nor the absolute position (vs. the Fc$^{+}/0$ couple) changed with any clearly discernable trend. The range of concentrations was used to assess whether the changing nature of the solvent medium (pure acetonitrile to acetonitrile/methanol mix) had an influence on the heterogeneous electron transfer constant – no effect was observed. The lack of clear peak broadening is indicative of no KIE and so a CPET mechanism is not supported.

![Graph]

**Figure 6.10.** KIE study comparing the PCET peak width and $E_{1/2}$ at 1 V/s of solutions containing 0.4 mM 1 and 0.4 mM 2-methylpyridinium (pKa = 13.32\textsuperscript{75}) and varying concentrations of either CH$_3$OH or CD$_3$OD. Data are the average of three separate experiments.
6.6 Conclusions

The PCET mechanism of a Mo complex previously found to undergo thermodynamically controlled electrochemical PCET was investigated. Through digital modeling and the lack of a clear H/D KIE, the mechanism is proposed to be stepwise across the pK_a regime. The specific stepwise route that PCET follows on the forward and return traces is hypothesized to vary with pK_a, with the mechanism in the middle of the PCET region of the diagram following an EC mechanism on both the forward and return scans. Near the pK_a of the intermediates 1 and 1(H)^+ it is expected that rapid thermal equilibrium can permit PCET to proceed through CE pathways. Further experiments – such as with acids other than 2-MePyH^+ to more fully probe PCET across the diagram – and digital modeling will be necessary to assign these mechanisms.
APPENDIX A. GENERAL EXPERIMENTAL METHODS


A.1 General Considerations

Acetonitrile (Fisher Scientific, HPLC grade, >99.9%) and diethyl ether (Fisher Scientific, >99%) were degassed with argon and dried using a Pure Process Technology solvent system followed by storage over activated 3 Å molecular seives. Aniline (Sigma-Aldrich), 4-chloroaniline (Aldrich, 98%), 4-tert-butylaniline (Sigma-Aldrich, 99%), 4-nitroaniline (Sigma-Aldrich, 99%), 4-methoxyaniline (Alfa-Aesar, 99%), 4-bromoaniline (Acros Organics, 96%), N,N-dimethylaniline (Sigma-Aldrich, 99%), benzoic acid (Aldrich, 99%), silver nitrate (Aldrich, 99+%), phenol (Sigma-Aldrich, ≥99%), pyridinium chloride (Alfa Aesar, 98%), p-toluenesulfonic acid (Sigma-Aldrich, ≥98.5%), trichloroacetic acid (TCI America, >99%), triethylammonium chloride (Aldrich, 98%), trifluoromethanesulfonic acid (Acros Organics, 99%), 2-nitrophenol (Alfa Aesar, 98%), 3-nitroaniline (TCI, >98%), methyl orange (Aldrich), tetraethylammonium p-toluenesulfonate (TCI America, >98%), decamethylferrocene (Acros Organics), benzoic acid (Aldrich, 99%), 2,4,6-tribromophenol (Sigma-Aldrich, 99%), 4-methoxypyridine (TCI America, >98%), 2-aminopyridine (TCI America, >99%), 2,4,6-trimethylpyridine (TCI America >98%), 2,3-diaminopyridine (Acros Organics, 98%), 2-aminobenzimidazole (Sigma-Aldrich, 97%), pentabromophenol (Sigma-Aldrich, 96%), 4-dimethylaminopyridine (Alfa Aesar, 99%), water for polishing (Fisher Scientific, HPLC grade) and 200 proof ethanol (Decon Labs, Inc.) were used as received. 2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenol (Sigma-Aldrich, 95%), 2,6-lutidine (Aldrich, 99+%), aniline (Sigma-Aldrich), 4-Chloroaniline (Aldrich, 98%), benzylamine (Acros, 99%), pyridine (Sigma-Aldrich, >99%), 2-methylpyridine (Alfa Aesar, 98+%), tetrafluoroboric acid diethyl ether complex (Aldrich), and 2,4,6-trimethylpyridine (TCI America, >98%) were degassed with three freeze-
pump-thaw cycles. 2-Methylpyridine and pyridine were further dried over activated 3 Å molecular sieves.

Salicylic acid (Aldrich) was recrystallized from boiling distilled tap water, filtered, washed with cold water, and dried under vacuum at 85-90 °C for 14 hours. Tetrabutylammonium hexafluorophosphate (TCI, >98%) was recrystallized from hot ethanol, filtered, washed with cold ethanol, and dried at room temperature under vacuum for 19 hours. Dimethylformamidium triflate was prepared as reported. Acetic acid (Fisher Scientific, 99.9%) and triethylamine (Acros, 99%) were dried over activated 3 Å molecular sieves and degassed with three freeze-pump-thaw cycles. Triethylamine was further dried by passage through activated alumina and by storage over activated 3 Å molecular sieves. Trifluoroacetic acid (Sigma-Aldrich, 99%) and water (from a Milli-Q system) were degassed with three freeze-pump-thaw cycles. CD$_3$CN (Cambridge Isotopes Laboratories, Inc., 99.8%) was stored over activated 3 Å molecular sieves.

Elemental analysis was performed by Atlantic Microlabs, Inc. NMR spectra were recorded on a Bruker 400, 500, or 600 MHz spectrometer and referenced to proteo solvent impurities. UV-vis spectra were recorded in a nitrogen-filled glovebox using fiber optic cables connected to an Agilent Cary 60 UV-vis spectrophotometer.

A.2 Electrochemical Methods

Electrochemistry was performed in a nitrogen-filled glovebox with either a Pine Instruments WaveNow or WaveDriver potentiostat using glassy carbon working electrodes, a platinum counter electrode, and a silver wire pseudoreference. The WaveNow potentiostat was pumped into the glovebox and connected to an external computer via a custom USB feedthrough while the WaveDriver potentiostat was kept external to the glovebox and the electrode leads were connected with a custom shielded electrode cable feedthrough. All scans were absolutely referenced to ferrocene using either ferrocene directly as an internal standard or decamethylerrocene (-0.505 V vs. Fc$^{+/0}$ as measured in our laboratory). Glassy carbon electrodes [CH Instruments, 1 mm or 3 mm diameter (used for the majority of experiments); and
eDAQ electrodes, 1 mm diameter and a BASi electrode, 3 mm diameter, were used for electrode comparison experiments with benzoic acid in Chapter 2] were polished with 0.3 micron alumina powder and 0.05 micron alumina powder (CH Instruments, contained no agglomerating agents) Milli-Q water slurries, rinsed and ultrasonicated briefly in HPLC grade water to remove residual polishing powder. The pseudoreference silver wire electrode was submerged in a glass tube fitted with a porous glass Vycor tip containing 0.1 or 0.25 M [Bu₄N][PF₆] in acetonitrile depending on the solution electrolyte concentration.

Each working electrode was pretreated with three cyclical scans from approximately 0.7 V to –2.8 V (the exact value varied in accordance with the silver wire pseudoreference) at 100 or 500 mV/s in 0.1 M [Bu₄N][PF₆]. The solution was agitated between scans. A potential window was initially established and refined with one working electrode to ensure that the reduction event was captured. For each subsequent scan, the working electrode was replaced with a fresh, pretreated working electrode and the voltammogram measured. For the water dependence experiments of Chapter 2, acid was added to yield a concentration of 25 mM, and the potential window of interest was determined with one working electrode. An additional scan was then taken with a fresh working electrode, using the established potential range, for comparison to the water scan. Subsequently, water was added to yield a concentration of 100 mM water and a voltammogram recorded with a third working electrode. Working electrodes were only reused in situations for which it was determined that no change was observed upon reuse of the electrode.

A.3 Anilinium and Triethylammonium Acid Syntheses

Syntheses were performed in a nitrogen filled glovebox. While syntheses of some of the aniliniums reported here have been reported previously, these reports lacked some details as well as NMR and elemental analyses to confirm purity. The general procedure was as follows: To a rapidly stirring 5 mL solution of diethyl ether containing 1.0 g of the respective substituted aniline (3 g in the case of aniline itself) was added 0.95 molar equivalent of
tetrafluoroboric acid diethyl ether complex (Sigma-Aldrich) in a dropwise manner, resulting in the precipitation of the tetrafluoroborate salt (*note: this reaction is exothermic and easily boils the diethyl ether*). The diethyl ether was removed under vacuum, and the precipitate was washed with two 5 mL portions of diethyl ether. The solid was then dissolved in approximately 3 mL of acetonitrile and reprecipitated by pouring into diethyl ether, followed by decanting the solution and drying the remaining solids under vacuum for approximately one hour. One recrystallization was sufficient except in the case of 4-nitroanilinium, where two recrystallizations were performed to remove a bright yellow impurity. The same synthetic procedure was followed for the preparation of triethylammonium tetrafluoroborate (1.0 g initial Et₃N). ¹H NMR characterization below. **Anilinium**: Yield 1.47 g, 27%. ¹H NMR (CD₃CN, ppm): 7.42-7.53 (multiple peaks, 5H, C₆H₅-), 8.14 (s, 3H, -NH₃). Anal. Calcd. for X = H: C, 39.83; H, 4.46; N, 7.74. Found: C, 40.08; H, 4.50; N, 7.83. **4-chloroanilinium**: Yield 0.68 g, 42%. ¹H NMR (CD₃CN, ppm): 7.41-7.54 (multiple peaks, 4H, -C₆H₄-), 8.17 (s, 3H, -NH₃). Anal. Calcd. for X = Cl: C, 33.46; H, 3.28; N, 6.50. Found: C, 33.63; H, 3.25; N, 6.55. **4-tert-butylanilinium**: Yield 0.30 g, 20%. ¹H NMR (CD₃CN, ppm): 7.33-7.56 (multiple peaks, 4H, -C₆H₄-), 8.05 (s, 3H, -NH₃), 1.32 (s, 9H, -C(CH₃)₃). Anal. Calcd. for X = C(CH₃)₃: C, 50.67; H, 6.80; N, 5.91. Found: C, 50.44; H, 6.67; N, 5.82. **4-nitroanilinium**: Yield 0.35 g, 23%. ¹H NMR (CD₃CN, ppm): 7.57-8.34 (multiple peaks, 4H, -C₆H₄-), 8.28 (s, 3H, -NH₃). Anal. Calcd. for X = Cl: C, 31.90; H, 3.12; N, 12.40. Found: C, 31.90; H, 3.12; N, 12.32. **4-methoxyanilinium**: Yield 1.06 g, 65%. ¹H NMR (CD₃CN, ppm): 7.05-7.31 (multiple peaks, 4H, -C₆H₄-), 8.01 (s, 3H, -NH₃), 3.79 (s, 3H, OCH₃). Anal. Calcd. for X = OMe: C, 39.85; H, 4.78; N, 6.64. Found: C, 40.03; H, 4.71; N, 6.66. **4-bromoanilinium**: Yield 0.69 g, 48%. ¹H NMR (CD₃CN, ppm): 7.35-7.69 (multiple peaks, 4H, -C₆H₄-), 8.16 (s, 3H, -NH₃). Anal. Calcd. for X = Br: C, 27.73; H, 2.72; N, 5.39. Found: C, 27.89; H, 2.71; N, 5.37. **4-cyanoanilinium**: Yield 0.37 g, 22%. ¹H NMR (CD₃CN, ppm): 7.59-7.89 (multiple peaks, 4H, -C₆H₄-), 8.37 (s, 3H, -NH₃). Anal. Calcd. for X = CN: C, 40.82; H, 3.43; N, 13.60. Found: C, 40.65; H, 3.51; N, 13.48. **N,N-dimethylanilinium**, Yield 1.10 g, 67%. ¹H NMR
(CD$_3$CN, ppm): 7.41-7.58 (m, 4H, -C$_6$H$_4$-), 8.87 (m, 1H, -NHMe$_2$), 3.24 (s, 6H, -NH(CH$_3$)$_2$). Anal. Calcd. for X = H: C, 45.98; H, 5.79; N, 6.70. Found: C, 45.69; H, 5.82; N, 6.73.

**Triethylammonium tetrafluoroborate**, prep modified such that no reprecipitation from CH$_3$CN was performed. Yield 1.49 g, 80%. $^1$H NMR (CD$_3$CN, ppm): 6.99 (broad s., 1H, (CH$_3$CH$_2$)$_3$N$^+$), 3.13 (q, 6H, (CH$_3$CH$_2$)$_3$NH$^+$), 1.24 (t, 9H, (CH$_3$CH$_2$)$_3$NH$^+$) Anal. Calcd. for X = H: C, 45.98; H, 5.79; N, 6.70. Found: C, 45.69; H, 5.82; N, 6.73.

**A.4 Pyridinium-Type Acid Syntheses**

2,6-Dimethylpyridinium tetrafluoroborate was prepared by dissolving 2,6-lutidine (1 g) in ca. 5 mL Et$_2$O in a nitrogen-filled glovebox and tetrafluoroboric acid diethyl ether complex (0.95 mol. eq.) added in a dropwise manner, effecting rapid precipitation of the desired tetrafluoroborate salt. After removal of the diethyl ether under vacuum, the solids were dissolved in ca. 3 mL acetonitrile and reprecipitated by pouring into diethyl ether, following by decanting the solution, rinsing the solids with diethyl ether, and drying the remaining solids under vacuum for about one hour. Yield: 1.163 g, 67%. $^1$H NMR (CD$_3$CN, ppm): 12.74 (broad s, 1 H), 8.28 (t, 1 H), 7.63 (d, 2 H), 2.70 (s, 6 H). Anal Calcd: C, 43.12; H, 5.17. Found: C, 43.13; H, 5.28.

Pyridinium tetrafluoroborate was prepared by dissolving in a nitrogen-filled glovebox 0.5 g of pyridine in ca. 10 mL Et$_2$O followed by portionwise addition of 0.9724 g of HBF$_4$-$Et_2$O (0.95 mol. eq.) with vigorous agitation. This effecte precipitation of white solids; 5 mL more Et$_2$O was added and the supernatant decanted. The solids were washed five times with ca. 10 mL Et$_2$O each time followed by drying under vacuum at room temperature for about 5 hours. Yield: 0.81 g, 81%. $^1$H NMR (CD$_3$CN, ppm): 13.09 (broad s, 1 H), 8.71 (d, 2 H), 8.62 (t, 1 H), 8.06 (m, 2 H). Anal Calcd: C, 35.98; H, 3.62. Found: C, 35.75; 3.66.

2-Methylpyridinium tetrafluoroborate was prepared by dissolving 1 g of 2-methylpyridine in ca. 4 mL CH$_3$CN followed by dropwise addition of 1.652 g HBF$_4$-$Et_2$O complex (0.95 mol. eq.). Addition of ca. 10 mL of Et$_2$O effected separation of a dense oil. The supernatant was decanted and the oil vigorously washed twice with 10 mL Et$_2$O followed by drying under vacuum at ca. 60
°C for twenty minutes to yield a very viscous liquid. Yield: 1.27 g, 69%. $^1$H NMR (CD$_3$CN, ppm): 12.42 (broad s, 1 H), 8.54 – 8.45 (two multiplets, 2 H), 7.85 (m, 2 H), 2.75 (m, 3 H). Anal Calcd: C, 39.83; H, 4.46. Found: C, 39.31; H, 4.48.

2-Aminopyridinium tetrafluoroborate was synthesized as for 2-methylpyridinium with 1 g of 2-aminopyridine and 1.635 g HBF$_4$-Et$_2$O (0.95 mol. eq.). As for 2-methylpyridinium, an oil initially formed after Et$_2$O addition; however, during the second Et$_2$O wash waxy white solids precipitated; these were dried under vacuum at about 60 °C for twenty minutes. Yield: 1.2 g, 65%. $^1$H NMR (CD$_3$CN, ppm): 10.71 (broad s, 1 H), 7.89 (m, 1 H), 7.78 (d, 1 H), 7.02 (d, 1 H), 6.88 (t, 1 H), 6.62 (broad s, 2 H). Anal Calcd: C, 33.01; H, 3.88. Found: C, 33.09; H, 4.01.

4-Methoxypyridinium tetrafluoroborate was prepared as for 2-aminopyridinium. The waxy solids isolated after the second Et$_2$O wash were briefly dried under vacuum followed by dissolution in a minimal amount of acetone. Diethyl ether was added dropwise until the solution became cloudy; acetone was then added until the solution became clear again. This solution was cooled at about -40 °C overnight to yield blocky white crystals. The crystals were crushed, washed twice with 10 mL Et$_2$O, and dried under vacuum at ca. 60 °C for twenty minutes. Yield: 0.12 g, 7%. $^1$H NMR (CD$_3$CN, ppm): 12.10 (broad s, 1 H), 8.48 (d, 2 H), 7.41 (d, 2 H), 4.09 (s, 3 H). Anal Calcd: C, 33.01; H, 3.88. Found: C, 36.50; H, 4.10.

2,4,6-Trimethylpyridinium tetrafluoroborate was prepared by dissolving 1 g of 2,4,6-trimethylpyridine in ca. 5 mL Et$_2$O followed by dropwise addition with stirring of 1.17 g of HBF$_4$-Et$_2$O (0.95 mol. eq.), effecting precipitation of white solids. The solvent was removed under vacuum. The solids were dissolved in a minimal amount of CH$_3$CN and Et$_2$O added until solids precipitated. After decanting, the solids were washed three times with ca. 15 mL Et$_2$O followed by drying under vacuum at ca. 60 °C for 30 minutes. Yield: 1.2 g, 73%. $^1$H NMR (CD$_3$CN, ppm): 11.48 (broad s, 1 H), 7.42 (s, 2 H), 2.62 (s, 6 H), 2.51 (s, 3 H). Anal Calcd: C, 45.98; H, 5.79. Found: C, 46.25; H, 5.96.
2-Aminobenzimidazolium tetrafluoroborate was prepared by suspending 1 g of 2,4,6-trimethylpyridine in ca. 5 mL Et₂O followed by dropwise addition with stirring of 1.155 g of HBF₄-Et₂O (0.95 mol. eq.) with 2 mL Et₂O, effecting precipitation of white solids. The reaction vial was capped and shaken vigorously to ensure adequate mixing. The solvent was removed under vacuum. The solids were dissolved in a minimal amount of CH₃CN and Et₂O added until solids precipitated. After decanting, the solids were washed three times with ca. 15 mL Et₂O followed by drying under vacuum at ca. 60 °C for 30 minutes. Yield: 0.35 g, 22%. ¹H NMR (CD₃CN, ppm): 10.03 (broad s, 2 H), 7.45 – 7.42 (m, 2 H), 7.30 – 7.28 (m, 2 H), 6.81 (broad s, 2 H). Anal Calcd: C, 38.05; H, 3.65. Found: C, 38.17; H, 3.67.

A.5 ¹H NMR Spectra of Acids

Figure A.1. ¹H NMR spectrum of 4-bromoanilinium tetrafluoroborate in CD₃CN.
Figure A.2. $^1$H NMR spectrum of 4-chloroanilinium tetrafluoroborate in CD$_3$CN.

Figure A.3. $^1$H NMR spectrum of 4-nitroanilinium tetrafluoroborate in CD$_3$CN.
Figure A.4. $^1$H NMR spectrum of 4-tert-butylanilinium tetrafluoroborate in CD$_3$CN.

Figure A.5. $^1$H NMR spectrum of anilinium tetrafluoroborate in CD$_3$CN.
Figure A.6. $^1$H NMR spectrum of dimethylformamidium triflate in CD$_3$CN.

Figure A.7. $^1$H NMR spectrum of N,N-dimethylanilinium tetrafluoroborate in CD$_3$CN.
Figure A.8. $^1$H NMR spectrum of 4-methoxyanilinium tetrafluoroborate in CD$_3$CN.

Figure A.9. $^1$H NMR spectrum of 4-cyanoanilinium tetrafluoroborate in CD$_3$CN.
Figure A.10. $^1$H NMR spectrum of triethylammonium tetrafluoroborate in CD$_3$CN.

Figure A.11. $^1$H NMR of pyridinium tetrafluoroborate in CD$_3$CN.
Figure A.12. $^1$H NMR of 2-methylpyridinium tetrafluoroborate in CD$_3$CN.

Figure A.13. $^1$H NMR of 2,6-lutidinium tetrafluoroborate in CD$_3$CN.

Figure A.14. $^1$H NMR of 4-methoxy pyridinium tetrafluoroborate in CD$_3$CN.
Figure A.15. $^1$H NMR of 2-aminopyridinium tetrafluoroborate in CD$_3$CN.

Figure A.16. $^1$H NMR of 2,4,6-trimethylpyridinium tetrafluoroborate in CD$_3$CN.

Figure A.17. $^1$H NMR of 2-aminobenzimidazolium tetrafluoroborate in CD$_3$CN.
APPENDIX B. PREPARATION AND CHARACTERIZATION OF COMPOUNDS

Portions of this appendix (i.e., NiP$_2$S$_2$ synthesis) adapted with permission from McCarthy, B. D., Donley, C. L., Dempsey, J. L. *Chem. Sci.* 2015, 6, 2827-2834. Published by The Royal Society of Chemistry.

Multiple metal complexes and ligands were prepared during the course of this dissertation; the majority of these did not exhibit desired PCET reactivity. The syntheses of complexes described in prior chapters in this work are described here alongside complexes not previously mentioned. Electrochemical characterization is also presented for those complexes that were not discussed in the preceding chapters.

B.1 Literature Complexes and Ligands

![Structures of literature complexes and ligands.](image)

- [Ni(bdt)$_2$][Bu$_4$N] 
- Ni(PNP)S$_2$
- pyrazine-2,3-dithiol
- 4,4'-dimalonimidazoline
- 4-(pyridin-4-yl)-1,3-dithiol-2-one
- MoCp$_2$(4-pedt)

*Figure B.1.* Structures of literature complexes and ligands.

$[\text{Ni(bdt)}$_2$][\text{Bu}_4\text{N}],^{199}$ Ni(PNP)S$_2,^{132}$ pyrazine-2,3-dithiol, 4,4’-(C$_2$H$_5$CO$_2$)$_2$-2,2’-bipyridine,$^{200}$ 4-(pyridin-4-yl)-1,3-dithiol-2-one,$^{201}$ and MoCp$_2$(4-pedt)$^{202}$ were prepared by literature methods. The Ni(PNP)S$_2$ complex was found to show similar electrochemistry with added acid as that of the NiP$_2$S$_2$ complex discussed in Chapters 3.

B.2 Novel Complexes

The synthesis and characterization of novel compounds (*Figure B.2*) are reported below. Electrochemical characterization for complexes not discussed in the prior chapters is also shown.
Figure B.2. Structures of novel ligands and complexes prepared for this dissertation.

**PSP Synthesis**

Procedure was adapted from the analogous SiMe bridgehead bisphosphine synthesis. In a nitrogen-filled glovebox, 0.6683 g (5.1 mmol) bis(chloromethyl)sulfide (TCI America) and ca. 10 mL THF were added to an oven-dried 100 mL Schlenk flask equipped with a stir bar. A pressure-equalizing addition funnel was attached to the Schlenk flask and loaded with 20 mL of 0.5 M potassium diphenylphosphide in THF (Aldrich) and ca. 30 mL THF. Apparatus was removed from the glovebox and put under positive N₂ flow on a Schlenk line. The Schlenk flask was cooled in an acetone dry ice bath followed by dropwise addition of the potassium diphenylphosphide solution over a period of one hour. The solution was allowed to warm to room temperature and stirred overnight. Under nitrogen, the solution was filtered three times through alumina to remove a red byproduct and the filtrate dried under vacuum. The residue was extracted with ca. 60 mL total pentane and this extract cooled at -35 °C for multiple days until white needle crystals formed, followed by decanting the supernatant and washing the crystals with cold pentane and drying under vacuum for ca. 7 hours. Yield: 0.522 g, 70%. \(^1\text{H} \) NMR (CD₃CN, ppm): 7.42 (b. multiplet, 8H), 7.36 (b. multiplet, 12H), 3.31 (d, 4H). \(^{31}\text{P}^{(1}\text{H}) \) NMR (CD₃CN, ppm): -19.8.
Figure B.3. $^1$H NMR spectrum of PSP in CD$_3$CN (400 MHz).

Figure B.4. $^{31}$P($^1$H) NMR spectrum of PSP in CD$_3$CN (400 MHz).

NiP$_2$(S$_2$-pyz) Synthesis

To a glass stir bar equipped Schlenk flask under nitrogen loaded with 0.0097 g (0.42 mmol) sodium metal ca. 15 mL degassed ethanol was added and the solution stirred until no solids were observed. In a separate flask 0.03 g (0.21 mmol) pyrazine-2,3-dithiol was suspended in ca. 15 mL ethanol and degassed by sparging followed by transfer of the sodium ethoxide solution to this flask, resulting in dissolution of the pyrazine-2,3-dithiol. This clear solution was transferred back to the Schlenk flask. In a separate Schlenk flask ca. 20 mL
ethanol and 0.05 g (0.21 mmol) nickel dichloride hexahydrate were degassed by sparging followed by addition under positive nitrogen flow 0.084 g (0.212 mmol) 1,2-bis(diphenylphosphino)ethane. This nickel solution was heated at reflux for ca. 1 hour, forming an orange solution, followed by cooling to room temperature and addition of the pyrazine solution under nitrogen, resulting in an air-stable red solution. The solvent was removed under reduced pressure and the residue dissolved in ca. 8 mL dichloromethane, filtered, and removal of solvent under vacuum. The solids were washed twice with diethyl ether (ca. 30 mL total), twice with pentane (ca. 40 mL total), and dried at ca. 50 °C. Yield: 0.094 g, 74%. $^1$H NMR (d-DMSO, ppm): 7.82-7.82 (overlapping s and m, 10H), 7.6-5.55 (overlapping multiplets, 12H), 2.67 (d, 4H). $^{31}$P{$^1$H} NMR (CD$_3$CN, ppm): 61.3.

Figure B.5. $^1$H NMR of NiP$_2$(S$_2$-pyz) in d-DMSO (500 MHz).
Figure B.6. $^{31}$P($^1$H) NMR of NiP$_2$(S$_2$-pyz) in CD$_3$CN (400 MHz).

Figure B.7. Cyclic voltammogram of 0.5 mM NiP$_2$(S$_2$-pyz) at 100 mV/s in acetonitrile with 0.25 M [Bu$_4$N][PF$_6$].

Figure B.8. Cyclic voltammogram of 0.5 mM NiP$_2$(S$_2$-pyz) at 100 mV/s in acetonitrile with 0.25 M [Bu$_4$N][PF$_6$] with and without 0.5 mM benzoic acid. Red and blue traces were performed with separate switching potentials.
NiP$_2$(4-pedt) Synthesis

To a stir bar equipped 25 mL Schlenk flask under nitrogen loaded with 0.019 g (0.84 mmol) sodium metal ca. 15 mL degassed methanol was added and the solution stirred until no solids were observed. In a separate flask 0.082 g (0.42 mmol) 4-(pyridin-4-yl)-1,3-dithiol-2-one was dissolved in ca. 15 mL methanol and degassed by sparging followed by transfer to the sodium methoxide Schlenk flask. In a separate Schlenk flask ca. 30 mL ethanol and 0.1 g (0.42 mmol) nickel dichloride hexahydrate were degassed by sparging followed by addition under positive nitrogen flow 0.169 g (0.42 mmol) 1,2-bis(diphenylphosphino)ethane. This nickel solution was heated at reflux for ca. 1 hour, forming an orange solution, followed by cooling to room temperature and addition of the sulfur ligand solution under nitrogen, giving a reddish-brown solution that was stirred overnight under nitrogen. Under air, the suspension was filtered and the collected solids washed with ca. 25 mL ethanol. Solvent was removed from the combined filtrates under reduced pressure and the residue dissolved in ca. 30 mL acetonitrile, filtered, and recrystallized via vapor diffusion using diethyl ether. After crystal formation (several days), the supernatant was decanted and the crystals discarded. The supernatant was dried under vacuum, dissolved in ca. 15 mL acetonitrile, and chilled at -40 °C for five days resulting in crystal formation. The supernatant was decanted and the crystals washed three times with ca. 10 mL diethyl ether followed by drying under vacuum. Yield: 0.05 g, 19%. $^1$H NMR (d-CD$_3$CN, ppm): 8.28 (bs, 1H), 7.77 (m, 7H), 7.55-7.41 (multiple m, 13H), 2.54-2.49 (m, 4H). $^{31}$P{$^1$H} NMR (CD$_3$CN, ppm): 59 (q).
Figure B.9. $^1\text{H}$ NMR of NiP$_2$(4-pedt) in CD$_3$CN (400 MHz).

Figure B.10. $^{31}\text{P}(^1\text{H})$ NMR of NiP$_2$(4-pedt) in CD$_3$CN (400 MHz).
Figure B.11. Cyclic voltammogram of 0.5 mM NiP2(4-pedt) at 100 mV/s in acetonitrile with 0.25 M [Bu₄N][PF₆].

Figure B.12. Cyclic voltammogram of 0.5 mM NiP₂(4-pedt) at 100 mV/s in acetonitrile with 0.25 M [Bu₄N][PF₆] with 0.5 mM 2,4,6-Br₃-PhOH or Et₃NH⁺.

**NiP₂S₂ Synthesis**

Attempts to synthesize NiP₂S₂ in the same manner as the previously reported analogous compound with a N-Me at the bridgehead of the phosphine¹³² were unsuccessful due to difficulty removing the [Et₃NH][BF₄] byproduct. Consequently, solid beads of ion exchange resin
with amine functionalities were used instead of Et₃N. In a nitrogen-filled glovebox, 0.4 g (0.84 mmols, 1 eq) of [Ni(CH₃CN)₆](BF₄)₂ and 15 mL of CH₃CN were added to a 100 mL oven-dried Schlenk flask equipped with a stir bar. While stirring, 0.3275 g (0.79 mmols, 0.95 eq) of bis(diphenylphosphino)propane dissolved in 10 mL of CH₃CN were added quickly dropwise, turning the solution red. Resin base (3.19 g) suspended in 25 mL of CH₃CN was added followed by 0.1085 g (1.00 mmols, 1.2 eq) of 1,3-propanedithiol dissolved in 5 mL of CH₃CN. After stirring for two days at room temperature, solvent was removed under vacuum and the remaining sludge extracted with 20 mL of CH₃CN and filtered. To the filtrate was added ca. 22 mL Et₂O and the solution cooled at -35 °C for six days to yield dark red crystals. After decanting the supernatant the solids were washed three times with ca. 2 mL of Et₂O. Additional crystals were obtained by drying the supernatant under vacuum, adding ca. 4 mL CH₃CN and 1 mL Et₂O, cooling for seven days at -35 °C, decanting, and washing the crystallized solids three times with ca. 2 mL Et₂O. The solids from both recrystallizations were combined and dried under vacuum for 6.5 hours. Yield 0.069 g, 15%. ¹H NMR (CD₃CN, ppm): 7.74 (multiplet, 8H), 7.44-7.34 (b. multiplet, 12H), 2.36 (multiplet, 4H), 2.21 (multiplet, 4H), and 1.80 (multiplet, 4H). ³¹P{¹H} NMR (CD₃CN, ppm): 12.40. Full ¹H and ³¹P{¹H} assignments are given below. Anal. Calcd.: C, 62.41; H, 5.59. Found: C, 62.45; H, 5.64.

**NiP₂S₂** was characterized by ¹H, ³¹P{¹H}, ¹H-¹H gradient enhanced COSY, and ¹H-³¹P HMQC (below). This data, along with elemental analysis and comparison to the NMR spectrum of a reported analog of **NiP₂S₂** where the phosphine bridgehead methylene is replaced with an N-Me,¹³² support the structural assignment of **NiP₂S₂**.

![Figure B.13](image-url) **Figure B.13.** Compound NiP₂S₂ with expected unique ¹H peaks.
Figure B.14. $^1$H NMR of NiP$_2$S$_2$ in CD$_3$CN (400 MHz) with proton assignments per Figure B.13.

Figure B.15. $^{31}$P($^1$H) NMR spectrum of NiP$_2$S$_2$ in CD$_3$CN (400 MHz).
Figure B.16. $^1$H-$^1$H gradient enhanced COSY NMR of NiP$_2$S$_2$ in CD$_3$CN (400 MHz).

Figure B.17. Upfield region of $^1$H-$^1$H gradient enhanced COSY NMR of NiP$_2$S$_2$ in CD$_3$CN (400 MHz). This spectrum reveals that the broad multiplet at 1.8 ppm is actually two overlapping signals, as evidenced by the off-diagonal peaks with both the e and f sets of protons. The two overlapping peaks are consequently assigned as the bridgehead methylenes of both the phosphine and dithiolate ligands, while e is assigned as the four methylene protons next to phosphorus on the phosphine and f the four methylene protons next to sulfur on the dithiolate.
Figure B.18. $^1$H-$^{31}$P HMQC NMR spectrum (CD$_3$CN, 400 MHz) of NiP$_2$S$_2$. The interaction of the phosphorus signal with the aromatic protons c and the methylene protons e is visible, supporting assignment of e as the methylene protons on the phosphine.

(tnam)(BF$_4$)$_2$ Synthesis

Adapted from the synthesis of (tmam)(PF$_6$)$_2$.$^{204}$ In a flask, 0.441 g (1.3 mmol) 4,4'-bis(bromomethyl)-2,2'-bipyridine was suspended in ca. 20 mL ethanol. With stirring, three mL of aqueous 45% trimethylamine (excess) was added. After three hours, the solution was removed under reduced pressure, the solids suspended in ca. 30 mL of acetonitrile, and 0.502 g (2.58 mmol) silver tetrafluoroborate added followed by stirring in the dark for two hours. The solution was filtered and the filtrate dried under vacuum to yield a white powder. Yield: 0.466g, 76%. $^1$H NMR (d-CD$_3$CN, ppm): 8.85 (d, 2H), 8.58 (s, 2H), 7.57 (dd, 2H), 4.52 (s, 4H), 3.10 (s, 18H).
Figure B.19. $^1$H NMR of (tmam)(BF$_4$)$_2$ in CD$_3$CN (500 MHz).

[Ni(tmam)(4-pedt)](BF$_4$)$_2$ Synthesis

To a glass stir bar equipped 25 mL Schlenk flask under nitrogen loaded with 0.012 g (0.53 mmol) sodium metal ca. 10 mL degassed methanol was added and the solution stirred until no solids were observed. In a separate flask, 0.052 g (0.27 mmol) 4-(pyridin-4-yl)-1,3-dithiol-2-one was dissolved in ca. 15 mL methanol and degassed by sparging followed by transfer to the sodium methoxide Schlenk flask. In a separate Schlenk flask, ca. 30 mL acetonitrile and 0.1 g (0.29 mmol) [Ni(H$_2$O)](BF$_4$)$_2$ and 0.127 g (0.27 mmol) (tmam)(BF$_4$)$_2$ were degassed by sparging. This nickel solution was heated at reflux for ca. 45 minutes followed by cooling to room temperature, addition of the sulfur ligand solution under nitrogen, and heating at reflux for ca. 25 minutes. Under air, the solvent was removed under reduced pressure, ca. 200 mL acetonitrile added followed by filtration and washing of the black solids with ca. 150 mL acetonitrile. Solvent was removed from the combined blue filtrate under reduced pressure, the solids extracted with ca. 50 mL acetonitrile, and the extract poured into ca. 400 mL diethyl ether, forming a precipitate. The supernatant was decanted and the solids washed with ca. 100 mL diethyl ether. The solids were dried under vacuum, dissolved in a minimal amount of
acetonitrile, and recrystallized through vapor diffusion of diethyl ether. The blue crystals were washed with pentane and dried under vacuum for one hour to yield the crude product. Yield: 0.108 g, 58%. $^1$H NMR (d-CD$_3$CN, ppm): 9.08-8.98 (bd, 1H), 8.84 (s, 1H), 8.58 (s, 1H), 8.41 (s, 3H), 7.72 (m, 2H), 7.56-7.52 (m, 2H), 6.96 (s, 1H), 6.96 (s, 1H), 3.12 (s, 12H).

Figure B.20. $^1$H NMR of [Ni(tmam)(4-pedt)](BF$_4$)$_2$ in CD$_3$CN (500 MHz).

Figure B.21. Cyclic voltammograms of 0.5 mM [Ni(tmam)(4-pedt)](BF$_4$)$_2$ and (tmam)(BF$_4$)$_2$ at 100 mV/s in acetonitrile with 0.25 M [Bu$_4$N][PF$_6$].
APPENDIX C. ADDITIONAL DATA FOR CHAPTER 2


C.1 Measurement of pKₐs by spectrophotometric titrations

UV-vis spectroscopy was used to monitor titrations of colorimetric indicators of known pKₐs with acids of unknown pKₐs, following literature procedure. Extinction coefficients of the colorimetric indicators methyl orange and 3-nitroaniline were determined in acetonitrile, as well as the protonated forms by titration with excess tetrafluoroboric acid diethyl ether complex. Extinction coefficients were found by measuring the absorbance of five independent solutions of varying known concentrations, finding the extinction coefficient, and averaging across all solutions.

![Extinction coefficients of methyl orange and protonated methyl orange in acetonitrile.](image)

**Figure C.1.** Extinction coefficients of methyl orange and protonated methyl orange in acetonitrile.
Figure C.2. Extinction coefficients of 3-nitroaniline and 3-nitroanilinium in acetonitrile.

UV-vis analysis of 4-tert-butylniliniline, 4-tert-butylnilinium, 4-chloroaniline, and 4-chloroanilinium showed that none absorbed above 350 nm. Consequently, methyl orange was titrated with 4-tert-butylnilinium, and the concentrations of all species were determined by finding the concentration of methyl orange at 384 where only methyl orange strongly absorbs and assuming mass balance for the remaining species.

Figure C.3. UV-vis monitored titration of methyl orange with 4-tert-butylnilinium in acetonitrile.
The resulting plot of \([\text{protonated methyl orange}]^{*}[4\text{-}\text{tert-butylaniline}]/[4\text{-}\text{tert-butylanilinium}]\) versus \([\text{methyl orange}]\), Figure S4, showed a linear dependence and a slope of 0.2872.

**Figure C.4.** Plot of \([\text{protonated methyl orange}]^{*}[4\text{-}\text{tert-butylaniline}]/[4\text{-}\text{tert-butylanilinium}]\) versus \([\text{methyl orange}]\).

Using the relation\(^{205}\)

\[pK_a(\text{anilinium}) = pK_a(\text{protonated methyl orange}) - \log(\text{slope})\quad (1)\]

the \(pK_a\) of 4-\text{tert}-butylanilinium was determined, relative to the \(pK_a\) of methyl orange (10.6\(^{206}\)), to be 11.1.

The same approach was used to find the \(pK_a\) of 3-chloroanilinium by titration of 3-nitroaniline with 4-chloroanilinium (Figure S5).
Plotting [protonated methyl orange][4-tert-butylaniline]/[4-tert-butylanilinium] versus [methyl orange], Figure S6, showed a linear dependence and a slope of 0.009.

Using equation 1 and the pKₐ of 3-nitroanilinium (7.68⁻⁷⁵), the pKₐ of 4-chloroanilinium was found to be 9.7 (note: omitting the data point near x = 195 μM gives a pKₐ of 9.8).
C.2 Cyclic voltammogram of silver nitrate

![Cyclic voltammogram of silver nitrate](image)

**Figure C.7.** Cyclic voltammogram of 0.05 mM silver nitrate in 100 mM [Bu₄N][PF₆] acetonitrile solution. At lower concentrations no clear reduction waves are visible and the oxidation wave position was often more negative (e.g., -0.24 V). Not ohmic drop corrected; albeit the small currents passed would result in negligible error.

C.3 Representative cyclic voltammograms of all acids studied at 100 and 1000 mV/s

*Notes: Ohmic drop corrected. For all cases the background at the appropriate scan rate is included.*

![Representative cyclic voltammograms](image)

**Figure C.8.** Cyclic voltammogram of 25 mM 4-bromoanilinium at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
Figure C.9. Cyclic voltammogram of 25 mM 4-bromoanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile.

Figure C.10. Cyclic voltammogram of 25 mM 4-chloroanilinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile.

Figure C.11. Cyclic voltammogram of 25 mM 4-chloroanilinium at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile.
Figure C.12. Cyclic voltammogram of 25 mM 4-nitroanilinium at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.13. Cyclic voltammogram of 25 mM 4-nitroanilinium at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.14. Cyclic voltammogram of 25 mM 4-tert-butylanilinium at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
Figure C.15. Cyclic voltammogram of 25 mM 4-tert-butylanilinium at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.16. Cyclic voltammogram of 25 mM acetic acid at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.17. Cyclic voltammogram of 25 mM acetic acid at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
Figure C.18. Cyclic voltammogram of 25 mM anilinium at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.19. Cyclic voltammogram of 25 mM anilinium at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.20. Cyclic voltammogram of 25 mM benzoic acid at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
Figure C.21. Cyclic voltammogram of 25 mM benzoic acid at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.22. Cyclic voltammogram of 25 mM dimethylformamidium triflate at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.23. Cyclic voltammogram of 25 mM dimethylformamidium triflate at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
Figure C.24. Cyclic voltammogram of 25 mM N,N-dimethylanilinium at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.25. Cyclic voltammogram of 25 mM N,N-dimethylanilinium at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.26. Cyclic voltammogram of 25 mM 4-methoxyanilinium at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
Figure C.27. Cyclic voltammogram of 25 mM 4-methoxyanilinium at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.28. Cyclic voltammogram of 25 mM 4-cyanoanilinium at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.29. Cyclic voltammogram of 25 mM 4-cyanoanilinium at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
Figure C.30. Cyclic voltammogram of 25 mM phenol at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile.

Figure C.31. Cyclic voltammogram of 25 mM phenol at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile.

Figure C.32. Cyclic voltammogram of 25 mM pyridinium at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile.
Figure C.33. Cyclic voltammogram of 25 mM pyridinium at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.34. Cyclic voltammogram of 25 mM salicylic acid at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.35. Cyclic voltammogram of 25 mM salicylic acid at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
Figure C.36. Cyclic voltammogram of 25 mM p-toluenesulfonic acid monohydrate at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile.

Figure C.37. Cyclic voltammogram of 25 mM p-toluenesulfonic acid monohydrate at 1000 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile.

Figure C.38. Cyclic voltammogram of 25 mM trichloroacetic acid at 100 mV/s in 100 mM [Bu$_4$N][PF$_6$] acetonitrile.
Figure C.39. Cyclic voltammogram of 25 mM trichloroacetic acid at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.40. Cyclic voltammogram of 25 mM triethylammonium at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.41. Cyclic voltammogram of 25 mM triethylammonium at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
Figure C.42. Cyclic voltammogram of 25 mM trifluoromethanesulfonic acid at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.43. Cyclic voltammogram of 25 mM trifluoromethanesulfonic acid at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

Figure C.44. Cyclic voltammogram of 25 mM trifluoroacetic acid at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
**Figure C.45.** Cyclic voltammogram of 25 mM trifluoroacetic acid at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

**Figure C.46.** Cyclic voltammogram of 25 mM 2-nitrophenol at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

**Figure C.47.** Cyclic voltammogram of 25 mM 2-nitrophenol at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
**Figure C.48.** Cyclic voltammogram of 25 mM water at 100 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.

**Figure C.49.** Cyclic voltammogram of 25 mM water at 1000 mV/s in 100 mM [Bu₄N][PF₆] acetonitrile.
C.4 Cyclic voltammograms of all acids with and without 100 mM added water

Note: Each CV current profile in this section was converted to current density using the measured surface area of the specific electrode used for that scan. All are ohmic drop corrected.

Figure C.50. Cyclic voltammogram of 2-nitrophenol at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.51. Cyclic voltammogram of 4-bromoanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.
Figure C.52. Cyclic voltammogram of 4-chloroanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.53. Cyclic voltammogram of 4-cyanoanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.54. Cyclic voltammogram of 4-methoxyanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.
Figure C.55. Cyclic voltammogram of 4-nitroanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.56. Cyclic voltammogram of 4-tert-butylanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.57. Cyclic voltammogram of acetic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.
Figure C.58. Cyclic voltammogram of anilinium at 100 mV/s with and without 100 mM added water in 100 mM \([\text{Bu}_4\text{N}]\text{[PF}_6]\) acetonitrile solution.

Figure C.59. Cyclic voltammogram of benzoic acid at 100 mV/s with and without 100 mM added water in 100 mM \([\text{Bu}_4\text{N}]\text{[PF}_6]\) acetonitrile solution.

Figure C.60. Cyclic voltammogram of dimethylformamidium at 100 mV/s with and without 100 mM added water in 100 mM \([\text{Bu}_4\text{N}]\text{[PF}_6]\) acetonitrile solution.
Figure C.61. Cyclic voltammogram of N,N-dimethylanilinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.62. Cyclic voltammogram of phenol at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.63. Cyclic voltammogram of p-toluenesulfonic acid monohydrate at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.
Figure C.64. Cyclic voltammogram of pyridinium at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.65. Cyclic voltammogram of salicylic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.66. Cyclic voltammogram of trichloroacetic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.
Figure C.67. Cyclic voltammogram of triethylammonium chloride at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.68. Cyclic voltammogram of trifluoroacetic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.

Figure C.69. Cyclic voltammogram of trifluoromethanesulfonic acid at 100 mV/s with and without 100 mM added water in 100 mM [Bu₄N][PF₆] acetonitrile solution.
C.5 Reaction of trifluoromethanesulfonic acid with acetonitrile

Trifluoromethanesulfonic acid was reacted with a 1.2 molar excess of acetonitrile (passed through activated alumina immediately prior to the experiment) in a nitrogen filled glovebox. Within a few minutes the solution turned yellow, and enough CD$_3$CN (first passed through activated alumina) was added to yield a solution with a total concentration of 125 mM trifluoromethanesulfonic acid. The $^1$H NMR spectrum below at 0.3 hours clearly shows the formation of unknown species and the spectrum at 69 shows an apparent loss of the original acidic proton signal at 13.75, tentatively assigned as either CF$_3$SO$_3$H or a protonated acetonitrile species.

![Figure C.70](image)

**Figure C.70.** $^1$H NMR spectra taken at 0.3 and 69 hours of 1.2 molar excess of acetonitrile reacted with trifluoromethanesulfonic acid for ca. three minutes followed by addition to CD$_3$CN such that the final concentration of trifluoromethanesulfonic acid equaled 125 mM. Spectra normalized to the height of the acetonitrile peak.
APPENDIX D. BULK ELECTROLYSIS METHODS

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Glassy carbon plates (1 x 1 x 0.1 cm) were treated for 10 minutes in a solution of 0.4 mM 1 (of Chapter 3) and 10 mM [Et$_3$NH][BF$_4$] at a potential of -1.7 V vs. Fc/Fc$^+$. After thorough rinsing of the electrode, the plate was held at -1.7 V vs. Fc/Fc$^+$ in a bulk electrolysis cell (Figure D.1) containing 25 mM [Et$_3$NH][BF$_4$] for 15 minutes. A 1 mL Vici Pressure-Lok Precision Analytical Syringe was used to sample 1 mL of the gas headspace and used to inject three ca. 0.3 mL samples into a Varian 450-GC with a pulsed discharge helium ionization detector and the average integrated hydrogen peak area calculated. A calibration curve made from samples of 0.5, 1.0, 3.0, and 5.0 v/v % H$_2$ in air for this specific instrument$^{128}$ was used to determine the volume fraction of hydrogen. Consequently, the number of moles of hydrogen produced was determined using the known headspace volume of the central compartment. Henry’s Law was used to estimate the number of moles of dissolved hydrogen in the working compartment solution and added to the moles of headspace hydrogen to find the total amount of hydrogen produced. The Henry’s Law constant for hydrogen in acetonitrile was estimated to be 5700 atm from literature values for the mole fraction solubility of hydrogen measured at different partial pressures of hydrogen at 298 K.$^{207}$ The Faradaic efficiency was then found by the ratio of the moles of hydrogen produced divided by the theoretical amount of hydrogen produced from integration of the total current passed. The experimental Faradaic efficiency was approximately 100%.
Figure D.1. Photo of three-compartment bulk electrolysis cell used to produce hydrogen for detection by bulk electrolysis. Cell was custom made by Allen Scientific Glass, Inc. The Pt coil counter electrode was purchased from BioLogic Science Instruments.
APPENDIX E. ADDITIONAL DETAILS FOR CHAPTER 4

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E.1 Estimation of diffusion limited rate of reaction of 1− and [Et₃NH][BF₄]

The diffusion limited bimolecular rate of reaction of 1− and [Et₃NH][BF₄] was estimated using the Debye-Smoluchowski relation:

\[ k_{diff} = 4\pi N_A (D_1 + D_2)\beta \]

where \( N_A \) is Avogadro’s number, \( D_1 \) and \( D_2 \) are the diffusion coefficients of the two reacting species (here 1 and Et₃NH⁺) and \( \beta \) is the effective reaction radius, taken as the sum of the radii for 1 and Et₃NH⁺ and estimated to be 8.5 Å. The diffusion coefficient of 1− was assumed to be equal to that of 1 which was obtained electrochemically to be 1 x 10⁻⁵ cm² s⁻¹ (see Chapter 3) while the diffusion coefficient of Et₃NH⁺ was estimated by ¹H DOSY NMR to be 2.2 x 10⁻⁵ cm² s⁻¹. As both reactants 1− and Et₃NH⁺ are charged, \( \beta \) was further modified to reflect electrostatic interactions via:

\[ \beta = \frac{R_c}{(\exp(R_c/R) - 1)\exp(R_c\kappa)} \]

where the Onsager radius \( R_c \) is given by

\[ R_c = (z_1 z_2 e^2 / 4\pi\varepsilon_r \varepsilon_0 k_B T) \]

where \( R \) is the reactant radius (as above, approximated for 1− and Et₃NH⁺ as 8.5 Å) \( z_1 \) and \( z_2 \) are the respective charges of the two species (here -1 and +1 for 1− and Et₃NH⁺), \( e \) is the elementary charge, \( \varepsilon_r \) is the relative permittivity of the solvent, \( \varepsilon_0 \) the permittivity of vacuum, \( k_B \) the Boltzmann constant, and \( T \) temperature. The relative permittivity of CH₃CN at room temperature is approximately 36.1.

The Debye length \( \kappa \) is given by:
\[ \kappa = \sqrt{\frac{2e^2N_a 1000}{\varepsilon_r \varepsilon_0 k_B T}} l_c \]

where \( l_c \) is the ionic concentration, e.g., the electrolyte concentration (mols/L).

The diffusion limited rate of \( 1^- \) and \( \text{Et}_3\text{NH}^+ \) was consequently estimated as \( 4.5 \times 10^{10} \) mols\(^{-1}\) s\(^{-1}\).

### E.2 Simulation details for \( \text{E}_i\text{C}_i\text{E}_i \) mechanism

The simulated \( \text{E}_i\text{C}_i\text{E}_i \) peak shift data depicted was simulated using \textit{DigiElch}. The following parameters were used:

**Table E.1.** Parameters used to simulate the data show in Chapter 4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental value</th>
<th>Estimated value</th>
<th>Rationale for estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) (1(^{st}) E)</td>
<td>0.3, 0.5, or 0.7</td>
<td>normal range for ( \alpha ) values(^{39} )</td>
<td></td>
</tr>
<tr>
<td>( \alpha ) (2(^{nd}) E)</td>
<td></td>
<td>0.5</td>
<td>assumed to be close to the average ( \alpha ) value(^{39} )</td>
</tr>
<tr>
<td>( k^0 ) (1(^{st}) E)</td>
<td></td>
<td>0.1 cm s(^{-1})</td>
<td></td>
</tr>
<tr>
<td>( k^0 ) (2(^{nd}) E)</td>
<td></td>
<td>0.1 cm s(^{-1})</td>
<td>assumed to be similar to ( k^0 ) for the first E</td>
</tr>
<tr>
<td>( D_p )</td>
<td>( 1 \times 10^{-5} ) cm(^2) s(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D_A )</td>
<td>( 2.2 \times 10^{-5} ) cm(^2) s(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([P] = [A])</td>
<td>0.005 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A )</td>
<td>0.071 cm(^2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_1 ) (1(^{st}) E)</td>
<td>-1.92 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_2 ) (2(^{nd}) E)</td>
<td>-1.42 V</td>
<td>The value of the 2(^{nd}) E was not found to significantly affect the peak position (see \textit{Figure E.1} and associated discussion)</td>
<td></td>
</tr>
</tbody>
</table>
Figure E.1. Simulated CVs for the E_CEi mechanism using the parameters in Table E.1 (except E_1 was set as 0 V instead of -1.92 V). The value of E_2, which from experimental data is likely more positive than E_1, was varied from 0 V to 1 V. Very little difference in the peak shift was observed; consequently, E_2 was set as -1.42 V for the simulation of the data shown in Chapter 4.
**APPENDIX F. ADDITIONAL DETAILS FOR CHAPTER 5**

**F.1 Cyclic voltammetry data for PCET reaction of MoCp₂(4-pedt) (1) and acids**

<table>
<thead>
<tr>
<th>acid</th>
<th>pKₐ(CH₃CN)</th>
<th>E₁/₂ for 1 + acid (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethylformamidium triflate</td>
<td>6.1</td>
<td>0.005</td>
</tr>
<tr>
<td>4-cyanoanilinium tetrafluoroborate</td>
<td>7</td>
<td>0.009</td>
</tr>
<tr>
<td>4-trifluoromethylaminilinium tetrafluoroborate</td>
<td>8.03</td>
<td>0.008</td>
</tr>
<tr>
<td>p-toluenesulfonic acid monohydrate</td>
<td>8.6</td>
<td>0.005</td>
</tr>
<tr>
<td>4-(methylbenzoate)anilinium tetrafluoroborate</td>
<td>8.62</td>
<td>0.004</td>
</tr>
<tr>
<td>4-trifluoromethoxyanilinium tetrafluoroborate</td>
<td>9.28</td>
<td>0.008</td>
</tr>
<tr>
<td>4-bromoanilinium tetrafluoroborate</td>
<td>9.43</td>
<td>0.005</td>
</tr>
<tr>
<td>4-chloroanilinium tetrafluoroborate</td>
<td>9.7</td>
<td>0.005</td>
</tr>
<tr>
<td>anilinium tetrafluoroborate</td>
<td>10.62</td>
<td>-0.003</td>
</tr>
<tr>
<td>4-tertbutylanilinium tetrafluoroborate</td>
<td>11.1</td>
<td>-0.005</td>
</tr>
<tr>
<td>4-methylanilinium tetrafluoroborate</td>
<td>11.4</td>
<td>-0.010</td>
</tr>
<tr>
<td>N,N-dimethylanilinium tetrafluoroborate</td>
<td>11.43</td>
<td>-0.010</td>
</tr>
<tr>
<td>4-methoxyanilinium tetrafluoroborate</td>
<td>11.86</td>
<td>-0.015</td>
</tr>
<tr>
<td>pyridinium tetrafluoroborate</td>
<td>12.53</td>
<td>-0.058</td>
</tr>
<tr>
<td>trifluoroacetic acid</td>
<td>12.65</td>
<td>-0.044</td>
</tr>
<tr>
<td>2-methylpyridinium tetrafluoroborate</td>
<td>13.32</td>
<td>-0.088</td>
</tr>
<tr>
<td>2,6-dimethylpyridinium tetrafluoroborate</td>
<td>14.13</td>
<td>-0.130</td>
</tr>
<tr>
<td>4-methoxypyridinium tetrafluoroborate</td>
<td>14.23</td>
<td>-0.137</td>
</tr>
<tr>
<td>2-aminopyridinium tetrafluoroborate</td>
<td>14.47</td>
<td>-0.160</td>
</tr>
<tr>
<td>2,4,6-trimethylpyridinium tetrafluoroborate</td>
<td>14.98</td>
<td>-0.162</td>
</tr>
<tr>
<td>2-aminobenzimidazolium tetrafluoroborate</td>
<td>16.08</td>
<td>-0.193</td>
</tr>
<tr>
<td>4-trifluoromethyl-2,3,5,6-tetrafluorophenol</td>
<td>16.62</td>
<td>-0.185</td>
</tr>
<tr>
<td>pentabromophenol</td>
<td>17.83</td>
<td>-0.195</td>
</tr>
<tr>
<td>triethylammonium tetrafluoroborate</td>
<td>18.82</td>
<td>-0.205</td>
</tr>
<tr>
<td>2,4,6-tribromophenol</td>
<td>20.35</td>
<td>-0.205</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>21.51</td>
<td>-0.202</td>
</tr>
</tbody>
</table>
In the following cyclic voltammograms decamethylferrocene is present as an internal reference (-0.505 V vs. Fc<sup>+</sup>/<sup>-</sup> as measured in our lab).

**Figure F.1.** Cyclic voltammogram of 0.2 mM 1, 0.2 mM dimethylformamidium triflate, and decamethylferrocene in 0.25 M [Bu<sub>4</sub>N][PF<sub>6</sub>] CH<sub>3</sub>CN solution at 100 mV/s.

**Figure F.2.** Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-cyanoanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu<sub>4</sub>N][PF<sub>6</sub>] CH<sub>3</sub>CN solution at 100 mV/s.
Figure F.3. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-trifluoromethylanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s.

Figure F.4. Cyclic voltammogram of 0.2 mM 1, 0.2 mM p-toluenesulfonic acid monohydrate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s.

Figure F.5. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-(methylbenzoate)anilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s.
**Figure F.6.** Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-trifluoromethoxyanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M \([\text{Bu}_4\text{N}]^{+}[\text{PF}_6]^{-}\) CH$_3$CN solution at 100 mV/s.

**Figure F.7.** Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-bromoanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M \([\text{Bu}_4\text{N}]^{+}[\text{PF}_6]^{-}\) CH$_3$CN solution at 100 mV/s.

**Figure F.8.** Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-chloroanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M \([\text{Bu}_4\text{N}]^{+}[\text{PF}_6]^{-}\) CH$_3$CN solution at 100 mV/s.
Figure F.9. Cyclic voltammogram of 0.2 mM 1, 0.2 mM anilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution at 100 mV/s.

Figure F.10. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-tertbutylanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution at 100 mV/s.

Figure F.11. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-methylanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution at 100 mV/s.
Figure F.12. Cyclic voltammogram of 0.2 mM 1, 0.2 mM \(N,N\)-dimethylanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M \([Bu_4N][PF_6]\) \(CH_3CN\) solution at 100 mV/s.

Figure F.13. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-methoxyanilinium tetrafluoroborate, and decamethylferrocene in 0.25 M \([Bu_4N][PF_6]\) \(CH_3CN\) solution at 100 mV/s.

Figure F.14. Cyclic voltammogram of 0.2 mM 1, 0.2 mM pyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M \([Bu_4N][PF_6]\) \(CH_3CN\) solution at 100 mV/s.
Figure F.15. Cyclic voltammogram of 0.2 mM 1, 0.2 mM trifluoroacetic acid, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s.

Figure F.16. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2-methylpyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s.

Figure F.17. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2,6-lutidinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s.
Figure F.18. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-methoxypyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution at 100 mV/s.

Figure F.19. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2-aminopyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution at 100 mV/s.

Figure F.20. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2,4,6-trimethylpyridinium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution at 100 mV/s.
Figure F.21. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2-aminobenzimidazolium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu4N][PF6] CH3CN solution at 100 mV/s.

Figure F.22. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 4-trifluoromethyl-2,3,5,6-tetrafluorophenol, and decamethylferrocene in 0.25 M [Bu4N][PF6] CH3CN solution at 100 mV/s.

Figure F.23. Cyclic voltammogram of 0.2 mM 1, 0.2 mM pentabromophenol, and decamethylferrocene in 0.25 M [Bu4N][PF6] CH3CN solution at 100 mV/s.
Figure F.24. Cyclic voltammogram of 0.2 mM 1, 0.2 mM triethylammonium tetrafluoroborate, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s.

Figure F.25. Cyclic voltammogram of 0.2 mM 1, 0.2 mM 2,4,6-tribromophenol, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s.

Figure F.26. Cyclic voltammogram of 0.2 mM 1, 0.2 mM benzoic acid, and decamethylferrocene in 0.25 M [Bu₄N][PF₆] CH₃CN solution at 100 mV/s.
F.2 Modeling PCET of 1 with acids as stepwise ET-PT or PT-ET mechanisms

F.2.1 Thermochemistry of an EC Reaction Mechanism

In an EC reaction mechanism, electron transfer at the electrode is coupled to a follow-up first-order (or pseudo first-order) homogeneous reaction. The EC reaction scheme for \([1(H)]^{1+}\) is depicted in Figure F.27, where the reversible oxidation of \([1(H)]^{1+}\) yields an equilibrium mixture of \([1(H)]^{2+}\) and \([1]^{1+}\):

\[
\begin{align*}
[1(H)]^{1+} + \text{H}^+ &\rightarrow [1]^{1+} + \text{H}_2 \quad \Delta G^\circ = (1.37 \text{ kcal mol}^{-1}) pK_a([1(H)]^{2+}) \\
-([\text{HA} \rightarrow \text{A}^- + \text{H}^+]) &\quad \Delta G^\circ = (1.37 \text{ kcal mol}^{-1}) pK_a(\text{HA}) \\
[1(H)]^{2+} + \text{A}^- &\rightarrow \text{HA} + [1]^{1+} \quad \Delta G_{\text{PT}} = -(1.37 \text{ kcal mol}^{-1}) [pK_a(\text{HA}) - pK_a([1(H)]^{2+})] \\
\end{align*}
\]

The equilibrium constant \(K_{\text{EC}}\) can be readily related to the free energy change associated with the deprotonation of \([1(H)]^{2+}\) by the conjugate base of HA:

\[
K_{\text{EC}} = e^{-\Delta G_{\text{PT}}/RT}
\]
For a reversible chemical reaction following the oxidation of \([1(H)]^{1+}\) to \([1(H)]^{2+}\) (zone DE), a reversible Nernstian wave centered around a new formal potential \(E_{1/2}\) is anticipated, which is related to \(K_{EC}\) and \(E^{o'}\) (the formal potential of the \([1(H)]^{2+/1+}\) couple) by:\(^{40,54}\)

\[
E_{1/2} = E^{o'} ([1(H^{+})]^{+} / 0) - \frac{RT}{F} \ln (1 + K_{EC})
\]

The new formal potential will appear at potentials cathodic to \(E^{o'}\) for an oxidative process (Figure F.28).\(^1\) At \(pK_a(HA)\) values < ca. 10, \(E_{1/2} \approx E^0\). In the region 10 < \(pK_a(HA)\) < 13, the \(E_{1/2} - pK_a\) relationship has curvature. For \(pK_a(HA)\) values > ca. 13, a linear relationship between \(E_{1/2}\) and \(pK_a(HA)\) is observed, with a slope of 59 mV/decade, consistent with the relationship predicted by Equation 12 in Chapter 5.

Figure F.28. The predicted relationship between \(E_{1/2}\) and the \(pK_a\) of HA for an EC reaction (+) reveals a linear region (---) with a slope of 59 mV/decade for \(pK_a\) values greater than ca. 13.

---

\(^1\) The relationship between \(E_{1/2}\) and \(K_{EC}\) has been derived for a reductive process. In this case, \(E_{1/2}\) appear at potentials anodic to \(E^{o'}\) and the relationship is defined by \(E_{1/2} = E^{o'} + \frac{RT}{F} \ln (1 + K_{EC})\). For an oxidative process, the sign should change and \(E_{1/2}\) should appear cathodic of the oxidative wave defined by \(E^0\).
F.2.2 Thermochemistry of a CE Reaction Mechanism

In a CE reaction mechanism, a first-order (or pseudo first-order) homogeneous reaction is followed by an electron transfer at the electrode. The CE reaction scheme for 1 is depicted in Figure F.29, where 1 and [1(H)]^{1+} are in equilibrium and 1 can be oxidized to [1]^{1+}:

**Figure F.29.** CE mechanism for oxidation of 1.

When electrode electron transfer is fast (such that the kinetics of the homogeneous reaction and diffusion are rate limiting), the electrochemical response is a function of the equilibrium constant ($K_{CE}$) and the dimensionless kinetic parameter $\lambda$.

\[
K_{CE} = \frac{k_+}{k_-}
\]
\[
\lambda = \frac{RT}{F} \frac{k_+ + k_-}{k} = \frac{RT}{F} \frac{k}{u}
\]

The equilibrium constant $K_{CE}$ can be readily related to the free energy change associated with the deprotonation of [1(H)]^{1+} by the conjugate base of HA:

\[
[1(H)]^{1+} \rightarrow [1] + H^+ \quad \Delta G^\circ = (1.37 \text{ kcal mol}^{-1}) \ pK_a([1(H)]^{1+})
\]
\[
-(HA \rightarrow A^- + H^+) \quad \Delta G^\circ = (1.37 \text{ kcal mol}^{-1}) \ pK_a(HA)
\]
\[
[1(H)]^{1+} + A^- \rightarrow HA + [1] \quad \Delta G_{PT}^\circ = -(1.37 \text{ kcal mol}^{-1}) \ [pK_a(HA) - pK_a([1(H)]^{1+})]
\]
\[
K_{CE} = e^{-\Delta G_{PT}^\circ / RT}
\]
In zone DE (large values of $\lambda$, small to moderate $K_{CE}$), a reversible Nernstian wave centered around a new formal potential ($E_{1/2}$), anodic to $E^{o'}([1]^{+/0})$, is expected.\(^2\) $E_{1/2}$ is related to $K_{CE}$ and $E^{o'}([1]^{+/0})$ by:\(^{40,54}\)

$$E_{1/2} = E^{o'}([1]^{+/0}) - \frac{RT}{F} \ln \left( \frac{K_{CE}}{1 + K_{CE}} \right)$$

At pK\(_{a}\) values $> ca. 16.5$, $E_{1/2} \approx E^o$. In the region $16.5 < pK_{a}(HA) < 14.25$, the $E_{1/2}$–pK\(_{a}\) relationship has curvature. For pK\(_{a}\)(HA) values $< ca. 14.25$, a linear relationship between $E_{1/2}$ and pK\(_{a}\)(HA) is observed (Figure F.30), with a slope of 59 mV/decade, consistent with the relationship predicted by Equation 12 in Chapter 5.

![Figure F.30](image.png)

**Figure F.30.** The predicted relationship between $E_{1/2}$ and the pK\(_{a}\) of HA for a CE reaction ($\bullet$) reveals a linear region (---) with a slope of 59 mV/decade for pK\(_{a}\) values less than ca. 14.25.

### F.2.3 Unifying EC and CE mechanisms

As demonstrated above, both of the EC and CE mechanisms predict a 59 mV/decade dependence of the observed redox wave on the acid pK\(_{a}\). Both also predict curvature near the

---

\(^2\) The relationship between $E_{1/2}$ and $K_{CE}$ has been derived for a reductive process (Ref. 12). In this case, $E_{1/2}$ appear at potentials cathodic to $E^0$ and the relationship is defined by $E_{1/2} = E^{o'} + \frac{RT}{F} \ln \left( \frac{K_{CE}}{1 + K_{CE}} \right)$. For an oxidative process, the sign should change and $E_{1/2}$ should appear anodic of the oxidative wave defined by $E^{o''}$. 
pK_a of [1(H)]^+ and [1(H)]^{2+}. These results are consistent with the predicted slope of in Equation 12 of Chapter 5 and the curvature observed in the experimental potential-pK_a diagram of 1. If the simulated peak shifts of the EC and CE mechanisms are overlaid on the same plot it is clear that it is a quantitative match for the experimental potential–pK_a diagram of 1 (Figure F.31). The observed curvature can be explained by the equilibrium that exists near the pK_a values of the two intermediates [1(H)]^+ and [1(H)]^{2+}.

**Figure F.31.** Overlay of the predicted relationship between $E_{1/2}$ and the pK_a of HA for both the CE (•) and EC (+) mechanisms.

Thermochemically, the match between the EC and CE mechanisms as well as the adherence of the experimental data for 1 to Hess’s law confirm that a thermochemical cycle can be made relating the two mechanisms. This also confirms that the concerted reaction (EC) is thermodynamically accessible. The overlapping predictions of the EC and CE simulated redox shift strongly hints that the mechanism is pK_a-dependent. The possibility of a concerted pathway at some pK_a is also possible.
F.3 Cyclic voltammetry data for PCET reaction of 2 and acids

Table F.2. Summary of acids used for electrochemical PCET with 2 and average $E_{1/2}$ for PCET.

<table>
<thead>
<tr>
<th>acid</th>
<th>$pK_a$(CH$_3$CN)</th>
<th>ref. for $pK_a$</th>
<th>Avg. $E_{1/2}$ for 2 + acid (V)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-trifluoromethylanilinium</td>
<td>8.03</td>
<td>75</td>
<td>-0.681</td>
</tr>
<tr>
<td>$p$-toluenesulfonic acid</td>
<td>8.6</td>
<td>190</td>
<td>-0.725</td>
</tr>
<tr>
<td>4-bromoanilinium</td>
<td>9.43</td>
<td>75</td>
<td>-0.785</td>
</tr>
<tr>
<td>4-chloroanilinium</td>
<td>9.7</td>
<td>179</td>
<td>-0.794</td>
</tr>
<tr>
<td>anilinium</td>
<td>10.62</td>
<td>75</td>
<td>-0.85</td>
</tr>
<tr>
<td>4-tert-butylanilinium</td>
<td>11.1</td>
<td>179</td>
<td>-0.878</td>
</tr>
<tr>
<td>4-methoxyanilinium</td>
<td>11.86</td>
<td>75</td>
<td>-0.896</td>
</tr>
<tr>
<td>trifluoroacetic acid</td>
<td>12.65</td>
<td>72</td>
<td>-0.902</td>
</tr>
<tr>
<td>2,6-lutidinium</td>
<td>14.13</td>
<td>75</td>
<td>-0.918</td>
</tr>
<tr>
<td>2,4,6-trimethylpyridinium</td>
<td>14.98</td>
<td>75</td>
<td>-0.915</td>
</tr>
<tr>
<td>4-CF$_3$-2,3,5,6-F$_4$-PhOH</td>
<td>16.62</td>
<td>190</td>
<td>-0.916</td>
</tr>
<tr>
<td>triethylammonium</td>
<td>18.82</td>
<td>75</td>
<td>-0.915</td>
</tr>
</tbody>
</table>

$^a$Unless otherwise stated, acids used had tetrafluoroborate counteranions. $^b$Average of at least three CVs at different scan rates where both reduction and oxidation could be observed.

Figure F.32. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 4-CF$_3$-anilinium, at varying scan rates. Recorded in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.
Figure F.33. Cyclic voltammograms of 0.45 mM 2 with one molar equivalent of p-toluenesulfonic acid, at varying scan rates. Recorded in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.

Figure F.34. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 4-bromoanilinium at various scan rates. Recorded in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.

Figure F.35. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 4-chloroanilinium at various scan rates. Recorded in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.
Figure F.36. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of anilinium at various scan rates. Recorded in 0.25 M [Bu₄N][PF₆] CH₃CN solution.

Figure F.37. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 4-tert-butylanilinium at various scan rates. Recorded in 0.25 M [Bu₄N][PF₆] CH₃CN solution.

Figure F.38. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of trifluoroacetic acid at various scan rates. Recorded in 0.25 M [Bu₄N][PF₆] CH₃CN solution.
Figure F.39. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 2,6-lutidinium at various scan rates. Recorded in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.

Figure F.40. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of 2,4,6-trimethylpyridinium at various scan rates. Recorded in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.

Figure F.41. Cyclic voltammograms of 0.5 mM 2 with one molar equivalent of 4-CF$_3$-2,3,5,6-F$_4$-PhOH at various scan rates. Recorded in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.
Figure F.42. Cyclic voltammograms of 0.45 mM 2 with and without one molar equivalent of triethylammonium at various scan rates. Recorded in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.
F.4 Cyclic voltammetry data for PCET reaction of 3 and acids

Table F.3. Summary of acids used for electrochemical PCET with 3 and average $E_{p,c}$ or $E_{1/2}$ for PCET.

<table>
<thead>
<tr>
<th>acid</th>
<th>$pK_a$(CH$_3$CN)</th>
<th>ref. for $pK_a$</th>
<th>Average $E_{p,c}$ for 3 + acid (V)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzylammonium</td>
<td>16.91</td>
<td>75</td>
<td>-1.581</td>
</tr>
<tr>
<td>triethylammonium</td>
<td>18.82</td>
<td>75</td>
<td>-1.671</td>
</tr>
<tr>
<td>2,4,6-tribromophenol</td>
<td>20.35</td>
<td>190</td>
<td>-1.725</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>21.51</td>
<td>190</td>
<td>-1.781</td>
</tr>
<tr>
<td>acetic acid</td>
<td>23.51</td>
<td>190</td>
<td>-1.847</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>25.44</td>
<td>72</td>
<td>-1.925</td>
</tr>
<tr>
<td>o-cresol</td>
<td>27.5</td>
<td>72</td>
<td>-1.947</td>
</tr>
<tr>
<td>2,4,6-tri-tert-butylphenol</td>
<td>28</td>
<td>23</td>
<td>-1.954</td>
</tr>
<tr>
<td>phenol</td>
<td>29.14</td>
<td>78</td>
<td>-1.942</td>
</tr>
</tbody>
</table>

$^a$Unless otherwise stated, acids used had tetrafluoroborate counteranions. $^b$Average of three CVs at 100 mV/s where only reduction could be observed. $^c$Average of at three CVs at 100 mV/s with fresh electrodes where both reduction and oxidation could be observed.

Note: Each cyclic voltammogram was obtained three times with freshly polished electrodes and either the average $E_{peak,cathodic}$ or $E_{1/2}$ determined for that set of three. Below are sample CVs; very little variation was observed from scan to scan.

Figure F.43. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of benzylammonium at 100 mV/s. Taken in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.
Figure F.44. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of triethylammonium at 100 mV/s. Taken in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.

Figure F.45. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of 2,4,6-tribromophenol at 100 mV/s. Taken in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.

Figure F.46. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of benzoic acid at 100 mV/s. Taken in 0.25 M [Bu$_4$N][PF$_6$] CH$_3$CN solution.
Figure F.47. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of acetic acid at 100 mV/s. Taken in 0.25 M [Bu₄N][PF₆] CH₃CN solution.

Figure F.48. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of 4-chlorophenol at 100 mV/s. Taken in 0.25 M [Bu₄N][PF₆] CH₃CN solution.

Figure F.49. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of o-cresol at 100 mV/s. Taken in 0.25 M [Bu₄N][PF₆] CH₃CN solution.
Figure F.50. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of 2,4,6-tri-tert-butylphenol at 100 mV/s. Taken in 0.25 M [Bu₄N][PF₆] CH₃CN solution.

Figure F.51. Cyclic voltammogram of 0.3 mM 2 plus one molar equivalent of phenol at 100 mV/s. Taken in 0.25 M [Bu₄N][PF₆] CH₃CN solution.
APPENDIX G. ADDITIONAL DETAILS FOR CHAPTER 6

G.1 Estimation of diffusion coefficients

Diffusion coefficients for reversible electron transfers can be estimated using the Randles-Sevcik equation: \( i_{\text{peak}} = (2.69 \cdot 10^5)n^{3/2}A D_0^{1/2} C_0^* u^{1/2} \)

where \( n \) is the number of electrons transferred, \( A \) is the electrode surface area, \( D_0 \) is the diffusion coefficient, \( C_0^* \) the bulk concentration of the species, and \( u \) the scan rate. By plotting \( i_{\text{peak}} \) versus the square root of the scan rate, the slope of the resulting line is used to determine the diffusion coefficient.

CVs were obtained of 1 and 1(H)^1+ in 0.25 M [Bu4N][PF6] over a range of scan rates. Figure G.1 and Figure G.2 show the resulting plots of background-subtracted cathodic peak current versus the square root of the scan rate for 1 and 1(H)^1+, respectively. Using slopes determined through linear fits, the diffusion coefficients of 1 and 1(H)^1+ were calculated to be 1.2 x 10^-5 cm^2 s^-1 and 1.5 x 10^-5 cm^2 s^-1, respectively.

![Graph](image)

**Figure G.1.** Background subtracted cathodic peak currents for 0.4 mM 1 plotted versus the square root of the scan rate.
G.2 Estimation of heterogeneous electron transfer rates

The Nicholson method\textsuperscript{133} was used to estimate $k_s$ for 1 and 1(H)$^{1+}$. CVs were collected at a variety of scan rates and the peak-to-peak separation determined ($\Delta E_p$) (Table G.1 and Table G.2). Using these values, the dimensionless charge transfer parameter $\psi$ was calculated using:\textsuperscript{133} $\ln(\psi) = 3.69 - 1.16\ln(\Delta E_p - 59)$.

The heterogeneous electron transfer rates ($k_s$ values) can then be found using the following expression:

$$k_s = \psi \left(\pi D_0 F v \frac{\nu}{RT}\right)^{1/2} \left(D_R/D_O\right)^{\alpha/2}$$

where $D_R$ and $D_O$ are the diffusion coefficients of the reduced and oxidized forms (here assumed to be equal), respectively, $v$ is the scan rate, $F$ the Faraday constant, $T$ the temperature, $R$ the gas constant, and $\alpha$ is the transfer coefficient, here assumed to be 0.5.
To minimized influence from solution resistance, CVs were collected with 1 mM diameter electrodes (reducing overall current) and with 0.25 M [Bu₄N][PF₆] for a 0.X mM solution of 1⁺⁺₀ and 1(H)²⁺⁻¹⁺ (generated in situ with excess dimethylformamidium triflate). Average values of $k_s$ for 1 and 1(H)²⁺⁻¹⁺ are shown in Table G.1 and Table G.2, respectively.

### Table G.1.

Measured peak-to-peak separation for 1 as a function of scan rate. Psi and $k^0$ values calculated as described in text.

<table>
<thead>
<tr>
<th>(V/s)</th>
<th>ΔEp (mV)</th>
<th>ψ</th>
<th>$k_s$ (cm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>61</td>
<td>14.2</td>
<td>0.39</td>
</tr>
<tr>
<td>2</td>
<td>64</td>
<td>6.5</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
<td>6.2</td>
<td>0.47</td>
</tr>
<tr>
<td>6</td>
<td>67</td>
<td>3.8</td>
<td>0.35</td>
</tr>
<tr>
<td>8</td>
<td>66</td>
<td>4.2</td>
<td>0.46</td>
</tr>
<tr>
<td>10</td>
<td>66</td>
<td>4.3</td>
<td>0.52</td>
</tr>
</tbody>
</table>

| average: | 0.4 |
| stdev:   | 0.1 |

### Table G.2.

Measured peak-to-peak separation for 1(H)¹⁺ as a function of scan rate. Psi and $k^0$ values calculated as described in text.

<table>
<thead>
<tr>
<th>(V/s)</th>
<th>ΔEp (mV)</th>
<th>ψ</th>
<th>$k_s$ (cm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>63</td>
<td>7.06</td>
<td>0.21</td>
</tr>
<tr>
<td>1</td>
<td>62</td>
<td>11.63</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>64</td>
<td>6.29</td>
<td>0.38</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
<td>5.96</td>
<td>0.51</td>
</tr>
<tr>
<td>6</td>
<td>63</td>
<td>8.61</td>
<td>0.90</td>
</tr>
<tr>
<td>8</td>
<td>66</td>
<td>4.16</td>
<td>0.50</td>
</tr>
<tr>
<td>10</td>
<td>66</td>
<td>4.16</td>
<td>0.56</td>
</tr>
</tbody>
</table>

| average: | 0.6 |
| stdev:   | 0.2 |

Estimation of diffusion coefficient of 2-methylpyridine
The diffusion coefficient of 2-methylpyridine was estimated by $^1$H DOSY NMR with a 500 MHz Bruker spectrometer. The pulse width was calibrated by varying the pulse width until null peaks were observed for all 2-methlypyridine peaks, with the calibrated 90° pulse found to be 8.43 μs. The DOSY dataset was processed in TopShim (© Bruker) and yielded an average diffusion coefficient of 2-methylpyridine of $3.3 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$ (Figure G.3).

Figure G.3. $^1$H DOSY NMR spectrum of a CD$_3$CN solution of 2-methylpyridine.
REFERENCES


(58) Martin, D. J.; McCarthy, B. D.; Rountree, E. S.; Dempsey, J. L. Qualitative Extension of the EC’ Zone Diagram to a Molecular Catalyst for a Multi-Electron, Multi-Substrate Electrochemical Reaction. *Dalt. Trans.* 2016, 45 (24), 9970–9976.


